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Assessing Friction Stress on a Liquid Lubricant by Stable Isotope Analysis

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14. ABSTRACT Compound-specific stable isotope analysis (CSIA) was applied to a pentaerythritol ester lubricant to determine if predictable fractionation effects could be related to friction stress. A pin-on-disk tribometer was used to expose the lubricant to five doubly-increasing sliding distances (up to 36 km). PCA was used to ordinate multivariate data and test if significant isotopic shifts or FTIR spectral changes could be related to sliding cycles. $\delta^{13}\text{C}$ Isotope ratios only were found to be statistically different ($P < 0.05$) between treatments. PCA gave a primary score (PC1) containing 44% of the ^{13}C -isotopic variability, which correlated exponentially with sliding cycles ($r^2 = 0.96$). A peak, not present in unexposed lubricant, became evident and showed increasing ^{13}C depletion with increasing length of sliding exposure.								
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Assessing friction stress on a liquid lubricant by stable isotope analysis

1. Introduction

Wear and tear of moving mechanical parts is costly to individuals, companies and nations, scaling from the thousands to billions of dollars in annual loss [1]. Lubricants are the front line of defense against mechanical failure. Therefore, most large organizations develop lubrication management plans to ensure equipment reliability, reduce down-time, and minimize both waste generation and energy use [2]. A proactive strategy, referred to as condition-based maintenance, involves performing preventative maintenance only when operating conditions warrant (*e.g.* [3]). Implicit in this strategy is the availability of a range of independent methods for analyzing and monitoring machine and lubricant condition.

Lubricant degradation analysis generally follows two basic strategies; (1) determine the distribution pattern of components of the lubricant itself (lubricant and additives), or (2) determine the contaminants from wear within the lubricant matrix (*e.g.* metals, fuel, moisture, etc.). The latter may provide a hardware condition snapshot and is by far the most common test in terms of both historical and present use. In addition, most sensor development technologies revolve around assaying wear components and contaminants in the lubricating oil matrix (*c.f.* [4]).

Lubricant component analyses may be less intuitive to interpret and assess. However, it may be most applicable to determining the lubricant's or additive's useful life and may provide information on degradation rates and states. Techniques have been developed to assess structural changes to lubricant and additive chemistries or component evolution. The most widely applied techniques have been infrared (IR) absorption, Raman scattering and ultraviolet fluorescence [5]. Advances in both IR [5-8] and fluorescence spectroscopy [5] coupled with multivariate statistics have enabled lubricant breakdown tracking from modeled friction stress. Tribological investigations using spectral techniques have allowed correlations between friction stress (engine use, heat, etc.) and component oxidation, decomposition of ester functionality, additive breakdown, and breakdown product emergence [5, 8-10]. While each of the aforementioned methods has strengths, additional indices which can relate wear (under varying conditions) to lubricant spectral characteristics would be of both economic and scientific importance.

In mechanical systems, energy may be converted into friction where parts move in relation to one another. This frictional energy can then be transferred to a lubricant under all fluid film lubrication regimes (*i.e.* hydrostatic, hydrodynamic, boundary, etc.) [11]. Friction and associated heat may be sufficient to initiate lubricant decomposition. If decomposition involves the breaking of bonds (*e.g.* oxidation, ester cleavage, etc.), reactions have the potential to involve kinetic isotope effects (KIE). For chemical reactions, the mass difference of heavier isotopes relative to lighter isotopes of the same element necessitates higher initial activation energies (for review see [12]). For instance, there is an 8% mass difference between the heavy carbon isotope (^{13}C) relative to the light isotope (^{12}C). The heavy isotope of hydrogen (deuterium, or ^2H) is 100% heavier than the light isotope: ^1H . In a chemical reaction, this phenomenon may lead to isotopically-lighter products and an isotopically-heavier residual pool of initial compound during degradation [12].

While originally employed in enzymology, kinetic isotope effects have recently been used in “field” studies, principally to assess biological contaminant degradation [13]. In these studies, if the “original” contaminant pool becomes isotopically-heavier as its concentration decreases, biological degradation (*i.e.* bond cleavage) is inferred. Additionally, using multivariate chemometric methods to assess isotopic variation in multi-component compound mixtures, one can determine if two sources are or are not statistically related [14]. If the transfer of frictional energy to lubricants and subsequent oxidation or bond-cleavage imparts an isotope effect, isotopic shifts in lubricant components could serve as a friction exposure diagnostic. To our knowledge, this hypothesis has not been tested. We thus hypothesize that lubricant component and degradation product hydrogen and carbon isotope ratios will be impacted by friction stress and that multivariate statistical models can be applied to allow an independent index of lubricant sliding exposure, perhaps providing a novel test mechanism and allowing independent validation of other lubricant wear tests.

2. Methods

2.1. Lubricant tests

A pentaerythritol ester lubricant (Hercolube-A, Hercules, Inc) was chosen which has a widespread military use (aviation) and demonstrated readily identifiable peaks via standard temperature gas chromatography (GC) analysis. Hercolube-A (Herc-A) was diluted at a 1:100 (v/v) ratio with dichloromethane for GC and FTIR analysis. A pin-on-disk tribometer (CSEM, Neuchâtel, Switzerland) was used for exposing the lubricant to friction stress. A 10 μL neat aliquot of Herc-A was pipetted through the center of the ball holder onto the slowly rotating disk at the beginning of each experiment in a manner similar to Dugger et al [15]. Both ball (1/4” diameter) and disk were AISI 52100 steel, and a 5 N load was applied for the duration of each experiment. Runs were made in ambient air at 25 ± 3 °C; relative humidity was kept below 10% by addition of desiccant in the tribometer chamber. The sliding radius was fixed at 15 mm for each run, and at 100 cycles/min resulted in a linear sliding speed of 0.15 m s^{-1} . Triplicate runs were conducted for the annotated cycles (Table 1). After completion of each run and a 0 cycle control, the ball and disk were immersed in dichloromethane and sonicated for 30 minutes for thorough lubricant to solvent transfer. The Herc-A containing solvent was then transferred to a calibrated tube and dried down to 1 mL using a Zymark[®] TurboVap system supplied with N_2 gas.

