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Surface Characterization and Contamination Analysis

by

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INTRODUCTION

The research activity for this first year has focussed on three distinct activities:

1. the use of an integrating sphere to improve upon the gathering of spectral data from a variety of surfaces,
2. the use of optical fiber spectrometry to determine levels of contamination from tape residues on critical bonding surfaces and
3. an exploratory activity in the use of spectroscopic ellipsometry for the analysis of thin films of contaminants on critical surfaces has also begun.

The work presented here was performed by Charles Hughes and Brad Wittington, graduate students in Physics. Dr. William Arendale, Professor Emeritus in Chemistry and co-founder of JMBL Associates, assisted in performing many of the chemometrics analyses for these NIR studies. Ms. Yadilett Garlington also assisted in the chemometrics analyses of these NIR data sets.

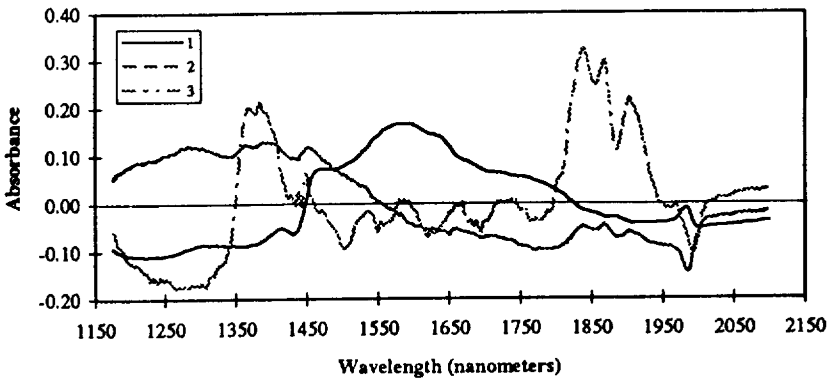
INTEGRATING SPHERE STUDIES

A major accomplishment was achieved in earlier research activities, funded by MSFC on NAS8-36809 and by Thiokol Corporation, by demonstrating that NIR optical fiber spectrometry was capable of quantitatively determining levels of contamination of HD2 and silicone contaminants on D6AC and aluminum alloys. In addition experiments using the 9-10 optical fiber probe were run to study the time/temperature/humidity effects on surface features of D6AC steel and aluminum alloys and to determine what effect surface hydroxides and oxides would have on bonding characteristics. The use of chemometric approaches for the analysis of the spectral observations from these studies showed that physical surface features (such as surface roughness) could provide a larger effect on the spectral features than the chemical species. This conclusion is shown as a result of the factor analysis of the spectra variation over time. The surface feature provides the largest influence on the data set. To illustrate this effect the first five factors from that work are reproduced here in figures 1 and 2.

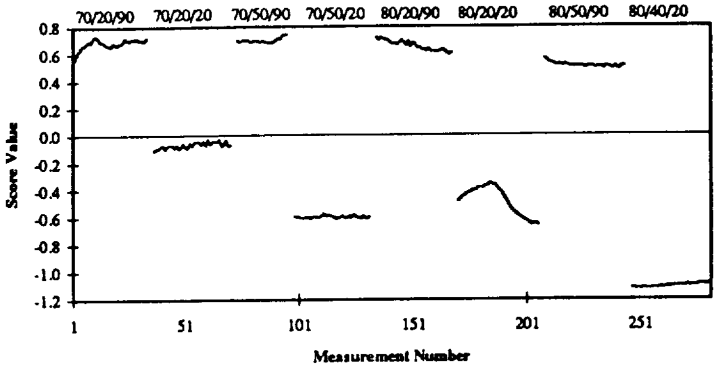
The first three factors which appear in the analysis for the D6AC study can be assigned as variances due to grit blast angle, relative humidity, and temperature in that order. Note that the scores chart for the first factor labels the groupings for the variables (temperature/relative humidity/grit blast angle). Since the loadings associated with the first two factors are rather broad and featureless, little chemistry can be derived from the observed features. Spectra features resembling previously observed moisture peaks on D6AC begin to show up with factor 3. This is probably due the effect of the temperature on the increasing significance of hydrolysis with respect to time in the course of the experiments. Since the model is centered on the mean, both positive and negative features show up in the loadings. Factors 4 through 6 do show some trends and spectral features which can be interpreted as due to hyrolysis effects on the surface layer of the D6AC steel;

