Designation: E2412 – 04

Standard Practice for
Condition Monitoring of Used Lubricants by Trend Analysis Using Fourier Transform Infrared (FT-IR) Spectrometry[1]

1. Scope

1.1 This practice covers the use of FT-IR in monitoring additive depletion, contaminant buildup and base stock degradation in machinery lubricants, hydraulic fluids and other fluids used in normal machinery operation. Contaminants monitored include water, soot, ethylene glycol, fuels and incorrect oil. Oxidation, nitration and sulfonation of base stocks are monitored as evidence of degradation. The objective of this monitoring activity is to diagnose the operational condition of the machine based on fault conditions observed in the oil. Measurement and data interpretation parameters are presented to allow operators of different FT-IR spectrometers to compare results by employing the same techniques.

1.2 This practice is based on trending and distribution response analysis from mid-infrared absorption measurements. While calibration to generate physical concentration units may be possible, it is unnecessary or impractical in many cases. Warning or alarm limits (the point where maintenance action on a machine being monitored is recommended or required) can be determined through statistical analysis, history of the same or similar equipment, round robin tests or other methods in conjunction with correlation to equipment performance. These warning or alarm limits can be a fixed maximum or minimum value for comparison to a single measurement or can also be based on a rate of change of the response measured (**1**).[2] This practice describes distributions but does not preclude using rate-of-change warnings and alarms.

NOTE 1—It is not the intent of this practice to establish or recommend normal, cautionary, warning or alert limits for any machinery. Such limits should be established in conjunction with advice and guidance from the machinery manufacturer and maintenance group.

1.3 Spectra and distribution profiles presented herein are for illustrative purposes only, and are not to be construed as representing or establishing lubricant or machinery guidelines.

1.4 This practice is designed as a fast, simple spectroscopic check for condition monitoring of used lubricants and can be used to assist in the determination of general machinery health through measurement of properties observable in the mid-infrared spectrum such as water, oil oxidation, and others as noted in 1.1. The infrared data generated by this practice is typically used in conjunction with other testing methods. For example, infrared spectroscopy cannot determine wear metal levels or any other type of elemental analysis. The practice as presented is not intended for the prediction of lubricant physical properties (for example, viscosity, total base number, total acid number, etc.). This practice is designed for monitoring used lubricants and can aid in the determination of general machinery health and is not designed for the analysis of lubricant composition, lubricant performance or additive package formulations.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D445 Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)

D2896 Test Method for Base Number of Petroleum Products by Potentiometric Perchloric Acid Titration

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D5185 Test Method for Determination of Additive Elements, Wear Metals, and Contaminants in Used Lubricating Oils and Determination of Selected Elements in Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

D6304 Test Method for Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fischer Titration

E131 Terminology Relating to Molecular Spectroscopy

E168 Practices for General Techniques of Infrared Quantitative Analysis

E1421 Practice for Describing and Measuring Performance of Fourier Transform Mid-Infrared (FT-MIR) Spectrometers: Level Zero and Level One Tests

E1655 Practices for Infrared Multivariate Quantitative Analysis

2.2 *ISO Document:*

ISO/TC 108 N 605 Terminology for the Field of Condition Monitoring and Diagnostics of Machines[4]

3. Terminology

3.1 *Definitions*—For definitions of terms relating to infrared spectroscopy used in this practice, refer to Terminology E131.

3.1.1 *Fourier transform infrared (FT-IR) spectrometry, n*—a form of infrared spectrometry in which an interferrogram is obtained; this interferrogram is then subjected to a Fourier transform to obtain an amplitude-wavenumber (or wavelength) spectrum. **E131**

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *condition monitoring, n*—a field of technical activity in which selected physical parameters associated with an operating machine are periodically or continuously sensed, measured and recorded for the interim purpose of reducing, analyzing, comparing and displaying the data and information so obtained and for the ultimate purpose of using interim result to support decisions related to the operation and maintenance of the machine (**2, 3**).

3.2.2 *machinery health, n*—a qualitative expression of the operational status of a machine sub-component, component or entire machine, used to communicate maintenance and operational recommendations or requirements in order to continue operation, schedule maintenance or take immediate maintenance action.

3.2.3 *trend analysis, n—as applied in this practice*, monitoring of the level and rate of change over operating time of measured parameters (**1**).

3.2.4 *used oil, n—as applied in this practice*, a lubricating oil that is present in a machine which has been at operating temperature for at least one hour.

3.2.4.1 *Discussion*—Sampling a used oil after at least one hour of operation will allow for the measurement of a base point for later trend analysis.

3.2.4.2 *Discussion*—Any subsequent addition of lubricant (for example, topping off, may change the trending baseline) which may lead to erroneous conclusions.

3.2.5 *new oil, n*—an oil taken from the original manufacturer's packaging, prior to being added to machinery.

3.2.6 *reference oil, n*—see *new oil*.

4. Summary of Practice

4.1 Periodic samples are acquired from the engine or machine being monitored. An infrared absorbance spectrum of the sample is acquired, typically covering the range of 4000 to 550 cm⁻¹, with sufficient signal-to-noise (S/N) ratio to measure

absorbance areas of interest. Exact data acquisition parameters will vary depending on instrument manufacturer but most systems should be able to collect an absorbance spectrum adequate for most measurements in less than one minute. Features in the infrared spectrum indicative of the molecular level components of interest (**1,8**) (that is, water, fuel, antifreeze, additive, degradation, and so forth) are measured and reported. Condition alerts and alarms can then be triggered according to both the level and the trends from the monitored system.

5. Significance and Use

5.1 Periodic sampling and analysis of lubricants have long been used as a means to determine overall machinery health. Atomic emission (AE) and atomic absorption (AA) spectroscopy are often employed for wear metal analysis (for example, Test Method D5185). A number of physical property tests compliment wear metal analysis and are used to provide information on lubricant condition (for example, Test Methods D445, D2896, and D6304). Molecular analysis of lubricants and hydraulic fluids by FT-IR spectroscopy produces direct information on molecular species of interest, including additives, fluid breakdown products and external contaminants, and thus complements wear metal and other analyses used in a condition monitoring program (**1,4-8**).

6. Apparatus

6.1 *Required Components*:

6.1.1 *Fourier Transform Infrared Spectrometer (FT-IR)*—Instrument is configured with a source, beamsplitter and detector to adequately cover the mid-infrared range of 4000 cm⁻¹ to 550 cm⁻¹. Most work has been done on systems using a room temperature deuterated triglycine sulfate (DTGS) detector, air-cooled source and Germanium coating on Potassium Bromide (Ge/KBr) beamsplitter. Alternate source, beamsplitter and detector combinations covering this range are commercially available but have not been investigated for use in this practice. Other detectors may be suitable but should be used with caution. In particular, liquid nitrogen cooled Mercury Cadmium Telluride (MCT) detectors are known to exhibit significant nonlinearities.

6.1.2 *Infrared Liquid Transmission Sampling Cell*—Sampling cells can be constructed of zinc selenide (ZnSe), barium fluoride (BaF₂), potassium bromide (KBr), or other suitable window material, with a pathlength of 0.1 mm (100 μm), parallel (<0.5° variance) cell spacer. Acceptable pathlength ranges are from 0.080 to 0.120 mm. Outside this range, poor sensitivity or data non-linearity can occur. For the data provided in this document, the cells used were ZnSe, NaCl, or KBr as the measurements ranged from 4000 cm⁻¹ to 700 cm⁻¹. Some cell material information is given below.

Material	Comments	Transmission Range, cm⁻¹
ZnSe	see 6.1.2.1	4000 – 550
KBr	susceptible to water damage	4000 – 400
NaCl	susceptible to water damage	4000 – 650
BaF₂	ammonium salts can damage	4000 – 850
CaF₂	ammonium salts can damage	4000 – 1100

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[4] Available from International Organization for Standardization (ISO), 1 rue de Varembé, Case postale 56, CH-1211, Geneva 20, Switzerland.

Results should be corrected to 0.100 mm pathlength to account for cell path variation and improve data comparison to other instruments using this practice.

6.1.2.1 Due to the large refractive index change when the infrared beam passes from air into the ZnSe windows, fringe reduction is necessary to provide consistent results. Fringe reduction can be achieved electronically, optically or mechanically for ZnSe cells. For further explanation, see Appendix X1. Care should be taken in selecting window materials to ensure that the desired parameters can be measured within the transmission region of that material and compatibility with the specific application; for example, salt windows (KBr, NaCl, KCl) can be used and may not require fringe correction but are susceptible to damage from water contamination in the oil. Coates and Setti (4) have noted that oil nitration products can react with salt windows, depositing compounds that are observed in later samples.

6.1.3 *Cell Flushing / Cleaning Solvent*—The ideal solvent to flush the cell between samples to minimize carryover should have no significant absorption in the condition monitoring areas of interest, and quickly dry when air is pumped through the system. Typical wash solvents used for common petroleum and some synthetic lubricants are technical grade, light aliphatic hydrocarbons such as heptane or cyclohexane. Other solvents may be required for more specialized synthetic lubricants. Health and safety issues on using, storing, and disposing of these solvents will not be covered here. Local regulations and Material Safety Data Sheets (MSDS) should be consulted.

6.2 *Optional Components*:

6.2.1 *Sample Pumping System*—A pumping system capable of transporting the sample to the transmission cell, emptying the cell and flushing the cell between samples may be used. Many commercial vendors offer various configurations of pump types, tubing and transmission cells for this type of application. It should be noted that non-homogeneity might occur if the oils are left standing for too long.

6.2.2 *Filter*—The use of a particulate filter (for example, 0.090 mm) to trap large particles is strongly recommended to prevent cell clogging when using a pumping system. If a particulate filter is not used, the cell should be back flushed regularly to prevent clogging.

6.2.3 *Sealed Sample Compartment*—The system configuration should be consistent with preventing harmful, flammable or explosive vapors from reaching the IR source.

6.2.4 *Hydrocarbon Leak Alarm*—When using a sample pumping system, an independent flammable vapor sensor and alarm system should be used to alert the operator when a leak occurs in the tubing, connectors or transmission cell. This alarm system is strongly recommended when a pumping system is used to pump samples and wash solvents into an enclosed area.

6.2.5 *Check Fluid*—A check fluid or quality control fluid can be analyzed as needed for individual laboratory quality control and procedure issues and for comparison to other laboratories. One IR manufacturer has used heptane and a commercial product is available.[5] A check sample should be a material that provides consistent results using the methods presented in the annexes to this practice. The purpose of this quality control fluid is to verify proper operation of the FT-IR spectrometer/transmission cell combinations, as well as any associated sample introduction and cleaning hardware.

7. Sampling and Sample Handling

7.1 *Sample Acquisition*—The objective of sampling is to obtain a test specimen that is representative of the entire quantity. Thus, laboratory samples should be taken in accordance with the instructions in Practice D4057.

7.2 *Sample Preparation*—No sample preparation is required. Laboratory samples should be shaken or agitated to ensure a representative sample is taken from the bottle.

8. Instrumentation Preparation

8.1 *Spectral Acquisition Parameters*:

8.1.1 *Spectral Resolution*—8 cm^{-1} or better (lower numeric value).

8.1.2 *Data Point Spacing Resolution*—4 cm^{-1} or better (lower numeric value).

8.1.3 *Typical Range*—4000 to 550 cm^{-1} (see 6.1.2).

8.1.4 *Spectral Format*—Absorbance as a function of wavenumber.

8.1.5 *Other Optical, Electronic Filtering and Interferogram Computational Parameters*—These parameters should be as recommended by the manufacturer or as determined necessary for adequate measurement quality. Individual parameters and settings will vary depending on instrument manufacturer but most FT-IR spectrometers should be able to collect an adequate spectrum in less than one minute.

NOTE 2—Identical scanning acquisition parameters should be used for all samples to be trended.

8.2 *Background Collection*:

8.2.1 The single beam background collection (empty system reference scanned and stored on an FT-IR spectrometer) should be performed frequently enough such that ambient changes in atmospheric water vapor levels and other changing ambient conditions do not significantly affect the sample results (see Practice E1421). The frequency of background checks should be determined by the individual laboratory conditions and sampling technique; for example, at the completion of each run when using autosamplers.

8.2.2 Note that changing water vapor levels will have the strongest effect, as water vapor is a strong infrared absorber. A water vapor check may be included in the software to monitor the intensity of the water vapor in the single beam background spectrum. For example, using the average of baseline points at 1609 to 1582 cm^{-1} and measuring the water vapor bands superimposed on the single beam spectrum at 1540, 1559, and 1652 cm^{-1} relative to the average baseline. Acceptable limits for operation can be set; for example, measured peaks due to water vapor superimposed on the single beam background should not be more than 10 % of the single beam intensity.

8.2.3 Most of the research and development work used in the development of this practice used a background collection at least every 2 hours. Individual parameters and settings will vary depending on instrument manufacturer but most FT-IR spectrometers should be able to collect an adequate spectrum in less than one minute.

8.3 *Cell Pathlength Check*—A cell pathlength check is needed to verify the pathlength consistency of the cell. Results are referenced to 0.100 mm as mentioned in 6.1.2. This check is particularly important for water-soluble salt cell windows (for example, KBr). For systems using a fixed flow cell, the check can be performed at the same time as the background collection. Different instrument manufacturers may use different techniques for cell pathlength checks that may require the use of a reference or calibration fluid(s). A fringe-based method for determining cell pathlength is discussed in the appendix. Manufacturers' instructions and recommendations should be considered.

