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FTIR Condition Monitoring of In-service lubricants: Ongoing Developments and Future Perspectives

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Abstract:

Condition monitoring of used lubricants by FTIR spectroscopy is reviewed and placed in context of the recently approved ASTM Practice E 2412-04 developed by the Joint Oil Analysis Program (JOAP) as a standardized means of trending oil/lubricant condition. A new *spectral reconstitution* procedure is presented and evaluated as an alternative means of executing this ASTM Practice, its objective being to minimize sample handling issues associated with the high viscosity of most in-service oils. Used diesel crankcase oils were analyzed in both their neat and diluted forms in 100 and 200 μm KCl cells, respectively, and the coefficient of variation (CV) for accuracy of the spectral reconstitution procedure was < 5% for all the parameters evaluated. Spectral reconstitution simplifies and facilitates sample handling, avoiding the need for peristaltic or syringe pumps, allowing up to 120 samples/h to be analyzed. The need for a solvent rinse between samples is avoided with cell clogging and tubing wear effectively eliminated. The spectral reconstitution technique also makes the ASTM Practice compatible with newer FTIR systems which are capable of quantitative determination of AN, BN and moisture.

Key Words: Condition monitoring, FTIR spectroscopy, spectral reconstitution, ASTM, automated analysis, lubricant analysis.

Introduction

In the field of lubricant analysis, condition monitoring is a general term used to describe analyses of in-service lubricants to provide an indication of the quality of a particular fluid to operate in its designed function. These analyses can include measurements of oil viscosity, wear metals, particle count, acid number (AN), base number (BN), moisture (H_2O), soot, nitration, sulfation, glycol contamination, oxidation, additive depletion, diesel or gasoline contamination, etc.. Such information can be correlated to engine, machinery and component failures and ensures that lubricants are changed only when required, usually when a critical parameter is out of specification. For crankcase lubricants the critical parameters are generally AN (indicative of oil oxidation), BN (measure of reserve alkalinity used to counteract acidity developed by oxidative processes, moisture (resulting in corrosion and/or lubricant failure) and soot load (resulting in increased wear and viscosity). In other mechanical systems, such as compressors, wear metals and AN are crucial, especially in relation to bearing wear and corrosion. For synthetic ester based hydraulic oils, ester breakdown products and moisture are critical parameters. The American Society for Testing and Materials (ASTM) has standardized analytical procedures designed to determine the more common condition monitoring parameters associated with lubricant quality.

IR spectroscopy has always played an important role in lubricant formulation and evaluation because of the detailed information on chemical composition provided by this technique, even though specific scientific literature on IR lubricant analysis is relatively sparse. In the case of in-service lubricants, most of the early work was related to observing bulk spectral changes, usually associated with additive depletion or gross oxidative changes in the oil (1-3). In 1983, Coates suggested the use of IR spectroscopy as a means of routinely monitoring the condition of used oils, based on studies of oxidative degradation of crankcase lubricants using both conventional IR and newly emerging FTIR instrumentation (4). In particular, he foresaw the potential utility of FTIR spectroscopy as a condition monitoring tool (5), and the inherent advantages of FTIR over conventional IR instrumentation, including simpler instrumentation, faster spectral acquisition, and spectral data manipulation capabilities, all which led to its rapid development.

In the late 1980's, Nicolet Instrument (now Thermo Instruments) marketed an FTIR-based Used Oil Analyzer. This system was a benchtop FTIR spectrometer equipped with a manually loaded attenuated total reflectance (ATR) sample handling accessory and included dedicated software to make spectral measurements considered to be related to condition monitoring parameters using spectral subtraction. This system was adopted by Caterpillar Inc. to analyze diesel engine crankcase oils as part of a warranty based predictive maintenance program. The screening capability of FTIR instrumentation was of particular interest to the U.S. Armed Forces as a potential means of reducing physical property testing (PPT), which was part of the mandate of the Technical Support Center (TSC) of the tri-service Joint Oil Analysis Program (JOAP). The main focus of JOAP was the coordinated use of atomic emission spectrometry to monitor wear metals in critical machinery, backed up in part by PPT. A critical assessment of FTIR condition monitoring was undertaken, starting with the Nicolet ATR system and later included Digilab (now Varian) and Nicolet transmission based systems. The study focused on defining FTIR methodology more rigorously, standardizing the analytical protocol and broadening its scope beyond petroleum-based crankcase oils to include synthetic lubricants (6). All the FTIR systems were designed primarily to track condition monitoring parameters for truck fleets and industrial equipment (7,8) and qualitatively assess whether the spectrum of a crankcase oil showed any evidence of excessive soot, water, oxidation products or the depletion of additives. Initial procedures advocated by the instrument manufacturers required that the spectrum of a used oil sample be analyzed in relation to its original fresh formulation or reference oil (9,10), which would be pre-recorded and archived in a data base. Thus with this approach a differential spectrum (11) rather than the used oil spectrum alone is the basis on which changes in oil chemistry are monitored. Although differential spectroscopy is considered a scientifically sound and rigorous approach to monitoring changes, in practice it has proved problematic and unworkable for used oils of undefined provenance. This was the conclusion of the JOAP studies (12, 13), determining that direct qualitative FTIR measurements of in-service oils in conjunction with simple straight trending of the data effectively monitors oil condition changes and substitutes for most PPTs (14). The procedural methodology developed came to be known as the JOAP protocol and was ultimately adopted by the U.S. military because of its simplicity as well as better overall reproducibility for the analysis of used oils relative to the differential approach (15). However, as there is merit to both approaches, depending on product, need and circumstance, both the reference oil based differential spectroscopic as well as JOAP type straight trending procedures are in use today (15, 16).