2.1. Carbon GC-Quadrapole MS and GC-Combustion-Isotope Ratio MS analysis

Herc-A was analyzed using a custom-configured GC-Combustion-Isotope Ratio MS (GC-C-IRMS) system similar to one previously reported [14]. The configuration consisted of a Hewlett Packard 6890 GC - 5973 quadrapole MS outfitted with a 250 μm ID 30 m Supelco SPB-05 capillary column. A post column 4-way splitter (Valco) allowed a 20:80 split between the quadrapole MS and the IRMS, respectively. IRMS flow was routed through a Finnigan GC combustion interface, which in turn interfaced to a Finnigan MAT Delta S IRMS. Injections were splitless to minimize potential isotope

fractionation in the inlet [16]. The inlet was set isothermally at 280 °C and operated at 35 psi pulsed pressure for the first 30 seconds of each run. Flow was set for 2 mL min⁻¹ throughout each run. Oven operating conditions were as follows: 150 °C for 5.00 min, ramp to 280 °C at 16 °C min⁻¹, hold 10 min, ramp to 310 °C at 5 °C min, hold 12 min. Each sample was spiked with an internal isotopic standard (*n*-tetracosane, -31.548 ± 0.23 ‰), which eluted immediately before lubricant peaks and calibrated by thermal conversion elemental analyzer (TCEA)-IRMS against NBS-22. An isotopic reference CO₂ gas (-22.805 ± 0.12 ‰) was injected in triplicate directly into the IRMS source at the beginning and end of each run.

2.2. Hydrogen GC -Isotope Ratio MS analysis

Herc-A was analyzed in as close as possible GC conditions as for δ¹³C analysis (*see above*). Setup for continuous flow δD measurements was as previously described [17]. Briefly, combined replicates were run in triplicate on a Varian 3400 GC coupled to a reduction furnace held at 1450 °C. In this configuration, the pyrolysis interface converted hydrocarbons to H₂/HD gas which passed through a Nafion[®] dryer before flowing into an open split interface to a Finnigan DelatPlus XL IRMS. H₂ reference gas was injected through an open split at the beginning and end of each run for calibration. Duplicate runs were made.

2.3. FTIR analysis

To determine if FTIR analysis was comparable with CSIA to assess lubricant friction stress, each lubricant sample was analyzed both with sliding exposure alone and with the addition of two common fuels (which might likely contaminate lubricants under real-world operational conditions). For the fuel contamination tests, 0.4% (v/v) diesel or JP8 fuel was added to the original and friction stressed Herculube A. The "original" wear series (Table 1) and fuel-added series were pipetted into a CaF₂ window FTIR cell with a 0.1mm spacer and analyzed using a Mattson IR-10110 FTIR spectrometer. Raw data were corrected for the methylene chloride solvent (run alone) and exported to Matlab[®] for modeling and analysis.

2.4. Data Analysis

Isotope ratio values were calculated and output in spreadsheet format by IsoDAT NT software (Thermo-Fisher). Isotope ratio data for each identified peak were collated, transferred to Matlab[®] software, and corrected for the internal isotopic standard (IIS) *n*-tetracosane using equation 1 for carbon and equation 2 for hydrogen:

$$\delta^{13}\text{C}_{\text{peak}} + (-35.458 - \delta^{13}\text{C}_{\text{IIS}}) \quad (1)$$

$$\delta\text{D}_{\text{peak}} + (-22.792 - \delta\text{D}_{\text{IIS}}) \quad (2)$$

Two general statistical tests were applied to triplicate isotope data. First, in order to determine if there were significant differences between each treatment, a stepwise coupled principal components analysis – multiple analysis of variance (PCA-MANOVA)

was conducted [14]. Second, to determine if wear cycles could be related to isotopic data, a PCA model was performed on the raw columnar data. In the PCA analysis, data were autoscaled by dividing each value by its column standard deviation. Finally, peak(s) which appeared in chromatograms after wear exposure were assessed for isotopic shifts.

FTIR data were analyzed by PCA and the resultant scores were related to wear cycles. The loadings from the PCA models were also plotted against wavenumber to assign structural information to regions which varied in response to wear treatment.

3. Results and Discussion

3.1. Hydrogen isotope ratio shifts

Ten major peaks were identified and used to perform statistical analyses. Corrected δD values ranged from ~ -163 to -47 ‰. Statistical analysis revealed only one instance in which there was a significant difference between samples (Table. 2). This difference was between the initial starting material and the lowest sliding cycle exposure sample (24,000 cycles). This appears to be anomalous, as one would expect higher levels of sliding exposure to also show significant differences. The presence of carbon isotopic shifts during wear tests (see below) but not hydrogen isotope shifts indicated that C-H bonds were not likely involved in initial lubricant degradation. This could occur if the friction-induced ester degradation behaved similarly to hydrocarbon thermal cracking, in which C-C bond cleavage occurs preferentially to C-H bond cleavage. Because C-C bond energies are ~ 200 - 300 kJ mol^{-1} while C-H bond energies are ~ 300 - 500 kJ mol^{-1} , the weaker bonds should break preferentially. Considering molecular orbital theory, the carbon radical in a C-C bond break would have higher stability than a hydrogen radical in a C-H bond break [18].

3.2. Carbon isotope ratio shifts

Twenty seven discreet peaks were identified in the isotope ratio chromatogram collection. Of these, three were not found in every chromatogram, thus were not included in the PCA-MANOVA analyses. The PCA-MANOVA model showed significant differences between each treatment (0, 24, 48, 96, 192, and 384k wear cycles) with probabilities usually less than 0.01 (Table 3).

In order to observe trends and deconvolve tabular data, a PCA model was created. The initial PCA model showed inflection at 3 and 6 components. The 6 component model had eigenvalues greater than 1.0, and captured 85% of the variability in the dataset. A two component model was "suggested" by the software. No discernable trends were seen in any PCA scores aside from PC1 (with models from 2 to 6 components). Average scores on PC1 (from triplicate analyses), which accounted for 44% of the variation in the compiled data, displayed an exponential increase over sliding cycles (Fig. 1). The fit was significant with a 0.96 goodness of fit statistic (r^2). A biplot showing scores and loadings demonstrated that certain peaks were instrumental in driving the model PC1 scores between 0 and 384k cycles (Fig. 2). Herc-A components at retention times (indicated by blue squares) in region "A" and region "B" (outlined in magenta on the figure) were

responsible for increases or decreases in isotopic ratios between native and friction stressed lubricant.

Screening Herc-A components at wavelengths highly loaded along PC1 (both positive and negative) showed components (at retention times shown in figures) whose isotopic ratios increased (Fig. 3) and decreased (Fig. 4) as a function of sliding cycles. In order to be consistent with the kinetic isotope model, an increase in any residual lubricant peak isotope ratio would be expected (*i.e.* isotope ratios of peaks that decrease in abundance due to friction-induced degradation should become more positive in value). Under the relatively mild friction conditions applied to Herc-A, one “new” peak was observed after 24K cycles. The $\delta^{13}\text{C}$ values for this peak decreased logarithmically in relation to wear cycles (see peak 944 in Fig. 4; $r^2 = 0.96$, $P < 0.01$). A linear relation also had a relatively high goodness of fit ($r^2 = 0.91$, $P < 0.01$).