9. Procedures, Calculation, and Reporting

9.1 *Sample Introduction*—A representative sample is introduced into the infrared transmission cell, either manually or by an automatic pumping system. Autosamplers that hold a variety of oil sample container sizes are available from several manufacturers.

9.2 *Sample Integrity Check*—To ensure accurate and consistent results, the infrared spectrum of the sample should be checked to prevent partial filling of the cell or air bubbles passing through the cell during data collection from affecting the results. Multiple, automatic, computerized interpretation methods exist for this procedure. A wavenumber range from 3000 to 1090 cm^{-1} will assess multiple lubricant types. The exact absorbance intensity will depend on the spectral resolution and the pathlength of the cell being used. The manufacturer's suggestions and recommendations should be considered.

9.2.1 Petroleum based lubricants have their maximum absorbance in the 3000 to 2800 cm^{-1} range (or transmittance value close to 0 %T).

9.2.2 Ester based lubricants have their maximum absorbance in the 1390 to 1090 cm^{-1} range (or transmittance value close to 0 %T).

9.3 *Sample System Cleaning and Checks*—To ensure the minimum amount of sample cross-contamination or sample carry-over, either a minimum volume of the next sample can be flushed, or a volatile solvent can be flushed through the cell and the cell dried. If the cell is dried, the amount of absorbance from either the previous sample or residual wash solvent in the sample cell can be checked. This check is performed by the same spectral analysis operation as described above. The maximum absorbance intensity should be below a preset threshold in the monitoring region (that is, CH stretch in petroleum based fluids). For most petroleum and synthetic lubricants and wash solvents, this intensity will be less than 0.2 absorbance units. The optimal threshold will depend upon the specific system configuration, in that some systems are designed to "push-out" the residual oil sample and wash solvent with the next sample. The manufacturer's suggestions and recommendations should be considered.

9.4 *Data Processing*—All spectra will be processed in units of absorbance as a function of wavenumber. Calculated data must be corrected to the reference pathlength of 0.100 mm prior to reporting to account for cell pathlength variation that will be seen in commercially available cells. Any other spectral data treatment should occur prior to calculating results from the spectrum.

9.4.1 Spectral data processing results can be trended directly from the used oil spectrum (direct trending). The only spectral data treatment is the correction of the spectrum or results to the 0.100 mm reference pathlength and the application of fringe reduction algorithms to the spectrum, if required.

9.4.2 Spectral data processing results can also be obtained by spectral subtraction processing which requires a reference spectrum (spectral subtraction). Where spectral subtraction is used, processing of results is done from the difference spectrum that is generated by subtracting the appropriate new oil reference spectrum from the used oil sample. The used oil spectrum and new oil reference spectrum must both be corrected to the reference pathlength of 0.100 mm prior to subtraction and a 1:1 subtraction factor used. The subtracted spectral results can be trended over time and treated in a manner similar to those collected using the direct infrared method.

9.4.2.1 The most commonly used reference is a sample of new oil. If possible the new oil should be the same lot and drum as the used oil. An alternate approach that might yield a more representative reference would be to take a sample of oil one hour after reaching operating temperatures.

9.4.3 Post analysis data treatment can use simple multipliers and other scaling techniques; for example, "value $\times$ 100" at the request of maintenance personnel for ease in evaluation and presentation (see Annex A1).

9.5 *Spectral Analysis of Sample Data*—Selected spectral regions containing information relevant to condition monitoring are measured and reported. The regions analyzed are specific to different lubricating fluid types. New oil sample parameters can be used as the point from which to trend when initially implementing an analysis process for a lubricant type. Statistical analysis shown in the annexes also provides examples. Details of the spectral analysis process can be found in the annexes to this practice.

10. Effects of Oil Formulation

10.1 Differences in oil formulations can affect the results reported for the various measurements described in Annex A1. For example, Fig. 1 shows spectra of four 10W-30 oils in the carbonyl region where oxidation for petroleum lubricants is observed. In this example, absorbances for carbonyl containing additives in these unused oils formulations contribute nearly a factor of 2 difference in the oxidation result measured by direct trending.

10.2 Results should be:

10.2.1 Interpreted relative to values measured for unused oil of the same formulation, or

10.2.2 Trended directly from the component sample history.

10.3 Distribution profiles for results for different oil formulations should typically not be combined unless justified by field experience in condition monitoring programs.
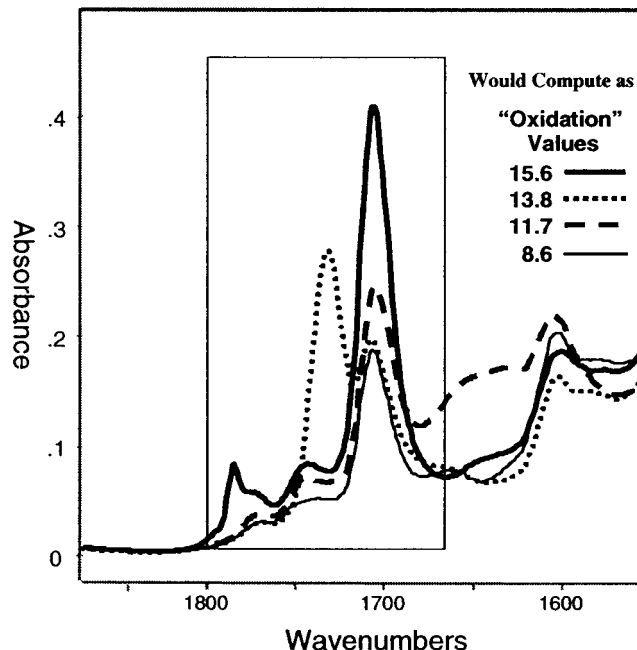
**FIG. 1 Example of Carbonyl Containing Components in New Oil
Formulations**

11. Keywords

11.1 additive packages; base stock degradation; condition monitoring; contamination; Fourier transform infrared; FT-IR; fuel; glycol; infrared; IR; lubricating oils; nitration; oxidation; petroleum based extreme pressure lubricants; petroleum lubricants; polyol ester synthetic lubricants; soot; sulfates; trend analysis; water

ANNEXES

(Mandatory Information)

A1. MEASUREMENT OF MOLECULAR PARAMETERS IN VARIOUS SYSTEMS—DIRECT TRENDING

A1.1 This annex does not purport to discuss all lubricant types. Measurement parameters for petroleum lubricants (for example, crankcase), extreme pressure petroleum lubricants and polyol esters are presented. As data becomes available, other lubricant types can be added to the annex.

NOTE A1.1—It is not the intent of this practice to establish or recommend normal, cautionary, warning or alert limits machinery or fluids. Such limits should be established in conjunction with advice and guidance from the machinery manufacturer and maintenance group.

A1.2 *Petroleum Lubricants (Typically Diesel Engines)*— Monitoring of diesel crankcase oil is one of the most common applications of lubricant condition monitoring. Condition monitoring in these systems is divided into contaminant monitoring (typically water, soot, fuel, glycol) and oil degradation monitoring (typically oxidation and nitration). Sulfation degradation products may arise from lubricant component breakdown but commonly arise from the by-products of sulfur containing diesel fuels. Measuring contamination from gaso-line is also possible but not as widely applied as comparatively few gasoline engines are enrolled in condition monitoring programs. In addition, monitoring of the zinc dialkyl dithiophosphate (ZDDP) based antiwear component of the additive package is also possible. The most common FT-IR condition monitoring parameters for crankcase engines are presented in Table A1.1, with some spectral measurement examples presented as a guide in using band areas. Throughout these examples, the use of integrated band area is preferred as noted in Practice E168 because it has been "found to be more accurate than peak-height measurements because one is, in effect, averaging multipoint data."

A1.2.1 *Water*:

A1.2.1.1 Water contamination is monitored in diesel crankcase lubricants by measuring the hydrogen-bonded OH stretch region given in Table A1.1. An example of varying levels of water contamination is shown in Fig. A1.1. In the following examples (except soot) the infrared spectrum is shaded down to

TABLE A1.1 Petroleum Lubricant (for example, Crankcase) Condition Monitoring Parameters—Direct Trending

Component	Measurement Area, cm⁻¹	Baseline Point(s), cm⁻¹	Reporting[A]
Water	Area 3500 to 3150	Minima 4000 to 3680 and 2200 to 1900	Report Value as Measured
Soot Loading	Absorbance intensity at 2000	None	Value × 100
Oxidation	Area 1800 to 1670	Minima 2200 to 1900 and 650 to 550	Report Value as Measured
Nitration	Area from 1650 to 1600	Minima 2200 to 1900 and 650 to 550	Report Value as Measured
Antiwear Components (Phosphate based, typically ZDDP)	Area 1025 to 960	Minima 2200 to 1900 and 650 to 550	Report Value as Measured
Gasoline	Area 755 to 745	Minima 780 to 760 and 750 to 730	Report Value as Measured
Diesel (JP-5, JP-8)[B]	Area 815 to 805	Minima 835 to 825 and 805 to 795	(Value + 2) × 100
Sulfate by-products	Area 1180 to 1120	Minima 2200 to 1900 and 650 to 550	Report value as measured
Ethylene Glycol Coolant	Area 1100 to 1030	Minima 1130 to 1100 and 1030 to 1010	Report value as measured

[A] Reporting values in absorbance/0.1 mm (see 6.1.2).
[B] Spectral characteristics of diesel and other noted fuels have been found to vary. Work is currently active on other IR measurement areas and techniques. The measurement listed can be used as a guideline but is not intended to be the only infrared based fuel contamination measurement. Checking suspect fuel sources is suggested to verify presence of indicator absorbance bands.
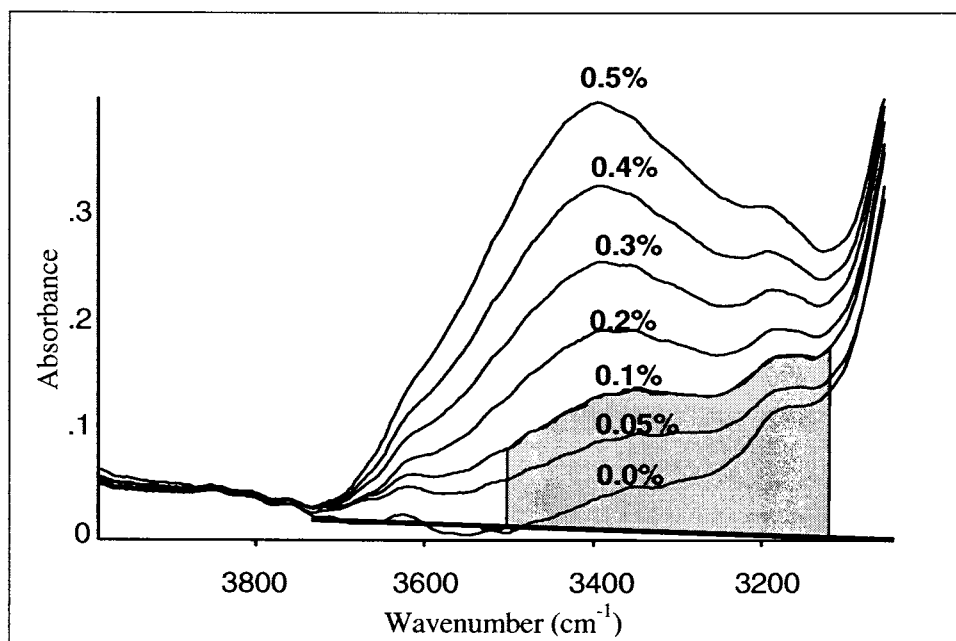

FIG. A1.1 Example of Integrated Band Measurement Area for Water in Crankcase Oil

the described baseline, giving a visual example of how the integrated absorbance area is measured. Measurement of these band areas by computer assisted techniques is common in most infrared manufacturers' software packages. For the water measurement in crankcase oils, the area under the curve between 3500 and 3150 cm⁻¹ is shaded, showing an example of the measurement described above.

A1.2.1.2 *Water Interferences*—High soot levels (~10 % w/w solids) may interfere with water measurements in diesel engines, but interference has not been seen until the soot limit has been exceeded (that is, > 3 to 5 % w/w solids). As a condition limit (soot) has already triggered, action should be taken irrespective of water. Exact quantitative measurement of soot is difficult (that is, % w/w) due to multiple infrared contributing factors as well as the many different soot measurement methods available.

A1.2.2 *Soot*:

A1.2.2.1 Soot loading is measured from the baseline offset at 2000 cm⁻¹ as described in the table above. Fig. A1.2 shows

some examples of spectra showing low, intermediate, high and very high soot loading levels (increasing levels from 1 through 5).

A1.2.2.2 *Soot Interference*—High water levels have been observed to interfere with the measurement of soot in internal combustion engine crankcases. However, this interference does not become significant until the water level is on the order of >5 % (50 000 ppm), levels which will immediately condemn the lubricant and require immediate maintenance action irrespective of any other indicators.