Figure 1. Loadings and scores for factors 1-3 derived from the D6AC spectral data. The labels for the scores are listed in the order of (temperature/humidity/grit blast angle)

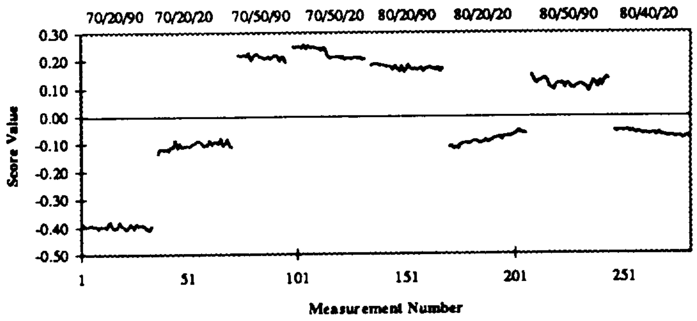
a.) loadings for factors 1-3.



b.) scores for factor 1



c.) scores for factor 2.



d.) scores for factor 3.

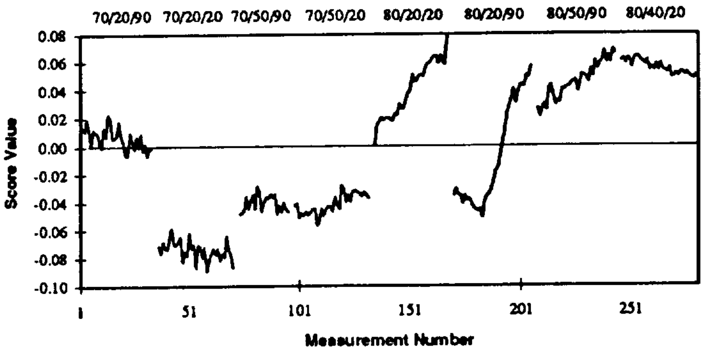
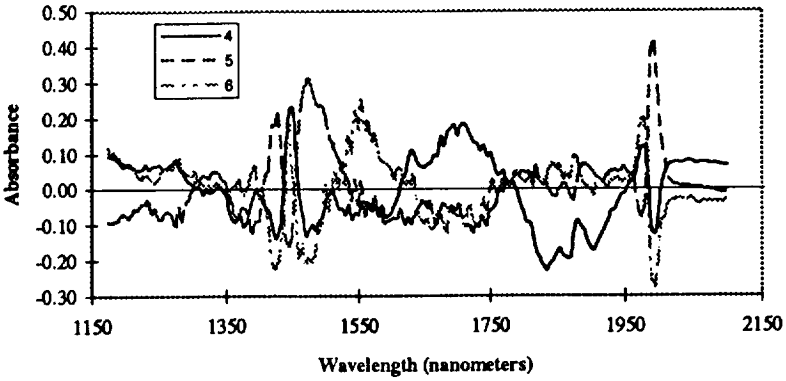
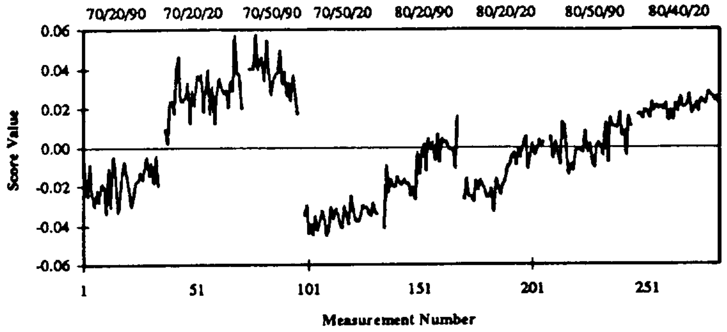


Figure 2. Loadings and scores for factors 4-6 derived from the D6AC data. The labels for the scores are again listed in the order of (temperature/humidity/grit blast angle).

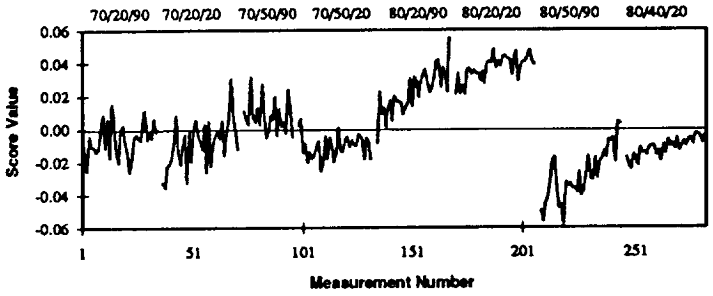
a.) loadings for factors 4-6.



