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7. Abstract This report discusses work done to investigate the feasibility of using optical spectroscopic methods, combined with multivariate Partial Least Squares (PLS) calibration modeling, to quantitatively predict the moisture content of the crust material in Hanford's waste tank materials. Experiments were conducted with BY-104 simulant material for the 400-1100 nm (VIS), 1100-2500 (NIR), and 400-4000 cm ⁻¹ (IR) optical regions. The test data indicated that the NIR optical region, with a single PLS calibration factor, provided the highest accuracy response (better than 0.5 wt%) over a 0-25 wt% moisture range. Issues relating to the preparation of moisture samples with the BY-104 materials and the potential implementation within hot cell and waste tanks are also discussed. The investigation of potential material interferences, including physical and chemical properties, and the scaled demonstration of fiber optic and camera types of applications with simulated waste tanks are outlined as future work tasks.		
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Prepared by

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Center for Process Analytical Chemistry (CPAC)

University of Washington, Seattle, WA

under

Westinghouse Hanford Company Contract Number

MLR-SVV-562951

Executive Summary

This report describes the work done at the Center for Process Analytical Chemistry (CPAC) as the Phase 1 work scope of Westinghouse Hanford Company (WHC) contract MLR-SVV-562951. The main emphasis of the Phase 1 project was to investigate the feasibility of using spectroscopic methods, combined with multivariate calibration, to quantitatively predict the moisture content of the crust material in the Hanford waste tanks. This task was to look at several wavelength regions, including the visible (VIS), the near-infrared (NIR), and the mid-infrared (IR) spectral regions in order to determine the best wavelength range for further investigation in later work. The overall goal of the project is to develop a monitoring system for moisture in the waste tanks.

All the spectroscopic data presented in this report was collected on commercially available spectrometer systems. The VIS and NIR studies used a spectrometer system capable of scanning a wavelength range from 400-2500 nm with 2 nm resolution and separate visible Si (400 to 1100 nm) and PbS NIR detectors (1100 to 2500 nm). All VIS and NIR spectra were collected in reflectance mode using a standard powder sample cup and were co-averaged over 32 scans to increase the signal-to-noise. For the IR studies, a FT-IR spectrometer system with a DTGS detector capable of scanning over the range from 350-7800 cm^{-1} with up to 0.5 cm^{-1} resolution was used. The IR spectra were collected using a diffuse reflectance accessory at a resolution of 4 cm^{-1} and each spectrum was the result of 40 co-added scans over the spectral range of 400-4000 cm^{-1} . All the FT-IR spectra described in this report are referenced to the diffuse reflectance spectrum of dry KBr powder and are reported in absorbance units.

All experiments were conducted using the BY-104 Salt Cake Simulant provided to CPAC by WHC. The samples were prepared by first drying the bulk surrogate material for forty-eight hours at 160°C in an oven. The BY-104 material was ground by hand using a ceramic mortar and pestle before and after drying to

remove any large chunks and provide a fairly uniform granular powder. The influence of particle size on the moisture determination will be investigated in Phase 2 of this project. Standard additions of water were added to the samples of dried surrogate by spraying a fine mist of de-ionized water on the dry material followed by thorough mixing. The sample was weighted before and after the water additions to find the weight of water added. All the water concentrations are reported as a weight percent (wt%) water in the total sample and ranged from zero wt% (dry starting material) to approximately twenty-five wt%.

All the calibration models discussed in this report were developed using the multivariate method of Partial Least Squares (PLS) regression. Cross validation was used to determine the number of factors to use in the PLS models and to avoid the overfitting problem in the calibration models. The second derivatives of the reflectance spectra in both the VIS and NIR regions were generated to eliminate baseline shifts due to changes in scatter and sample position. For the IR spectral data, several different baseline correction and preprocessing methods were investigated before forming the PLS models.

The results of the various models are presented in Table 1 below. From the table, one can see that the NIR model gave the best prediction results with the simplest model. For all the other approaches, additional model factors were required to account for nonlinear behavior in the relationship between the measured spectra and the moisture concentration. However, all the models had prediction errors that were better than 1.5 wt% water over the full moisture concentration range (0-25 wt%). For the IR spectra, it was observed that there were marked spectral differences between samples with water content above and below approximately 10 wt% water. This roughly corresponds to the saturation level for moisture in

	Number of Factors in Model	Standard Error of Prediction	Slope of Regression (R ²)	Persons's Correlation Statistic	Standard Error of Estimation
VIS Spectra	2	1.474	0.979	0.98	1.27
NIR Spectra	1	0.476	0.997	0.99	0.42
Raw IR Spectra	2	1.415	0.961	0.98	1.31
IR Mean Normalize	4	1.529	0.957	0.98	1.36
IR Area Normalize	3	1.710	0.944	0.97	1.55
IR First Derivative	3	1.297	0.968	0.98	1.18
IR Second Derivative	3	1.141	0.975	0.98	1.04
IR Kubelka- Munk	4	1.319	0.968	0.98	1.18
IR MSC (each set)	3	1.192	0.972	0.98	1.09
IR MSC (combined)	4	19.67*	0.972	0.98	1.10
IR LOW Model	3	0.412	0.978	0.99	0.34
IR HIGH Model	3	1.328	0.891	0.94	1.10
IR LWR Model	6	0.680	0.989	0.99	0.677

Table 1. Summary of regression statistics for the VIS, NIR and IR models. Please see the full text for a description of the various model treatments.

the BY-104 crust surrogate (i.e., the subjective point where visual inspection suggested that additional moisture added to the dry surrogate was not being fully adsorbed). The IR LOW and IR HIGH models are derived from the spectra of those

samples with water content above and below 10 wt%, respectively. The low water model gave very good results while the higher water model was about the same as the best full set models. Finally, the nonlinear method of locally weighted regression (LWR) was investigated to account for the nonlinear IR response in the two moisture concentration domains. The LWR model gave very good results even without any preprocessing of the spectral data.

In this phase of the study, we have concentrated on answering the question related to the prediction of moisture content using spectral information. Since this preliminary study was only aimed at establishing the feasibility of the approach, many aspects of experimental design were chosen to eliminate factors that could complicate this relationship. Variations due to differences in the compositional makeup of the crust material, particle size effects, and experimental setup were not investigated. All these factors could complicate the prediction of moisture from the spectral measurements. These effects will be fully explored in the next phase of the work. Based on the results obtained in this preliminary study, the optical determination of moisture content is certainly possible. Although many issues remain to be resolved, we believe these results establish the basic feasibility of the approach and it is anticipated that moisture in the Hanford waste tanks can be determined from optical reflectance measurements made on the crust material.

