

TG-FTIR METHODS FOR THE EVALUATION OF LUBRICANT CONTAMINATION

Anthony S. Bonanno, Rosemary Bassilakis and Michael A. Serio

Advanced Fuel Research, Inc.
87 Church Street
East Hartford, CT 06108

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ABSTRACT

A typical Air Force base will produce several thousand gallons per year of used turbine engine lubricants (1-5). The potential for contamination of the collected lubricants, particularly with halogenated compounds such as degreasing solvents and other fluids, reduces the effectiveness of a previously developed reclamation process. In this project, the feasibility of using two different thermal/FT-IR analysis methods in combination with advanced data analysis techniques to detect contamination in used turbine engine lubricants was investigated. The first method, TG/FT-IR combined with advanced data analysis routines, was shown to be capable of detecting the presence of several different types of contaminants in synthetic lubricants at concentrations of about 5%. It was demonstrated that data analysis routines based on factor analysis (SIMCA) and neural networks could be used for identifying the presence of a contaminant. The second method, TG/secondary oxidation/FT-IR, was developed specifically for detecting trace levels of chlorinated contaminants in lubricants. Optimization of this method using existing instrumentation led to a detection limit of about 300 ppm (w/w) organic chlorine in the lubricant. Further improvements in hardware and software components could lead to detection limits of <10 ppm. This instrumentation could also be used to characterize used motor oils, cooking oils or pyrolysis oils.

INTRODUCTION

The Dalton Process is a proprietary process for reclaiming synthetic ester based turbine lubricants (MIL-L-7808 and MIL-L-23699) for reuse (1,3,4). Under controlled collection of the used lubricants, this process has been shown to give as high as 95% yield of virgin lubricant (4). However, contamination of the used lubricants greatly reduces the yield of the reclamation process, and since supervised collection of used lubricants is not feasible, methods are required to rapidly determine the presence of unacceptable levels of contamination. Likely contaminants are volatile hydrocarbons in the form of kerosene type turbine fuels, domestic paraffins, petroleum naphthas, and chlorinated degreasing agents such as trichloroethylene. Previously used methods of identifying contaminated lubricant samples involved classifying the samples on the basis of appearance and odor (normal or abnormal), and subjecting the samples to a series of analytical tests in order to determine parameters such as volatile contaminant content, volatile hydrocarbon content, mineral oil content, and foaming propensity (3). The results of these analyses were used to specify whether a used lubricant sample was suitable for reclamation. A more rapid and objective method of classifying used lubricants and related materials is needed. Thermogravimetric (TG) analysis combined with Fourier Transform Infrared (FT-IR) analysis of evolved products has been used at Advanced Fuel Research, Inc. (AFR) and elsewhere for characterization of a variety of hydrocarbon materials (6,7). The objective of the current study was to investigate the application of TG-FTIR methods for the evaluation of lubricant contamination.

The successful development of a TG-FTIR based lubricant evaluation instrument would allow non-technical Air Force personnel to rapidly and reproducibly determine whether used lubricants are suitable for reclamation or reuse. This type of instrumentation would also find several uses in the commercial sector. These include analysis of used motor oils and of oils produced from post-consumer plastics. The processing of corn oil and cotton seed oil often results in the contamination of residual "soapstock" with chlorinated hydrocarbons, which prevents recovery of the useable oil through acidulation. The recovery of useable motor oil by supercritical fluid extraction is currently being evaluated. The value of the recovered oil is directly related to the amount of residual organochlorine in the extract.

EXPERIMENTAL

Sample Selection and Preparation

The Air Force provided two types of synthetic turbine lubricants (MIL-L-7808 and MIL-L-23699) from two different sources (Mobil and Hatco). The contaminants of primary interest were halogenated compounds, therefore, three chlorinated compounds were selected as representative contaminants for this work: trichloroethylene (TCE), dichloromethane, and *ortho*-dichlorobenzene (o-DCB). Other contaminants of interest included fluids that could routinely be found at an Air Force base and could potentially contaminate the used lubricants. A set of representative fluids was collected from commercial sources. These included methanol, motor oil (Castrol GTX 10W30), hydraulic jack oil (Gold Eagle),

brake fluid (Prestone), turbine fuel (Jet A), diffusion pump silicone oil, and Dow-Corning silicone oil (DC-200). The primary constituents of these fluids are given in Table 1.