To assess overall concentration changes during friction stress, peak areas were normalized to the surrogate standard (tetracosane) for each treatment. For “heavier” components, which became ^{13}C -enriched during sliding exposure, an overall decrease was sometimes observed - however, considerable error (particularly with the 192,000 cycle samples) made it difficult to observe a model-fitting trend (Fig. 5). Similarly, some lighter peaks showing ^{13}C -depletion during sliding exposure increased in concentration (Fig. 6). Again, large standard errors often made any trend statistically insignificant. Even with sonication and attempted full recovery, quantitative analysis was difficult. A PCA analysis did not show any significant trends - due to the relatively high replicate variability (data not shown). Because a ^{13}C enrichment in some higher molecular weight components was observed with a concomitant ^{13}C depletion in some lighter components (Figs. 3-4), and at least in some cases concentrations of these components co-varied with isotopic shifts, we hypothesize that either terminal branched C-C or backbone C-C bonds might have been cleaved during wear exposure - or some combination thereof. A higher degree of friction stress and detailed component structural analysis could likely help resolve the exact relationship between lubricant use and shifts in concentrations and carbon isotope ratios. However, in this study, analyzing shifts in isotopic ratios appeared more robust in response to friction stress than monitoring changes in component concentrations.

3.3. Comparison to “standard” FTIR analyses

FTIR analysis has been used to assess lubricant degradation and contaminant accumulation [19, 20]. FTIR analysis is relatively inexpensive, rapid and is able to discern regions within a lubricants molecular structure undergoing change. FTIR was conducted in this study to potentially validate results from isotopic analysis. In order to understand changes due to friction stress, solvent-corrected FTIR spectra were combined, classed and modeled by PCA. The first component (PC1) accounted for 89% of the spectral variation but only showed statistically-significant variation ($P < 0.05$ with friction stress at 384,000 cycles (Fig. 7). To account for potential lubricant contamination, two fuels were added, diesel and JP8 (Herc-A is an aviation lubricant). Fuel contaminants are often found in used lubricants and have been shown to bias FTIR spectra [20]. Lubricants are generally higher in molecular weight than fuels, so these contaminants would not influence the GC-C-IRMS results (elute far earlier than lubricant

peaks). Therefore concomitant fuel additions were not analyzed by GC-C-IRMS. The fuel-contaminated samples demonstrated different variation with friction stress - JP8 contaminated FTIR spectra showed an initial increase along PC1 with a final decrease at 384,000 cycles. Diesel-contaminated lubricant showed significant change along PC1 after 96,000 cycles, however, PC1 accounted for only 67% of the spectral variation (Fig. 7).

While the FTIR data did not allow a robust model linking spectral features to friction stress, the PC1 loadings did show spectral changes occurred in the CH₃ and CH₂ regions as well as C=O, other carbon-oxygen bonds and O-H bonds. The O-H bond loading appeared to vary significantly between neat lubricant and added fuel contaminants (Fig. 8) - showing no friction-stress changes in neat lubricant, but perhaps spurious changes with fuel-contaminated lubricant (Fig. 8; ~3200-3400 cm⁻¹). Aside from the O-H bond assignment, spectral variation as modeled in PC1, was within similar bond assignment regions for each friction stress treatment. Most regions appeared to not be impacted by fuel contaminants. Overall, the PCA model(s) from either neat or fuel-contaminated lubricant did not offer robust linear or exponential relationships to friction stress (Fig. 7). Within the neat samples, the variation seen primarily in C-C bonds, the FTIR analysis supports results seen in the stable isotope ratios suggesting primarily C-C bonds (and not bonds involving hydrogen) were primary regions of change due to friction stress on the lubricant.

4. Conclusions

This manuscript explores whether isotopic shifts might be a viable alternative method for assessing the friction stress “history” in lubricants. We observed statistically-significant shifts in collective isotope ratios under relatively mild sliding conditions. A modified MANOVA analysis showed each level of friction stress significantly altered the collective carbon isotope ratios of the lubricant components ($P < 0.01$). A PCA model was formulated that demonstrated a nonlinear relation between $\delta^{13}\text{C}$ and friction stress. This model was quite good ($r^2 = 0.96$) and by analyzing the loadings, showed several lubricant components became ¹³C-enriched while others became ¹³C-depleted in response to friction stress. Changes in concentration were not easily modeled, while FTIR spectra showed no statistically-significant change (but did demonstrate bonds most impacted by friction stress).

Isotopic analysis may be an independent means to assess lubricant changes relative to friction stress and may offer another alternative in an overall lubricant management plan. In order for stable isotope analysis to be effective, several conditions must exist, 1) the lubricant must be amenable to GC-C-IRMS analysis - having multiple individual components resolvable by GC column coatings and run conditions, 2) the lubricant must be able to be tested in its unused state to obtain a baseline isotopic signature, and 3) each new batch of lubricant must be tested as isotopic ratios vary based on different base feedstocks. The overall advantages of the proposed method are that it:

- does not require accurate quantitative recovery of lubricants or ad hoc development of peak area ratios;
- is not sensitive to fuel contaminants in the lubricant as components are separated by GC during the analysis,

- may be more sensitive to small changes in lubricant components as isotopic models related to friction stress proved more robust and statistically significant than peak area shifts or FTIR analysis.
- does not require an a priori knowledge of lubricant components - only that they can be separated reliably by retention time.
- does not require absolute isotope calibration - the statistical tests need only be relative to a surrogate standard (which can be set to an isotopic value of 0).

The overall disadvantages to the method are

- higher overall cost relative to FTIR or standard GC separations
- each lubricant batch needs to be fingerprinted prior to use
- initial modeling could be expensive and may lead to less significant models for a given lubricant (this paper reports on a proof of concept).