Standardization of the Methodology

The JOAP report (6) placed many aspects of the FTIR analytical condition monitoring protocol in the public domain, defining spectral regions and baselines based on standard addition experimentation, for three oil categories; petroleum, synthetic (ester), and hydraulic oils. The JOAP studies established trend relationships between conventional PPTs and spectral changes associated with three oil categories based on the assessment of over 5,000 in-service oils. Further assessment and standardization of this methodology was undertaken by ASTM Committees E13 (Molecular Spectroscopy and Chromatography). When FTIR condition monitoring became part of the ASTM Inter-laboratory Crosscheck Program run by D02 (Petroleum Products and Lubricants), it became apparent that without adherence to any standard, competing FTIR systems produced incomparable data for the same sample.

Although the spectral regions used by these systems to measure such oil condition parameters were generally similar, differences in methodology as well as in reporting formats were such that the FTIR data were only interpretable within individual laboratories or defined laboratory programs such as JOAP and Caterpillar. Thus, while FTIR analysis served well as a screening tool that allowed more expensive chemical or physical analyses to be limited to oils that were found to be problematic, the need for a standardized methodology to allow for inter-laboratory comparison of FTIR data also became apparent.

Ongoing work, directed by A. Toms, formerly of JOAP-TSC, led to the formulation of an ASTM E13 Practice which was submitted for ballot and officially approved in late 2004, entitled " E 2412-04 Standard Practice for Condition Monitoring of Used Lubricants by Trend Analysis using Fourier Transform Infrared (FT-IR) Spectrometry" (17). This practiced sets out the analytical parameters for condition monitoring of in-service oils using either straight trending or differential spectroscopic procedures for petroleum, hydraulic, and synthetic oils. ASTM Committee D02 is presently in the process of documenting, establishing and assessing a variety of used oil specific methodologies which will build on the foundation provided by the Practice. To better evaluate this FTIR Practice, Committee D02 is in the process of revising its Inter-laboratory Crosscheck Program to use collected spectra rather than the numerical data output provided by commercial FTIR systems. By processing the raw spectra, they can be normalized to a standard path length (100 μm) and resolution (8 cm^{-1}) and analyzed in accordance with the ASTM Practice (summarized in Table 1 for the category of petroleum-based crankcase oils) to provide comparable data for the unambiguous assessment of FTIR condition monitoring reproducibility and performance. Furthermore, commercial laboratories are increasingly making use of this standardized protocol to develop and market their oil analysis programs. Thus, with the advent of a defined practice and better means of its evaluation through the cross-check program, FTIR spectroscopy is positioned to continue its evolution towards becoming an ASTM method for the condition monitoring of lubricants.

Increasing Sample Throughput

For centralized laboratories, speed of analysis is paramount but even with the use of newer automated systems, FTIR condition monitoring it is presently limited to 2-3 min/sample largely due to the viscosity of the oils being analyzed. In this section, research conducted by the McGill IR Group in collaboration with Thermal-Lube on a new sample-handling procedure designed to facilitate and increase the sample throughput of FTIR oil condition monitoring is described. This work was undertaken following the development of new FTIR *quantitative* methods for the determination of AN, BN and moisture (H_2O) in new and used lubricants (18-19). What is common to these new methods is that the oils are pre-diluted and thus of low viscosity, allowing a simple low volume pumping/tubing system to be used (Fig. 1). On the other hand, such a system is not suited to handling neat, sooty or viscous oils routinely encountered in conventional FTIR condition monitoring analysis, which requires a peristaltic or syringe pump to pass oils through the system. Thus, an FTIR system configured to analyze oils for AN, BN, and H_2O cannot be used for conventional ASTM FTIR condition monitoring analysis. The possibility of applying the new ASTM Practice to diluted oils was thus investigated as a means of overcoming this incompatibility, with the attendant benefits of increasing the sample throughput and eliminating cell clogging and the need for solvent rinses.

To accomplish these objectives, the concept of "spectral reconstitution" has been developed and evaluated, taking advantage of the high precision spectral data available from FTIR spectrometers. This involves the dilution of an oil with a solvent containing an IR marker, the IR absorption of the marker being measured and used to mathematically remove the solvent spectral contribution and then to "reconstitute" the spectrum of the undiluted oil. In effect, one passes a diluted sample through the IR system but effectively make measurements as if the sample was neat. In the balance of this paper the spectral reconstitution procedure is described and assessed in relation to the ASTM Practice E 2412-04 for the analysis of diesel crankcase oils to determine whether similar data and analytical reproducibility are obtained as in conventional procedures that are designed to analyze neat oils.