Table 1. List of the lubricants and contaminants analyzed.

Type of Fluid	Primary Constituents
MIL-L-7808, MIL-L-23699	polyol esters
motor oil, hydraulic oil	mineral oils
brake fluid	polyalkylene glycol ethers
turbine fuel (Jet A)	aliphatic hydrocarbons
diffusion pump oil	poly(dimethyl/diphenyl siloxane)
DC-200 silicone oil	polydimethylsiloxane

A preliminary spectral analysis revealed that the MIL-L-7808 and MIL-L-23699 lubricants were quite similar. Consequently, further study was limited to the Mobil MIL-L-23699 lubricant. The samples analyzed included the pure lubricant, the pure "contaminants," and the lubricant spiked with a known amount of a given contaminant. The spiked samples were prepared by pipetting the required volume of the contaminant into a graduated cylinder and topping off with the lubricant. In order to minimize errors due to loss of volatile components, each sample was prepared immediately prior to analysis.

Lubricant Analysis Studies

TG/FT-IR Instrument - The combined thermal/FT-IR analysis technique is an extension of the TG/FT-IR (thermogravimetric analysis with FT-IR analysis of the evolved species) instrumentation developed by AFR and sold commercially by Bomem, Inc. as the "TG/Plus". The details of the TG/FT-IR method and instrumentation have been described previously in the literature (6-8), but a brief description will be given here. The apparatus, illustrated schematically in Figure 1, consists of a sample pan suspended from a balance within a furnace. As the sample is heated, the evolving volatile products are carried out of the furnace by an inert gas stream directly into a 5-cm diameter multi-pass gas cell (heated to 150 °C) for analysis by FT-IR. Spectra are obtained at specified time intervals in order to quantitatively determine the evolution rate and composition of the evolved products. The sample can be subjected to programmed temperature ramp rates between 3 °C/min and 100 °C/sec, with a temperature range of 20 to 1000 °C. The system monitors the time dependent evolution of specific gases, the heavy liquid evolution rate and its infrared spectrum with identifiable bands from the functional groups, the mass loss during the run, and the mass of the non-volatile residue remaining at the end of the run. An analysis of C, H, N and S in the residue can be obtained at the end of the pyrolysis experiment by introducing oxygen and analyzing the combustion products.

TG/FT-IR analysis of lubricant samples - Two specific problems were encountered during the initial TG/FT-IR analysis of the synthetic lubricant samples (9). It was found that the lubricant samples volatilized very rapidly, thus resulting in a high concentration of aerosol in the FT-IR gas cell. The high aerosol concentration resulted in significant scattering, and therefore the spectra appeared to be distorted. Additionally, the sample condensed on the quartz tube between the furnace and the flow cell, and then re-volatilized as the furnace reached a higher temperature. This limited the ability to correlate between the FT-IR data and the TG balance data. A method was developed that would result in slower evolution of the sample in order to improve the results. The lubricant was adsorbed onto pre-pyrolyzed sand and was crimped in a stainless steel boat. This was found to significantly slow the rate of evolution of the lubricant, and also limited the condensation of evolved products.

Using this sample introduction method, several samples were run in the standard TG/FT-IR mode using a temperature profile with a ramp rate of 30°C/min and a sample size of about 10 mg. The samples included the Mobil 23699 lubricant, the contaminants listed in Table 1, and the lubricant spiked with the contaminants (usually at a concentration of 5%). The spectra obtained during the runs were then converted to a format compatible with Spectra Calc data processing software (Galactic Industries, Salem, NH) for further analysis.

TG/secondary oxidation/FT-IR analysis of lubricant samples - TG/FT-IR with secondary oxidation or pyrolysis allows the evolved species to be oxidized or further pyrolyzed before passing into the FT-IR gas cell. The secondary oxidation unit consists of a quartz tube through which the evolved species flow prior to entering the gas cell. The tube houses a resistive platinum element which is used to heat the evolved species to 800-900 °C. A 15 mL/min flow of preheated gas is introduced just prior to the heater; helium is used for the secondary pyrolysis mode, and oxygen is used for the secondary oxidation mode.