Tribometric tests appropriate to the lubricant's use (*i.e.* high temperature, high or low speed, differing boundary conditions, etc) would need to be conducted for a given lubricant at relevant conditions to vet the method within a lubricant management program. Results from these experiments could then be modeled (PCA, for instance) and perhaps scaled to process control level chemometrics so that routine analyses could be conducted at appropriate timescales. Tests involving lubricant component isotope ratios would be independent of other protocols currently employed to assess lubricant friction stress. Isotope evaluation could be coupled to lubricant efficacy tests and may thus serve as an indicator of lubricant senescence. Additional experiments would need to be conducted, probably using more aggressive friction stress. In addition, a lubricant management plan would need to annotate initial sampling of all "new" lubricant batches for wear comparisons. At present, this proof of concept study demonstrates using isotopic ratio shifts as an independent method for assessing friction stress in lubricants.

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Table 1. Tribometer run characteristics

Cycles (X 1000)	Run Time (<i>hr</i>)	Linear Distance (<i>km</i>)
0	0	0
24	4	2.26
48	8	4.53
96	16	9.05
192	32	18.1
384	64	36.2

Table 2. Probabilities that δD values represent the same means among wear cycle treatments.

Sample 1	Sample 2	<i>P</i>	<i>C.I.</i>
0 cycles	24K cycles	0.031	0.0027
0 cycles	48K cycles	0.85	0.022
0 cycles	96K cycles	0.52	0.027
0 cycles	192K cycles	0.47	0.020
0 cycles	384K cycles	0.14	0.0037
24K cycles	48K cycles	0.61	0.042
24K cycles	96K cycles	0.11	0.0037
24K cycles	192K cycles	0.20	0.0054
24K cycles	384K cycles	0.22	0.011
48K cycles	96K cycles	0.49	0.011
48K cycles	192K cycles	0.32	0.010
48K cycles	384K cycles	0.33	0.0087
96K cycles	192K cycles	0.71	0.030
96K cycles	384K cycles	0.97	0.11
192K cycles	384K cycles	0.93	0.19

Table 3. Probabilities that $\delta^{13}\text{C}$ values represent the same means among wear cycle treatments.

Sample 1	Sample 2	<i>P</i>	<i>C.I.</i>
0 cycles	24K cycles	0.0005	0.00001
0 cycles	48K cycles	0.0023	0.00004
0 cycles	96K cycles	0.0012	0.00002
0 cycles	192K cycles	0.0076	0.00010
0 cycles	384K cycles	0.0405	0.00124
24K cycles	48K cycles	0.0310	0.00384
24K cycles	96K cycles	0.0011	0.00001
24K cycles	192K cycles	0.0007	0.00001
24K cycles	384K cycles	0.0014	0.00003
48K cycles	96K cycles	0.0036	0.00003
48K cycles	192K cycles	0.0013	0.00001
48K cycles	384K cycles	0.0062	0.00007
96K cycles	192K cycles	0.0020	0.00009
96K cycles	384K cycles	0.0128	0.00032
192K cycles	384K cycles	0.0054	0.00021

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Figure 1. PCI scores from d13C PCA model related to wear cycles

Figure 2. Bi-plot for d13C PCA model. Regions (A) and (B) show heavily loaded regions along PC1

Figure 3. $\delta^{13}\text{C}$ enrichment related to friction stress for various components

Figure 4. $\delta^{13}\text{C}$ depletion related to friction stress for various components

Figure 5. Change in relative peak area related to friction stress for various components

Figure 6. Change in relative peak area related to friction stress for various components

Figure 7. FTIR PC1 scores related to friction stress

Figure 8. PC1 loadings for FTIR spectral changes in response to friction stress

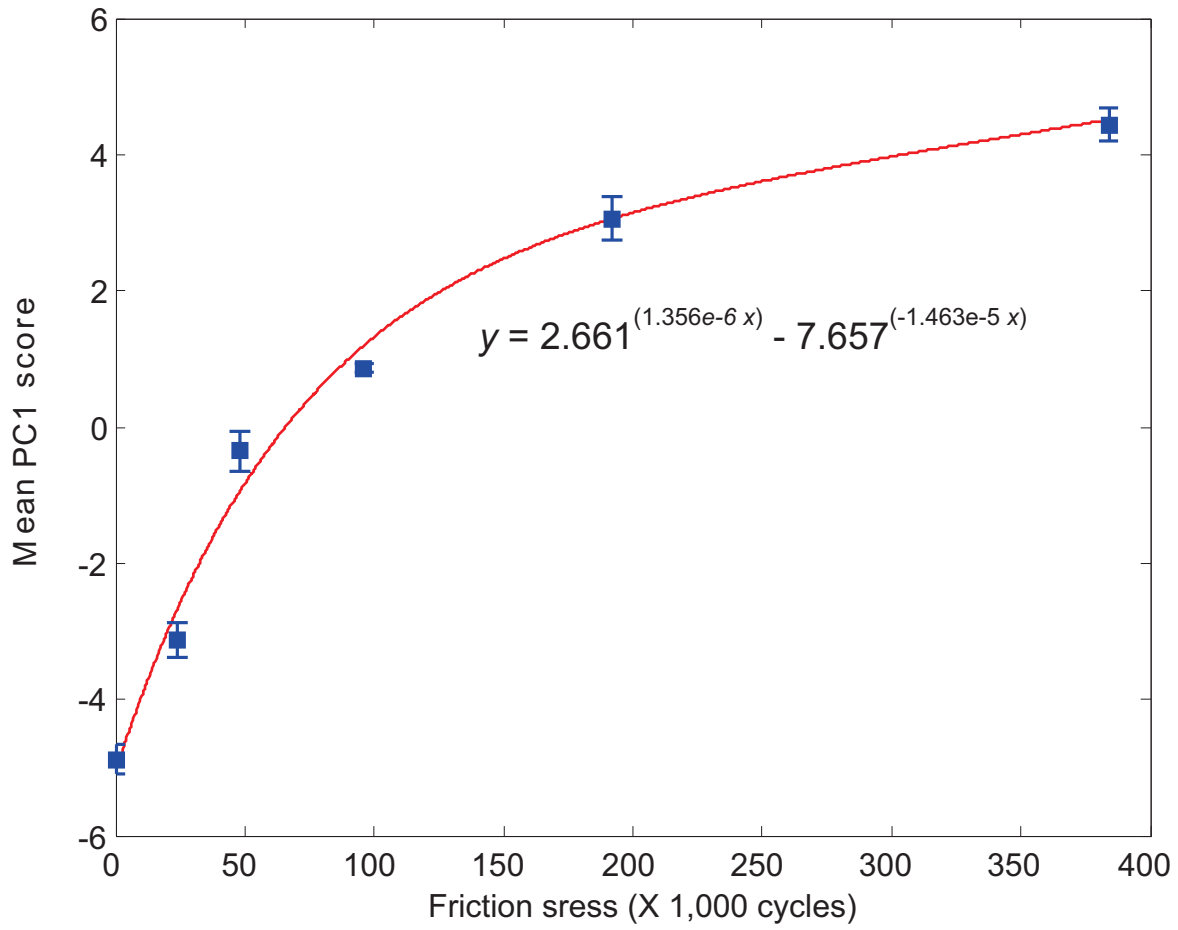


Figure 1.