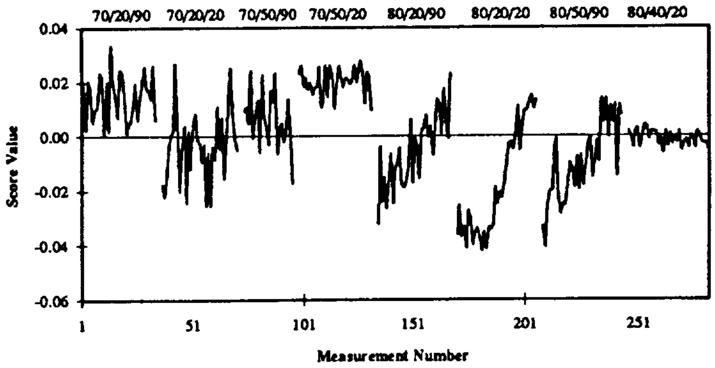
b.) scores for factor 4



c.) scores for factor 5



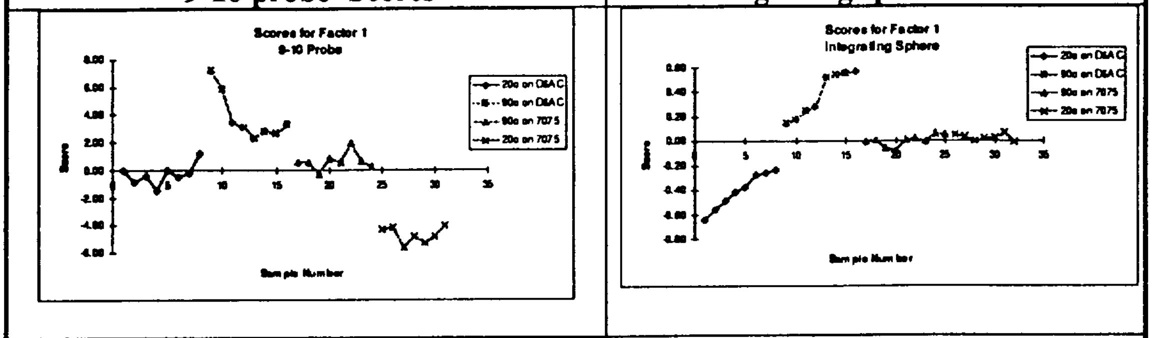
d.) scores for factor 6



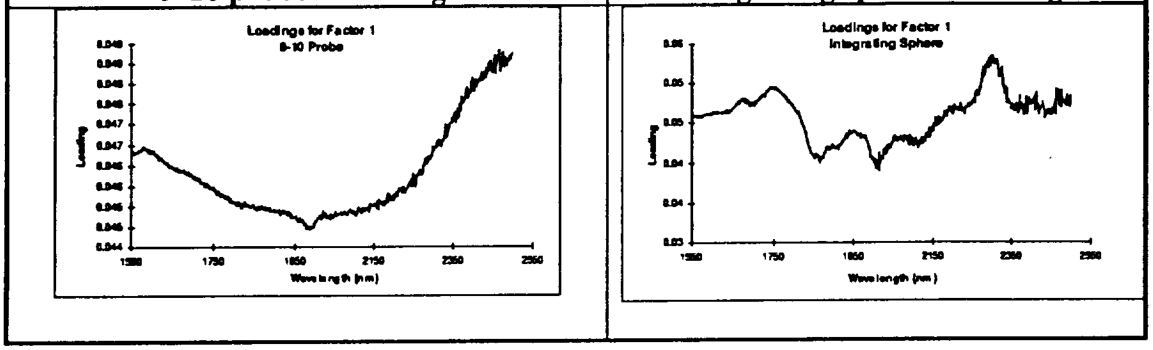
however, interpretation confirmed by results published in the open literature is not available at this time. The results of the aluminun 7075 alloy showed a similar influence of the surfaces features although not as prominent as the D6AC steel. This is probably due to the difference in hardness between the two materials.

