

## STUDY OF SURFACES USING NEAR INFRARED OPTICAL FIBER SPECTROMETRY

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### ABSTRACT

The measurement and control of cleanliness for critical surfaces during manufacturing and in service provides a unique challenge for fulfillment of environmentally benign operations. Of particular interest has been work performed in maintaining quality in the production of bondline surfaces in propulsion systems and the identification of possible contaminants. This work requires an in-depth study of the possible sources of contamination, methodologies to identify contaminants, discrimination between contaminants and chemical species caused by environment, and the effect of particular contaminants on the bondline integrity of the critical surfaces.

This presentation will provide an introduction to the use of optical fiber spectrometry in a nondestructive measurement system for process monitoring and how it can be used to help clarify issues concerning surface chemistry. Correlation of the Near Infrared (NIR) spectroscopic results with Optical Stimulated Electron Emission (OSEE) and ellipsometry will also be presented.

### INTRODUCTION

Optical fiber spectrometry offers unique capabilities for detection and identification of contaminating species on aerospace flight hardware and other critical surfaces, either stand-alone or in conjunction with other inspection processes such as Optically Stimulated Electron Emission (OSEE). Much progress has been made in understanding spectral features observed from surface films with optical fiber probes, yet the interpretation of spectral features on surfaces continues to be the major challenge for this spectrometric tool. The complexity of the interactions due to thin film reflection/absorption phenomena still requires some chemical and physical knowledge about the surface being analyzed. In addition considerable expertise is still required to sort through the spectral features obtained, to pick out the significant features and determine the origin of these features. It is anticipated that the evolving methodologies resulting from the work presented here, will become more easily absorbed into the production arena with a little more development and implementation activities.

Continuing work with both NASA/MSFC and Thiokol has provided the opportunity to apply the capabilities of optical fiber NIR techniques to the following cases:

A summary of the path used to optimize upon an analytical approach used are presented in figure 3. The approaches most frequently used are derived from the current interest in applying chemometric techniques to solve real-world problems. All of the software packages used in this work are commercially available and used by a large number of spectroscopists and others who need to analyze large spectroscopic data sets.

**Figure 3. Data analysis concepts used in this work.**

## **DATA ANALYSIS CONCEPTS**

- **Experimental Constraints**
  - Low signal levels
  - Variable reflectivity among sample plates
  - Silica spectral domain
- **Digital Filtering**
  - Savitsky-Golay Smoothing Routines
- **Principal Component Analysis (PCA) and Partial Least Squares (PLS1 and PLS2)**
  - Provide number of factors that influence the observed spectra
  - Identify the real factors
  - Detect clusterings of data
  - Identify spectra due to each factor
  - Predict new data and/or verify model.

The procedures followed in obtaining spectral data and performing the analysis were fairly consistent. Deviations in the use of specific routines for data smoothing or to bring out certain anticipated features were implemented as required. Once a series of NIR spectra were obtained from the experiments described in this report, a variety of chemometric techniques were employed to isolate significant spectral features as factors using either Principal Component Analysis (PCA) or Partial Least Squares (PLS) techniques. Iterative smoothing routines were sometimes performed back-to-back to improve the S/N ratio of the observed spectra. Complementary analysis techniques were used in order to trade off advantages over disadvantages of various techniques. For instance, optical fiber spectral scans were performed with the Guided Wave 260, which can obtain the highest resolution possible either by reducing the spectral bandwidth or by signal averaging. Either choice requires relatively longer scan times. Hence trade-offs between resolution and scan time had to be used in optimizing spectral scans with OSEE scans in the studies performed in the environmental chamber. At the level of resolution used, sequential smoothing routines would allow for good peak definition.

- HD2 and silicone films on D6AC steel and 7075 aluminum
- Mixtures of HD2 and silicone films on D6AC steel and 7075 aluminum
- D6AC steel and 7075 Aluminum plates in controlled temperature and humidity for extended periods of time.