Experimental

Samples and Reagents. Oil samples used for evaluating the spectral reconstitution procedure consisted of a variety of commercial multi-grade petroleum based motor oils as well as used bus oils obtained from the Montreal transit authority. Odorless mineral spirits (OMS), obtained from Thermal-Lube Inc. (Pointe Claire, PQ), was used as the oil diluent and spiked with chromium hexacarbonyl (Aldrich, Milwaukee, WI), which served as an IR measurable spectral marker.

Instrumentation. The instrument used for this study was an ABB Bomem WorkIR Fourier transform infrared (FTIR) spectrometer (Bomem, Quebec, PQ, Canada) equipped with a Model 223 Gilson autosampler (Gilson, Inc., Middleton, WI). A positive displacement micro-pump (Vissers Sales Corp., Aurora, Ont.) was used to pump the diluted oil samples from the autosampler into a 200-μm KCl transmission flow cell (International Crystal Laboratories, Garfield, New Jersey). A 3-way stainless steel valve (Vannes et Raccords Laurentian Ltée., Montreal, PQ) was used to switch the COAT® system from pumping lubricant samples to an air purge line supplied by a small air pump (5L/min), the air used to clear the cell and lines of sample as required (e.g., to take a cell background). The spectrometer, micro-pump and autosampler were all controlled by an IBM-compatible PC running proprietary Windows-based UMPIRE® (Universal Method Platform for InfraRed Evaluation) software (Thermal-Lube, Pointe-Claire, PQ, Canada) which automatically loaded solutions and collected and co-added 4 scans at a resolution of 8 cm^{-1} and a gain of 1.0. The software also processed the spectral data so as to reconstitute the spectrum of the undiluted sample and subsequently analyze it to obtain the ASTM E 2412-04 Practice condition monitoring parameter values as outlined in Table 1. The same samples in their neat form were also run manually in a 100 µm KCl cell and the resulting spectra processed directly as per the ASTM Practice.

Sample Preparation and Analysis. Samples were prepared for analysis by filling 20 ml plastic autosampler vials ~1/3rd full with oil and dispensing ~10 ml of OMS diluent containing the marker with a re-pipette so as to attain an oil/diluent ratio of ~1:2. The diluted samples were placed in autosampler racks each containing 14 vials, the autosampler tray holding 4 racks comprising a total of 56 vials. All the vials in each rack were then covered with a rubberized plate held in place and the tray was inverted several times to thoroughly mix the oil and diluent. The samples were then loaded into the autosampler tray for analysis and each autosampler run (56 vials) was initiated with the first two vials containing only diluent.

The first vial of diluent was used to ensure the IR cell was clean, with the second used to measure the cell path length (microns) employing a calibration previously devised by relating a distinctive OMS band to cell interference fringe counts. After pumping the first vial of diluent through the FTIR, the 3-way valve was switched to allow air to blow the lines and cell clean and dry (~45 sec). Subsequently, a "clean cell check routine", was run based on measuring the residual CH absorptions (< 30 mA units) to verify that the cell was clean and ready for a background spectrum to be taken. A single-beam background spectrum was taken through the empty cell, saved, and used to produce absorbance spectra from the single beam spectra of the subsequent samples to be analyzed.

After resetting the 3-way valve to the sample flow position, the autosampler proceeds to pump the second vial of diluent through the FTIR system and the spectrum recorded is used to calculate the cell pathlength and peak height of the marker. The analytical run then proceeds to automatically pump each sample into the cell, scan it, ratio its spectrum against the cell background and produce an absorbance spectrum. A "cell full routine" check is simultaneously executed to ensure there are not air bubbles in the cell. The UMPIRE software measures the height of the marker in the diluted sample to calculate how much OMS is present, then ratios out the OMS spectral contribution and corrects for dilution of the oil to reconstitute the neat oil spectrum. The reconstituted spectrum is then evaluated for its ASTM condition monitoring parameter values and outputs the data to file and computer monitor. This procedure is repeated until all the samples have been analyzed (~30 sec/sample). The run is concluded with a vial of diluent to clean the lines and cell. For the analysis of neat oils the samples were loaded manually, their single beam spectra taken and ratioed against an empty cell background and the spectra analyzed using the ASTM Practice.