A1.2.3 *Oxidation, Nitration and Sulfation*:

A1.2.3.1 Unlike the previous examples, oxidation, nitration and sulfation breakdown products in crankcase oils can not be easily quantified by comparison to pure prepared standards. Here, there are a large number of different oxidation and nitration compounds that can be produced and gradually build up in the oil. Fig. A1.3 shows the measurement areas for oxidation and nitration product buildup monitoring, with the sulfation region highlighted in Fig. A1.4.
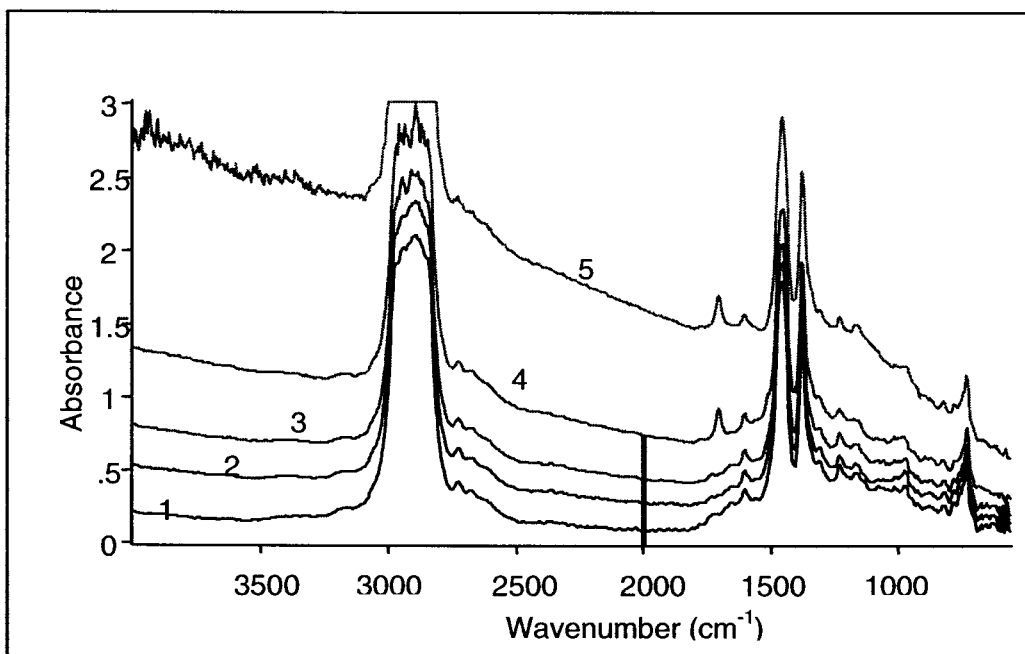
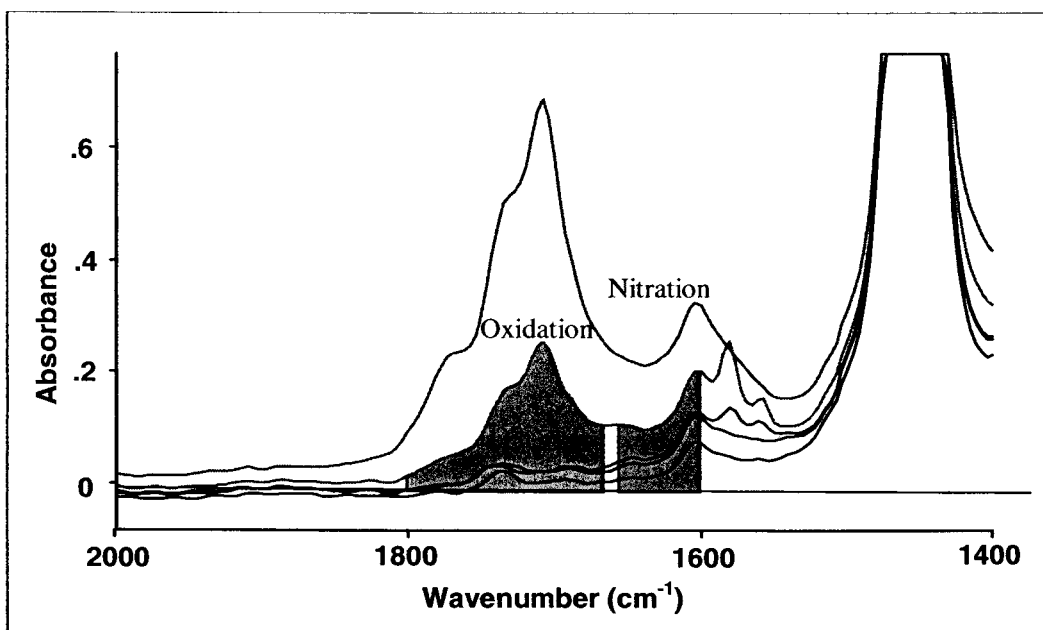FIG. A1.2 Soot Measurement in Diesel Crankcase Oils

FIG. A1.3 Oxidation and Nitration Measurement in Crankcase Oils

A1.2.3.2 *Oxidation, Nitration and Sulfation Interferences*—As in the soot measurement, very high water levels can generate false positives for oxidation and nitration. However, water levels of this magnitude will immediately condemn the lubricant. Very high (>5 %) glycol levels in a crankcase oil may start interfering with sulfation measurement, but again contaminant levels of this magnitude would dictate immediate maintenance action. Various additive packages, such as detergents, dispersants, antioxidants, overbase addi-

tives, etc. may also generate significant absorbance in the condition monitoring regions of interest. Blends of petroleum lubricants with significant amounts of ester whether part of the base stock package or as an additive will absorb strongly in the oxidation area. These lubricants are not presented at this time.

A1.2.4 *Fuel Contamination*:

A1.2.4.1 The possibility of fuel contamination may be indicated in diesel crankcase lubricants by measuring the peak at 810 cm^{-1}. Spectral characteristics of diesel (Fig. A1.6) and
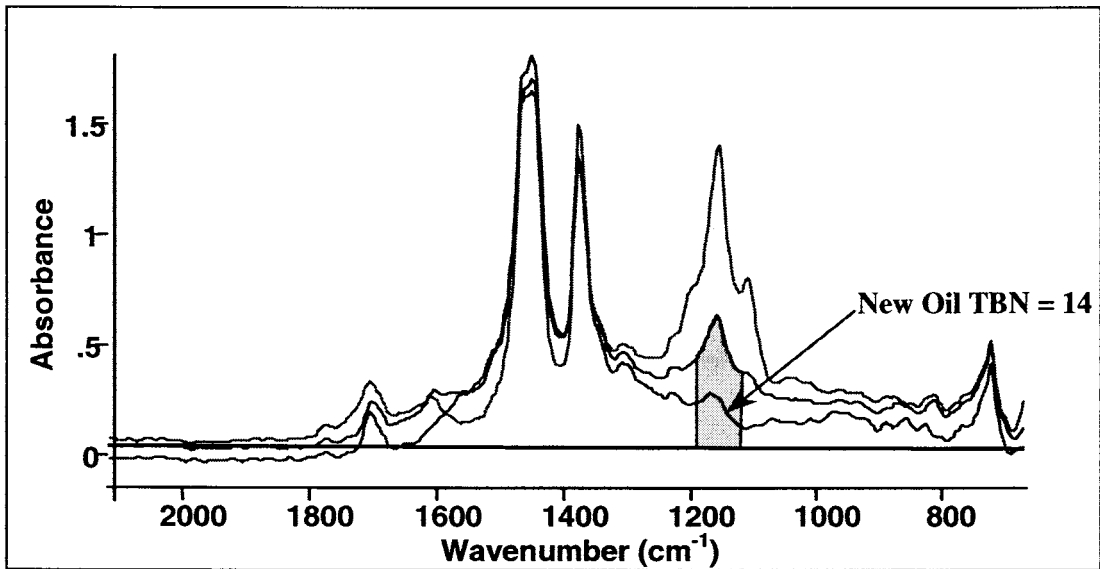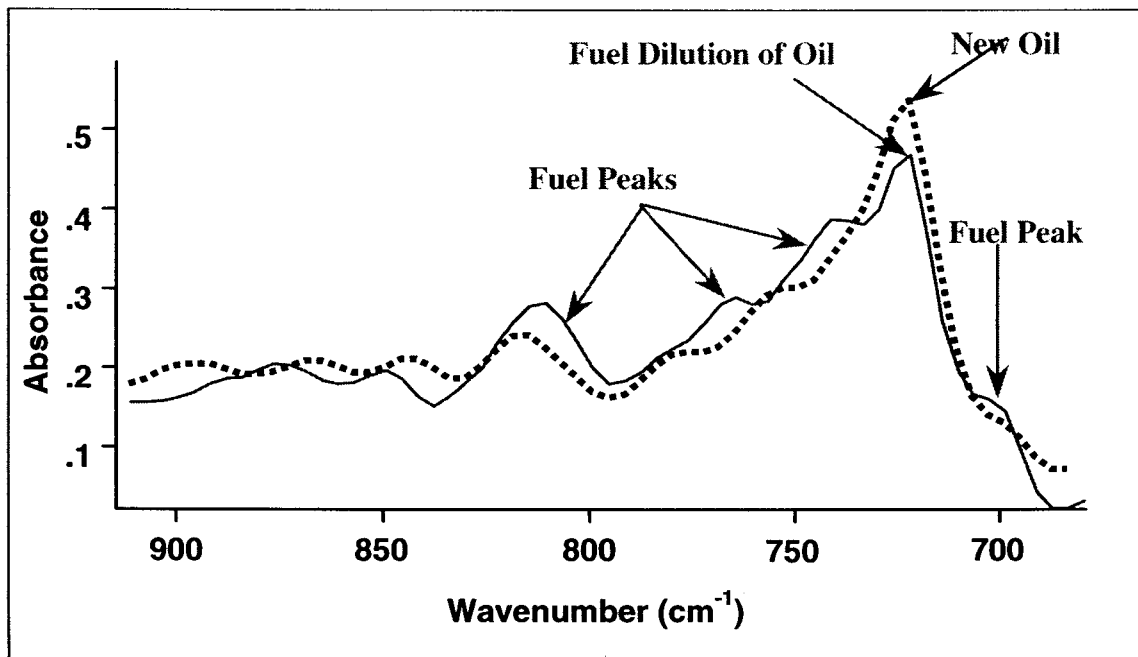
FIG. A1.4 Sulfation Measurement in Crankcase Oils

FIG. A1.5 Fuel Measurement in Crankcase Oils

other fuels noted in Table A1.1 have been found to vary. Work is currently active on other IR measurement areas and techniques. The measurement listed can be used as a guideline but is not intended to be the only infrared based fuel contamination measurement. An independent test, such as viscosity change, flash point, or gas chromatography can be used to confirm an indication of fuel presence by the FT-IR.

A1.2.5 *Glycol Antifreeze Contamination*:

A1.2.5.1 Glycol contamination is monitored in diesel crankcase lubricants by measuring the carbon-oxygen stretch region as noted in Table A1.1. Spectral characteristics of glycol contamination are shown in Fig. A1.6.

A1.2.5.2 Ethylene glycol will interfere with the ability to accurately quantify water level when present since it also contains hydroxyl groups. However, the converse is not true since glycol has other spectral features that are used for detection and quantification. Therefore, when glycol is present, water can be detected but not be reliably quantified using FT-IR. This is not considered a problem because of the greater significance the presence of glycol has to engine operation. As with fuel, the presence of glycol can be confirmed by gas chromatography or a colorimetric test or more commonly, corroborated using elemental analysis results from sodium and boron.
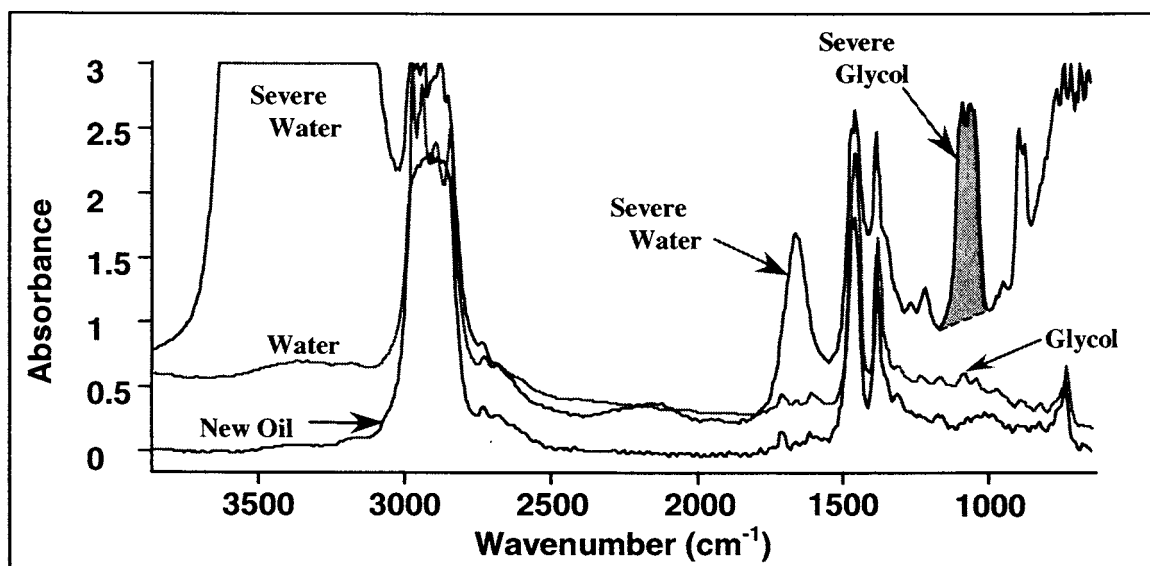
8

FIG. A1.6 Glycol Contamination Measurement in Diesel Engine Oils

A1.3 *Extreme Pressure (EP) Fluids (Typically Petroleum Gear or Hydraulic Fluids)*:

A1.3.1 In addition to the above crankcase oil analysis, condition monitoring of gear and hydraulic oil is also widely applied. In these systems, the most common parameters measured are water contamination and oxidative breakdown of the oil, which are presented in Table A1.2.