Since different spectral regions were studied in this Phase of the project, one can make some general observations as to the relative merits of each spectral region concerning moisture monitoring. For the NIR region the standard error of estimation is roughly half a weight percent for water while for the VIS spectral region it is about three times larger and the IR results are somewhere between the two (depending on the preprocessing used). The NIR and IR models were also better suited to predicting the low, or zero, water concentration samples than the

VIS model. Finally, the NIR model was the simplest model in that the nonlinear corrections (requiring additional factors in the VIS and IR models) were not required for the NIR model.

While the visible model was not able to achieve the same level of performance, the results obtained using this spectral region may prove to be more than adequate for the monitoring needs in the waste tanks. Certainly a visible light sensing system has some attractive aspects in terms of low cost and simplicity. While the IR results showed that good calibration models can be developed with suitable preprocessing, there are also some inherent drawbacks to the IR technology as a remote sensing system. First and perhaps most important, the IR radiation will have a very limited effective interaction path with the solid crust material. Variations due to changes in the compositional makeup of the crust material, particle size effects, and experimental setup will all most certainly complicate the prediction of moisture from the IR spectral measurements. Of course the other spectral regions are also affected by these parameters albeit not as stringently. Also one has to consider the cost of instrumentation, ease of use and calibration, and suitability to the monitoring environment all of which are slightly against the IR technology. The NIR spectral region has the advantages of more light interaction with the surface and sub-surface material due to the inherently greater penetration depth of the NIR radiation, simpler calibration procedures, and potentially more accessible and cheaper hardware required for remote sensing or fiber optic sensing.

Therefore, we recommend that the further development work for the moisture monitoring effort concentrate on the NIR spectral region. Our results show that NIR gave very good predictive models and its many advantages for working in the tank environment make it the most likely candidate for successful implementation as an on-line monitoring method. Issues remaining to be resolved are the effects

of surface topography, variation between waste tanks, and probe design and deployment. These issues will be addressed in the planned future phases of the project.

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Introduction

This report describes the work done at the Center for Process Analytical Chemistry (CPAC) as partial fulfillment of the Phase 1 work scope of Westinghouse Hanford Company (WHC) contract MLR-SVV-562951. The main emphasis of the Phase 1 project was to investigate the feasibility of using spectroscopic methods, combined with multivariate calibration, to quantitatively predict the moisture content of the crust material in Hanford waste tanks. This task was to look at several wavelength regions, including the visible (VIS), the near-infrared (NIR), and the mid-infrared (IR) spectral regions to determine the best wavelength range for moisture sensing. The overall goal of the project is to develop a remote monitoring system for measuring moisture in waste tank materials (sludge, cake, etc.). This report will present the results for all three spectral regions (the IR, the NIR, and the VIS). The main criteria for evaluation will be the predictive ability of the calibration models derived from the spectral measurements in estimating moisture. This report represents the completion of the Phase 1 study to determine initial feasibility.

The rationale for this project stems from the Unreviewed Safety Question (USQ) regarding the potential for ferrocyanide to react with oxidizing materials, such as nitrates and nitrites, under certain conditions to produce uncontrolled exothermic reactions leading to explosive conditions. It has been determined that the presence of water in excess of 12 wt% will suppress the ferrocyanide propagating reactions at ferrocyanide concentrations up to 26 wt% (dry basis).¹ Furthermore, the ferrocyanide reaction will not initiate below 220° C and will not propagate if the fuel concentration is below about 13 wt% (dry basis). Sufficient moisture levels will contribute to the overall safety of these tanks by 1) diluting the

reactants below the stoichiometric levels needed for reaction, 2) providing a heat sink to maintain tank temperatures at a safe level, and 3) provide the quenching needed to prevent the postulated runaway reactions.

Therefore, knowledge of the moisture content of ferrocyanide bearing waste tanks is important to determine the safety status of a tank. Continued monitoring of the moisture content of the tanks may be required to demonstrate that a tank is being maintained in a state of controlled safety. It is the continued long-term monitoring aspect that is addressed by this project. In order to monitor the waste material moisture in a cost effective manner, remote non-invasive sensing is preferred. There are a number of tanks that potentially need to be monitored and access to the tank interior is restricted. Due to the nature of the waste stored in the tanks, direct sampling of the tank material for moisture determination is problematic in terms of sampling, worker safety, analysis cost, and waste disposal.

Remote optical spectroscopy, combined with chemometrics methods for calibration, has been shown to be very useful for monitoring manufacturing processes. CPAC has developed many such applications for our industrial sponsors. It is expected that much of the same technology could be applied to the moisture monitoring of the ferrocyanide tanks. There are three main issues that need to be resolved prior to implementing the on-line moisture monitoring utilizing optical methods. These are:

- Feasibility must be established showing that optical measurements from tank crust material can be related to changes in the moisture content. Wavelength regions that are sensitive to the water content of the waste must be identified and quantitative models developed to predict the moisture within a satisfactory accuracy. That is the focus of this report and Phase 1 of this project.

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- Characterize the factors that influence the optical measurements, such as compositional effects, scattering, refractive index, and matrix effects, which could affect the performance of the moisture prediction. Associated with this effort would be work to prove the feasibility of remote monitoring within the geometry's of the waste tanks. This is the subject of the Phase 2 work scope.
- Engineering required to implement the remote monitoring optical system in the tank farm environment. Associated with this issue is design of the sensing system, resolution of environmental effects, such as head space humidity and scatter, transfer of the moisture calibration methods from the laboratory to field systems. These issues are deferred until Phase 3 and are largely dependent on the success of the earlier phases.

Associated with this project will be the need to relate the moisture determined through optical measurements from the tank crust surface to moisture within the bulk material in the tanks. Since it is anticipated that the optical measurements will only be able to sample the uppermost crust material, it will remain up to WHC to establish that the crust moisture represents a bounding condition for the bulk moisture. In order to establish this relationship, it may be necessary to monitor the bulk moisture through secondary means, such as a pennetrometer or core hole. Homogeneity of the tank will be an issue in resolving this question but extensive bulk sampling of the tanks is not feasible.