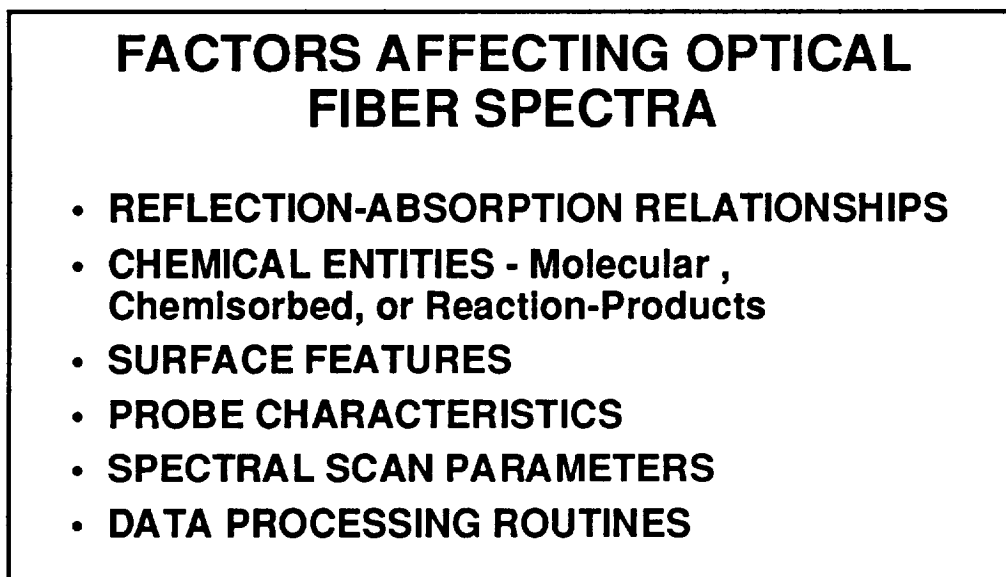
The primary results of these observations has been to show that NIR spectrometry is able to:

- Discriminate between HD2 and silicone greases in single or mixed applications, both qualitatively and quantitatively.
- Detect the various water/hydroxide species that occur on both D6AC and aluminum surfaces under variable humidity and temperature conditions.
- Detect levels of contamination by tape residues used in the manufacturing operations of the RSRM.

#### **Optical Fiber Spectrometry Considerations:**

Optical fiber spectrometry provides a number of challenges for accurate surface analysis. A number of the factors which can affect the signals observed, and correspondingly the interpretation of its chemistry, are shown in Figure 1 below.

**Figure 1. Factors affecting the interpretation of spectra observed from surfaces.**



The underlying physics associated with the reflection/absorption characteristics of the multitudinous films which may occur on a surface are always going to be part of the unknown in any analysis performed on solid rocket motors. Objectively, the data processing techniques used in this work, have been oriented such that these phenomena

can be factored out to provide spectral features associated with both the chemical species and physical parameters represented on the surface. These chemical entities can be oxides, hydroxides, or any other materials. In the spectral region in which this work has been performed, 1.0 - 2.5 microns, the -OH stretching vibration is the major peak observed for species which result from hydrolysis or hydration. This spectral band represents the second harmonic or combination bands of features normally observed in the mid-IR using FTIR or other infra-red instruments. In most cases, the -CH stretching vibration is also observed in this region as combination bands. This observation, for example, allows us to differentiate between HD2 and silicone greases. Spectral observations in the mid-IR can not always do as well in differentiating between similar species.

In this work, the chemical entities which are observed in the spectral scans are primarily hydrated species which result from the presence of water on the surface of the metal or contaminants purposely placed on the surface. The chemistry associated with hydrolysis of D6AC steel and aluminum 7075, obviously becomes a very important part of the interpretation of the spectra observed in these experiments. In the case of D6AC steel, very little work on hydrolysis at ambient temperatures has been found in the literature so far. Aluminum; however, provides a large number of data presented in the literature which makes the interpretation of the spectral observations somewhat easier.