A1.3.2 *Water*:

A1.3.2.1 As water is the most common contaminant in crankcase oils, it is also the most common contaminant in gearboxes and hydraulic systems. In these systems, unlike the crankcase oils, water interacts differently with the EP additives, resulting in a different infrared response, and thus water is measured differently than in the crankcase lubricants. Fig. A1.7 demonstrates this different response. Water contamination is manifested as a general, horizontal baseline offset of the entire infrared spectrum. Here, the integrated area for the spectrum representing 3000 ppm (0.3 %) water is shaded. While this measurement becomes the principal water measurement in EP fluid systems, very high water levels (greater than 2 %) will begin to show a similar hydrogen-bonded OH stretch band as seen in the crankcase oils.

A1.3.2.2 *Water Interferences*—As the principal water measurement is based on the integrated absorbance with no local baseline correction, soot, dirt and high concentrations of infrared scattering particulates will generate higher than expected readings for water. However, typical gearboxes and hydraulic systems will not contain particulate levels high enough to cause a significant baseline offset and tilt. Wear metal analysis, particle counting or other applicable tests

should condemn gear and hydraulic systems that manifest such extreme particulate levels.

A1.3.3 *Oxidation*:

A1.3.3.1 The oxidative breakdown measurement shown in Fig. A1.8 in petroleum EP fluids is the same as in the petroleum-based crankcase fluids discussed in A1.2.3.2. Note that while Fig. A1.8 also shows an increase in sulfation by-products, not all EP systems will show this effect.

A1.4 *Synthetic Polyol Ester Lubricants (Typically Aero-Derivative Gas Turbines)*:

A1.4.1 Condition monitoring of high-performance aircraft turbine engines is widely applied in both the military and commercial aviation maintenance industries. In addition, many aero-derivative gas turbines are used in power generation, marine transport and other non-aeronautical applications. In these systems, the primary lubricant is a synthetic polyol ester and is available under a variety of different military specifications and commercial item descriptions and brand names. Table A1.3 lists the condition monitoring properties of interest measured by FT-IR along with the band measurement area and the baseline point(s).

A1.4.2 *Water*:

A1.4.2.1 Just as the infrared measurement for water was adjusted to account for the different interactions in the formulations in crankcase and EP oils, a different water measurement area is also required for the polyol esters. Fig. A1.9 shows the area under the curve that is integrated for the determination of water contamination in these systems, with the measurement highlighted for a sample containing 1000 ppm of added water.

TABLE A1.2 Petroleum Based EP Fluid Condition Monitoring Parameters—Direct Trending

Component	Measurement Area, cm⁻¹	Baseline Point(s), cm⁻¹	Reporting[A]
Water	Area 3400 to 3250	No Baseline	Value × 20
Oxidation	Area 1800 to 1670	Minima 2200 to 1800 and 650 to 550	Report Value as Measured

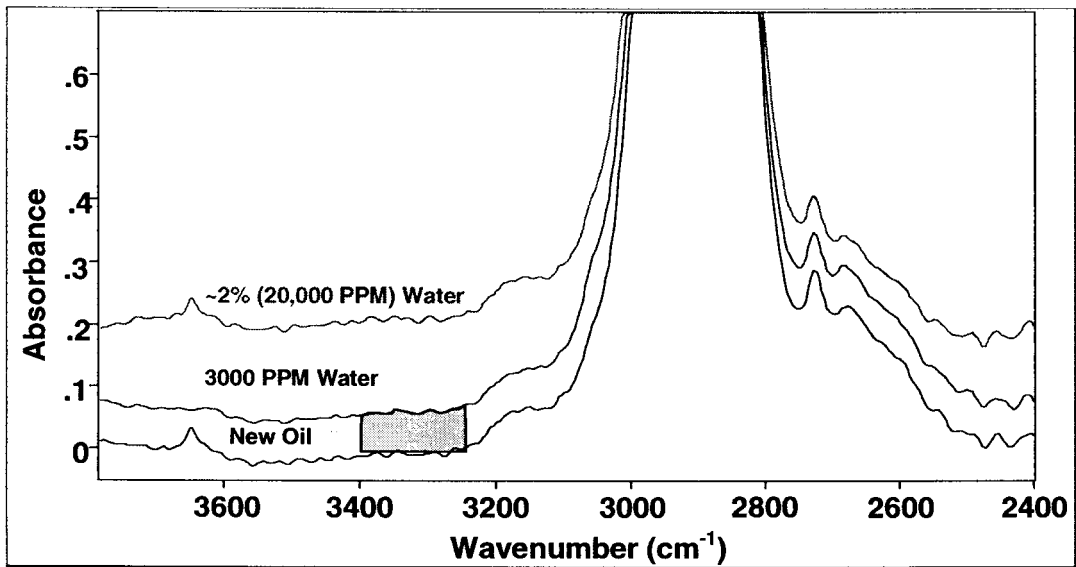[A] Reporting values in absorbance/0.1 mm (see 6.1.2).

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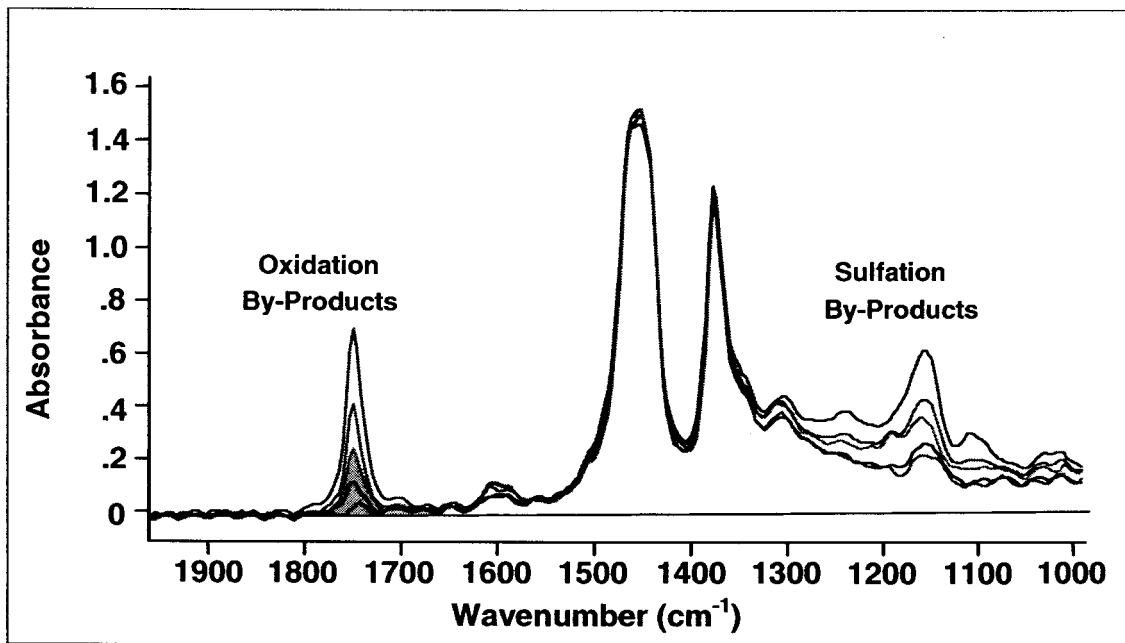FIG. A1.7 Water Contamination Measurement in EP Fluids

FIG. A1.8 Oxidation Measurement in EP Fluids

Note that the water in these systems shows up as a broad band, similar to the crankcase oils, but the strongest response occurs at higher frequencies than the crankcase oil (~3700 to 3600 cm^{-1} for polyol esters versus 3500 to 3150 cm^{-1} for crankcase oils).

A1.4.2.2 *Water Interferences*—The most significant interference found in the determination of water is interference from the polyol ester lubricant breakdown I (see A1.4.3). Under severe conditions of lubricant degradation, this band will begin to overlap and contribute to the integrated water

measurement area. As seen below in Fig. A1.10 however, this effect is only seen when the lubricant is already severely degraded, which dictates maintenance action from the degradation irrespective of the actual water level.

A1.4.3 *Ester Base-Stock Breakdown*:

A1.4.3.1 As the polyol esters are a different chemical system than petroleum based lubricants, degradation of the polyol ester lubricant produces different breakdown products.

TABLE A1.3 Polyol Ester Fluid Condition Monitoring Parameters—Direct Trending

Component	Measurement Area, cm⁻¹	Baseline Point(s), cm⁻¹	Reporting[A]
Water	Area 3700 to 3595	Minima 3950 to 3770 and 2200 to 1900	Value x 10
Ester Base-Stock Breakdown I	Area 3595 to 3500	Single point at 3595	Value x 10
Ester Base-Stock Breakdown II	Area 3330 to 3150	Minima 3950 to 3770 and 2200 to 1900	Value x 10
Antiwear Components (typically TCP)	Area 1025 to 960	Minima 2200 to 1900 and 650 to 550	Report value as measured
Fuel (JP-4, JP-5, JP-8)[B]	Area 815 to 805	Minima 835 to 825 and 805 to 795	(Value + 2) x 100
Other Contaminants in Polyol Ester Synthetics (for example, Petroleum Lubricants and Hydraulic Fluids)	Area 1425 to 1390 and 1090 to 1030[C]	None	Report value as measured

[A] Reporting values in absorbance/0.1 mm (see 6.1.2).
[B] Spectral characteristics of noted fuels have been found to vary. Work is currently active on other IR measurement areas and techniques. The measurement listed can be used as a guideline but is not intended to be the only infrared based fuel contamination measurement. Checking suspect fuel sources is suggested to verify presence of indicator absorbance bands.
[C] Alternate multivariate techniques such as PCR, PLS and factor analysis such as given in Practice E1655 can also be used.
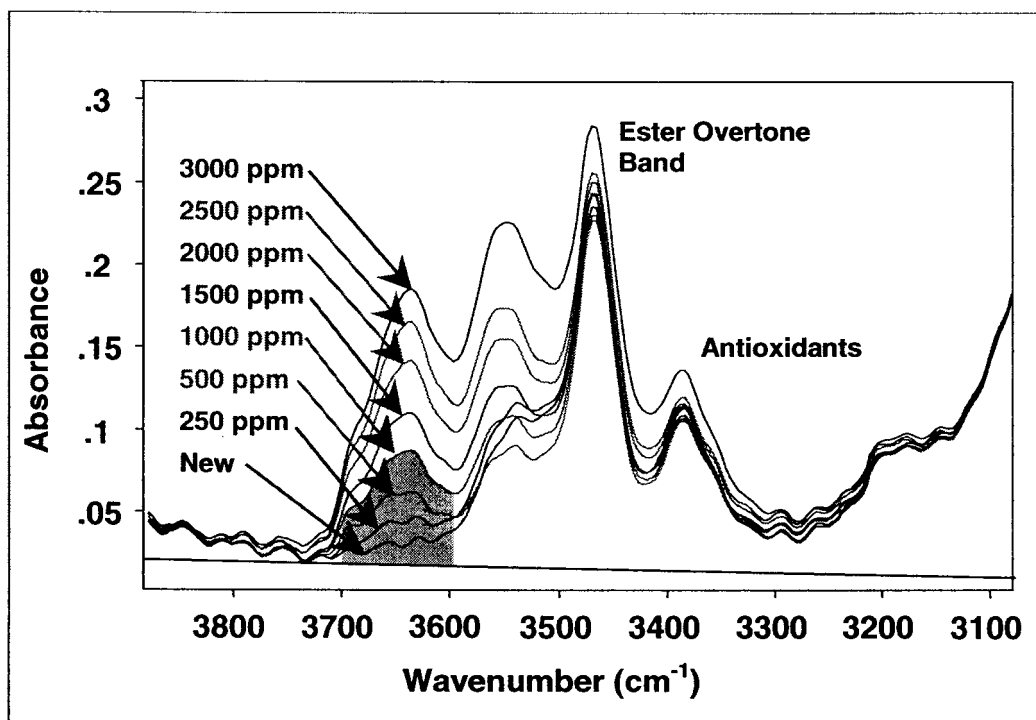

FIG. A1.9 Water Contamination Measurement in Polyol Ester Lubricants

The most common degradation pathway in ester based lubricants is the conversion of the ester into organic acids and alcohols.

A1.4.3.2 *Ester Base-Stock Breakdown I*—The resulting polyol ester degradation products are first seen between 3595 and 3500 cm⁻¹, and the measurement is noted as ester base-stock breakdown I in Table A1.3 and highlighted in Fig. A1.10. As this area is closely associated with the water measurement area, a localized, single point baseline at 3595 cm⁻¹ provides a correction for low levels of water buildup (Fig. A1.10).

A1.4.3.3 *Ester Base-Stock Breakdown II*—In addition to the breakdown area I, a second area associated with the traditional OH stretch (as measured for water in crankcase oils) also increases as the lubricant breaks down. This ester base-stock breakdown II area is also monitored as a measurement of degradation of the polyol ester lubricants. The breakdown II region is also highlighted in Fig. A1.10.

A1.4.3.4 *Ester Base-Stock Breakdown Interferences*—As noted above in A1.4.2.2 where excessive base-stock breakdown interferes with the water measurement, a similar effect has also been noted with the lubricant breakdown measurement. Excessive water levels may cause the lubricant breakdown reading to be higher than the actual level. Once again however, water levels of this magnitude will condemn the lubricant irrespective of the actual breakdown level.