Experimental

The spectroscopic data presented here was collected on commercially available spectrometer systems. For the VIS and NIR studies a spectrometer system capable of scanning a wavelength range from 400-2500 nm with 2 nm resolution was used. The instrument contains a visible Si detector that covers the spectral range from 400 to 1100 nm (visible and short-wavelength NIR) and a PbS NIR detector that covers the spectral range from 1100 to 2500 nm. The instrument is capable of operating in either the transmission or reflectance mode with separate detectors and amplifiers for each mode of operation. All spectra for this study were collected in reflectance mode using a standard powder sample cup and sample transport accessories. To increase the signal-to-noise, 32 scans over the full spectral range were co-averaged to obtain each of the reported spectra. The system uses an internal ceramic reference standard to automatically calibrate the wavelength axis and to ensure linearity of the wavelengths over time. The spectrometer and sample system were controlled by an IBM-PC class computer using the vendor supplied software.

For the IR study we used a FT-IR spectrometer system with a DTGS detector. This system is capable of scanning over the range from 350 - 7800 cm^{-1} with up to 0.5 cm^{-1} resolution. In this work we used a resolution of 4 cm^{-1} and each spectrum was the result of 40 co-added scans over the spectral range of 400-4000 cm^{-1} . All the IR spectra described in this report are referenced to the diffuse reflectance spectrum of dry KBr powder and are reported in absorbance units. The instrument and data collection are directly controlled through an interface to a standard IBM-PC style computer.

Initially, we proposed to use a direct reflectance fiber optic interface to the instrument for introducing the samples to the FT-IR optical beam. However, given

the spectral range to be covered, and the high cost and limited availability of suitable infrared fibers, the initial studies were conducted using a standard diffuse reflectance sampling accessory that fits directly in the optical beam of the instrument sample compartment. In retrospect, this arrangement makes more sense for the initial feasibility studies since we are able to obtain the spectral information without anomalies or problems associated with the fiber interface. It should be noted that MID-IR fibers are commercially available for selected wavelength ranges and could be used in further studies if needed, although the stability of these fibers to the radiation environment found in the waste tanks has yet to be established.

All experiments were conducted using the BY-104 Salt Cake Simulant provided to CPAC by WHC. The samples were prepared by first drying the surrogate material for forty-eight hours at 160°C in an oven. It was observed that the moisture content of the bulk surrogate was approximately 10 weight percent (wt%) as supplied by WHC (gravimetrically determined by weight difference before and after drying). The crust material was ground by hand using a ceramic mortar and pestle before and after drying to remove any large chunks and provide a fairly uniform granular powder. This grinding step was deemed necessary to facilitate even distribution of the added water and to remove the influence of particle size on the moisture determination. Without grinding, the crust material forms large aggregates, or chunks, during the drying process. The influence of particle size on the moisture determination will be investigated in Phase 2 of this project. This material was again oven dried and placed in a desiccator between experiments.

For the VIS and NIR experiments, standard additions of water were added to the samples of dried crust surrogate by spraying a fine mist of de-ionized water followed by thorough mixing. The sample was weighted before and after the water additions to determine the weight of water added at each addition as well as to account for any material lost during transfer to and from the sample cups. All

the moisture concentrations are reported as a weight percent (wt%) water in the total sample. Two spectra were measured for each of the water addition steps by removing the sample cup and reinserting it in a rotated orientation between scans to determine any dependence on sample orientation. Table 2 below shows the experimental data for the VIS and NIR experiments. For the IR experiments, materials were prepared in a similar manner except each sample was prepared directly from the dried surrogate rather than using successive standard additions of water. The samples were weighted before and after the water additions to find the weight of water added for each sample. Table 3 below shows the experimental data for the IR experiment.

Sample Number	Weight Before H ₂ O Added (g)	Weight After H ₂ O Added (g)	Weight H ₂ O Added (g)	Total Wt% H ₂ O
1 2 3 4	50.005	50.005	0.000	0.000
5 6	50.005	50.370	0.000	0.730
7 8	50.367	50.958	0.365	1.192
9 10	50.940	51.740	0.231	2.792
11 12	51.721	52.117	0.800	3.585
13 14	52.081	52.840	0.396	5.105
15 16	52.799	53.496	0.759	6.502
17 18	53.460	54.412	0.697	8.411
19 20	54.344	54.948	0.952	9.624
21 22	54.890	55.478	0.604	10.806
23 24	55.410	56.663	0.588	13.328
25 26	56.553	57.382	1.253	15.000
27 28	57.244	58.247	0.829	17.028
29 30	58.024	58.764	1.003	18.529
31 32	58.269	59.122	0.853	20.225
33 34	58.728	59.756	1.020	22.393
35 36	58.624	60.256	1.632	25.820

Table 2. Experimental design data for the VIS and NIR water standard addition experiment.

Using the instrument's standard sample cups for the VIS and NIR measurements limits the high water concentrations to about 25 wt% due to seepage of excess water from the sample containers. We have obtained a separate reflectance detector accessory for the instrument that will allow for more flexibility in making up the samples and their composition. This probe allows the detectors to be moved to the sample at any orientation and distance using a fiber optic to transmit the incident light. Unfortunately, this attachment was not obtained in time for it to be used in this first phase of the work. At any rate, the range of water concentrations measured adequately span the critical 12 wt% value cited above. Since the crust material is expected to be dryer than the bulk sludge material (reported to be 40 to 60 wt% water), we believe this experimental range is sufficient to establish the feasibility of the moisture calibration.

For the IR experiments, the surrogate plus water samples were loaded into the sample cup and leveled prior to insertion into the spectrometer. No attempt was made to ensure uniform a sample surface other than leveling the sample to the top of the sample cup. Since the samples ranged from a dry powder to a slurry (depending on the amount of water added), the relative packing of material, the surface roughness, and the effective particle size will all vary depending on the water content. The effect of these parameters on the obtained FT-IR spectra will be discussed further in the result section. Five FT-IR spectra were measured for each sample. Each of the five spectra is of the same sample but the sample was removed and reinserted in a rotated orientation between scans to help determine any dependence of the measured spectra on the sample orientation due to surface irregularities.

The data, consisting of the spectra collected from the spectrometer and the recorded weights, were transformed from the vendors binary data format to a MATLAB² compatible ACSII data format using the supplied software. The transformed data was then transferred from the PC to a UNIX workstation where

the analysis and calibration model development were done using MATLAB. The MATLAB scripts used in the analysis are available from CPAC upon request.