RESULTS AND DISCUSSION

Detection of General Contamination in Synthetic Lubricants

SIMCA analysis for contaminants - In the development of a methodology to detect contamination in used turbine engine lubricants, the data analysis routine must be designed to answer specific questions. If specific contaminants are likely to be encountered, for example, silicone oil, then one could ask "Is there any silicone oil in the lubricant?" Then a spectral analysis routine could be developed to look for the IR bands characteristic of silicone. The question being asked in this case is more general; "Is there anything out of the ordinary in the lubricant?" In this case the spectral analysis routine must be more general, and should be capable of not only identifying IR bands that do not arise from the lubricant, but also differences in the relative intensities of bands that might also indicate the presence of a contaminant. A discriminant analysis technique based on principal components analysis (PCA) was applied to the data obtained in order to detect the presence of an unspecified contaminant.

Several studies have employed PCA, also known as factor analysis, in the development of discriminant algorithms. Although PCA and its applications have been thoroughly described in the literature (10,11), a brief discussion will be given with an emphasis on its role in discriminant analysis techniques. PCA involves decomposing the original data matrix of n spectra by m measurements (or wavelengths) into a matrix of scores, and a matrix of factors, as given by: $X = SF + E$; where X is the mean-centered data matrix, S is the n by a matrix of scores, F is the a by m matrix of factors, and the decomposition was carried out to a factors. E is an n by m matrix that contains the residual values for each spectrum at each measurement. The factors are linear combinations of the original measurements and are chosen sequentially to represent the directions of maximum variance in the data set. Each spectrum in the data matrix has a set of scores that indicate the amount of each factor required to represent the initial spectrum. Although the decomposition can be carried out to use all of the degrees of freedom available, usually the significant variance in the data set can be represented by a smaller number of factors, and any further factors represent only random variations (noise). After decomposition, each of the n spectra in the training set can be described by the set of a scores instead of m measurements (usually with $a < m$). This not only reduces the dimensionality of the data set, but also improves the quality of the data since some of the noise is excluded from the primary set of factors.

Malinowski has discussed the determination of the optimum number of factors, a , that are needed to accurately represent the data matrix (12,13). He showed that, for a data matrix that is factor analyzable, there exists a primary set of factors that consists of a mixture of meaningful information and error, and a secondary set of factors that consists of pure error, or noise. Since it is the primary set that is of use in chemical analysis, rejection of the secondary set of factors will actually lead to an improvement of the raw data set. The problem lies in deciding where to separate the factors into primary and secondary sets. For multivariate quantitative calibration (e.g., partial least squares), the dependent variables can be used to monitor the progress of the decomposition. PCA decomposition, however, does not rely on dependent variables; the factors are selected solely on the basis of the variance within the data matrix. Malinowski derived several indicator functions which monitor the error via the eigenvalues associated with the factors (13). The eigenvalues give a measure of the amount of variance represented by each factor. The number of primary factors can be determined by starting with the least significant factor, and working backwards, until the point where the eigenvalues begin to represent more than the known experimental error. The factors beyond this point can be taken to be members of the primary set.

Once the training set data matrix has been decomposed by PCA, the scores can be used to develop a discriminant algorithm, similar to the way in which individual absorbance values can be used. Factorial discriminant analysis (FDA), which uses linear discriminating functions, has been demonstrated for several applications using NIR and mid-IR spectra (14-16). FDA uses the primary set of factors to define the space occupied by the training set. An alternative method, called soft independent modeling of class analogy (SIMCA), employs the information contained in the secondary set of factors (17). In SIMCA, the spectrum is reconstructed using the primary set of factors, and the residual spectrum is computed as the difference between the original and the reconstructed spectra. This is identical to computing the residual spectrum using the secondary set of factors but eliminates roundoff errors that can result from the small values in the secondary factors. The residual variance for a given spectrum is then computed as the sum of the squares of the values in the residual spectrum. An F -test can then be used to compare the residual variance for an unknown to the residual variances for the training set in order to statistically determine if the unknown is significantly different from the training set. Although FDA and SIMCA both employ PCA, the basic concept of the two techniques is quite different. FDA compares samples in a space that represents the significant variance of the training set, while SIMCA compares in the remaining orthogonal space. Van der Voet *et al.* have described these two spaces as inside-model space (IMS) and outside-model space (OMS), respectively (18). Both methods have certain merits, but the two are certainly suited to different types of applications. For example, FDA is best suited to an application that would discriminate against known sources of variation. This allows the PCA to accurately represent the space in which the variations will occur. SIMCA however is more suited to identify variations that are quite different from the inherent variance of the training set. The work of Gemperline *et al.* provides a

good example of this (19). Using SIMCA they successfully discriminated adulterated pharmaceutical raw materials from training sets of pure materials based on NIR reflectance spectra.