In order to demonstrate the improvment of the integrating sphere over the 9-10 probe we took spectra of D6AC steel and 7075 aluminum plates which had been cleaned and grit blasted at 20° and 90° angle. Figures 3 through 5 give a comparison of the first three principal components for data collected with the 9-10 probe in comaprison with the integrating sphere.

Figure 3. Factor 1 Scores and Loadings


9-10 probe -Scores

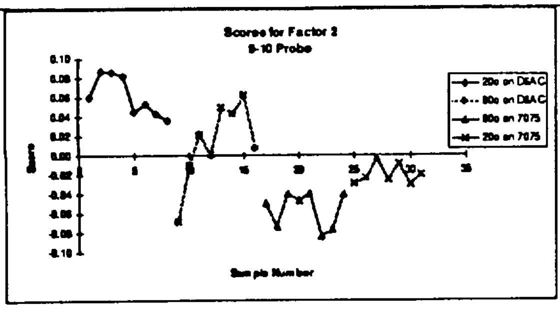
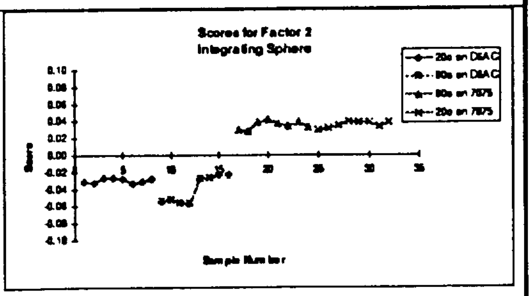
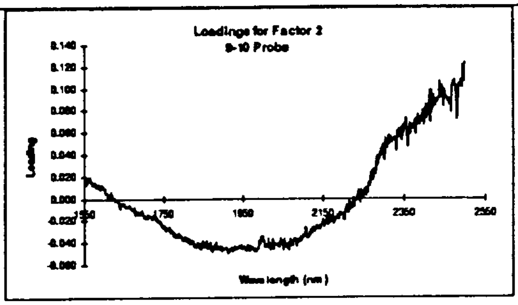
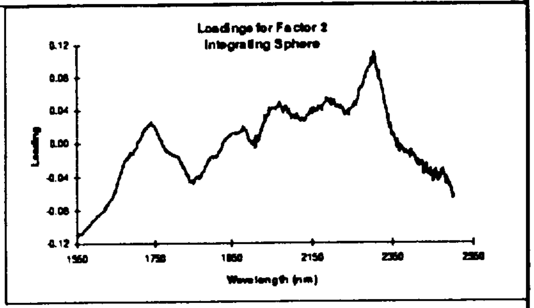
Integrating sphere -Scores