A1.4.4 *Antiwear Components*:

A1.4.4.1 While the antiwear compounds used in crankcase oils and polyol ester lubricants are typically different species, the most common compounds used for both oils have a phosphate functional group. For this reason, the measurement area developed for monitoring levels and trends of ZDDP has been found to be equally useful for monitoring tricresyl phosphate (TCP). Fig. A1.11 shows varying levels of TCP blended into a polyol ester lubricant. As previously noted,
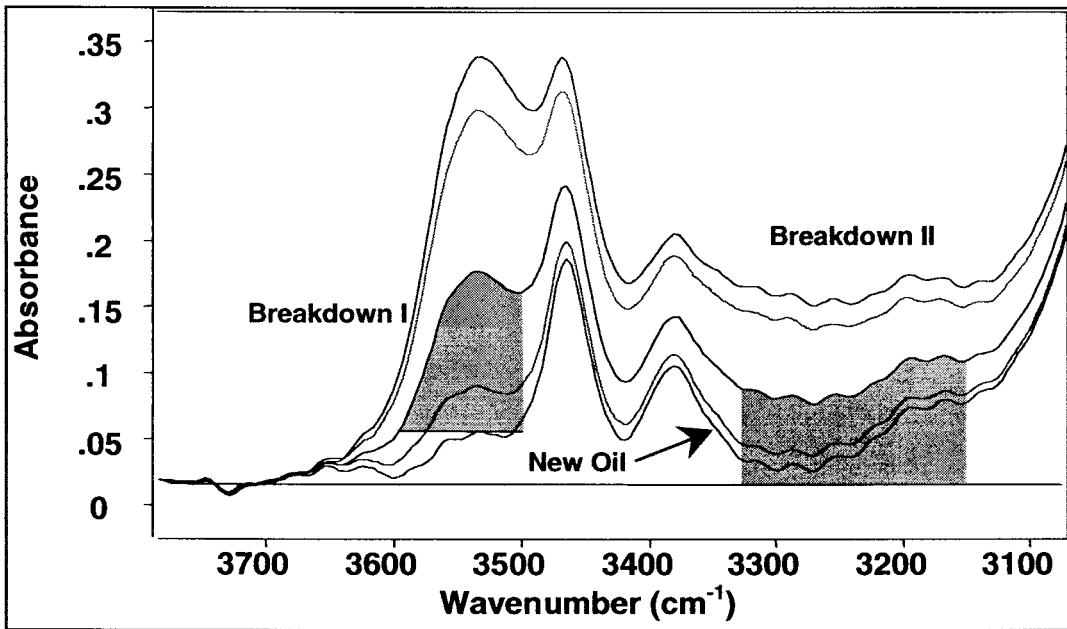
11

FIG. A1.10 Ester Base-Stock Breakdown Measurements in Polyol Ester Lubricants
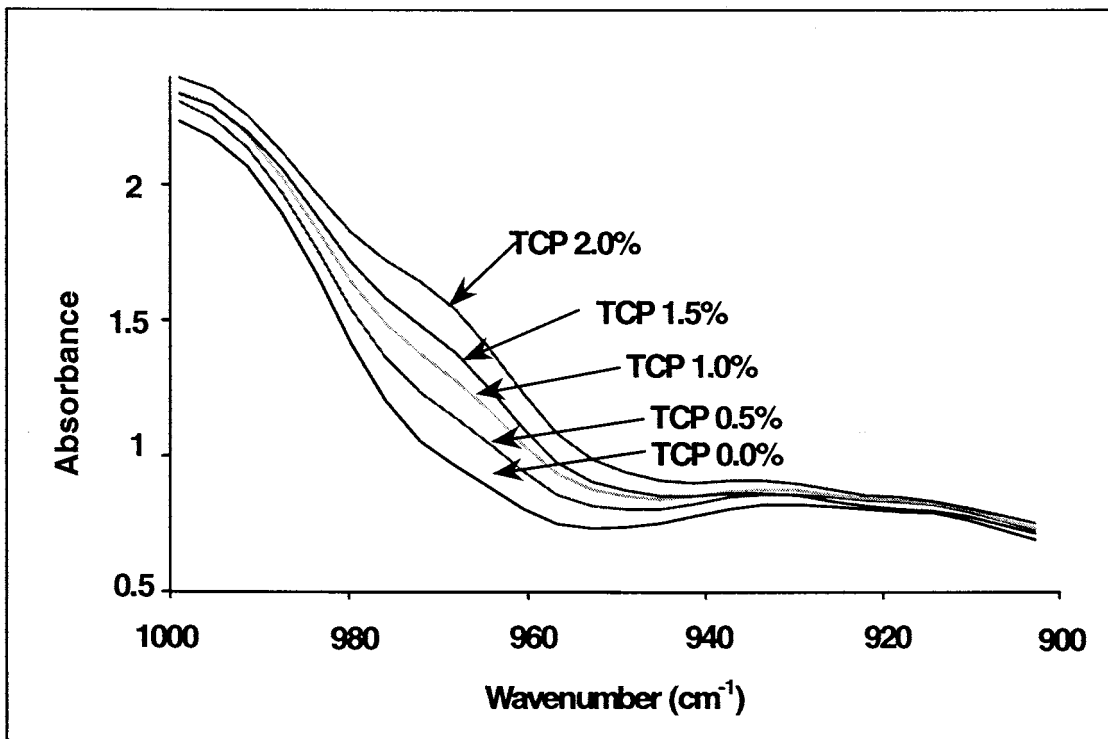

FIG. A1.11 Measurement of Antiwear (TCP) in Polyol Ester Lubricants

building calibration curves for measurement parameters (when pure or prepared standards are available) is possible. However, this is not necessary, as lubricant condition monitoring requires only reliable, repeatable measurements. Correlation of FT-IR measurements to physical values is not necessary.

A1.4.5 *Fuel Contamination*:

A1.4.5.1 Fuel contamination is monitored in polyol ester lubricants by measuring the peak at 810 cm^{-1} as given in section A1.2.4.
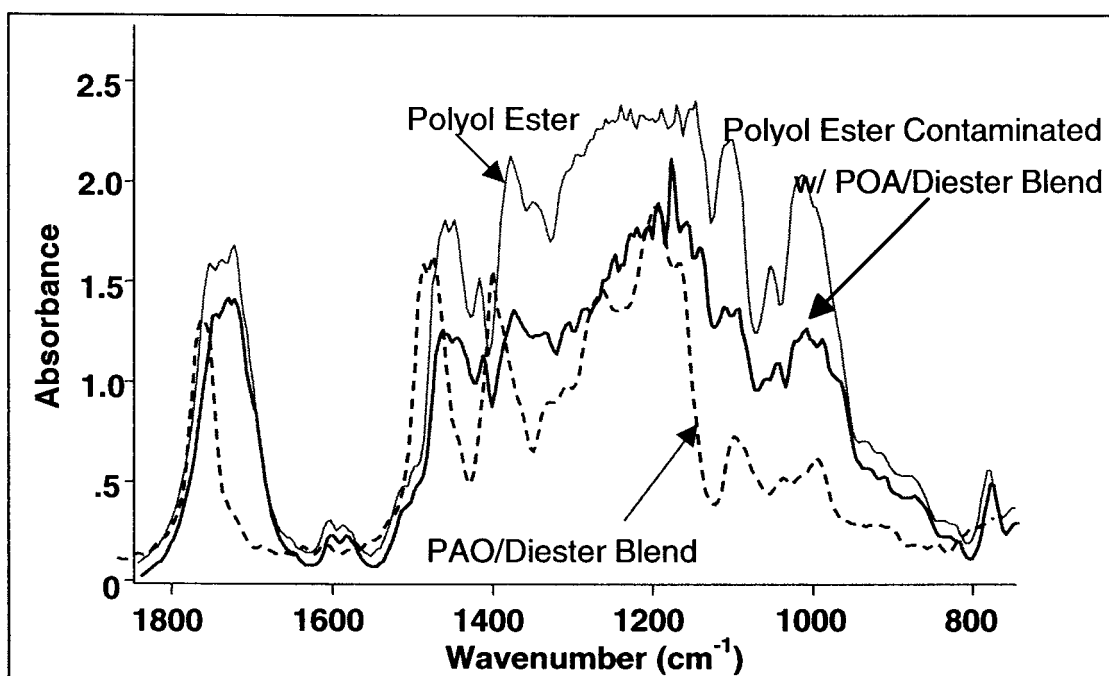
FIG. A1.12 Polyol Ester Lubricant Contaminated with PAO/Diester Oil

A1.4.6 *Other Fluid Contamination*:

A1.4.6.1 In addition to fuel contamination, foreign oils and hydraulic fluids may contaminate lubricating oils (for example, polyol ester contaminated by a petroleum based fluid). In most cases, identifying the presence of a foreign fluid is all that is required to generate an appropriate maintenance response. The wide variety of potential contaminates suggests an equally wide variety of measurement methods may be desirable. In addition, multiple frequency distributions may also be required and are not given here. The measurement areas given in Table A1.3 demonstrate the measurement used to indicate the presence of petroleum oils, phosphate ester oils, or polyalphaolefin (PAO)/diester blend oils contaminating polyol ester oils. Fig. A1.12 shows an example of polyol ester oil contaminated by a polyalphaolefin (PAO)/diester blend oil.

A2. MEASUREMENT OF MOLECULAR PARAMETERS IN VARIOUS SYSTEMS—SPECTRAL SUBTRACTION

A2.1 This annex does not purport to discuss all lubricant types. Measurement parameters for petroleum lubricants are presented. As data becomes available, other lubricant types can be added to the annex.

NOTE A2.1—It is not the intent of this practice to establish or recommend normal, cautionary, warning or alert limits for any machinery or fluids. Such limits should be established in conjunction with advice and guidance from the machinery manufacturer and maintenance group.

A2.1.1 Searching a spectral library to find the best selection for reference subtraction should not be used. This approach will generate incorrect results, particularly for antifreeze, fuel and water. It is better to make a choice of lubricant type and use it consistently if the oil type is not known. If an appropriate reference oil cannot be obtained, spectral subtraction should not be performed.

A2.2 *Petroleum-Based Crankcase Lubricants*—As stated in Annex A1, condition monitoring of crankcase oils is divided into contaminant monitoring and degradation monitoring. The analysis parameters for spectral subtraction are similar to those for the direct trending approach. Different laboratories have developed slight variation on these analyses. These different approaches are equally valid for trending, but will produce results that differ numerically. Consistent analyses should be applied for each application. Table A2.1 give examples of specific analysis parameters used to obtain data from difference spectra of used minus new oil. The information in the remainder of this section provides more detail about the individual parameters. The footnotes to Table A2.1 should be reviewed carefully.

A2.2.1 *Water Contamination*:

A2.2.1.1 Water has two characteristic absorptions in the infrared (3400 cm^{-1} and 1640 cm^{-1}) which make detection possible at around the 0.05 to 0.1-wt% level. While this is not as sensitive as some other techniques, it is at a level where problems from the presence of water in the crankcase could begin. Water is detected using a broad feature, centered around 3400 cm^{-1}, that is caused by stretching of the hydrogen-bonded hydroxyl (-OH) group. Water is measured as depicted in Fig. A2.1 using a single point baseline at 3700 cm^{-1} and at peak height at 3428 cm^{-1}. Alternatively, the water maximum can be measured relative to a two-point baseline drawn from 3740

TABLE A2.1 Petroleum Crankcase Lubricant Condition Monitoring Parameters—Spectral Subtraction

Component	Measurement (cm⁻¹)	Baseline (cm⁻¹)	Reporting Units	Footnotes
Water - A	Height at 3428	1 point at 3700	wt% (calibrated method)	9
Water - B	Maximum near 3400	2 point: 3120, 3740	A/cm or wt%, vol% calibrated method	1, 2, 3, 9
Soot - A	Height at 1950	No baseline	Abs/0.1 mm	4
Soot - B	Absorbance at 2000, 1950 or 1900	No baseline	A/cm or wt% (calibrated method)	5, 9
Oxidation - A	Max. Height 1800 to 1660	1 point: 1950	Abs/0.1 mm	6
Oxidation - B	Peak closet to 1709 in range of 1685-1725	1 point: 1900	A/cm	
Nitration	Max. Height 1650 to 1610	1 point at 1950	Abs/0.1 mm	7
Phosphate Antiwear	Min. Height 1020 to 930 (Negative peak height)	2 point 1020 and 930	Abs/0.1 mm	8
Gasoline	Area 734 to 721	2 point 734 and 721	wt% (calibrated method)	9, 10
Diesel	Area 817 to 804 Verification peak: Area 883 to 864	2 point 817 and 804 Verification peak: 883 to 864	wt% (calibrated method)	9, 10
Sulfation	Height at 1150	1 point at 1950	Abs/0.1 mm	
Ethylene Glycol	Height at 883 Verification peaks: Max ht 1098 to 1069 Max ht 1050 to 1030	1 point at 901 Verification peaks: Min 1110 to 1098 Min 1063 to 1051 Min 1029 to 1023	wt% (calibrated method)	1, 9, 11, 12

As noted in 9.4.2, for all components except soot, spectral subtraction is done followed by tilt correction over the range from 4000 to 650 cm-1. For soot, follow the specific recommendations in Table A2.1. After soot calculation, subtraction is done and a spectral tilt correction is applied from 4000 to 650.