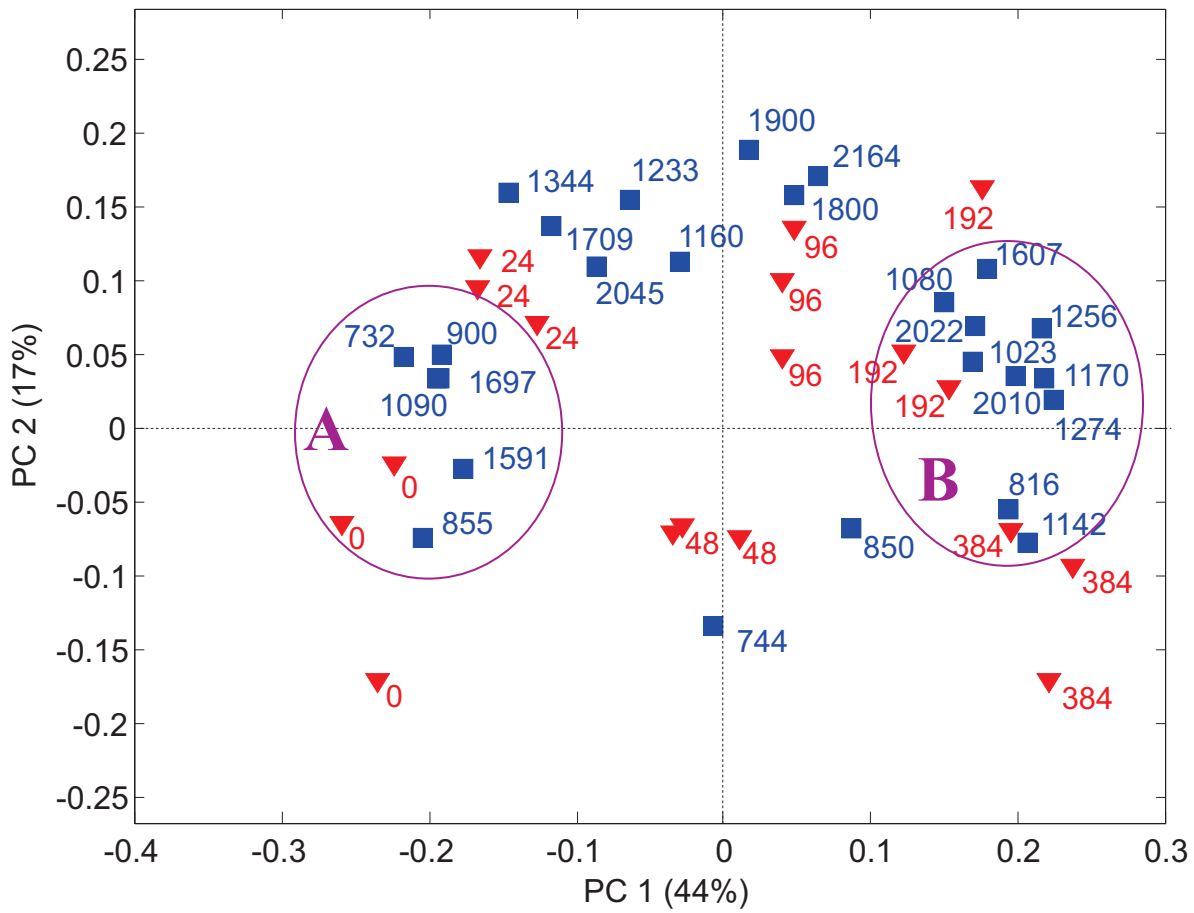


Figure 2.