The data that are obtained during a TG/FT-IR run differ somewhat from the data typically used in discriminant analysis. FT-IR spectra are measured as the components of the sample evolve, and therefore spectra obtained during the run can vary widely. Therefore, discriminant analysis in the IMS will not be very useful since the variations in the factor space for an uncontaminated sample will be quite large. However, if the primary factors accurately represent the species evolving from the uncontaminated lubricant, then the presence of contaminants in a lubricant should result in evolving species that spectrally fall outside of the IMS defined for the uncontaminated lubricant. In this case, a discriminant analysis routine that analyzes the OMS (such as SIMCA) should be capable of detecting the presence of a contaminant. It is important to note that this approach requires that the contaminant produces evolving species that are spectrally different from the species evolving from the uncontaminated lubricant. The magnitude of required spectral difference is dependent upon the implementation of the discriminant algorithm, and spectral pretreatment will be particularly important.

SIMCA was evaluated as a method of detecting contamination in used synthetic lubricants on the basis of the data collected during a standard TG/FT-IR analysis (no postoxidizer). The spectra obtained during a run of an uncontaminated lubricant were used as the training set. First derivative spectra were used in order to eliminate the effects of baseline variations resulting from scattering. After selection of the spectral region of interest, the mean-centered training set was decomposed, and the number of factors in the primary set was determined using Malinowski's IND function (13). The residual variance was then computed for each spectrum in the training set and for all the spectra obtained from the runs of all the other samples, including the uncontaminated lubricant, various pure contaminants, and various "contaminated" lubricants. The residual variance for each spectrum, and the residual variance for the training set, were then used to compute the *F*-statistic using the approach outlined by Gemperline et al., (19). Gemperline classified samples as members if *F* was below the 95% level, as non-members if *F* was above the 99% level, and as undecided if *F* was between the 95% and 99% levels.

An example of the results of the factor analysis is shown in Figure 2. Figure 2a shows a plot of the spectra obtained for an uncontaminated lubricant and the residual spectra that result from projecting the spectra onto the primary set of factors. In Figure 2b, the spectra and residual spectra are shown for a lubricant sample contaminated with 5% polydimethylsiloxane. The large features present in the residuals result from spectral features due to the contaminant. Since these features are of larger magnitude than can be attributed to noise, this sample is identified as containing a contaminant. Several spectral regions were used to develop discriminant analysis routines, and the best general results were obtained using a region containing 4000-2450 and 2250-890 cm^{-1} . The 2450-2250 cm^{-1} region was excluded in order to reduce the effects of variable CO_2 evolution profiles, and the region below 890 cm^{-1} was excluded due to the presence of large noise spikes. These two regions were found to adversely affect the performance of the discriminant routines.

In Figure 3, the *F*-values are plotted for lubricant samples contaminated with several fluids. The samples with 5% silicone (PDMS) oil and 5% brake fluid are easily identified as contaminated, but the samples with 5% jet fuel, 5% motor oil, and 5% hydraulic oil all fell in the region where no decision can be made. This can be explained by the fact that the silicone oil and the brake fluid both have unique spectral bands that result in significant contributions to the residual spectrum, while the spectra of the other samples only exhibit bands due to C-H vibrational modes which are also present in the lubricant. Since these samples are only present at a concentration of 5% the contribution to the residual spectrum is small. This is verified by the fact that the sample with 30% hydraulic oil is identified as contaminated. In future work, additional spectral pretreatment methods will be investigated in order to magnify the spectral differences between the lubricant and these types of contaminants. It has been demonstrated by Hasenoerhl et al. (20) that pretreatment routines such as variance scaling and feature weighting can vastly improve the performance of PCA-based discriminant analysis routines.