Sample Number	Weight Before H ₂ O Added (g)	Weight After H ₂ O Added (g)	Total Wt% H ₂ O
1 - 5	2.2750	2.2891	0.6160
6 - 10	1.5645	1.6005	2.2493
11 - 15	1.6173	1.6650	2.3694
16 - 20	2.3556	2.4133	2.3909
21 - 25	1.9054	2.0183	5.5938
26 - 30	1.7959	1.9360	7.2366
31 - 35	1.9464	2.0803	6.4366
36 - 40	2.1030	2.3472	10.4039
41 - 45	2.4367	2.8156	13.4572
46 - 50	2.2649	2.6270	13.7838
51 - 55	2.2395	2.6809	16.4646
56 - 60	2.3820	2.8074	15.1528
61 - 65	2.4937	2.9987	16.8466
65 - 70	2.2952	2.9520	22.2493
71 - 75	2.0049	2.4560	18.3673

Table 3. Experimental design data for the FT-IR water standard addition experiment.

Results and Discussion

All the calibration models were developed using the multivariate method of Partial Least Squares^{3,4,5} (PLS). This method is described in Appendix A. In order to develop the "best" calibration models, it is necessary to balance the desire to reduce the error of prediction with the need to avoid overfitting the calibration data. This was done by relying on the statistical method of cross validation to determine the number of factors to include in the PLS calibration models. Cross validation is a technique by which part of the calibration data is held aside when

developing the model and then using the model with the held aside data to predict the quantities of interest. Since one knows the correct values for the estimated parameters, the predicted residual error sum of squares (PRESS) or the standard error of prediction (SEP) can be estimated as a function of the number of factors in the model and the data splitting scheme. Several data splitting schemes were investigated and all gave essentially the same results.

VIS and NIR Spectra

Before the analysis of the spectroscopic data, several preprocessing steps were performed. First, the spectral data was split into the visible and NIR portions in order to assess separately the relative value of each spectral region in determining the moisture content of the crust surrogate. Secondly, the second derivatives of the reflectance spectra in both the VIS and NIR regions were generated in order to eliminate baseline shifts due to changes in scatter and sample position. This was accomplished using the `pka2nddv.m` MATLAB script written by CPAC. Finally, the spectral data were mean centered before developing the PLS models. While not strictly necessary, mean centering simplifies the interpretation of the models. Without mean centering, the models generally require an additional factor simply to describe the average spectrum in the calibration set. In practice, little difference was observed between the models developed with mean centered data and those developed with the uncentered data.

The next two sections will describe the PLS models obtained for the VIS and NIR spectral data, respectively. In both cases, the highest water samples (sample number 35 and 36) were found to be outlier samples in the PLS models. This is probably due to the problems related to moisture leakage from the sample cup mentioned above. Another possibility is that there is a nonlinear response of the water at higher concentrations. This will be investigated further with the remote

reflectance probe described above as part of the Phase 2 work. In the remaining analysis, these samples were removed from the calibration data set.

The outlier samples can clearly be seen in Figure 1 where the sample leverage versus the studentized residuals is plotted for the NIR PLS model. The leverage of a sample is related to the importance of that sample in determining the PLS model. The studentized residuals are simply the calibration set concentration residuals corrected for the leverage of each sample. The use of studentized residuals is preferred over the straight residuals since high leverage samples tend to have lower residuals due to their influence on the model⁶. In a plot of this type, the identification of outliers and clues about why they are identified as outliers can be accomplished. Samples with studentized residuals outside the limit lines (determined from standard t-test statistics at the 95% confidence level) are identified as outlier samples. There are several rules-of-thumb that can be used in interpreting these plots.

- If a sample has low leverage and low errors, it is considered a representative sample that is modeled adequately by the model. This would be considered a "normal" calibration sample.
- A sample with low leverage and high errors would most likely be an outlier in the reference concentration values (water wt%) since its spectral response is fairly typical (low leverage). This would be considered an outlier sample.
- A sample with high leverage but low error indicates that this sample has influential spectral response and but that the model influenced by that response does an adequate job of estimating the concentration values. This would be considered an influential sample but not an outlier. However, it may be advisable to collect more

samples in this region to reduce the model's dependence on relatively few high influence samples.

- If a sample has high leverage values and high errors, that sample is probably an outlier in the spectral response. The model has worked extra hard at incorporating the sample's information but still fails to give adequate estimates of their reference values. This sample could be considered either an outlier or an influential sample. It is hard *a priori* to figure out if these samples have errors in the spectra or concentrations or if they are simply extreme samples in the normal calibration space. At any rate, more samples should be collected to resolve the ambiguity.

Figure 1. Leverage versus studentized errors for the NIR PLS model (limit lines represent 95% confidence levels) indicating samples 35 and 36 as outliers

In this plot, one can see that the outlier samples (35 and 36) have both high leverage and high residuals. Therefore, they may be considered "unique" samples with either spectral responses or concentration values outside the range of the linear calibration model. The high leverage indicates that these samples were highly influential in determining the model, but the fit to the moisture concentration values was poor. Given that all the samples at the high and low water levels received high leverage in the model, these samples are probably outliers due to errors in the water concentration value. Samples 35 and 36 were the highest water concentration samples and a likely explanation for the water concentration error is water seepage from the sample cup (as explained in the Experimental section above). The water concentration errors are positive (indicating a predicted moisture value lower than the "true" values) which is consistent with this explanation. The analysis of Figure 1 displays the valuable insights into the calibration model one can obtain from this type of plot. These samples show the same characteristics in the leverage versus studentized error plot for the VIS PLS model as is shown above for the NIR model. In the remaining analysis, these two samples were removed from the VIS and NIR data sets.

VIS Calibration Results

The visible spectra, shown in Figure 2, consist of a broad band absorbance with several humps, or shoulders, related to the water features. No attempt was made to identify the specific electronic transitions responsible for the observed spectral features. In the plot, each line is really two separate spectra corresponding to the replicate measurements for each sample. The derivative spectra, shown in Figure 3, clearly show the spectral features due to the variation in the water concentration after the broad spectral trend has been removed. Note that the first 50 data points in the spectra have been zeroed because of the derivative operation.

Figure 2. VIS spectra for the calibration set.

Figure 3. Second derivative spectra for the VIS calibration set.