9-10 probe - Loadings

Integrating sphere -Loadings

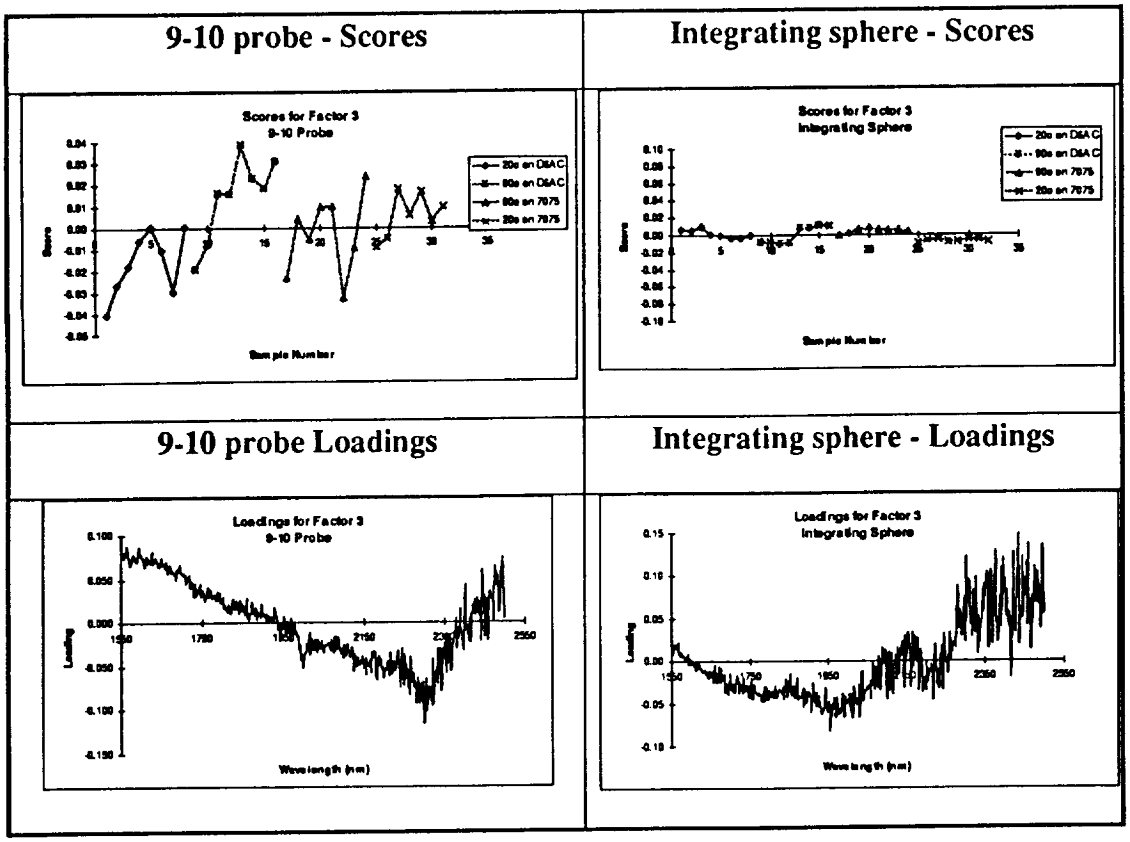
It can be seen that the spectral features for factor 1 are broad and contain no molecular information for the 9-10 probe, while the loadings for factor 1 with the integrating sphere do show absorption features. Also the scores for the 20 and 90 grit blast angle samples do cluster nicely, with both D6AC steel and Al 7075 separating out nicely.

Figure 4. Scores and Loadings for Factor 2

9-10 probe - Scores	Integrating sphere - Scores
	
9-10 probe. Loadings	Integrating sphere - Loadings
	

As can seen in figure 4, the scores and laodings for factor 2 exhibit similar characteristics as shown for factor 1. The loadings for the 9-10 probe are still featureless of molecular absorption while the integrating sphere does show good spectral detail. Also the scores for factor 2 show much less dependence upon the grit blast angle compared to factor 1 for both probes.

Figure 5-Scores and Loadings for Factor 3



9-10 probe - Scores

Integrating sphere - Scores

9-10 probe Loadings

Integrating sphere - Loadings

Spectra features, although not with much detail, begin to show up in factor 3 for the 9-10 probe. Clustering of the scores as to grit blast angle has disappered for both probes by the third factor. An important aspect of the analysis as shown in this data is that fewer factors are required for PCA because the physical features of the surface do not affect the variances observed in the data gathering.

TAPE RESIDUE STUDIES

Previous work on contract NAS8-38609 had demonstrated that a chemometrics analysis of spectra taken of witness panels, which had been quantitatively covered with known residues, could determine levels of contamination on both D6AC and AL 7076 surfaces. The extent of the demonstration at that time was that a PLS model obtained from the known levels of contamination was sufficient to determine levels of contamination on similar panels, treated as unknowns. More importantly, the PLS model allowed us to differentiate between the four types of residues:

1. Teflon tape used in the grit blast operation
2. Paint mask tape used in the painting operation
3. Vinyl tape used in the cleaning operation
4. Blast mask tape, also used in the grit blast opration.

The procedures developed in carrying out this work evolved into additional spectral observations on residues left from pulling the tape and the same residues after smearing with a cloth saturated with a solvent such as methyl chloroform.

Once again the Guided Wave 260 with the 9-10 probe was used to collect the spectral data. The data was obtained using the following parameters:

Spectral Averages	1
Point Averages	5
Dwell Angle	1
Wavelength Band	0.8 - 2.2 μ with a step of 2 nm
Detector	Germanium with a 0.5 mm slit <1.6 μ PbS with 0.5 mm slit above 1.6 μ

The data for this study was truncated to match the spectral range of the calibration data, which had been taken from 1.1 - 2.2 μ with a step size of 1 nm. In addition the calibration data was transformed to a 2 nm step size to match the step size of the current data. Neither change will affect the results of the analysis; however, the reduced data set does make the analysis less cumbersome.