The *F*-values were also plotted for another uncontaminated lubricant sample and samples contaminated with 5% methanol, 5% dichloromethane, and 5% trichloroethylene (TCE) (9). The discriminant analysis routine performed well for the uncontaminated sample and the methanol-contaminated sample. The two samples contaminated with chlorinated species were not detected as contaminated. This is due in part to the fact that the spectral region characteristic of C-Cl vibrational modes was excluded in order to limit the contribution of extraneous noise spikes. Results from analyses including this spectral region are poor due to the presence of these noise spikes, but do indicate that chlorinated contaminants can be detected at relatively high concentrations. As discussed below, much more sensitive detection of chlorinated contaminants can be achieved by using secondary oxidation to convert organic chlorine to HCl.

Artificial neural network analysis for contaminants - In the past decade, significant effort has been made to develop computing strategies that simulate biological systems. The resulting artificial neural networks (ANN) are grossly simple in comparison to biological networks, but are well suited for performing tasks such as pattern recognition, cost minimization, etc. (21). A typical ANN is made up

of three layers of processing units (nodes) and weighted connections between the layers of nodes. The input data is introduced at the input layer and is fed to the hidden layer through the weighted connections. Each node of the hidden layer sums its inputs and then applies an activation function to compute its output. The outputs of the hidden layer are then processed by the output layer, and their outputs are given as the output of the ANN. The function of the network is determined by the activation functions applied by the nodes and by the weights of the connections between the nodes. The weights can be strong or weak, and positive (excitatory) or negative (inhibitory). Typical activation functions are linear, step, and sigmoidal. Once the configuration of the ANN is defined for a given application, and the appropriate activation functions are selected, a network must be trained to perform the desired task. This is analogous to "learning" in a biological system. The usual method involves introducing training data to the ANN and comparing the output of the network to the correct or desired output. The error is then propagated back through the network in order to adjust the weights. This process is repeated until the error level falls below an acceptable level.

Recent applications of ANN technology to infrared spectral data fall into two primary classes: 1) multivariate quantitative analysis, and 2) classification. The primary advantage of ANNs for the development of quantitative models lies in the inherent capability to model nonlinearity. Classification networks applied to spectral data take advantage of the capability of ANNs to handle complex pattern recognition problems. Expert systems have been developed which employ ANNs to determine the functional groups present in a compound on the basis of its infrared spectrum (22). More specific classification networks have also been developed. Examples include sorting plastics encountered at a recycling plant based on their infrared spectra (23), and classifying woods as either hardwoods or softwoods on the basis of their FT-Raman spectra (24). These results are very promising and are indicative of the potential of using ANNs with spectral data to develop powerful classification techniques.

In order to investigate the potential of using a classification network to detect the presence of contaminants in synthetic lubricants, several networks were trained to recognize the presence of chlorinated solvents in the evolved species from a TG/FT-IR run. Training of the networks involved presenting examples of spectra from uncontaminated and contaminated runs. In order to provide a more general set of "contaminated" spectra, library spectra of dichloromethane and trichloroethylene (TCE) were added to the spectra obtained from the uncontaminated run.

Networks were developed and trained using the NeuralWorks ANN development package (NeuralWare, Pittsburgh, PA) in conjunction with custom C routines for data preprocessing and presentation. The network was trained using spectra from a TG/FT-IR run for an uncontaminated sample and spectra from the same run artificially spiked with library spectra. This was accomplished by writing a C program that presented either a spiked or unspiked spectrum to the network during training. The program was interfaced directly to the ANN development software in order to allow computation of new spiked spectra on the fly during training. At the beginning of each presentation, the program randomly chooses to present either a spiked or unspiked spectrum. If a spiked spectrum is to be presented, then a random fraction of a library spectrum is added to a randomly selected spectrum from the TG/FT-IR run. This presentation method allowed the training data to represent a large range of potential contamination conditions. Before presentation to the network, spectra were preprocessed with a Fourier filter routine to remove low frequency baseline variations and some of the high frequency noise, and the spectra were then normalized to unit vector length in order to give all spectra equal importance.