From the cross validation studies, it was found that a two-factor PLS model gave the best predictive model. In the cross validation tests the Standard Error of Prediction (SEP) was found to be 1.47 for the two-factor model. Table 4 shows the amount of spectral (X-block) and moisture concentration (Y-block) information resulting from each PLS factor of the model.

Factor #	X-Block		Y-block	
	This Factor	Total	This Factor	Total
1	96.721	96.721	91.761	91.761
2	2.025	99.026	5.024	99.785

Table 4. Percent variance described by the VIS PLS model factors.

The first factor of the model describes most of the information present in the spectral and concentration blocks while the second factor describes a relatively minor amount of additional variance. The combined 2-factor model accounts for over 99% of the information in each block. While there is only a single component of variation in the experimental design (i.e., the variation in the water content), the PLS model uses two factors in the calibration. Typically, the presence of the second small factor beyond the expected rank of the system is indicative of a small corrective term to account for some nonlinear behavior in the relationship between the spectral responses and the water concentration. Since PLS is an inherently linear regression method, it handles nonlinearities by adding additional factors. For a simple curve, PLS would use one factor to explain the least squares fit line of the curve and a second factor to describe the variance, or scatter, of the curve points off the least squares line of the curve. For more complex nonlinearity, the PLS model would approximate the curve by successive linear approximations.

The model estimation results for the calibration set are shown in Figure 4 where the actual water concentration is plotted against the values estimated by the model. In this plot, one can see that there is still some structure in the residuals (i.e., the variation off the regression line is non-random) especially for the low water concentration samples. Also note that the errors, or residuals, are generally larger for the samples at the lower range of the moisture concentration. This suggests that the 2-factor PLS model was not able to completely model the water concentrations from the spectral information. The prediction results for the calibration set are also listed in Table 5 below. Some regression statistics for the calibration model are given in Table 8 later in this section.

Sample Number	Actual Wt% H ₂ O	Mean Predicted Wt% H ₂ O	Mean Residual (Error)	Standard Deviation
1 2 3 4	0.000	-1.577	1.577	0.452
5 6	0.730	0.221	0.509	0.034
7 8	1.192	2.772	-1.580	0.122
9 10	2.792	5.180	-2.388	0.066
11 12	3.585	5.937	-2.352	0.052
13 14	5.105	6.128	-1.023	0.136
15 16	6.502	7.056	-0.554	0.146
17 18	8.411	6.652	1.760	0.252
19 20	9.624	8.448	1.176	0.247
21 22	10.806	10.556	0.250	0.084
23 24	13.328	12.339	0.989	0.000
25 26	15.000	13.846	1.157	0.046
27 28	17.028	17.768	-0.740	0.569
29 30	18.529	19.295	-0.766	0.642
31 32	20.225	21.007	-0.782	0.221
33 34	22.393	21.168	1.226	0.144

Table 5. Calibration model results for the VIS spectra using a 2 factor PLS model.

Figure 4. Actual versus predicted water percent weight values from the VIS 2-Factor PLS model.

In order to better understand the calibration model, it is instructive to look at plots of some model components. One of the most telling plots is to look at the X-block (spectral) scores versus the Y-block (concentration) scores for each of the two PLS factors. These are shown in Figures 5 and 6 for the first and second factors, respectively. In Figure 5 one can clearly see that there exists a nonlinear relationship between information described by the scores in the X and Y blocks. If the spectral response and concentration information described by this factor were perfectly described by a linear relationship, one would expect to see all the score values to fall along the 45° line. If the spectral response and the concentration were completely uncorrelated, one would expect to see a random distribution of the scores centered about zero (for mean centered data). In Figure 5, the modeled relationship is somewhere between these two extremes. Samples 9 through 32 follow a roughly linear relationship

but the low range water concentration samples are not well explained by the linear relationship between the spectral response and the water concentration. The highest water content samples are also not well explained by the first factor of the model. These high and low water concentration samples have score values that lie off the linear regression line (i.e., there is a significant bias in the modeled relationship for these samples).

Figure 5. X-block (spectra) versus Y-block (concentration) scores for the first factor of the VIS PLS model.

Figure 6 shows the same plot for the second PLS factor. In this plot, the differences between the middle water concentrations and the high and low water concentrations are explained. Although it is difficult to visualize in the plot, there is a progression, or "looping", of the score values related to the differences between the high and low water content samples and those samples with mid-range water content. The score values start out in the upper quadrant with samples 1-4, move toward the lower quadrant (samples 17-20), and then return

to the upper quadrant with samples 31-34. Therefore, this second factor can be interpreted as a correction to the first factor to account for the nonlinear optical response at the extreme ends of the water concentration scale.

Figure 6. X-block (spectra) versus Y-block (concentration) scores for the second factor of the VIS PLS model.

Figures 7 and 8 show the spectral response scores and loadings for the first PLS factor. In the scores plot, one can see the nonlinear progression of the low water concentration samples (recall that the first four samples are the zero water added samples). Samples 10 - 35 have scores that are steadily increasing. The loading plot shows the wavelength regions being described by this factor. Most of the information described by this factor is in the region below 800 nm with only a small contribution in the region between 900 and 1000 nm. As expected, the loadings closely correspond to the main features of the average derivative spectrum. Figures 9 and 10 show the response block scores and loadings for the second factor. Again, in Figure 9, one can see that this factor is mainly describing the difference between the mid-range water concentration samples and

Figure 7. VIS sample scores on the first X-block factor of the PLS model.

Figure 8. VIS spectral loadings on the first factor of the PLS model.

Figure 9. VIS sample scores on the second factor of the PLS model.

Figure 10. VIS spectral loadings on the second factor of the PLS model.

the spectra from those samples with high or low water concentrations. The loadings plot, Figure 10, shows that the correction represented by this factor is predominantly concerned with the wavelength regions from 525 to 650 nm, 900 to 1050 nm, and the leading edge of the absorption at 450 nm.

The regression coefficient estimated by the 2-factor PLS model is shown in Figure 11. This regression coefficient vector, when multiplied by the VIS spectra will yield the estimated water wt%. This regression coefficient vector is a linear combination of the first two factors loading vectors shown in Figures 8 and 10. Its main contributions come from the correlated spectral regions around 450 nm, 700 nm, and 980 nm and the region from 550 nm to 650 nm.

Figure 11. VIS calibration set regression coefficient vector for the 2-factor PLS model.