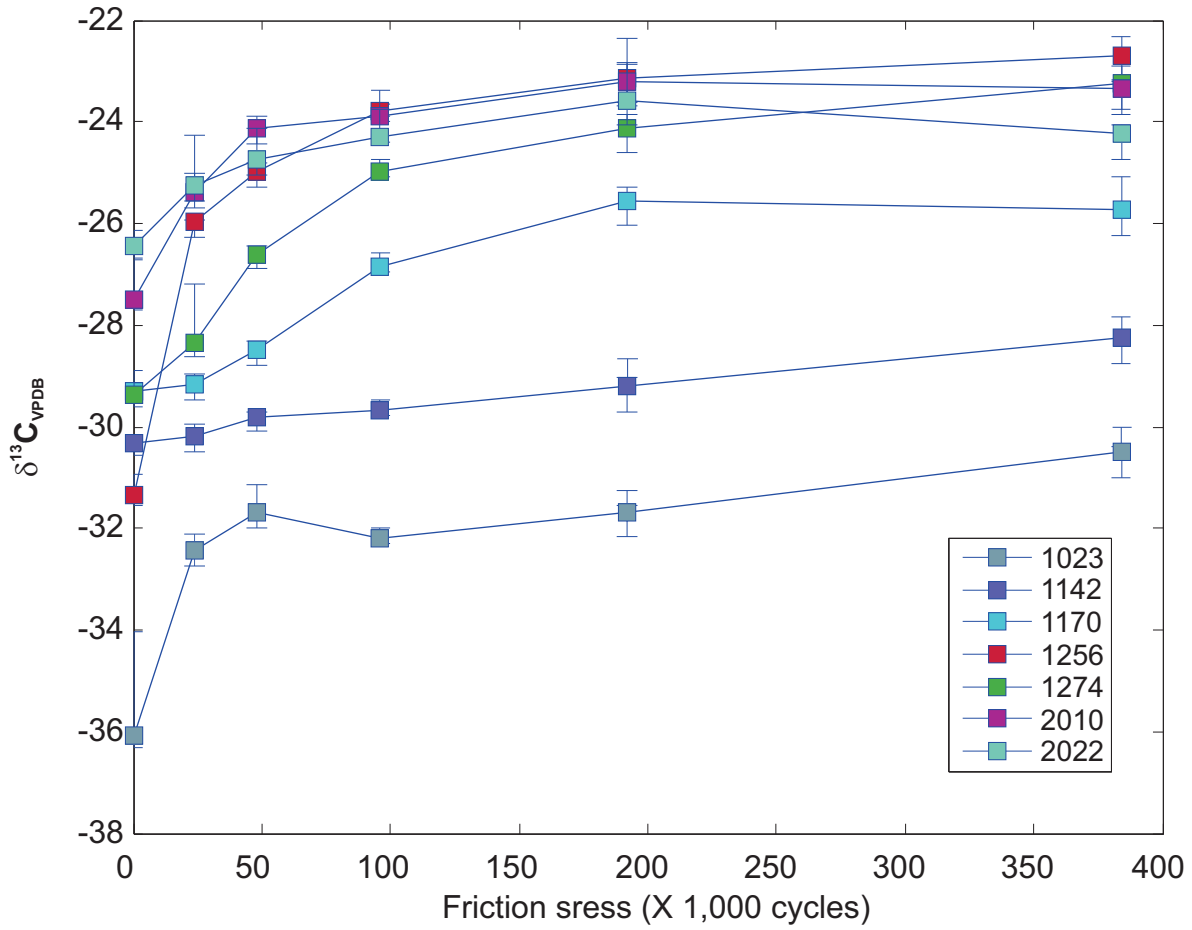


Figure 3.

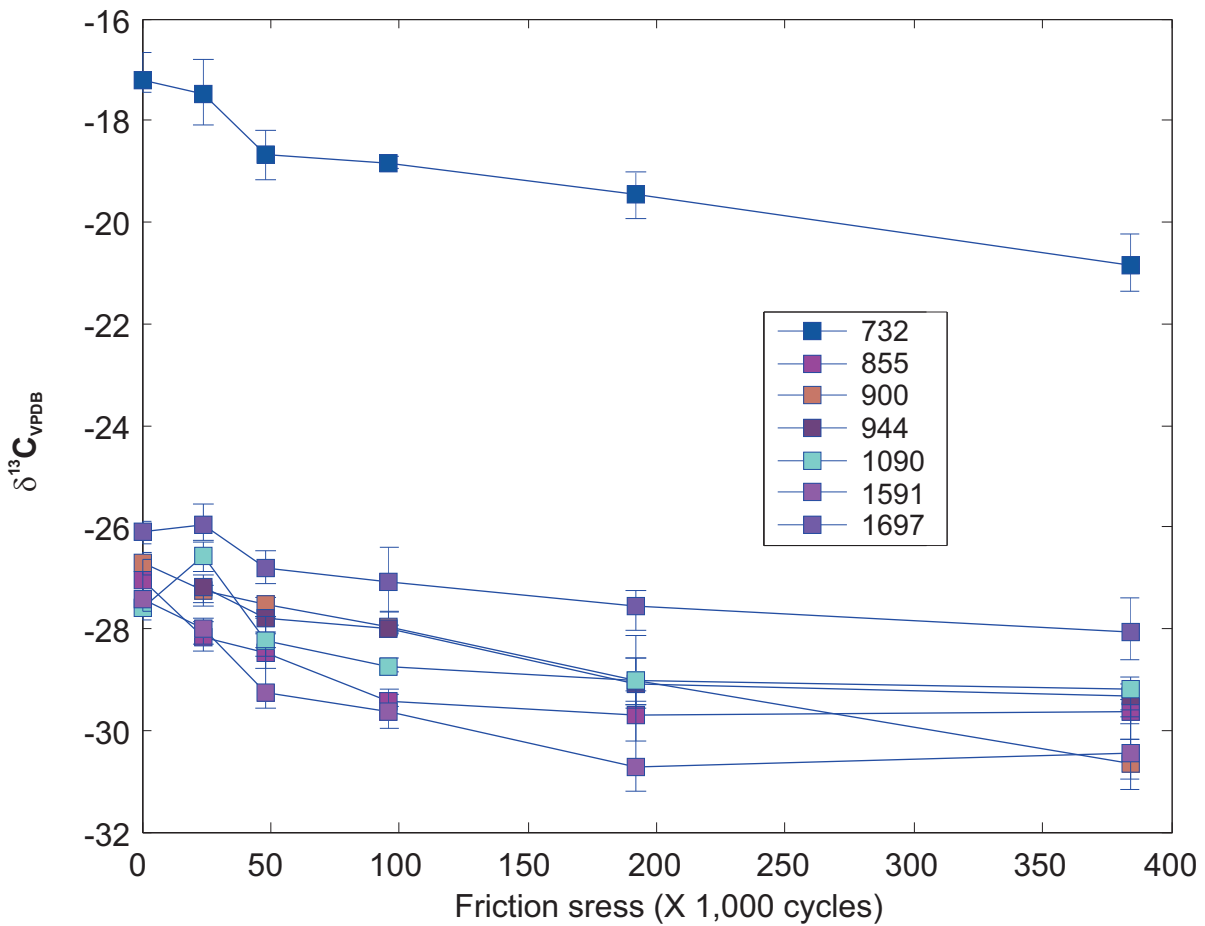


Figure 4.