Evaluation of Spectral Reconstitution Procedure. The basic premise associated with spectral reconstitution is that FTIR spectroscopy is both sensitive and accurate enough to effectively reconstitute the spectrum of the neat oil from its diluted counterpart. This can be assessed by comparing the reproducibility of both approaches as well as the accuracy by comparing the analytical results of the dilution technique relative to that of neat oils. In the case of spectral dilution, samples were diluted ~1:2 with OMS and measured in a 200 µm cell using the autosampling system, the data processed to produce "reconstituted" spectra and analyzed using the ASTM Practice. For the conventional procedure, neat oils were manually loaded into a 100um cell using a syringe, the spectra taken and processed using the ASTM Practice, with the cell thoroughly rinsed between samples with OMS. For reproducibility and accuracy, 10 samples of used motor oil were analyzed in duplicate on two separate days in both their neat and diluted forms. The data pairs obtained for each ASTM parameter were regressed against each other using a linear for both the diluted and neat sample sets. The correlation coefficients (R) and standard deviations (SD) obtained from the regressions as well as the mean difference (MD_r) and standard deviation of the differences (SDD_r) for the reproducibility ($_r$) between duplicate analyses were evaluated for both methods. To determine the accuracy of the spectral reconstitution technique, linear regressions were carried out between all diluted and neat oil results as well as determining the MD_a, SDD_a and coefficient of variation (CV) for accuracy ($_a$) for each component. In addition, the responsiveness of each ASTM condition monitoring parameter to Beer's law was assessed by the proportionate blending of new and used oils in ratios of 1:1, 2:1 and 1:2. The ASTM predictions of the mixtures were compared to the theoretical expected values calculated using the means of the individual new and used motor oil parameters.

Results

The spectral reconstitution procedure assumes that the use of a strong spectral marker in the diluent will allow one to extract the diluent spectrum and reconstitute the neat oil spectrum without significant loss of accuracy. The FTIR was programmed to measure the height of the spectral marker in the diluent spectrum and compare it to the height of the marker in the diluted sample spectrum and to remove the diluent spectrum from the spectrum of the diluted sample. The resulting sample spectrum was then corrected for dilution and normalized to a pathlength of 100μm and then assessed for the ASTM Practice parameters. To accommodate for the presence of the spectral marker, minor changes to some of the ASTM Practice regions and baselines were required; specifically the minima over the range of 2200 to 1900 cm^{-1} being adjusted to 2200 to 2030 cm^{-1} and the soot measurement was moved from 2000 to 2100 cm^{-1}. To allow direct comparison of both neat and spectrally diluted oil data, both were analyzed using these modified spectral regions to obtain comparable oil parameter data.

Reproducibility. Fig. 2a-d presents the between day reproducibility for oxidation (a,b) and moisture (c,d) for duplicate FTIR ASTM Practice analyses for neat oils and spectral diluted samples, respectively illustrating the linear relationship for between day reproducibility data for these and the other parameters. Table 2 summarizes the regression statistics as well as the mean differences for reproducibility (MD_r) for each of the eight ASTM parameters measured for diluted and undiluted samples. Most slopes and intercepts are close to the ideal of 1.0 and zero respectively, except for glycol and diesel. For all components, coefficient of variation (CV) of the diluted oils are quite similar to those of the undiluted oils and well under 5%, except for glycol where the mean is close to zero, resulting in large differences in the calculated CV values. For most of the parameters, the absolute MD_r values are similar to the regression SDs indicating that there is little bias between the duplicate runs. When the duplicate results for day-to-day reproducibility for all parameters combined are plotted against each other in a single graph for each method (Fig. 3a,b), it is clear that oil dilution with OMS does not degrade reproducibility to any apparent degree relative to that of direct spectral measurement of neat oils. The combined regression equations obtained for the undiluted and diluted oil samples, respectively are:

Results Day2 = 0.0009 + 0.9989 Results Day1 R = 0.9997 SD = 0.1528 [1]

Results Day2 = -0.0006 + 0.9891 Results Day 1 R= 0.9995 SD = 0.2359 [2]

Accuracy. To assess accuracy, the concordance between the spectral reconstitution data relative to the neat oil data was evaluated. Table 3 presents linear regression statistics for each component together with the mean differences of the values obtained for the undiluted and the diluted oils. The regression correlation coefficients and CV's, except for glycol, indicate excellent fits and accuracy, with the slopes indicating that the overall responsiveness of the dilution procedure is slightly greater than the neat samples. Comparing the magnitude of the MD_a values to the regression SDs indicates that there are biases associated with most of the parameters. Soot, diesel and water give higher average values in the dilution procedure. Fig. 4a,b are representative accuracy plots for the water and oxidation parameters illustrating the linear relationship obtained between the two methods as well as the relative extent of their slope and bias effects.

Fig. 5 combines the accuracy data for all parameters into a single plot, much like the combined comparative plots produced for reproducibility (Fig. 3,b). In contrast to Fig. 3a,b not all the points lie uniformly on a single line but appear to group into two linear segments, offset from each other. This is due to the parameters grouping into those having a negative bias (MD_a), such as soot, diesel and water in contrast to the rest of the parameters which have a slight positive bias relative to the neat oil parameter data. Although the source of these minor biases are not known, they do not detract from the individual linear relationships amongst the individual parameters and a regression through the grouped data in presented in Fig. 5 still results in a good relationship:

Neat Oils = - 0.311 + 1.032 Diluted Oils R = 0.9803 SD = 1.48 [3]

Since the accuracy concordance data presented in Table 3 was obtained using slightly modified spectral regions and baselines rather than those exactly specified by the ASTM Practice, the neat oil data was reprocessed using the exact ASTM specifications and compared to that that obtained using the diluent defined regions. This adjustment resulted in no significant changes to the CV's obtained for reproducibility or accuracy data presented in Tables 2 and 3, respectively.