NOTE 1—Calibrated methods for water and ethylene glycol are developed using standard preparations of water or ethylene glycol in appropriate used oil matrices.
NOTE 2—Peak maxima may be easily identified using second derivative spectra.
NOTE 3—Water measurements can be adjusted for glycol content.
NOTE 4—Soot calculated from unsubtracted sample spectrum.
NOTE 5—Soot calculated from subtracted spectrum, before tilt correction.
NOTE 6—Oxidation region for lubricant blends with diesters base oil can be adjusted to 1710 to 1660.
NOTE 7—Alternate method for nitration has been suggested to eliminate metal soap contribution using peak at 1630 with baseline minima in range 1655 to 1640 and 1620 to 1595.
NOTE 8—Phosphate antiwear is a negative peak height since it represents additive depletion compared to the new oil.
NOTE 9—Calibrated methods are based on standard linear regression models.
NOTE 10—Fuel calibrations are based on weathered fuel and need to be adjusted for local variation in fuels.
NOTE 11—Ethylene glycol calibrations based on 50:50 glycol:water mixtures.
NOTE 12—Glycol verification peak locations can best be derived from the second derivative spectrum.
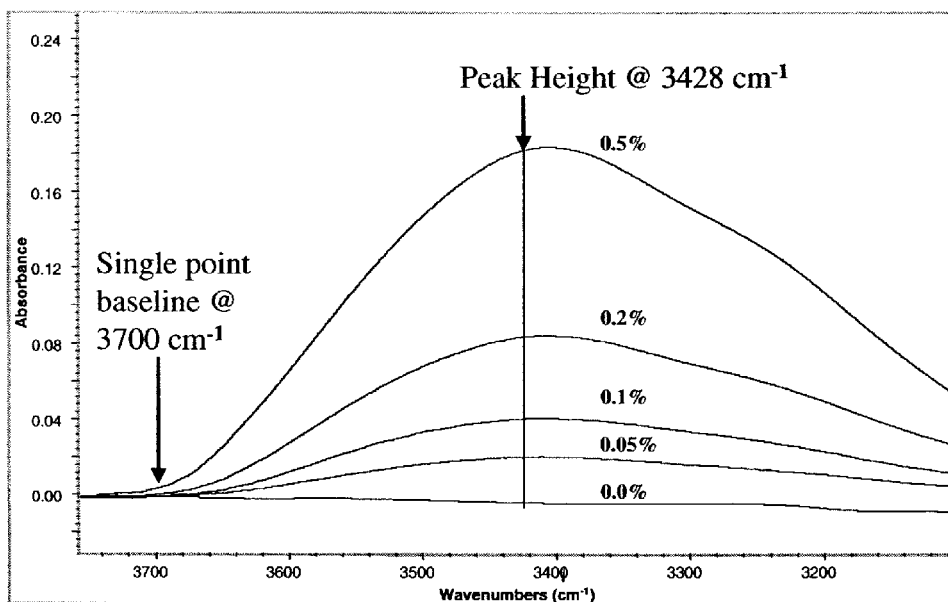

FIG. A2.1 Water Analysis Region for Petroleum Crankcase Lubricants

cm⁻¹ to 3120 cm⁻¹. The concentration values shown in the figure are for weight percent (wt%) water.

A2.2.1.2 *Calibration*—Calibration is typically done over the range from 0.05 to 0.5-wt%, but may go as high as 1.0 wt%

water. Beyond this point the behavior of water in petroleum lubricant becomes very non-linear when measured in lubricating oil by an optical measurement technique such as infrared. Standards are prepared locally by adding water to dry oil.

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Water standards should be freshly prepared and analyzed. Adequate mixing is necessary to obtain valid results. Mixing, sonicating or mechanical shaking for at least 15 minutes is considered adequate. Do not use plastic containers.

A2.2.1.3 *Interferences*—Ethylene glycol will interfere with the ability to accurately quantify water level when present since it also contains hydroxyl groups. However, the converse is not true since glycol has other spectral features that are used for detection and quantification. Therefore, when glycol is present, water can be detected but not reliably quantified using FT-IR. This is not considered a problem because of the greater significance the presence of glycol has to engine operation.

A2.2.2 *Soot Particles*:

A2.2.2.1 Suspended soot is the result of the incomplete combustion of fuel. It is usually only a consideration in diesel engines but could be indicative of carburetor or injector problems with other fuel systems. While soot has no specific frequency of absorption in the infrared spectrum, it causes a shift in the baseline of the spectrum due to absorption and scattering of light. Since there are no other spectral features in the region at 1950 cm^{-1}, this area is used to assess the level of soot in a sample as is shown in Fig. A2.2.

A2.2.2.2 In the case soot, the baseline absorbance is measured prior to reference oil subtraction. Because the soot absorbance obtained is a measure of the amount of tilt in the spectral baseline, a correction should be applied to the data to account for the contribution of the transmission cell to the baseline tilt if the background is taken without the cell in the beam path. This value can be significant in the case of a ZnSe cell, on the order of 0.2 absorbance units with clean oil in the cell as can be seen in the figure. The baseline shift caused by soot is affected by the amount of soot present and the effective particle size. The effective particle size is determined by the nature of the combustion system and the dispersants in the oil. This fact makes it difficult to directly assess or calibrate the

quantity of soot, so factors that relate the amount of soot to the infrared absorbance value must be established with the engines and lubricants of interest.

A2.2.3 *Oxidation (Carbonyl Oxidation Products)*:

A2.2.3.1 The broad feature centered at 1730 cm^{-1} is due to the presence of carbonyl-containing degradation products of oil. These have been identified as lactones, esters, aldehydes, ketones, carboxylic acids and salts. This feature is shown in Fig. A2.3. The baseline for carbonyl oxidation measurement, referred to as oxidation, is taken at 1950 cm^{-1} and the maximum peak height between 1800 and 1650 cm^{-1} is determined. Alternatively, some labs measure the absorbance of the peak closest to 1709 cm^{-1} relative to a single point baseline at 1900 cm^{-1}.

A2.2.3.2 For ester based synthetic oils; the measurement region can be shifted to range from 1710 to 1660 cm^{-1} to avoid the large carbonyl feature of the ester base oil. The broadness of the peak is a result of the wide variety of materials present. The point of maximum intensity will vary as the oil and conditions of its use are changed. The increase in peak height that occurs as the number of hours the oil has been run in the engine increases and has significance in the measurement of degradation related to TAN and viscosity.

A2.2.4 *Nitrogen Oxidation Products*:

A2.2.4.1 The sharp feature at 1630 cm^{-1} is the result of nitrogen oxide fixation into the oil as is shown in Fig. A2.3. The materials leading to this feature are nitrate esters. The measurement of the nitrogen oxide feature is done by choosing the maximum peak intensity over the range of 1650 to 1610 cm^{-1} with single point baseline at 1950 cm^{-1} or 1900 cm^{-1}.

A2.2.4.2 Because of the interference that can be seen over the same region from metal soap products, some people prefer to measure the sharp feature as a shoulder on the broad underlying feature as a more correct measure of nitration. The formation of nitrogen fixation products is most significant in
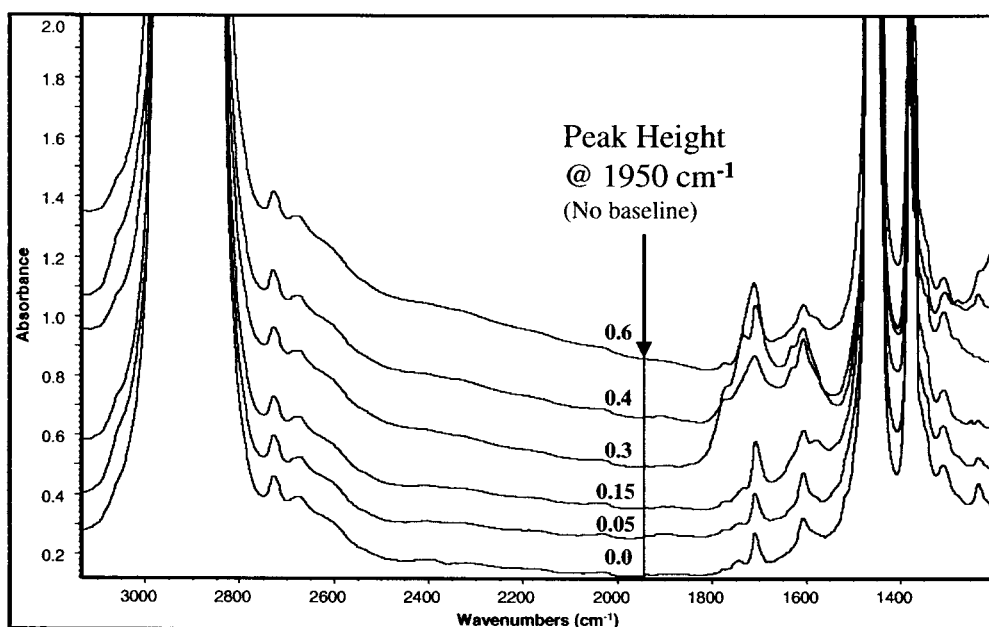

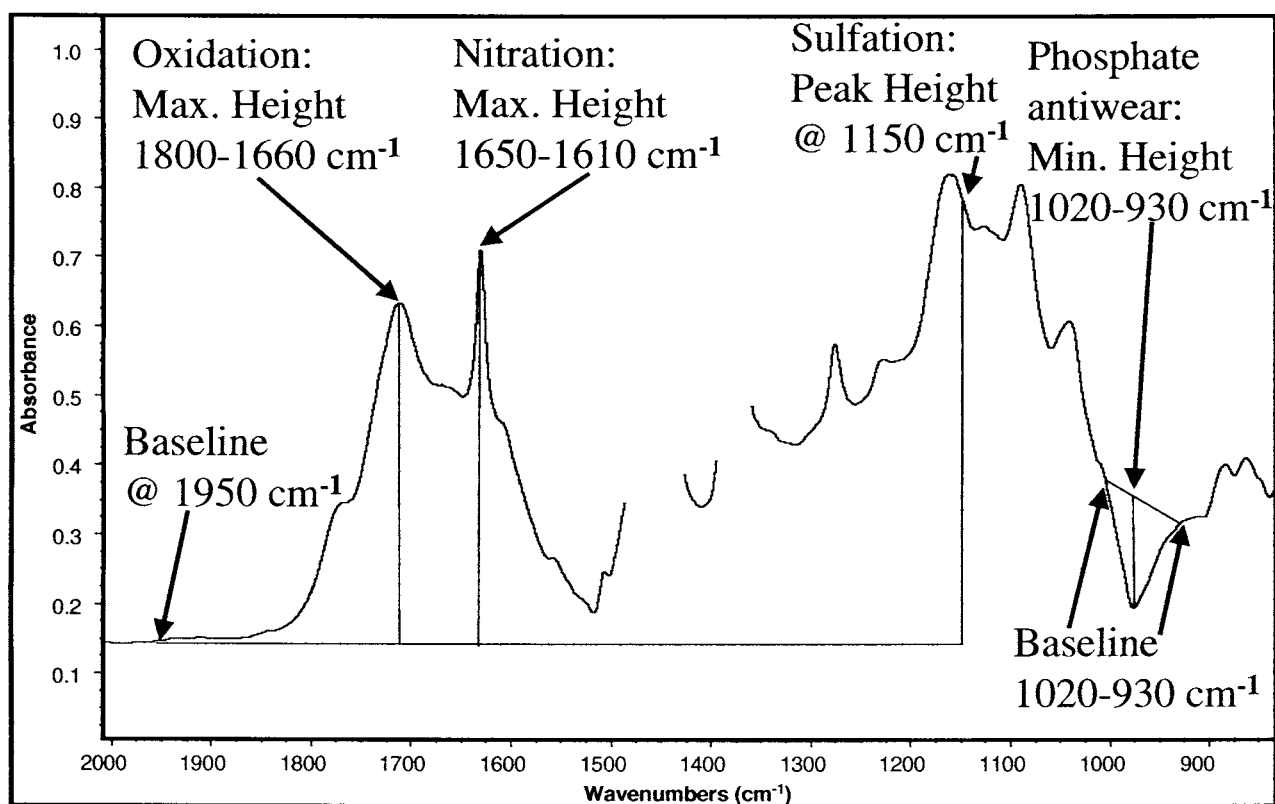**FIG. A2.2 Soot Analysis Region for Petroleum Crankcase Lubricants**

FIG. A2.3 Oxidation, Nitration, Sulfation, and Phosphate Antiwear Additive Analysis Regions

gasoline and natural gas engines as well as some diesel systems that use exhaust gas re-circulation.

A2.2.5 *Sulfur Oxidation Products*:

A2.2.5.1 Another broad spectral feature, centered around 1150 cm⁻¹ as shown in Fig. A2.3, is the result of sulfate compounds as well as overlap with oxidation products (carboxylate). A baseline point at 1950 cm⁻¹ is used.

A2.2.5.2 Sulfate material results from the introduction of sulfur from the combustion of diesel fuels or from the oxidation of sulfur from the base oil and additives in gasoline or natural gas engines. This band is a fairly specific measure of over basing additive consumption and directly relates to the TBN assay for engine oils.