The obvious goal of any spectral analysis is to obtain a quantitative measure of the interaction between the material being analyzed and the light used for interrogation. The physical features extracted in the factor analysis can be difficult to interpret with non-uniform surfaces, presenting another set of problems in the quantitative analysis of films on surfaces. Since the light may specularly reflect off the surface of the film or the surface of the metal more than once, one may obtain spurious intensity relationships from the spectral analysis. Also if the light reflected off the surface has passed through the film more than once, then one has difficulty providing a quantitative measurement of the properties of the film. In the case of the materials used in this study, solid rocket motor case materials were not intended to have mirror finishes, hence, diffuse scattering from randomly oriented surface features encompasses the primary thrust of this work. In general most the panels provided for spectral analysis had varying surface roughness and reflectivity, making calibration one of the most difficult tasks in the study.

In addition to the enhancement of the desired signals using physical improvements related to the optical and scan parameters, improved software approaches have also been used during this work, primarily in the use of chemometrics techniques to extract the useful information contained in a series of spectra acquired from the various samples under test. These methods fall under the category of multivariate analysis techniques and are used very successfully in a number of chemical and process industries. For example the idea is to analyse all the relevant spectral data at once and extract features which dominate the behavior of the data series. This is shown in figure 2 on the next page, in which the accumulated spectral data is analyzed by a multivariate analysis technique and the loadings (spectral features) and scores (influences) are extracted to determine how the system is changing chemically. This analysis is currently being performed with Unscrambler II.