Although the ASTM Practice is only considered a qualitative trending procedure, it is presumed that the methodology responds proportionately to changes made in the parameters being measured. To examine that dilution does not impinge on this expected response, new and used motor oils were blended gravimetrically and the resulting blends analyzed in triplicate and their means compared to the calculated ideal values expected based on data obtained from the neat samples. Table 4 presents the MD_a obtained for the blends analyzed for the eight ASTM Practice parameters relative to their ideal values, indicating that no significant biases appeared for any of the components relative to their calculated values. Fig. 6 illustrates that the expected proportionality of the IR response was not compromised by the dilution procedure relative to the analysis of neat samples producing the following regression equation:

$$\text{Theoretical} = -0.094 + 1.002\ \text{Actual} \quad R = 0.9998 \quad SD = 0.137 \quad [4]$$

Thus the overall results of this experimental work indicates that spectral reconstitution appears to be a promising alternative approach to carrying out condition monitoring of used petroleum based lubricants using the ASTM Practice.

Future Perspectives

FTIR oil condition monitoring is still an evolving analytical methodology and is finding wide application as a rapid oil quality screening technique. The original JOAP protocol is now being used by many commercial oil analysis laboratories and its recent acceptance as an official ASTM Practice will further standardize the procedure. This analytical capability is being supplemented by new quantitative FTIR procedures for the determination of AN, BN and H_2O, but which are incompatible with conventional condition monitoring sample handling systems. The results of this research indicate that high quality oil condition monitoring data can be obtained using spectral reconstitution and using this technique AN, BN, H2O as well as conventional condition monitoring procedures all now be carried out using the same instrument. For other systems, spectral reconstitution promises improved sample throughput (up to 120 samples/h) on automated FTIR systems without the need for peristaltic or syringe based pumping systems, thereby avoiding additional solvent rinses as well as minimizing cell clogging and wear.

The new ASTM practice, although generally applicable to petroleum hydrocarbons, some synthetic esters and glycol based hydraulic oils, addresses only a small part of the many classes of lubricants (20) found in the industry (Table 5). Although the three classes addressed in the ASTM Practice comprise a significant portion of the total lubricant volume commonly analyzed, only the FTIR condition monitoring of petroleum hydrocarbons is relatively well defined. The methodology becomes more tenuous as synthetic oils come into play, synthetic esters and glycols coming in many versions and combinations. As such, further refinement and evolution of FTIR condition monitoring methodology within the ester category (e.g., synthetic phosphate vs. carboxylic esters) is required as it is for glycols. In addition, further basic research is required to both define the condition monitoring parameters of interest to be trended for many of the oil categories outlined in Table 5 as well as how they should be measured spectrally. Given the spectral diversity of base oils and/or blends thereof, a more versatile approach might be to develop algorithms to categorize oils into predominant spectral types and define the parameters to be measured accordingly. Such algorithms have been developed to characterize and identify unknown bacteria (21) and similar approaches could well be used to categorize oils to implement an analytical protocol appropriate to the oil in question. Although the industry still has a long way to go before such methodology will be developed and approved, it is something to strive towards in the longer term. In the more immediate time frame, the acceptance of the ASTM practice is a definite step forward in this process and provides the foundation for development and defining a more rigorous ASTM method.

Even with the ASTM Practice approved, there are still a variety of issues which need to be addressed, including the standardization of instrument apodization, using a fixed instrument resolution (8 vs. 4 cm^{-1}), data spacing (4 vs. 2 cm^{-1}), the type of background (through cell vs. air), amongst others. The D02 Committee is actively pursuing changes in the FTIR portion of the Inter-laboratory Crosscheck Program for in-service lubricants. The intent is to collect absorbance spectra rather than examining instrument/software reported data, normalize all the spectra and then process the spectral data as per the ASTM Practice. This approach should yield a spectral database from which to gauge how reproducible FTIR can be between laboratories analyzing the same sample, a comparison which has effectively not been possible to date because reporting units and other variables (resolution, path length, etc.) vary for commercial FTIR based condition monitoring systems.

In terms of this work, spectral reconstitution appears to provide a very useful alternative means of obtaining data for the newly defined E 2412-04 ASTM practice, allowing improved sample throughput. This development allows FTIR instrumentation designed to automatically execute quantitative AN, BN and moisture analysis to also be used for routine condition monitoring analyses as well others to modify their FTIR spectrometers to facilitate more efficient and simpler operational protocols.

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List of Figures

Figure 1. COAT system for the quantitative FTIR analysis of AN, BN, H2O.

Figure 2a-d. Between day reproducibility for oxidation (a,b) and moisture (c,d) for duplicate FTIR ASTM Practice analyses for neat oils and spectrally reconstitued samples, respectively.