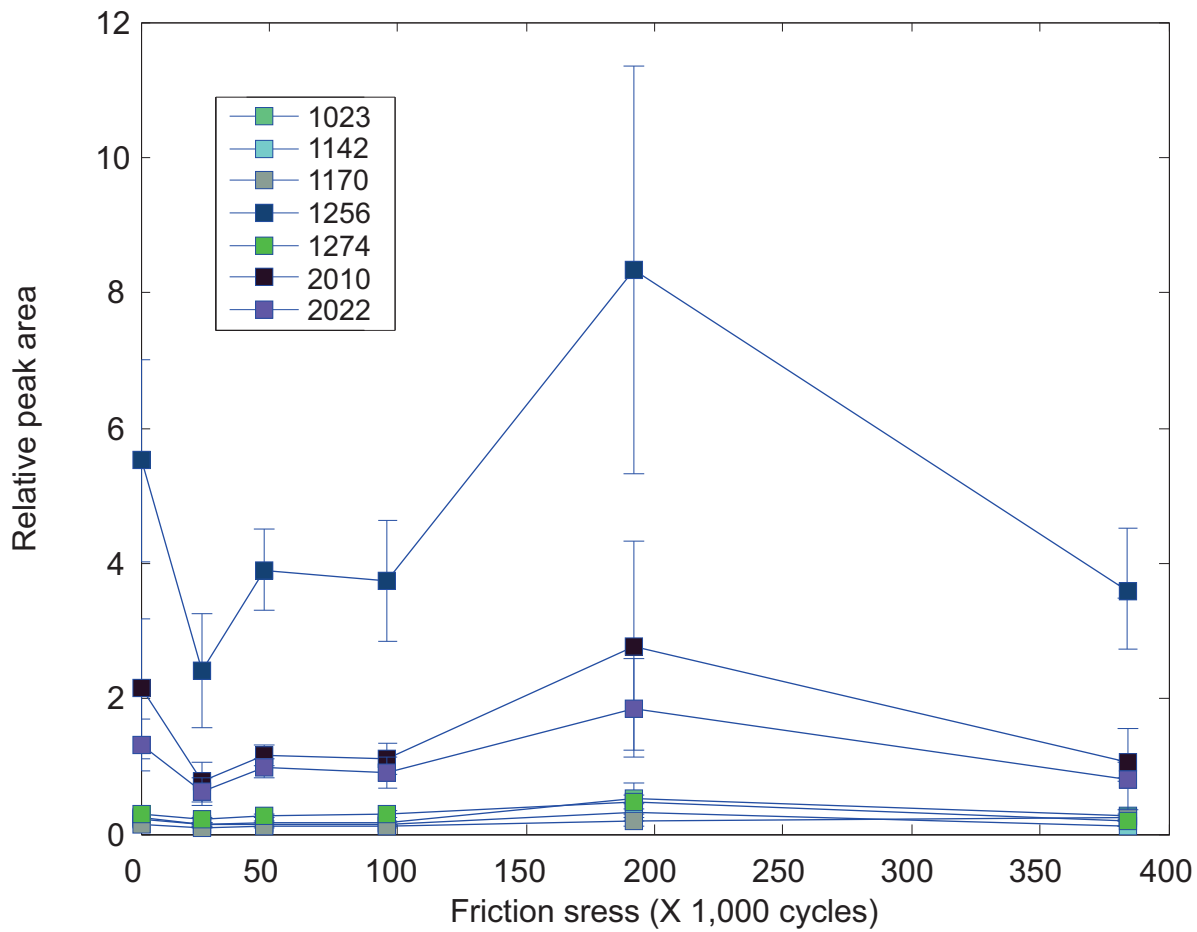


Figure 5.

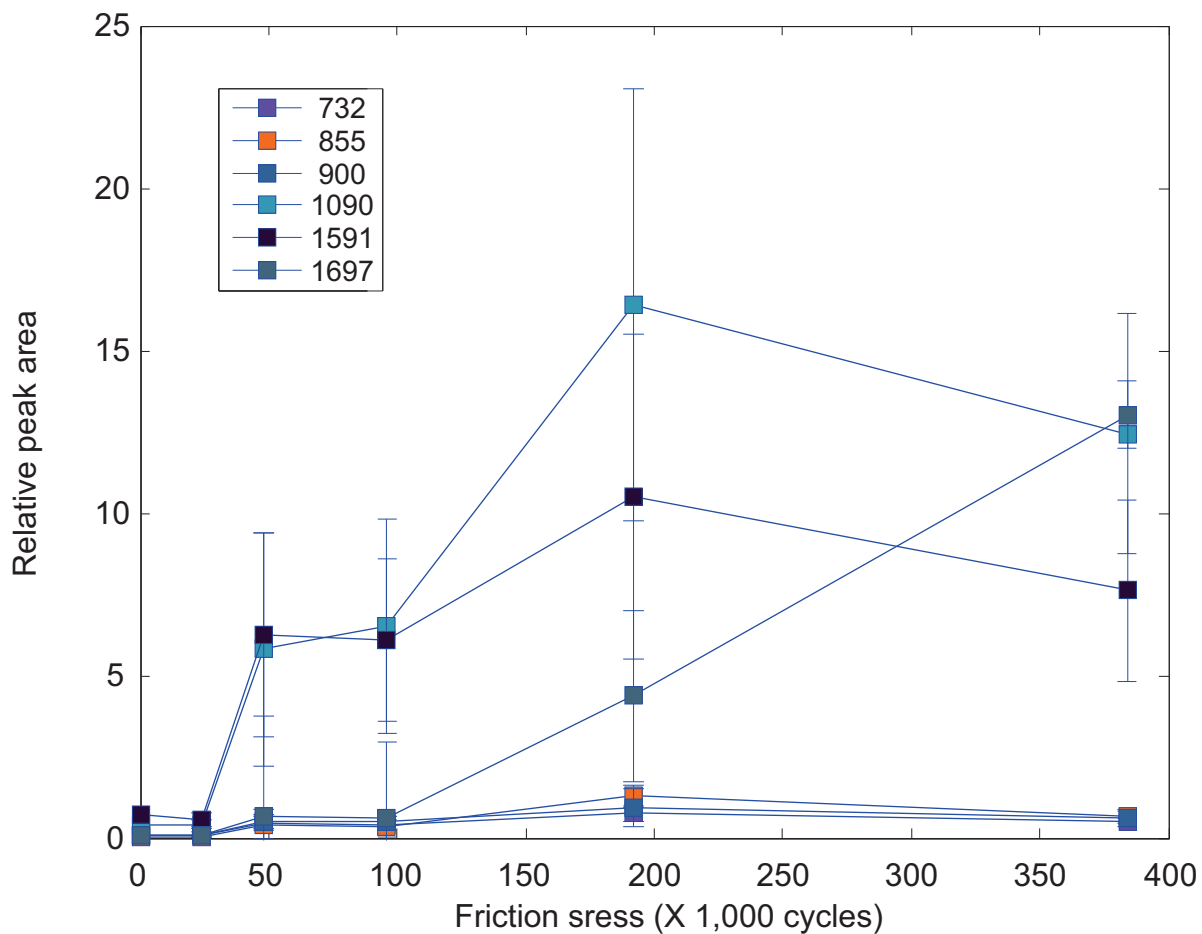


Figure 6.