A2.2.6 *Phosphate Antiwear Additive Depletion*:

A2.2.6.1 Monitoring the disappearance of phosphate anti-wear additive (typically zinc dithiodiphosphate) can indicate unusual wear or severe operating conditions. The depletion of these additives will occur prior to the point where the oxidation of the lubricant begins to accelerate, making its trending a useful indicator of the lubricant's remaining useful life. This component is monitored as a negative peak in the difference spectrum since the new oil will contain a greater concentration of the additive than the used oil. In this case the maximum negative peak in the range from 1020 to 930 cm⁻¹ with baseline points over the same range is used as shown in Fig. A2.3.

A2.2.7 *Fuel Residue*:

A2.2.7.1 As mentioned previously, the measurement of fuel residues or raw fuel is very difficult by any method. The main difference between the fuel and base oil is in molecular weight

or boiling range and the relative percentage of aromatic materials. Fuel has a lower boiling range and a higher percentage of aromatic material. Conventional methods such as gas chromatography or flash point make use of the lower boiling range, while the infrared approach examines the aromatic content to indicate if fuel is present.

A2.2.7.2 The spectral feature caused by aromatic bands over the range from 817 to 804 cm⁻¹ is used for this purpose. A peak area over this range is used as is depicted in Fig. A2.4. The figure shows the peak area increase as the wt% of weathered diesel fuel increases. In some cases, notably winter diesel fuel, the peak used for fuel residue is broader than that shown in Fig. A2.4. A wider range for the baseline points can be used to achieve better sensitivity, although this caused a reduction in the selectivity.

A2.2.7.3 The accuracy of measurement is strongly affected by the standard material used to calibrate the instrument and the level to which the fuel is evaporated within the engine crankcase. This is why weathered fuel should be used to calibrate the system and calibration of fuel should be done based on fuels obtained regionally. In addition there is a critical need to match the new-oil reference properly, as discussed earlier. It is the change in base oil aromatic content that is the major factor leading to errors from reference mismatch.

A2.2.7.4 Calibration for diesel fuel is typically done over a range from 2 to 10 weight percent and gasoline from 1 to 10 weight percent. Weathered fuel is used as the standard material. Procedures for preparing representative weathered fuel may vary, but the following should serve as a guideline: Diesel fuel
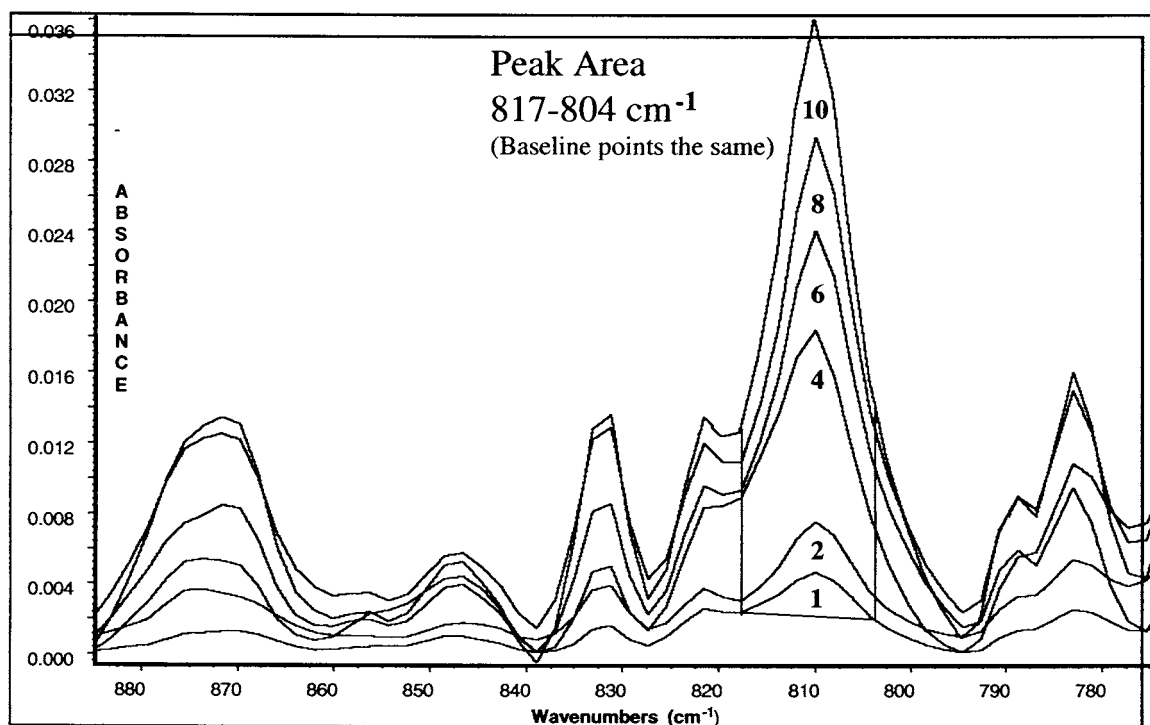
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FIG. A2.4 Diesel Fuel Analysis Regions for Petroleum Crankcase Lubricants

is brought to approximately 107 degrees Centigrade then held at this temperature for 30 minutes. This represents a loss of around 5 % of the original volume. Gasoline is heated at low temperature until around 40 % of the original volume is evaporated. Note: Great care should be taken when preparing these materials to avoid fire hazard or exposure to the vapors.

A2.2.7.5 Gasoline contamination detection is less problematic than for diesel fuel because of the higher relative aromatic content of gasoline. Gasoline is calibrated using a peak area over the range of 734 to 721 cm^{-1}.

A2.2.7.6 An independent test, such as viscosity change, flash point, or gas chromatography can be used to confirm an indication of fuel presence by the FT-IR.

A2.2.8 *Glycol Contamination*:

A2.2.8.1 This contaminant has characteristic absorptions in the infrared that make its detection possible at around the 0.1 % level. While this is not as sensitive as some other techniques, it is at a level where problems from the presence of these contaminants in the crankcase could begin. Glycol has the same broad hydroxyl (-OH) group feature, centered on 3400 cm^{-1}, that is seen in water. However, glycol has other characteristic peaks that differentiate it from water around 880, 1040, 1080 cm^{-1} as can be seen in Fig. A2.5.

A2.2.8.2 The peak height at 883 cm^{-1} with single point baseline at 917 cm^{-1} is used to quantify glycol since it is not subject to interferences to the same extent as the bands at 1040 and 1080 cm^{-1}. This effect can be seen by looking at Fig. A2.5 which shows a large sulfate band with glycol peaks on the right shoulder. Even though the peaks at 1040 and 1080 cm^{-1} are larger than the one at 880 cm^{-1}, it is very difficult to accurately

measure them in the presence of other oil breakdown product. Instead the peaks at 1040 and 1080 cm^{-1} are used to confirm the presence of glycol.

A2.2.8.3 In practice, a 2nd derivative spectrum can be used to find the correct peak location for these peaks and absorbance intensity limits can be used to trigger whether glycol appears to be present. Fig. A2.5 shows the intensity increase in the glycol bands at the concentration increases over the range from 0.05 to 0.8 wt%.

A2.2.8.4 *Interferences*—Glycol will interfere with the quantitation of water level when present, but the converse is not true. Therefore, when glycol is present, water cannot be reliably quantified using the FT-IR. This is not considered a problem because of the greater significance the presence of glycol has to engine operation. As with fuel, the presence of glycol can be confirmed by gas chromatography or a colorimetric test or more commonly, corroborated using elemental analysis results from sodium and boron.

A2.2.8.5 Glycol standards can be prepared over a range from 0.1 to 0.5 weight percent glycol using a 50:50 mixture of glycol-based antifreeze and water. Calculations should be made based on the actual amount of glycol-based antifreeze added, not on the amount of the 50:50 mixture. Glycol standards should be freshly prepared and analyzed. Adequate mixing is necessary to obtain valid results. Mixing, sonicating or mechanical shaking for at least 15 minutes is considered adequate. Do not use plastic containers.

A2.2.9 *Reporting of Data*—The values determined from the infrared spectrum for the components discussed in the preceding sections on spectral subtraction are reported in different ways because of the nature of the materials present. Certain of
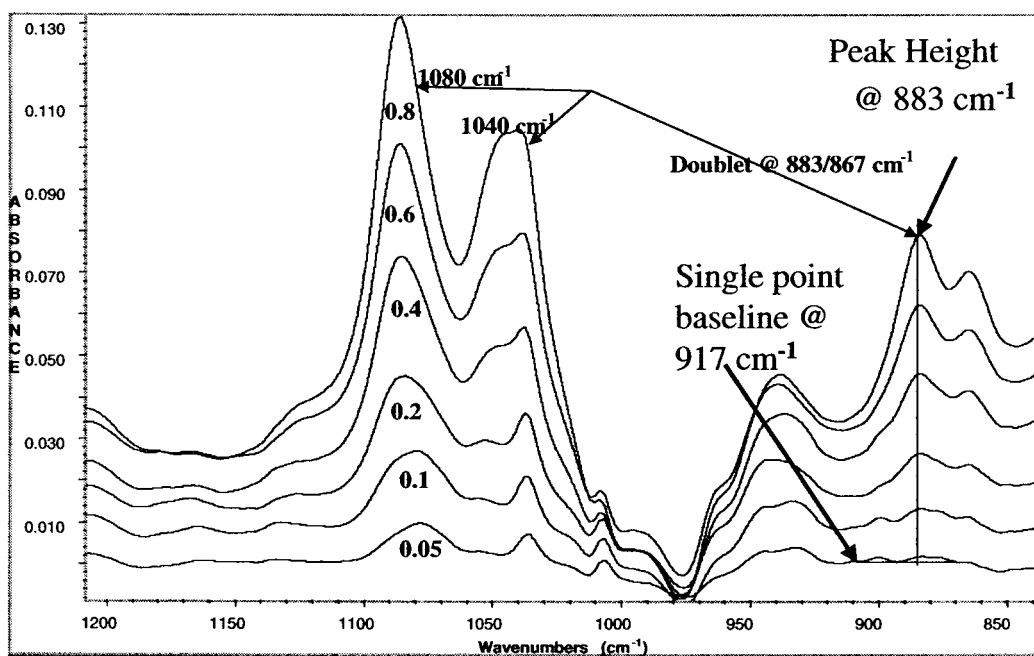
FIG. A2.5 Glycol Analysis Regions for Petroleum Crankcase Lubricants

the components are not calibrated, including oxidation, nitration, sulfation, soot, and phosphate antiwear additive. Others are calibrated, including diesel fuel, gasoline, water, and glycol. Recommendations for calibration procedures were included in previous sections of Annex A2.

A2.2.9.1 Oxidation, nitration and sulfation components are not reported as concentration values, because there are many different chemical compounds formed that contribute to the measured absorption. Since no single product is formed, standard materials are not available to generate the calibration curves needed to relate absorbance to concentration. Absorbance values related to the thickness of sample exposed to light are reported. The units used for reporting are absorbance per 0.1 millimeter (abs/0.1 mm), which relates directly to the peak intensities observed in the difference spectrum of used oil. The information for these components is most useful in trend analysis.

A2.2.9.2 The carbon particles that form soot do not cause localized absorption. Instead, an offset of the spectral baseline due to light scattering and absorption is observed. The magnitude of this offset is determined by the particle size of the soot as well as its concentration. The particle size observed is affected by the engine type and lubricant. Absorbance per 0.1 mm (abs/0.1 mm) values are reported as well.

A2.2.9.3 Phosphate antiwear additive, typically various forms of zinc dithio diphosphate in crankcase oils, is reported in absorbance per 0.1 millimeter (abs/0.1 mm) the same as the above oxidation components. However, the antiwear additive is reported as a negative value since in the used oil difference spectrum the peak is negative due to the depletion of the additive compared to the original reference oil.

A2.2.9.4 Fuel, water, glycol and gasoline are reported in weight percent values from calibrations with standards. The calibrations prepared for diesel fuel and gasoline may not accurately reflect the fuels in use in particular regions of the world. Because of this, these components should be calibrated with locally generated weathered fuel standards. In the case of water and glycol, these materials are typically very consistent since their chemical make-up does not typically change other than variation in the percent of glycol in antifreeze mixtures. These components should not be routinely calibrated locally because of the difficulty in making and analyzing standards.

A2.2.9.5 In practice, the approach taken to make use of the absorbance values for the non-calibrated components is to note their increase over time within an engine. From a plot or table of the change in absorbance with time, judgments about when to change the lubricant can be made.

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A3. DISTRIBUTION PROFILES AND STATISTICAL ANALYSIS

A3.1 Statistical analysis of historic data from a sufficiently large population of machinery can be used to explore possible relationships between condition monitoring test data and machinery failure modes. Such statistical analyses are a tool used in establishing alarm limits for condition monitoring tests. A thorough discussion of distribution profile analysis and alarm limit determination is beyond the scope of this practice. This annex merely provides a summary of distribution profile analysis for the interested user. More detailed descriptions can be found in Ref (1).

A3.2 *Frequency Distribution Plots—Histograms*:

A3.2.1 Distribution plots are a common tool used in the statistical analysis of condition monitoring data. The abscissa of the plot is the test data result, and the ordinate is the frequency at which a specific result occurs in the test population. Fig. A3.1 shows an example distribution plot. In this example, the data is from a population of 1910 diesel engine oils. The abscissa represents the integrated nitration result. A vertical bar is used to represent the number of oils for which the test result falls between the two abscissa values. For example, the tallest bar indicates that approximately 410 nitration values were between 7 and 8 cm^{-1}.