Figure 4 shows the prediction results from a network trained as described above. A network output of 1.0 indicates the evolution of a contaminant, and an output of -1.0 indicates that no contaminant is evolving. Figure 4a is the result for an uncontaminated lubricant run. While this result shows excellent prediction, this is the same data used to train the network, and therefore does not significantly demonstrate generalization. In Figure 4b, the result is shown for a TG/FT-IR run of a lubricant contaminated with TCE. The TCE evolving from 1-8 minutes is clearly identified as a contaminant, and the remainder of the run is accurately identified as uncontaminated. This result clearly demonstrates both the ability of the network to detect contamination and the ability of the network to generalize, i.e., accurately predict the uncontaminated portion of the run. The plot shown in Figure 4c shows the result for a TG/FT-IR run of a lubricant contaminated with dichloromethane. While the network clearly identified the contaminant evolving from 1-10 minutes, it did not successfully predict the absence of contaminant during the later part of the run (~45-70 minutes). This indicates that the network may produce false positives in the prediction of contamination.

Continuation of ANN development in future work will address the problem observed in Figure 4c. Further investigation of preprocessing routines should provide a solution to this problem. Additionally, other ANN architectures will be investigated. While the networks developed to date do not perform as well as desired, the results discussed above are promising, and indicate that further investigation may provide a powerful methodology for detecting contamination in synthetic lubricants.

Detection of Trace Chlorinated Contaminants in Synthetic Lubricants

While TG/FT-IR combined with the data analysis methods discussed above is well suited to identifying general contamination at relatively high concentrations, the detection of trace level contamination by chlorinated species is better accomplished using TG/FT-IR with secondary oxidation to convert the evolving organic chlorine to HCl. There are several factors that lead to greatly improved sensitivity for the detection of chlorinated species. Since the evolving species are converted to the gaseous combustion products (H₂O, CO₂, HCl), the quantitative analysis software can be vastly simplified. HCl can easily be measured by FT-IR in the presence of high concentrations of CO₂ and H₂O, since there is little spectral interference. Additionally, conversion of the evolving species to gaseous products eliminates the formation of aerosols in the gas cell, and therefore much larger samples of lubricant can be analyzed. This also allows for the use of a longer residence time in the gas cell and a faster temperature ramp in the furnace since there is less risk of condensation of heavy products on the gas cell mirrors and windows.

Two sets of samples contaminated with chlorinated compounds were run using the TG/FT-IR method with secondary oxidation. The first two samples were spiked with o-DCB and TCE, respectively, and ~45 mg samples were analyzed. The resulting spectra from the o-DCB contaminated sample are given in Figure 5. The spectra from this run shows the HCl evolving from 2-6 minutes into the run, along with high concentrations of H₂O evolving throughout the run. It is clear from the spectra that the relatively strong H₂O bands (4000-3000 cm⁻¹) will not obscure the weaker HCl bands between 3000 and 2600 cm⁻¹. As shown in Table 2, the measured HCl concentration agrees well with the expected concentration for the sample spiked with o-DCB, but is somewhat low for the sample spiked with TCE. It is believed that the bias observed for the TCE sample is a result of volatilization of the TCE during sample preparation.

Two ~200 mg samples contaminated with 1.3% and 0.13% o-DCB, respectively, were also run in order to increase the sensitivity of the method, and the quantitative analysis results are also summarized in Table 2. In the case of the ~200 mg samples, incomplete oxidation of the evolving lubricant led to the formation of significant amounts of methane, which can interfere with the quantitation of HCl. (Further tuning of the secondary oxidizer should allow for complete oxidation of samples of this size.) However, the HCl was still observed evolving from 2-6 minutes during the run (as was the case with the smaller samples), before the methane evolution becomes significant. It should be noted that a bias was observed for the 1.3% o-DCB sample, and it is believed that this is a result of an error in the preparation of the sample. The HCl concentration measured for the 0.13% o-DCB sample agrees well with the expected concentration of 0.065% HCl. This corresponds to 620 ppm (w/w) organic chlorine in the lubricant sample, and on the basis of the signal-to-noise ratio in the spectra, indicates a detection limit of about 300 ppm (w/w). On the basis of these results and projections of the gain that can be achieved with additional improvements the lower detection limit for organic chlorine in synthetic lubricant samples could be reduced to less than 10 ppm (9).