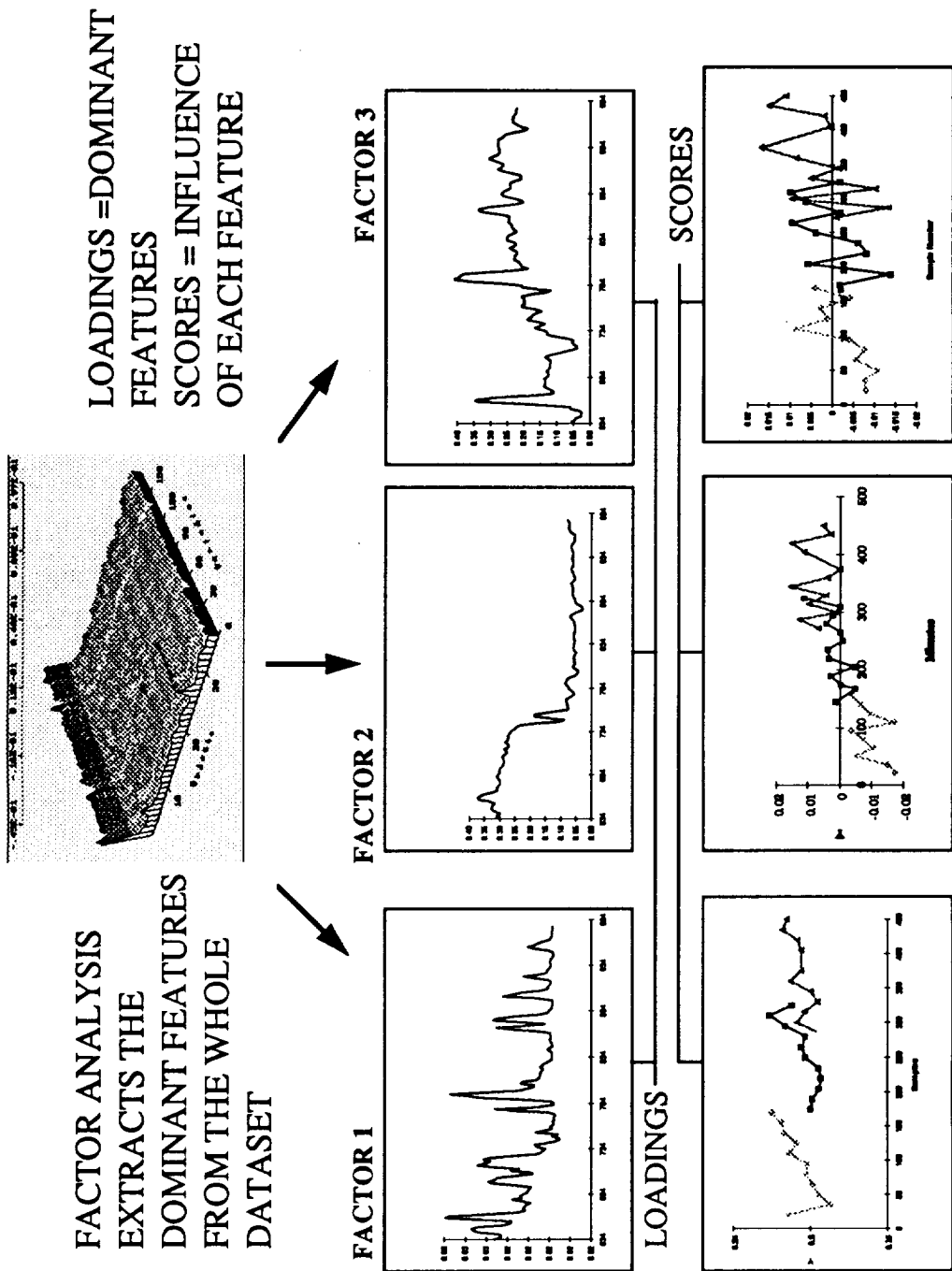
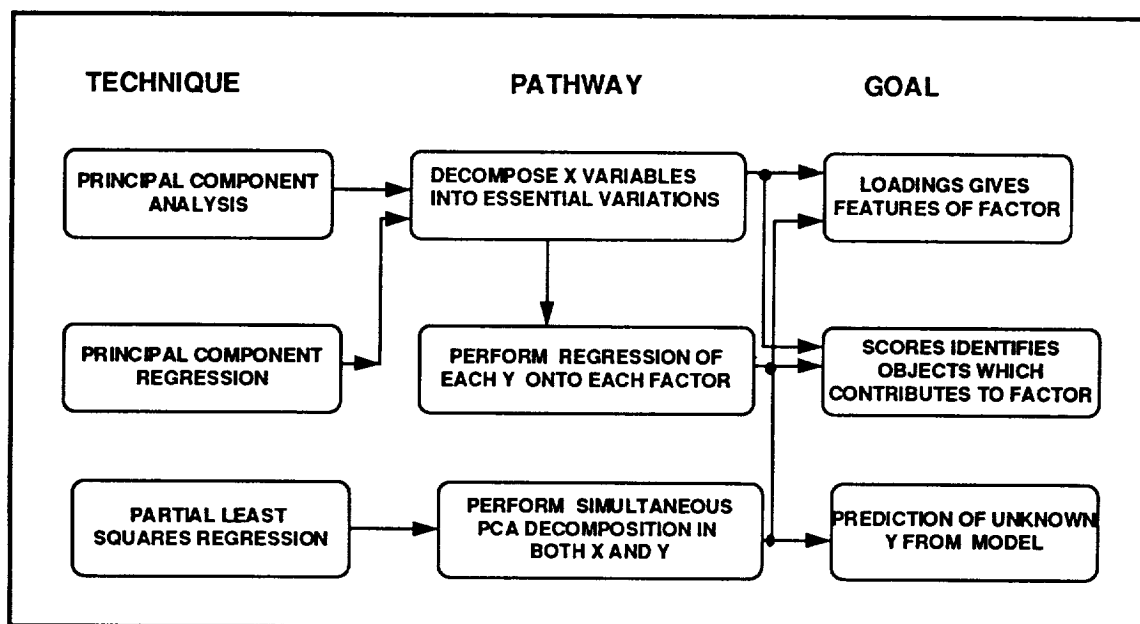


Figure 2. Loadings and scores are the dominant factors contained within a dataset.

The data handling routines for separating out the significant peaks were primarily by performing a PLS Analysis on the spectra, usually using the total spectra set to generate a model for any set of experiments. A schematic showing the possible approaches to perform either principal component or partial least squares analysis on the data sets is shown in Figure 4 below. In some cases verification of peaks and their occurrence in the experiments was obtained by taking the difference between any two spectra in a series.