Figure 3a,b. Combined plots for reproducibility of all parameters obtained for 200 (a) and 100 (b) µm cells in which diluted and neat oils were analyzed by the ASTM procedure. Diesel values were divided by 10 to keep them on the same relative scale as the other parameters.

Figure 4a,b. Plots of data for (a) oxidation and (b) water for neat oils analyzed in a 100µm cell vs. OMS-diluted oils analyzed in a 200µm cell corrected for dilution and pathlength.

Figure 5. Combined parameter plot for accuracy of the diluted oil results vs the neat oil results.

Figure 6. Plots of measured vs theoretical data for the fresh/used oil blends indicating that spectral reconstitution does not compromise the proportionate responses expected.

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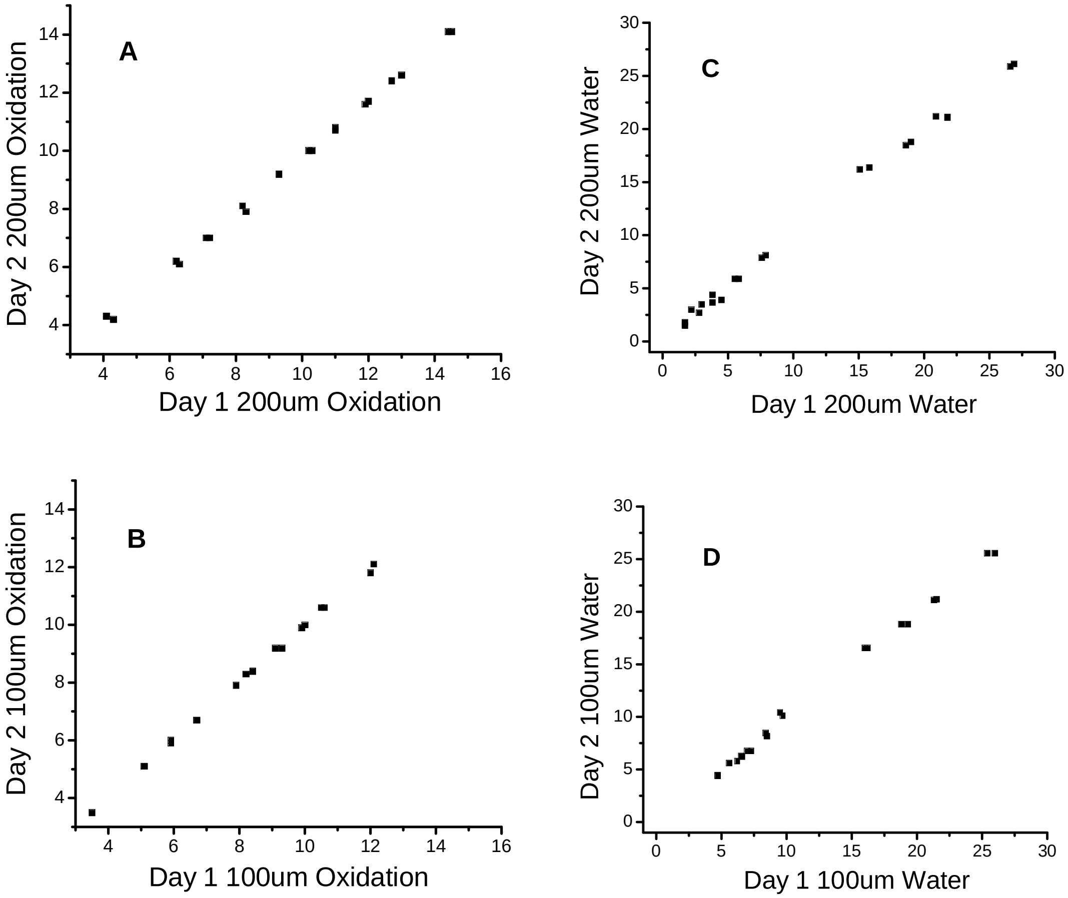

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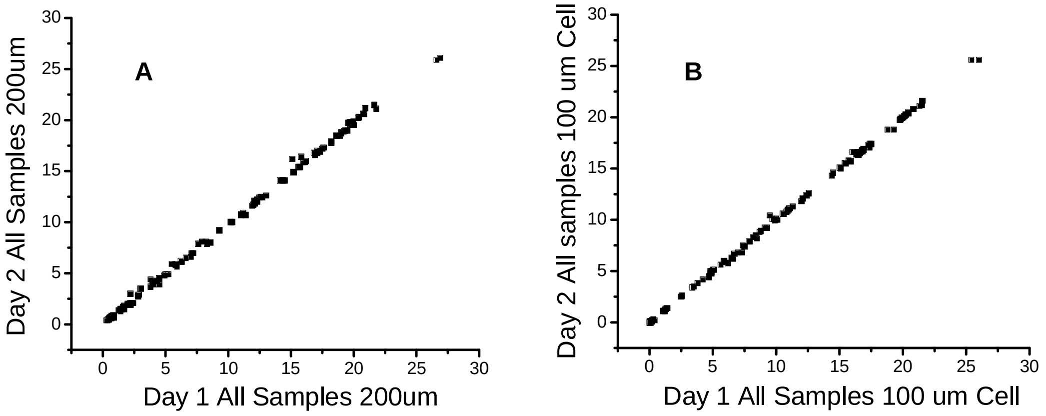