The procedures for analyzing the spectra data was the same as before: subtraction from a reference spectrum to obtain aborbance values and the transformed into Unscrambler format. Table 1. provides the resulting prediction matrix for the data set.

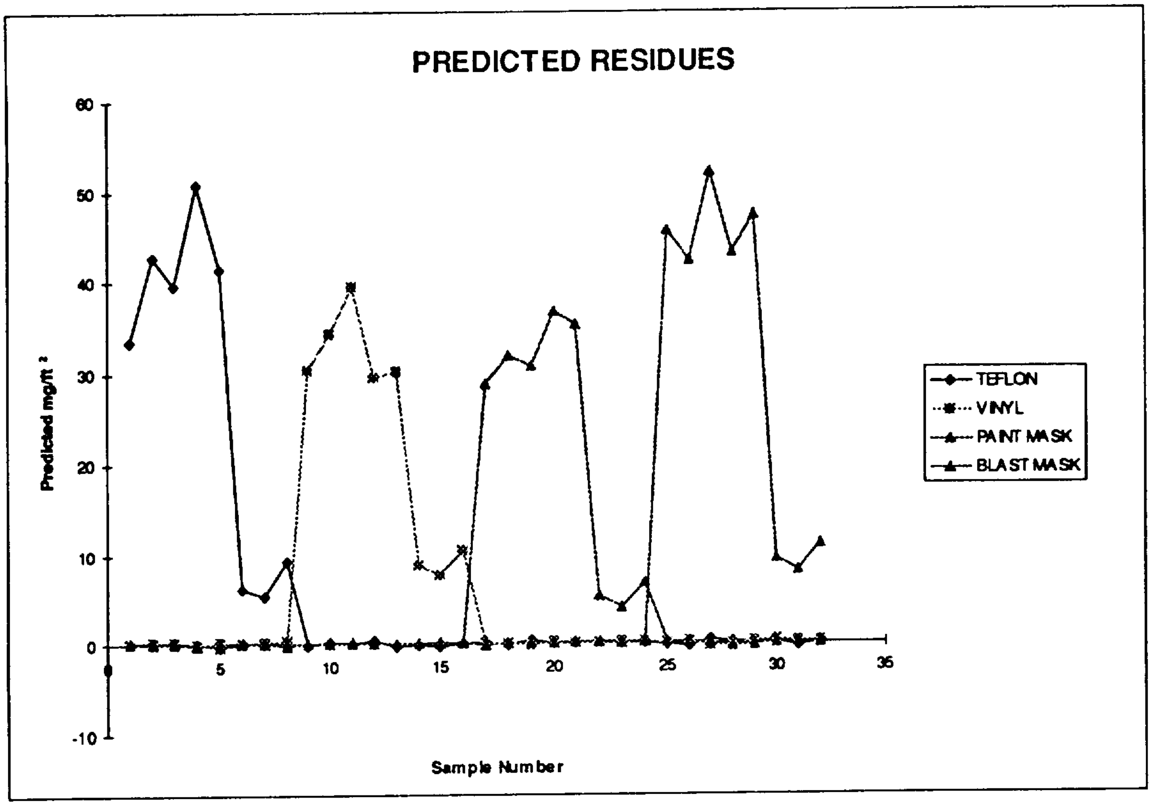
The results indicate that levels of each residue was detected for both test conditions and that the calibration set successively selected each residue type. In each case the results after wiping with the methyl chloroform resulted in removal of most of the residue, but not all. Because of the technique involved in the wipe procedure, where the cloth was lifted at the edge instead of wiping off the edge, it appears that more residue was left at

Table 1. - Numerical results for the predicted residue.