**Figure 4. Decision tree showing possible routes to obtain factors in the spectral analyses for this work.**



In the work presented here, the philosophy was to collect all the information for a particular substrate, chemical system and build the model based upon the most complete set of variables possible. In this manner, the Unscrambler software was much more likely to pick out the corresponding factors from the observed spectra.

The major software used to support this work included SpectraCalc and Unscrambler II. Typically spectra were recorded in units of watts and transformed into absorbance using the relationship:

$$A = \log \frac{I}{I_{ref}}$$

Much work was spent in the beginning of the research in determining what reference surfaces to use for calculating absorbances. The major problem that arises in this type of analysis is when a spectral feature goes negative; i.e.  $I < I_{ref}$  then most of the matrix multiplication techniques are not applicable. In practice, a negative absorbance is undefined, which means that the reference is not valid. Several reference surfaces used in

this work include an aluminum or gold mirror; i.e. totally or specular reflecting; barium sulfate i.e., diffuse reflecting, and native surfaces such as D6AC steel or aluminum.

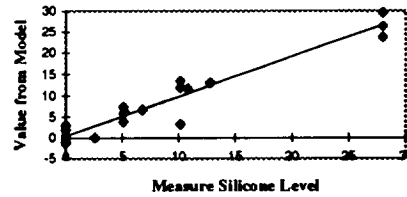
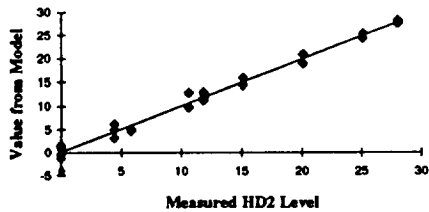
### Experimental Results:

The results of three different experiments are reported here. The first experiment is concerned with the quantitative identification of HD2 and silicone films on D6AC steel and 7075 Aluminum. A set of D6AC and aluminum 7075 panels were vapor degreased and grit blasted at 20° and contaminated at six levels with either HD2 or silicone or a combination of both. NIR spectra of the panels obtained and analyzed with PLS1 are shown in figure 5.

**Figure 5. Calibration curve for HD2 and silicone contaminants on D6AC Steel**

a. HD2 grease

b. Silicone

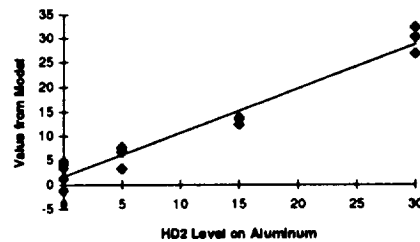
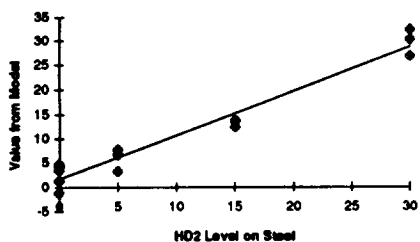


Another test was performed at Wasatch as a demonstration of capabilities with samples prepared by Thiokol personnel and the results are shown in figure 6.

**Figure 6. Results of NIR demonstration at Thiokol Wasatch.**

a. HD2 on D6AC Steel

b. HD2 on Aluminum 7075



Another series of experiments looked at the surface chemistry of D6AC steel and 7075 Aluminum plates in controlled temperature and humidity for extended period of time to determine the effects of relative humidity, temperature and grit blast angle on the bonding characteristics of both D6AC steel and Aluminum 7075. In both sets of experiments,