NIR Calibration Results

The original NIR calibration data spectral responses and their second derivative spectra are shown in Figures 12 and 13, respectively. The prominent features of the spectra are the water combination bands at 1925 nm and 2250 nm and the first overtone band at 1425 nm. It is interesting to note that the NIR spectra of the dry BY-104 simulant shows almost no spectral absorbencies in the NIR region. This feature makes the NIR region ideally suited for the moisture determination since interferences from other constituents are not likely to affect the NIR moisture calibration model. The presence of organics in the actual waste tank material may lead to other spectral features in the NIR spectra. However, the water bands are sufficiently sharp (due in part to the high alkaline nature of the waste material) that correction for the organic absorptions should be possible. This should be investigated in future work.

The offsets observed in the raw NIR spectra, shown in Figure 12, are mainly due to the variations in scatter and sample placement, as well as the absorption due to the variations in the water content. The net effect results in an increasing sloped baseline with increasing water content. This is commonly observed in NIR spectroscopy and is usually corrected by taking the second derivative of the recorded spectra. The derivative spectra, shown in Figure 13, clearly removes the baseline offset trend and reveals the spectral changes due to the varying water concentration. The shoulder on right of the OH first overtone band at 1425 nm may be indicative of the difference between free and bound water in the sample. As mentioned above, the sharpness of the water absorption bands is related to the pH of the sample and has been used to estimate the sample pH of highly alkaline solutions. In the planned Phase 2 work, we will investigate the pH effect and determine if NIR spectroscopy can be used to predict the pH as well as the moisture content in the waste tanks.

Figure 12. NIR spectra for the calibration data set.

Figure 13 NIR second derivative spectra for the calibration data set.

The optimal calibration model for the NIR spectra was found to have 1 PLS factor by cross validation. Since the experimental design involved only one planned source of variation (i.e., the water concentration) the inherent dimensionality, or rank, of the system should be one. Therefore, one would expect a single factor calibration model in the absence of interferences and nonlinear absorption effects. For the VIS calibration model (discussed in the section above) the calibration model was actually of rank two due to the inclusion of an additional factor to account for the nonlinear VIS spectral response over the calibration range. For the NIR spectral region, the spectral response to moisture variation is well described by a single linear factor (i.e., there are no nonlinearities that require a second factor to explain). In this sense, the NIR spectral region gives a simpler calibration model than the VIS region and therefore is more desirable from a calibration standpoint.

The percent variance described by this single factor model is given in Table 6 below. This single factor model accounts for over 99% of the spectral and water wt% information contained in the calibration set. The estimated water wt% values for the calibration data set are listed in Table 7 and the estimation results are plotted in Figure 14.

Factor #	X-Block		Y-block	
	This Factor	Total	This Factor	Total
1	99.260	99.260	99.660	99.660

Table 6. Percent variance described by the NIR calibration set PLS model.

Figure 14. Actual versus predicted percent water weight from the NIR 1-factor PLS model.

As can be seen in Figure 14 above, the single factor PLS model for the NIR region fits very well over the full moisture concentration range with only slightly higher errors for the first two low water samples and the highest water sample. Contrast these results with the visible spectra model results (shown in Figure 4 above) and it is clear that the NIR model performs significantly better, especially in the lower moisture concentration range. In the VIS model, the lower moisture samples were not well explained by the model with significant residual structure in the predicted concentrations. The NIR model shows very consistent prediction results over the full moisture concentration range with a prediction standard deviation typically less than 0.1 wt% water. This good performance is partly attributed to the lack of interfering absorptions from the surrogate material in the NIR spectral region. Since the dry BY-104 surrogate is nearly transparent in the NIR (in the sense that it exhibits no specific absorptions), the PLS calibration model can focus on the water absorptions without correcting for secondary interferences. Also, the NIR response to water concentration follows a linear relationship.

Sample Number	Actual Wt% H ₂ O	Mean Predicted Wt% H ₂ O	Mean Residual (Error)	Standard Deviation
1 2 3 4	0.000	-0.481	0.481	0.003
5 6	0.730	0.127	0.604	0.032
7 8	1.192	1.584	-0.392	0.093
9 10	2.792	3.449	-0.657	0.104
11 12	3.585	3.971	-0.386	0.037
13 14	5.105	5.380	-0.275	0.009
15 16	6.502	6.585	-0.083	0.027
17 18	8.411	8.456	-0.045	0.038
19 20	9.624	9.791	-0.167	0.032
21 22	10.806	10.864	-0.058	0.045
23 24	13.328	13.222	0.106	0.072
25 26	15.002	14.600	0.402	0.122
27 28	17.028	17.585	-0.557	0.449
29 30	18.529	18.552	-0.023	0.078
31 32	20.225	20.545	-0.320	0.054
33 34	22.393	21.553	0.841	0.013

Table 7. Calibration model results for the NIR spectra using a 1 factor PLS model.

Again, it may be useful to discuss some features of this model although with a single factor contributing to the model, the interpretation is straight forward. The single factor NIR model did not exhibit the same nonlinear response seen in the VIS model and so only a single factor was required. The regression coefficient is shown in Figure 15 and shows the contribution from the O-H combination band at 1900 nm, the O-H first overtone band at 1400 nm, and a minor contribution from the O-H combination band at 2200 nm. Since there is only one factor in this model, the regression coefficient vector is identical to the loading vector for the single factor of the model. It is interesting to note the shoulder on the peak at 1420 nm that may be indicating the difference between free and bound water, although further studies will be needed to verify this observation.

Figure 15. Regression coefficient vector for the NIR 1-factor PLS model.

Some summary statistics comparing the VIS and NIR calibration models are presented in Table 8. Clearly, the NIR model does a better job at predicting moisture than the VIS model, probably due to the lack of any nonlinear terms in the NIR model and the lack of interfering spectral features due to other sample constituents in the NIR region. These results will be discussed further in the conclusion section later in this report.

Regression Statistic	VIS	NIR
Slope	0.979	0.997
Y Intercept	0.133	0.031
R ²	0.969	0.997
Std. Error of Est.	1.274	0.424
Correlation (r)	0.985	0.998

Table 8. Regression statistics for the VIS and NIR PLS models.