SAMPLE	TEFLON		PAINT MASK		VINYL		BLAST MASK	
	Y-PRED	DEV	Y-PRED	DEV	Y-PRED	DEV	Y-PRED	DEV
1	33.5	2.41	0.1	2.56	0.2	1.73	0.2	2.01
2	42.6	2.37	0.2	2.62	0.0	1.49	0.2	1.83
3	39.5	2.33	0.2	2.48	0.1	1.66	0.3	1.92
4	50.7	2.37	-0.1	2.89	-0.1	1.91	0.1	1.95
5	41.3	2.32	0.3	3.12	-0.0	1.50	-0.2	1.92
6	6.2	3.40	0.0	3.02	0.2	1.49	0.1	1.80
7	5.4	3.00	0.2	2.56	0.1	1.78	0.0	1.99
8	9.3	2.92	0.4	2.45	0.1	1.80	-0.1	1.95
9	-0.1	2.81	30.3	2.67	0.1	1.90	-0.0	1.89
10	0.2	2.82	34.2	2.76	0.0	2.02	0.0	1.88
11	0.1	2.26	39.4	2.82	0.0	1.65	0.2	1.94
12	0.4	2.15	29.5	2.94	0.1	1.48	0.1	2.03
13	-0.3	2.58	30.2	2.93	0.1	1.52	0.1	1.86
14	-0.1	2.48	8.9	2.67	0.1	1.45	0.0	1.79
15	-0.2	2.72	7.6	2.93	-0.0	1.83	0.2	2.04
16	-0.0	2.64	10.4	2.99	0.2	1.79	0.1	2.02
17	0.2	2.10	0.0	2.87	28.8	1.72	-0.1	1.89
18	-0.1	2.44	0.1	2.86	31.9	1.65	0.1	1.92
19	0.4	2.75	-0.1	2.69	30.8	1.45	-0.0	1.88
20	0.1	2.33	0.2	2.72	36.7	1.79	0.1	2.01
21	0.0	2.13	0.1	2.63	35.2	1.67	0.2	2.03
22	0.2	2.43	0.1	2.46	5.3	2.11	0.3	1.98
23	0.2	2.45	0.3	2.85	4.0	1.93	0.1	1.95
24	0.1	2.67	0.2	2.91	6.9	1.82	0.2	1.97
25	-0.1	2.43	0.1	2.80	0.2	1.73	45.6	1.96
26	-0.3	2.56	0.2	2.90	0.2	1.68	42.4	2.01
27	0.4	2.46	-0.2	2.68	0.0	1.98	52.1	1.87
28	0.2	2.44	-0.1	2.68	-0.2	2.01	43.2	2.00
29	0.1	2.47	0.2	2.65	-0.1	1.91	47.3	2.03
30	0.2	2.13	0.4	2.69	0.0	1.65	9.4	1.92
31	-0.2	2.21	0.3	2.78	0.1	1.67	8.2	1.98
32	0.3	2.01	0.2	2.66	0.1	1.89	11.2	2.02

the end of the wipe. The numerical values reported for the tape residues from this test are probably not precise, since all of the the spectral data taken just after the tape pull and before the wipe is above the highest point in the data point in the calibration set. Hence these results are extrapolated beyond the calibration model. The relative values are reasonable and do indicate that the NIR method applied here does work with smaller sample amounts than the known levels used for the calibration model.

Figure 6. - Chart showing predicted tape residues.



Having the ability to quantitative measure levels of specific contaminatants in the solid rocket motor production facility is an excellent tool for the manufacturers. This study has extended the results beyond the calibration stage into smeared films which are more representative of an industrial occurrence.

In order to compare the levels shown in Table 1 and figure 6 with a clean plate, one can see from Table 2 what levels uncontaminated plates predict from using the PLS model.

Table 2. - Numerical results from clean plate.

SAMPLE	CLEAN D6AC STEEL	
	Y- PRED	DEV
33	0.3	1.45
34	0.2	1.41
35	0.3	1.39
36	0.1	1.44
37	0.1	1.38

Continuing work will include an NVR procedure to compare with current procedures in the manufacturing of SRB's and longer aging times before the tapes are pulled.

ELLIPSOMETRY ACTIVITIES

Two different studies were carried out during this time frame to determine the capabilities of ellipsometry for quantitative measurements on critical hardware. The instruments used in this study were the VASE and Gaertner instruments at MSFC and the tri-beam at UAH. In each case a set of measurements were made on a specfic film/substrate combination to determine the consistency of results that should exist with the combined data set. HD2 on silicon has been the most studied combination. However, since it is always going to be a three layer system (with SiO2 as the middle layer) the ellipsometer requires the capability to solve for the middle layer.

At the time of this report, the Gaertner and the VASE come fairly close in repeating optical values for two layer systems. The VASE does a better job on three layer systems due to its modelling capability for multi-layer systems. The tri-beam has an unusual (and unknown) methodology built into its software. We are currently trying to get a better grasp of what is already built in to the system to see if we can modify it to provide similar modelling capabilities as the VASE.