spectra subtraction between any two spectra showed peaks in the -OH vibration region that varied throughout the experiments. In the case of the D6AC steel, the lack of knowledge of what spectra features to expect made evaluation difficult. Aluminum has been studied substantially more and does provide spectral features which can be predicted from the literature. However, this approach does not provide much insight into the role of any of the variables in the experiment. Consequently more substance has been given to the PLS analysis in trying to interpret the observed spectral features. In each case the total collection of spectra for one substrate has been amassed into one data set to generate a PLS2 model. Then a PLS1 analysis was performed to isolate the significant features. In both cases, the principal components which appeared as the primary factor was grit blast angle. In the D6AC experiments temperature and relative humidity showed up nicely as factors 2 and 3. Spectral features that varied throughout the test then followed as the remaining principal components. For the aluminum data set, the temperature and relative humidity did not separate out quite as nicely. For that reason the interpretation for the aluminum-water chemistry is obviously quite complex. Fortunately the chemistry is better known and the literature provides more information to work with; however, the analysis of contaminating films is still difficult.

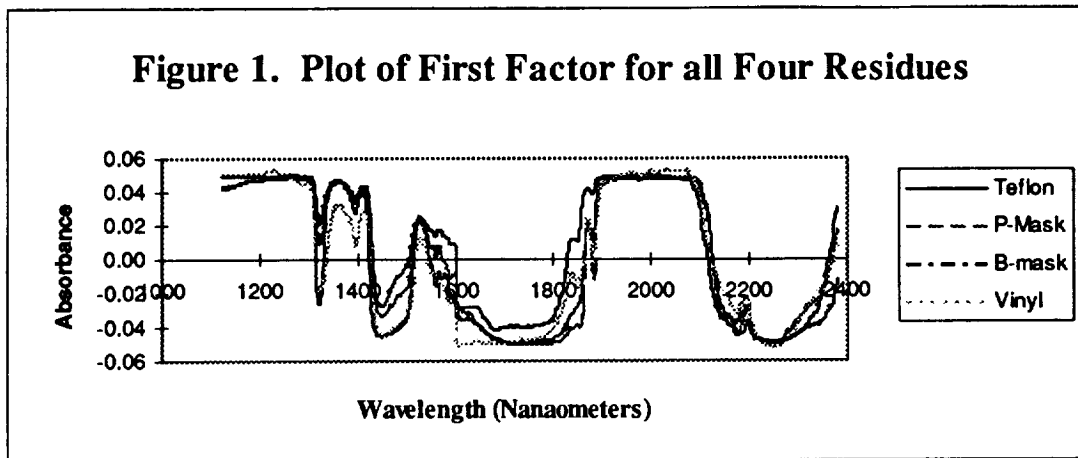
In the final sequence of experiments reported here, the residues of adhesives from four different tapes used by Thiokol in their manufacturing process were studied to determine if they could be quantitatively identified in the NIR. Data was collected from the samples of residue that might remain on a bonding surface after tape has been applied, then removed and the adhesive cleaned from the surface with solvent. The residues from four different tapes currently used by Thiokol were extracted using 1,1,1 Trichlorethane as a solvent. The four tapes studied, and their occurrence in the manufacturing process, are

- 1) Teflon tape, a tape used in the grit blast process;
- 2) P mask, a masking used in the painting operation;
- 3) B mask, a masking used in the grit blast process;
- 4) Vinyl tape, a tape used in the cleaning operation.

The residues were sprayed concurrently on large aluminum plates and witness foils. The gravimetric weights were determined for the witness foils from which conclusions about the levels on plates were deduced. Each residue was applied in two distinct levels of contamination, yielding eight contaminated levels, two for each type of contaminant. A blank panel was also processed similarly, except without contamination.

The PLS analysis confirmed that the tape residues from the four potential contaminants could be quantitatively identified in the NIR. The close similarity of the chemistry for the adhesives, for example a common plasticizer such as a phthalate was present in each residue, made the differentiation among the four a little more difficult; however, the PLS model did a fairly good job of differentiating between the tape residues.





### Summary

NIR spectrometry can provide a useful tool for the inspection of critical surfaces and the quantitative detection of contaminating materials. The utility of optical fiber system allows for flexible approach to using NIR in untraditional applications. In conjunction with chemometric tools, like PCA or PLS, the on-line approach is quite feasible and can provide a useful supplement to other techniques such as OSEE.

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