A3.2.2 To develop reliable alarm limits from statistical analysis of condition monitoring test data, the data must be approximately normally distributed. The histogram should have roughly a bell shaped appearance, and be free of multimodal features. The histogram in Fig. A3.1 shows an approximate normal distribution.

A3.2.3 When the FT-IR results are limited to non-negative values, and the median of the distribution is close to zero, the

distribution will not appear normal (see for example Fig. A3.2). While a mean and standard deviation can still be calculated, the user should verify that alarm limits based on these statistics are descriptive of the actual distribution. For example, only about 5 % of the values should fall above the mean plus two standard deviations.

A3.2.4 Multimodal distributions (Fig. A3.3) and broad, flat distributions (Fig. A3.4) should not be utilized for statistical analysis. Both examples are indicative of multiple sources of the same data, low ratio of normal data to failure data or poor measurement precision.

A3.3 *Sampling Considerations*:

A3.3.1 The data used in the statistical analysis should include a history of all machines of a like type for at least one overhaul period. The population should include a minimum of several hundred results for meaningful statistical analysis. If the population of machines is very large, less than one overhaul period may be sufficient.

A3.3.2 Unless analysis demonstrates otherwise, segregate and separately analyze results from different machine types and for machines using different oil formulations. Even machines with different sump sizes or different metallurgies should initially be analyzed separately. If the initial analyses yield similar limits for all test parameters, it may be appropriate to pool results.

A3.3.3 Random selection of samples does not necessarily provide for normally distributed results. Sequential samples over the course of the overhaul period are more likely to yield normally distributed results.
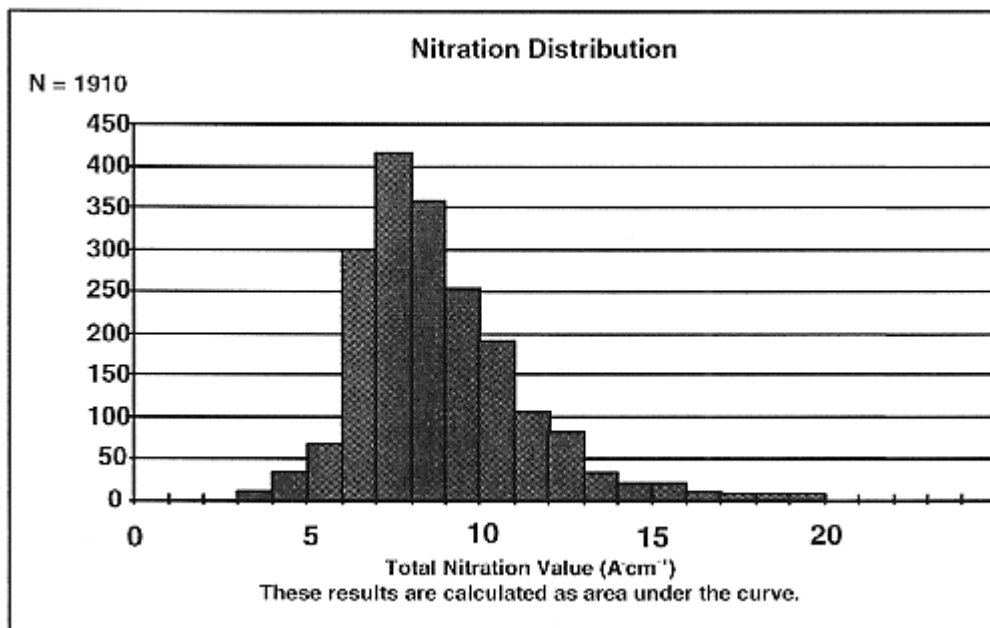

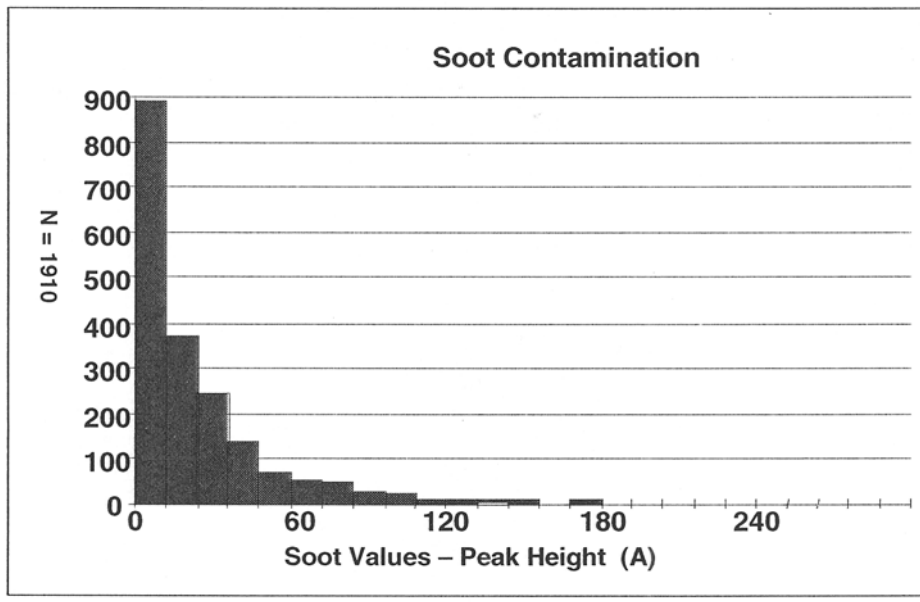**FIG. A3.1 Distribution of Nitration Measurements from ~1900 Diesel Engine Oils**

FIG. A3.2 Distribution of Measurements for Soot from ~1900 Diesel Engines
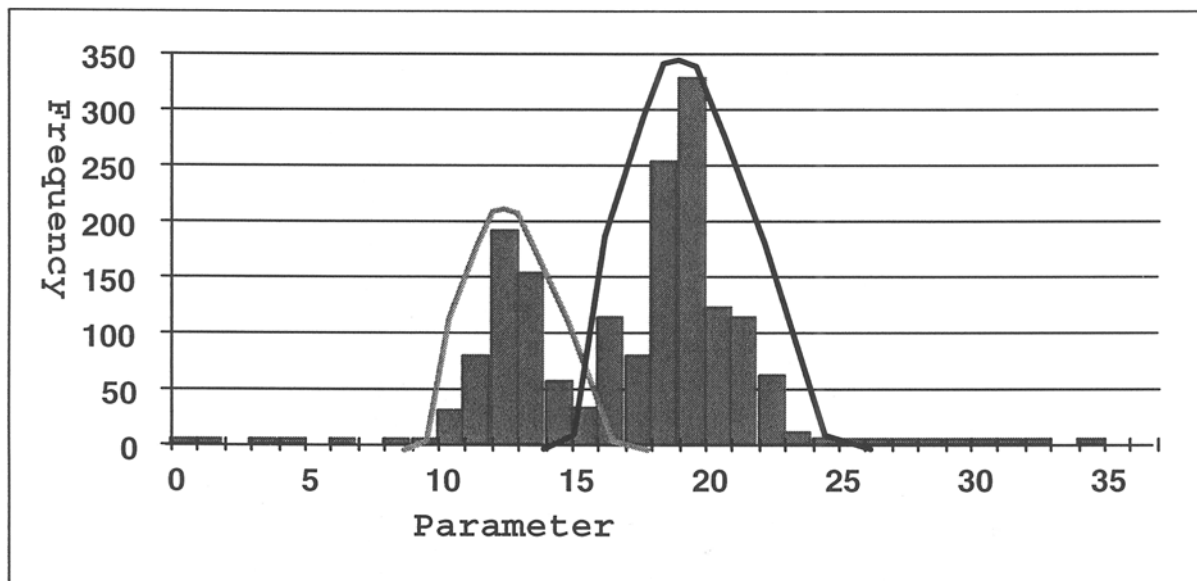

FIG. A3.3 Example of Multi-modal Distribution

A3.3.4 The population analyzed must include examples of all oil related failure modes, at typical failure rates. If too many examples of failures are included, the distribution may be broad and calculated limits may be too high. Alternatively, if failure modes are underrepresented, the distribution may be narrow, and the calculated limits may be too low.

A3.4 *Tentative Alarm Limit Calculations*—The specific calculations and limits used in a condition-monitoring program are established with advice and guidance from the machinery manufacturer and maintenance group. The following are provided only as an example.

A3.4.1 The user must first establish categories for test levels and alarms. Typically a warning or alert level will be used as an early indication of a potential problem, and an alarm level will be used as an indication of the need for immediate corrective action. More levels may be used, but at the expense of increased complexity.

A3.4.2 Plot the oil test result data on histograms, marking data that corresponds to oil related failures. Verify that the frequency distribution is approximately normally distributed.

A3.4.3 Calculate tentative limits based on the average and standard deviations of the oil test results.
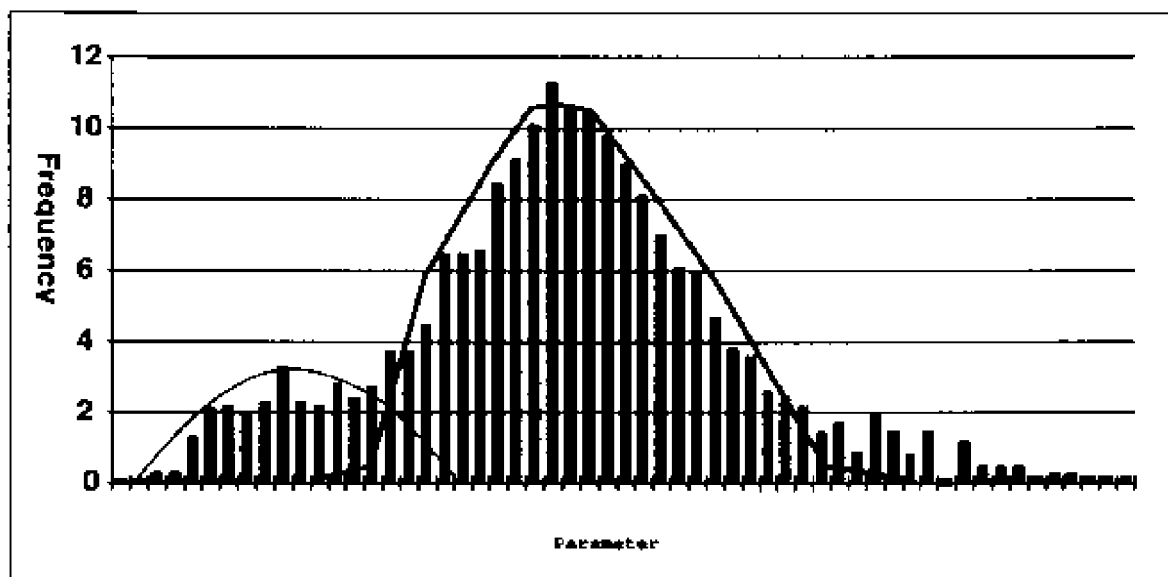
FIG. A3.4 Example of Broad, Flat Distribution

A3.4.3.1 Calculate a tentative alert (warning) limit as the average plus two standard deviations. This assumes a test result for which the value increases with time. For results where the value decreases with time, the limits would be the average minus the corresponding number of standard deviations.

A3.4.3.2 Calculate a tentative alarm limit as the average plus four standard deviations.

APPENDIX

(Nonmandatory Information)

X1. FRINGING EFFECTS IN INFRARED LIQUID TRANSMISSION SAMPLE CELLS

X1.1 When light passes from one material into another, its velocity changes as a result of the change in refractive index encountered. In addition, unless the refractive indices are an exact match, the amount of light transmitted through the interface is less than 100 %, as some reflection occurs. If the light passes through a thin film of material, such as a thin polymer sheet, there are two such interfaces encountered where reflections can occur. The result of this is that some light goes straight through and out the second surface, and some is reflected back at each side of the film. In addition, some of the light reflected from the second surface is again reflected back from the first surface, and then is traveling in the original direction. The result of such multiple internal reflections is that the pathlength of the radiation inside the film is increased, and the resulting light transmitted has suffered a phase delay from the original beam. This results in the two beams interfering (weakly) with each other. This interference is wavelength dependent and the result is that a spectrum plotted in wave-number shows a regular sine wave superimposed on the baseline.

X1.2 This effect is also observed when using a liquid

transmission cell because the air gap between the two windows creates the same interference effect as the polymer film described above. This optical effect can be used to measure the thickness of the empty cell, either from the spectral fringes or from the phase delay observed in the interferrogram (see Standard Practice E168). In the case where salt windows are used, when oil is introduced into the cell the fringe pattern is made much weaker because the refractive index of the salt window is relatively close to that of an oil sample. Thus, the fringe pattern essentially disappears from the spectrum. In the case where ZnSe windows are used, when the oil is introduced into the cell a significant fringe pattern is typically still observed because the refractive index of the ZnSe is much greater than that of an oil sample. If the empty cell is used to create the background spectrum, or when a ZnSe cell with exactly parallel window is used to collect the sample spectrum, these fringes will appear to be in the absorbance spectrum of the oil. Fringe reduction techniques can be used to avoid this problem. A common method is to locate the secondary (phase-delayed) centerburst in the interferrogram recorded for the empty cell and remove it by computer manipulation. The

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transformed single-beam spectrum then shows only minimal fringes. Other techniques based on computer fitting and removing the regular sine wave pattern in the absorbance spectrum, using cell windows with antireflective coatings, or slightly ″wedging″ the cell windows (<0.5° variance) have also been used to reduce fringing effects observed in the spectrum.

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