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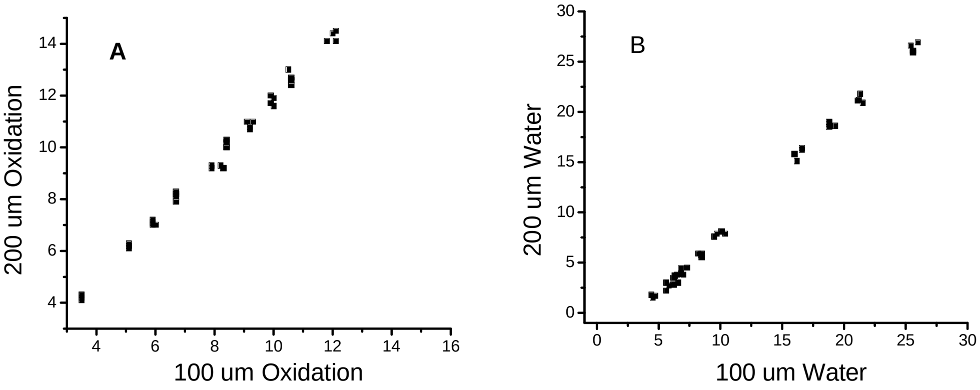

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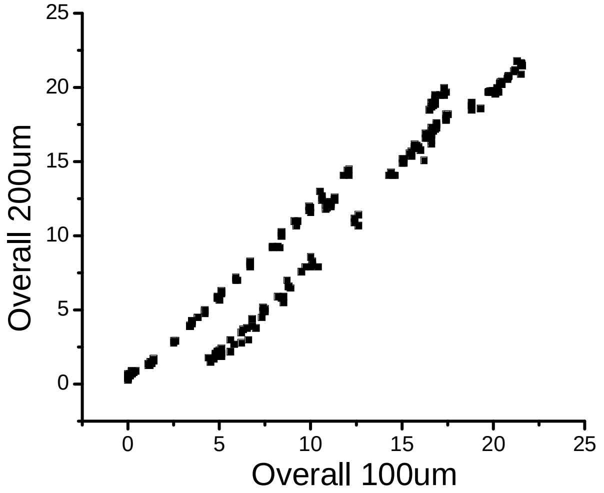

Figure 5. Combined parameter plot for accuracy of the diluted oil results vs the neat oil results.

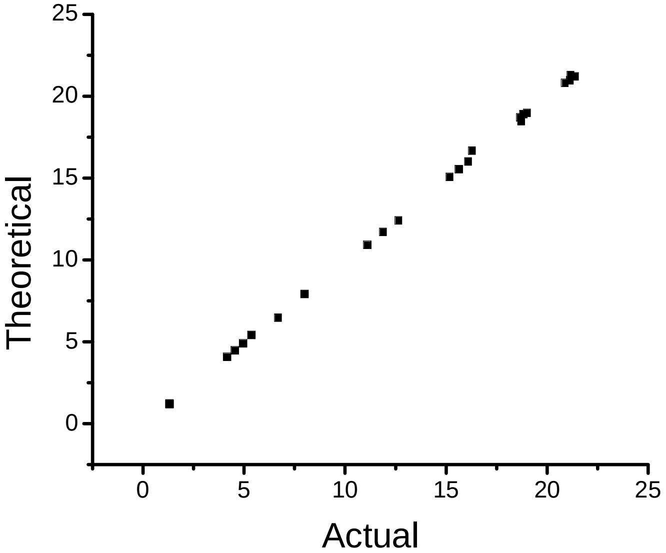

Figure 6. Plots of measured vs theoretical data for the fresh/used oil blends indicating that spectral reconstitution does not compromise the proportionate responses expected.

List of Tables

Table 1. ASTM E 2412-04 Practice components, their measurement regions, baselines and reporting for petroleum crankcase lubricants.

Component	**Measurement Region, 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	Abs at 2000	None	Value x 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	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[B] (JP-5, JP-8)	Area 815 to 805	Minima 835 to 825 and 805 to 795	(Value + 2) x 100
Sulfate by-products	Area 1180 to 1120	Minima 2200 to 1900 and 650 to 550	Report value as measured
Ethylene Glycol	Area 1100 to 1030	Minima 1130 to 1100 and 1030 to 1010	Report value as measured

[A] Reporting values in absorbance/0.1 mm

Table 2. Day-to-day parameter reproducibility statistics for undiluted (neat) and OMS-diluted oils.