IR Spectra

The FT-IR spectra for six successive scans of the dry surrogate base material are shown in Figure 16 below. The most interesting feature of this plot is the offsets observed for the various sample spectra. The only difference in the sample between these scans is the orientation of the sample cup in the diffuse reflectance accessory. Therefore, the observed baseline offsets are most likely due to differential scatter effects resulting from irregularities in the powder sample surface. It is well known that surface scattering effects are prominent in diffuse reflectance FT-IR and there are several "standard" methods available for correcting the scatter effect before calibration. Among these are area normalization, mean normalization, Kubelka-Munk corrections, spectral derivatives, and multiplicative scatter correction (MSC). The results of applying each correction to the spectra shown in Figure 16 are shown in the Figure 17 below.

Figure 16. Six FT-IR spectra of the dry surrogate material used as the starting base for the moisture experiments.

From the plots in Figure 17, it can be seen that qualitatively, the mean normalization and the MSC methods were best at removing the baseline offsets. A less subjective measure of the effectiveness of the various "scatter" correction methods will be given below where each method was applied before forming the calibration model.

Figure 17. Different baseline correction methods applied to the IR spectra shown in Figure 16. For each plot, the x-axis corresponds to wavenumber (cm⁻¹) and the y-axis to normalized, or arbitrary, absorption units.

Before the calibration results are presented, there are several interesting features of the FT-IR spectra that are worth noting. The most important observation is the sharp change in spectral features that occurs between samples with 7.23 wt% water and those with 10.49 wt% moisture added. This is shown in Figures 18 and 19. The spectral features between 1500 cm⁻¹ and 2900 cm⁻¹ are increasingly obscured, or reduced, at the higher water concentrations. Also, the absorbance

between 2900 cm^{-1} and 3100 cm^{-1} is further reduced at the higher water concentrations (which shows up as an increasingly negative peak relative to the average absorbance). This change in the FT-IR spectrum at about 10 wt% water corresponds to the point at which added moisture is no longer fully adsorbed into the dry base surrogate material. It is difficult to speculate as to the exact mechanism contributing to the change in spectral response.

Figure 18. FT-IR spectra showing the marked difference in spectral response. [Samples 28 and 38 having 7.23 and 10.4 wt% moisture, respectively].

As the base material becomes saturated with water the inter-particle spaces within the sample are close to being filled with free water. Consequently, the IR radiation (which has a very short effective penetration into the sample) will experience a much shorter mean free path before being adsorbed or diffusely scattered and detected. In essence, the IR beam will see less of the initial sample due to its reflection and/or adsorption by the free water. Without further studies

It would not be possible to determine if the change in the spectra actually corresponds to the difference between bound and free water in the sample. Indeed, the observed behavior may not be even be representative of results that might be obtained with the actual tank crust due to different crystalline and particle structure found in the actual waste tank. Further experiments would be needed to fully understand the mechanism of this observed phenomenon.

Figure 19. IR spectra of samples with water below 10 wt% and with water above 10 wt%. [Samples 3,8,13,18,23,28,33 in upper plot and samples 38,43,48,53, 58,63,68,73 in lower plot.]

Another possibility is that the difference in observed spectra is related to the increased specular reflectance, relative to the diffuse reflectance, caused by the increased surface smoothness of the wetter samples (which are more paste, or slurry, like in appearance than the drier samples. We performed some initial experiments that would tend to rule this out, however. The diffuse reflectance accessory used in this study incorporates a flat plate that can be rotated down to

set perpendicular across the sample surface. This plate bisects the sample and prevents the specular reflectance component of the scattered light from reaching the detector. When this plate was employed, we found no structural difference in either the high or low water content sample spectra. This would tend to suggest that the marked change in the observed spectra is due to some other phenomena of the light/surface interaction rather than an increased specular reflection component at the higher water content.

The second main point about the observed spectra is that the observed "baseline", or "average absorbance", is not strictly related to the water concentration. This is especially true at the lower water concentration as shown in Figure 20. This effect is most likely due to subtle differences in the sample level within the sample cup and positioning the cup at the same position within the diffuse reflectance accessory. The level of the reflecting surface within the diffuse reflectance apparatus is related to the total throughput of the spectrometer/accessory system. Ideally, the sample surface should be exactly at the focal point of the IR beam within the sample chamber. Difficulties in filling the sample cup to the same level with sample, and differences in sample surface "roughness" contribute to the variable offsets observed. Of the baseline correction methods discussed above, only the MSC method does a very good job of removing this type of offset. This is expected since the other methods work by only correcting the baseline of a single spectrum at a time while the MSC method estimates the correction over the entire set of spectra in the calibration set. In the calibration modeling result discussion below, we will describe how the baseline offset problem affects the calibration model results.

Figure 20. IR spectra showing the different offsets independent of the water content. The labeled spectra correspond to: 1) Sample #3 with 0.616 wt% water, 2) Sample #8 with 2.249 wt% water, and 3) Sample #13 with 2.865 wt% water.

The third observation from the measured FT-IR spectra is that, at low water concentrations, the thermal energy of the IR beam can actually dry the sample over the course of the spectral measurement. This can be seen in the spectra for the second set of data (water wt% of 2.25) as shown in Figure 21. It takes about one and a half minutes to complete the 40 scan averaging required to accumulate a single spectrum. However, the sample is exposed to the IR beam even while the instrument is not actively acquiring data while it is in the diffuse reflectance sample chamber. The fact that the IR beam is drying the sample is further verified by observing that the portion of the sample at the focus point of the IR beam is a lighter color than the sample near the edges of the sample cup. As the surrogate material is dried, it becomes almost sandy in appearance and as moisture is added it becomes increasingly darker brown or reddish.

Figure 21. Spectra of Sample #2 (2.25 wt% water added) showing the drying effect of the IR light beam (the numbers correspond to the order the spectra were collected and span an exposure time to the IR beam of approximately 10 minutes).

PLS Results for Raw Spectral Data

As a point of reference, the uncorrected baseline spectra were used to develop a PLS calibration model relating the wt% moisture to the measured FT-IR spectral responses. In all cases the data was mean centered before computing the PLS model. Cross validation studies were performed to estimate the optimal complexity, or order, for the PLS model. Adding additional factors the PLS model will always improve its ability to fit the calibration data. However, at some point adding more factors just fits the calibration data and provides no improvement in the ability of the model to predict new samples, and sometimes will actually degrade the model's predictive performance. This is known as the overfitting problem in regression.