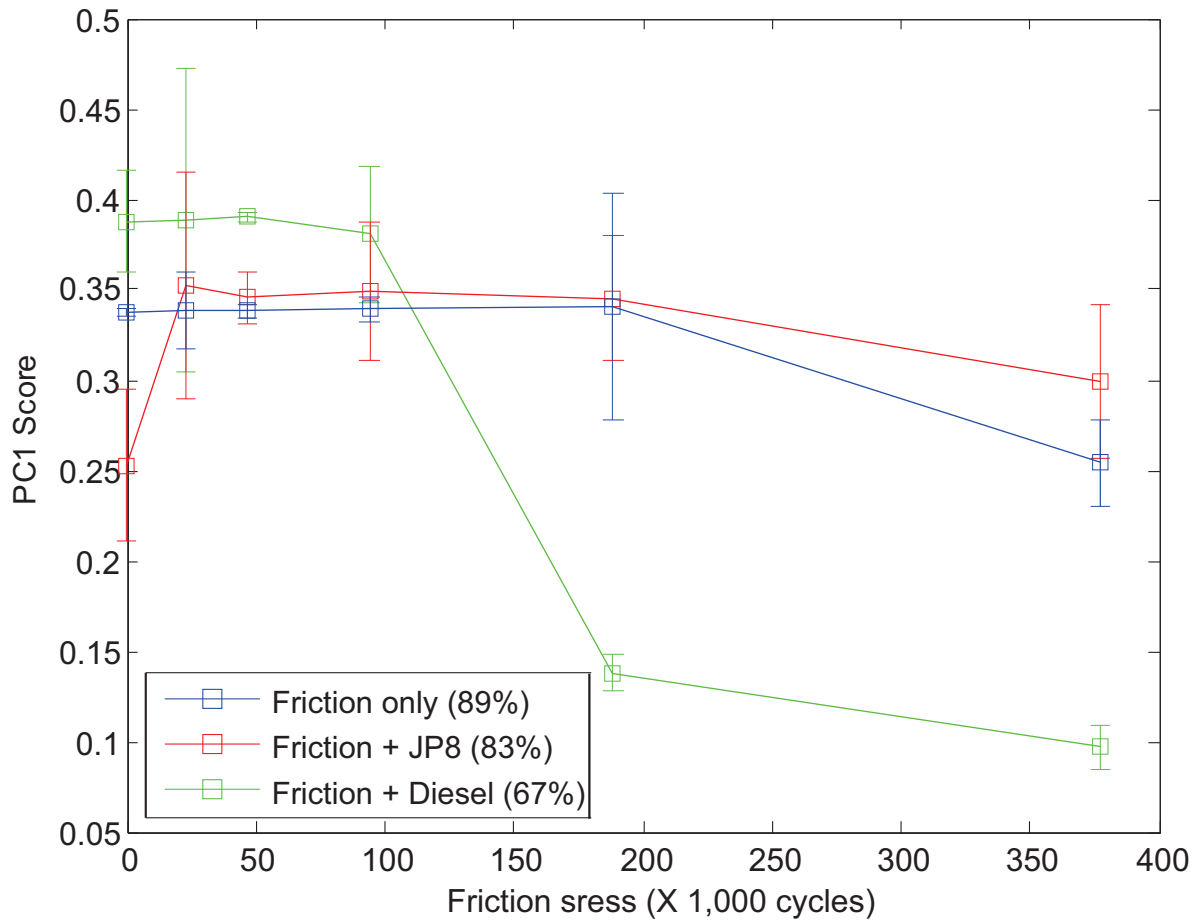


Figure 7.

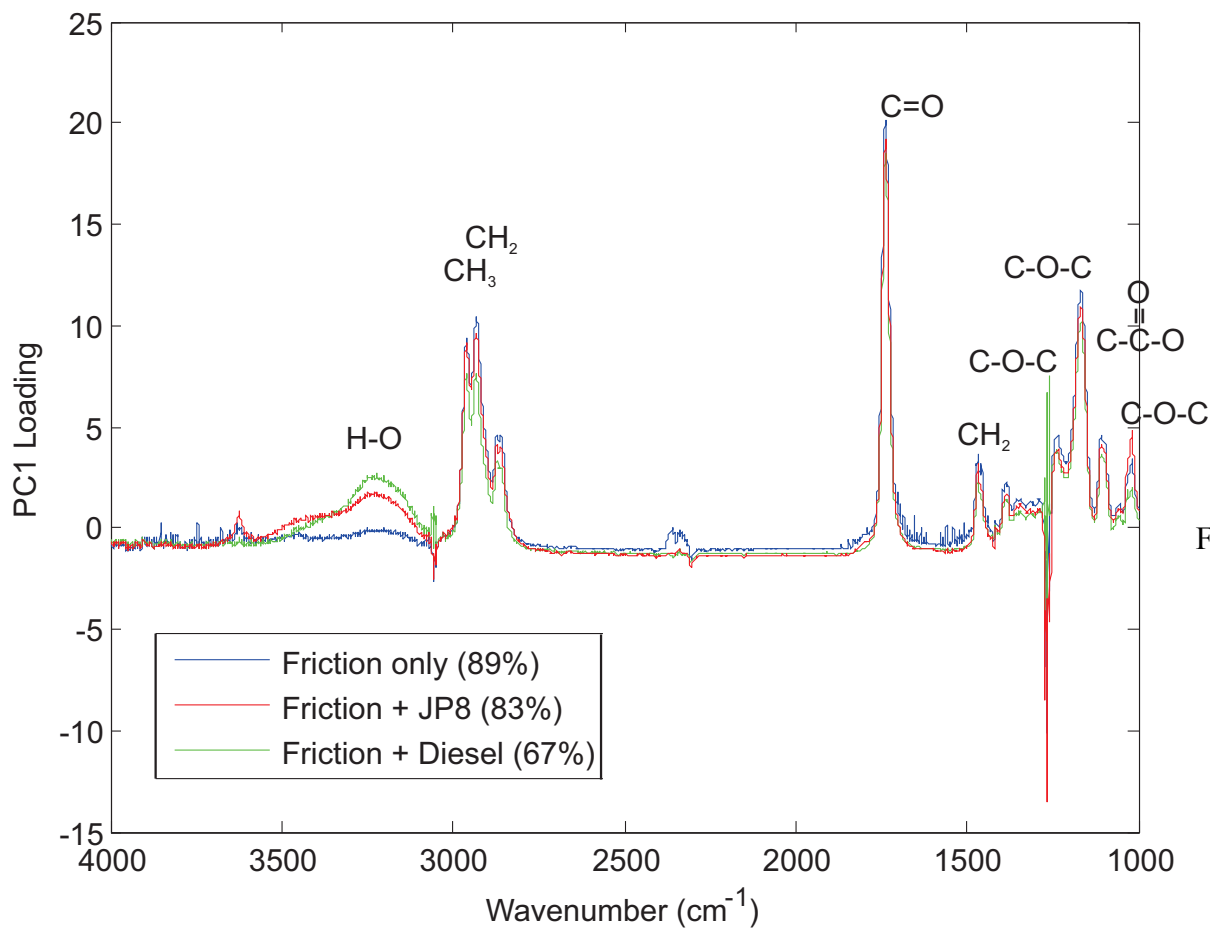


Figure 8.