Table 2. Summary of the quantitative analysis results for the TG/secondary oxidation/FT-IR analysis of lubricant samples spiked with chlorinated contaminants.

contaminant	sample size (mg)	Cl conc. (wt %)	HCl conc. (wt %)	measured HCl (wt %)
0.65 wt% o-DCB	41.2	0.31	0.33	0.35
0.65 wt% TCE	46.9	0.53	0.54	0.37
1.3 wt% o-DCB	198.5	0.62	0.65	0.35
0.13 wt% o-DCB	208.2	0.062	0.065	0.059

SUMMARY AND CONCLUSIONS

In this work, the feasibility of using two novel thermal/FT-IR analysis methods in combination with advanced data analysis techniques to detect contamination in used turbine engine lubricants was demonstrated. The first method, TG/FT-IR combined with advanced data analysis routines, was shown to be capable of detecting the presence of different types of contaminants in synthetic lubricants at concentrations of about 5%, and this sensitivity could probably be increased to about 1% with software and hardware improvements. It was demonstrated that data analysis routines based on factor analysis (SIMCA) and neural networks could be used for identifying the presence of a contaminant. The second method, TG/secondary oxidation/FT-IR, was developed specifically for detecting trace levels of chlorinated contaminants in lubricants. Optimization of this technique using existing instrumentation led to a detection limit of about 300 ppm (w/w) organic chlorine in the lubricant. Further improvements in the hardware and software components could lead to detection limits of <10 ppm.

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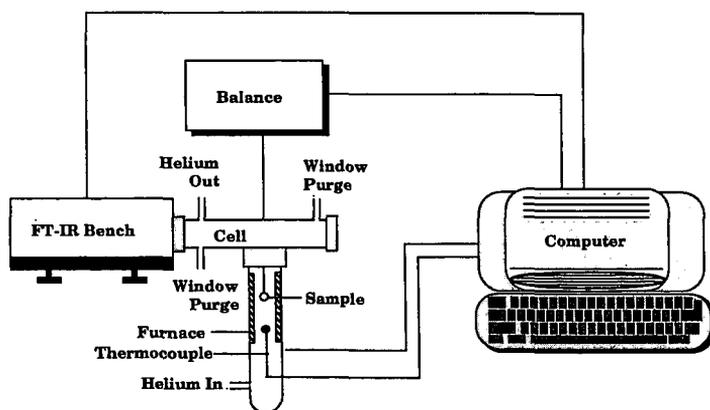


Figure 1. Schematic diagram of the standard TG/FT-IR instrument. The sample is suspended in the furnace, and, as the sample is pyrolyzed, the evolving species are swept into the FT-IR gas cell. The instrument was modified to include an oxidation zone before the gas cell.

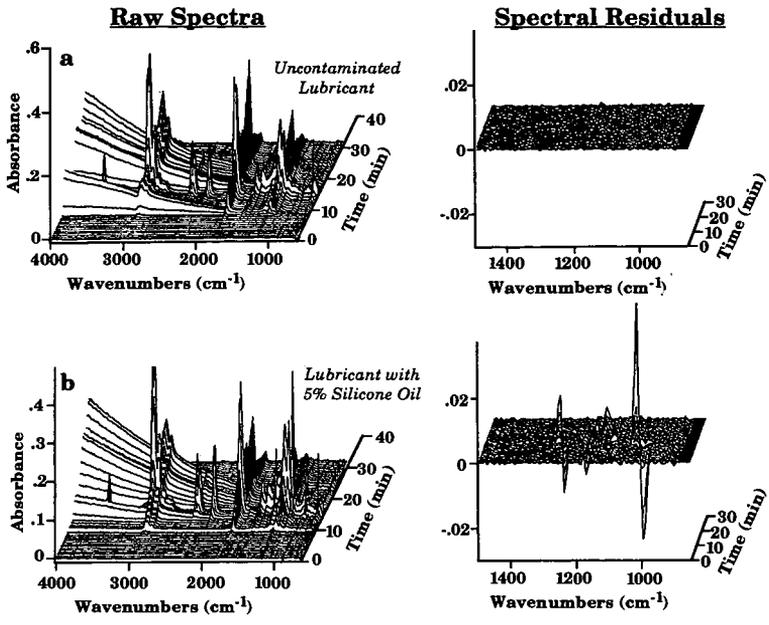


Figure 2. Examples of SIMCA analysis for TG/FT-IR runs of a) uncontaminated lubricant and b) lubricant with 5% polydimethyl siloxane. The raw spectra from the run are shown on the left, and the residual spectra resulting from projection onto the primary factors are shown on the right (note the expanded scale).