Parameter	Slope	Intercept	R	SD	MD_r	Mean	CV(%)
Glycol Diluted	0.74	0.18	0.85	0.07	0.02	0.66	12.06
Glycol Undiluted	0.70	0.01	0.85	0.05	0.02	0.12	43.33
Soot Diluted	0.96	-0.07	0.99	0.12	0.25	4.33	2.86
Soot Undiluted	0.99	0.09	0.99	0.08	0.05	6.85	1.21
Oxidation Diluted	0.96	0.15	0.99	0.10	0.21	9.46	1.06
Oxidation Undiluted	0.99	0.05	0.99	0.06	0.01	7.94	0.87
Nitration Diluted	0.96	0.09	0.99	0.06	0.00	2.94	2.35
Nitration Undiluted	1.01	-0.02	0.99	0.03	0.00	2.52	1.19
Antiwear Diluted	0.97	0.13	0.99	0.10	0.24	15.63	0.67
Antiwear Undiluted	0.98	0.24	0.99	0.07	0.03	13.91	0.52
Diesel Diluted	0.88	22.25	0.98	0.84	0.47	200.78	0.42
Diesel Undiluted	0.99	0.44	0.99	0.46	0.05	202.81	0.23
Sulfate Diluted	0.95	0.53	0.99	0.10	0.23	16.29	0.66
Sulfate Undiluted	0.97	0.36	0.99	0.10	0.02	16.04	0.63
Water Diluted	0.97	0.33	0.99	0.48	0.08	10.79	4.53
Water Undiluted	1.00	-0.10	0.99	0.39	0.07	12.43	3.20

Table 3. Accuracy assessed as the concordance between analytical results obtained for neat and OMS-diluted oils after correcting for dilution and pathlength.

Parameter	Slope	Intercept	R	SD	MD_a	Mean	CV(%)
Glycol	1.27	0.50	0.84	0.08	0.54	0.39	21.94
Soot	1.19	-3.83	0.99	0.21	-2.52	5.59	3.81
Oxidation	1.17	0.12	0.99	0.22	1.52	8.70	2.54
Nitration	1.17	-0.03	0.99	0.08	0.42	2.73	3.04
Antiwear	1.19	-0.99	0.99	0.16	1.72	14.77	1.09
Diesel	1.10	-24.1	0.95	1.70	-2.03	201.79	0.84
Sulfate	1.28	-4.31	0.98	0.16	0.25	16.16	1.03
Water	1.19	-4.04	0.99	0.41	-1.64	11.61	3.54

Table 4. Comparison of theoretical and actual values for blends of a fresh and used motor oil in a 1:1, 2:1 and 1:2 ratio.

Component	**MD_a**	**Mean**	**SD**	**Range**	**CV**
Water	0.09	18.77	0.421	11.40-26.03	2.2%
Soot	-0.08	6.63	0.155	2.73-10.63	2.3%
Oxidation	-0.18	11.76	0.012	9.57-14.17	0.1%
Nitration	-0.05	4.52	0.000	3.37-5.73	0.0%
Antiwear	0.03	18.85	0.045	18.33-19.33	0.2%
Diesel	-1.3	210.57	0.310	203.7-219.0	0.2%
Sulfate	-0.09	15.58	0.012	14.23-17.03	0.1%
Glycol	-0.09	1.23	0.00	1.30-1.30	NA

Table 5. Oil classification system adapted from Shubkin (20) relating the predominant functional groups which characterize them.

Hydrocarbon Based	
Ground Petroleum	CH
Synthetic Polyalphaolefins	CH
Alkylated Aromatics	CH, $\mathrm{CH}_{\mathrm{(aromatic)}}$
Monoalkylbenzenes	CH, $\mathrm{CH}_{\mathrm{(aromatic)}}$
Dialkylbenzenes	CH, $\mathrm{CH}_{\mathrm{(aromatic)}}$
Ester Based	
Carboxylic Acid Esters	
Dicarboxylic Acid Esters (Diesters)	CH, (O-C=O)
Dimer Acid Ester	CH, (O-C=O)
Polyols	CH, (O-C=O)
Polyoleates	CH, (O-C=O)
Phtalate	CH, $\mathrm{CH}_{\mathrm{(aromatic),}}$ (O-C=O)
Trimellitate	CH, $\mathrm{CH}_{\mathrm{(aromatic),}}$ (O-C=O)
Pyromellitate	CH, $\mathrm{CH}_{\mathrm{(aromatic),}}$ (O-C=O)
Phosphate Esters	
Trialkyl Phosphates	CH, O-P=O
Triaryl Phosphates	CH, $\mathrm{CH}_{\mathrm{(aromatic),}}$ O-P=O
Alkyl Aryl Phosphates	CH, $\mathrm{CH}_{\mathrm{(aromatic),}}$ O-P=O
Polyalkylene Glycols	
Monoalkyl ethers	CH, C-O-C, OH
Diol/Triol ethers	CH, C-O-C, OH
Silicone Based	
Silicone Oils	CH, Si-O-Si
Polysilicone oils (siloxanes)	CH, Si-O-Si
Silicate esters	CH, O-Si=O
Polyphenylethers	CH, $\mathrm{CH}_{\mathrm{(aromatic),}}$ C-O-C
PolyFluoroalkylethers	CF, C-O-C
Chloroflourocarbons	CF, CCl
Polymethacrylate/polyalphaolefin cooligomers	CH, O-C=O