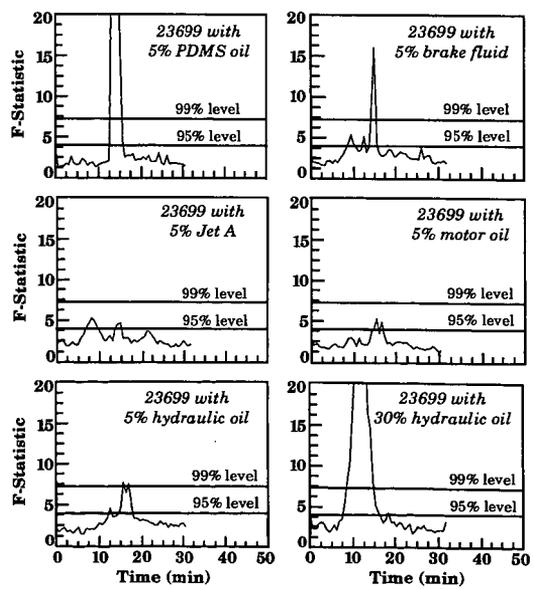


Figure 3. Results of SIMCA analysis for contamination in used synthetic lubricants. The *F*-values are plotted versus time for TG/FT-IR runs of lubricant samples contaminated with various fluids likely to be encountered at an Air Force base.

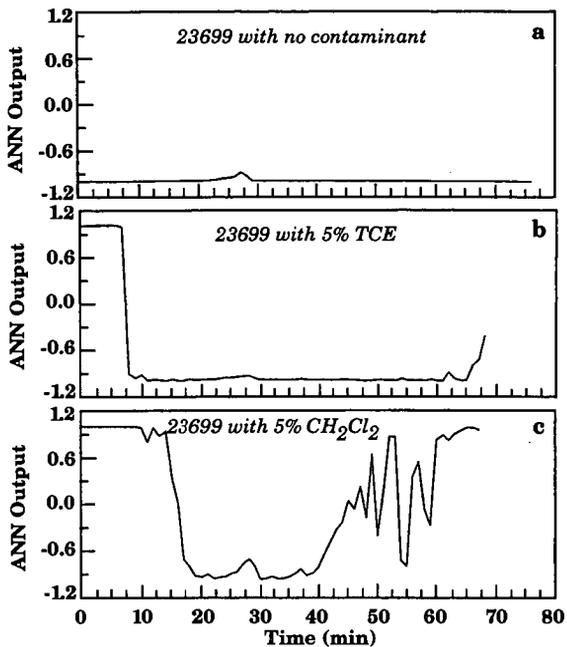


Figure 4. Neural network based prediction of chlorinated contaminants evolving during TG/FT-IR runs. A value of 1.0 indicates the presence of contaminant and -1.0 indicates the absence of contaminant. a) uncontaminated Mobil 23699; b) trichloroethylene contaminated Mobil 23699; c) dichloromethane contaminated Mobil 23699.

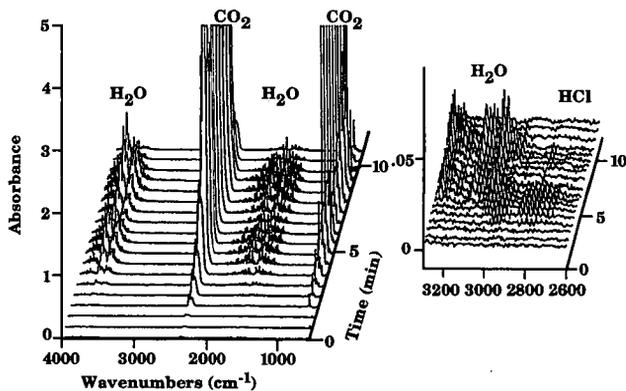


Figure 5. Spectra obtained during TG/secondary oxidation/FT-IR analysis of a 41.2 mg sample of lubricant spiked with 0.63% *o*-DCB. The scale is expanded in the plot on the right to show the evolution of HCl.