In cross validation, part of the calibration set data is held aside and not used to determine the model. The estimated model is then applied to the spectral responses of the held aside data to predict the concentration values. Since the actual concentrations for this held aside data are known, estimates of the prediction error can be obtained. This process is repeated multiple times, each time increasing the complexity of the PLS model by adding an additional factor to the model (up to some predetermined maximum number of factors). The prediction errors are then examined as a function of the number of factors in the estimating model. Generally, the prediction errors will drop rapidly with added model factors up to some point after which additional factors produce only minor error reduction. Additional factors can lead to slight increases in the prediction error due to calibration set "noise" being included in the model. Repeated cross validation studies are often run to ensure that the results would be representative for unknown spectral prediction by removing a different portion of the data for each cross validation study. While time consuming, this procedure provides the most reliable statistic for determining the predictive ability of a calibration model while protecting against overfitting the data. In all cases, we prefer to accept the somewhat pessimistic view that any increase in prediction error at a given number of factors is justification to stop adding more factors, even if additional factors eventually result in a lower total prediction error. While this criterion results in PLS models with higher SEP values, we feel it is justified in terms of the relatively small number of samples in the calibration set.

For the uncorrected spectral data, the cross validation studies indicated that a 2-factor PLS model was most appropriate. While the system we are studying has only one component of variation in the experiment, the amount of water, the above discussion of the observed spectral features would certainly lead one to expect that the real rank of the calibration set is greater than one. The percent variance described by each PLS factor in the spectra (X-block) and concentrations (Y-block) are given in Table 9 below. The first factor of the PLS model used about

half the information in the spectral responses to describe, or model, about 80% of the wt% water information. The second factor again uses about half the spectral information, but in this case describes only about 15% of the concentration information. Overall, the 2-factor PLS model accounts for most of the information in the spectral and concentration blocks of data. The summary statistics for the complete PLS model are given in Table 10 below. In general, the PLS model on the uncorrected spectra did surprisingly well considering the large spectral variations discussed above which are not, or only indirectly, related to the percent moisture content of the samples.

Factor #	X-Block		Y-Block	
	This Factor	Total	This Factor	Total
1	43.794	43.794	81.567	81.567
2	53.211	97.000	14.518	96.085

Table 9. Percent variance described by the FT-IR PLS model factors using the raw spectral responses (i.e., no baseline adjustment).

Standard Error of Prediction	1.4153
Slope of calibration line	0.9608
Y-axis intercept	0.402
R^2	0.9608
Standard Error of Estimation	1.309
Pearson's Correlation Coefficient	0.980

Table 10. Summary statistics for the PLS 2-Factor model based on the raw, or uncorrected baseline offset, FT-IR spectral responses. The standard error of prediction (SEP) is based on the leverage corrected residuals for the calibration set.

The actual regression model results are plotted in Figure 22 and listed in Table 11 below. As seen from the fit results, the PLS model does not do a very good job at fitting the spectra from the second set of samples (water wt% of 2.25) or the highest water content set of samples (water wt% of 22.24). These samples were all under estimated in the wt% water. The PLS model identified samples 9 and 8 (both from the second set of samples) as potential outliers in the leverage versus studentized error plot. Sample 66 was also identified as an outlier sample (in the spectral response) and the rest of the high water samples (67, 68, 69, and 70) were identified as high leverage samples just below the 95% limit for outlier classification. Sample 16 from the third set of samples (2.86 water wt%) was also flagged as a potential outlier in the same plot. When samples 66, 16, 9, and 8 were removed from the calibration set the SEP was improved from 1.413 wt% to 1.248 wt%. The model also over estimated the water wt% for the samples from the eighth set of spectra (10.4 wt% water). Again, samples from this set (36, 37, and 38) were very close to being outside the 95% confidence limit for outliers, although their leverage on the calibration model was average. Much of the poor performance of this model can be attributed to the separate problems of the baseline offset and different spectral responses for high and low water concentrations described above. Before we address solutions to these problems it may be useful to look at some information available about the PLS model.

Compared to the VIS and NIR models (described above), the raw IR model performed about as well as the VIS model but not nearly as well as the NIR model. Both the IR and VIS models require more than a single factor in the model while the NIR model achieved its better results using only a single factor. The IR model did perform more consistently over the full moisture concentration range than the VIS model which performed poorly at the low moisture range.

Figure 22. Actual wt% water versus predicted wt% water for the 2-Factor PLS model obtained from the uncorrected FT-IR spectra.

One of the most useful features of the PLS modeling method is the ability to graphically view the relationships between the spectral data (the X-block) and the concentration data (wt% moisture, Y-block) that are contributing to the regression model. This allows the analyst to not only derive a predictive model, but also to gain important insights into the understanding of the model. The PLS model decomposes each block of data into a set of orthogonal, or independent, basis vectors, or factors (often called latent variables), and bases the regression model on the relationships between these factors. Therefore, information is available on the inherent structure present in the spectral domain and how that structure is related to the structure in the concentration domain. For each factor of the PLS model, one can readily identify which samples and wavelengths are contributing to that factor and how that spectral information correlates to the variation of the concentration information for each sample.

Sample Number	Actual Wt. H ₂ O	Mean Predicted Wt. H ₂ O	Mean Residual (Error)	Standard Deviation
1 -- 5	0.6160	0.960	0.344	0.476
6 -- 10	2.2493	0.456	-1.793	1.075
11 -- 15	2.8694	4.249	1.384	0.518
16 -- 20	2.3909	3.922	1.531	0.746
21 -- 25	5.5938	5.010	-0.584	1.483
26 -- 30	7.2366	6.982	-0.255	1.028
31 -- 35	6.4366	5.868	-0.569	0.543
36 -- 40	10.4039	12.253	1.850	0.525
41 -- 45	13.4572	12.388	-1.069	0.705
46 -- 50	13.7838	14.265	0.481	0.771
51 -- 55	16.4646	15.460	-1.005	0.464
56 -- 60	15.1528	15.425	0.272	0.277
61 -- 65	16.8466	17.734	0.893	0.391
66 -- 70	22.2493	20.262	-1.987	0.624
71 -- 75	18.3673	18.874	0.507	0.487

Table 11. Calibration model results for the FT-IR spectra using a 2-factor PLS model.

One of the most interesting informational plots available from the PLS model is the relationship between the factors in the spectral domain and the factors in the concentration domain. Since we only have a single Y-block variable (the wt% water concentration), the Y-block loadings (the relationships among the variables within a block of data) will simply be a scalar for each factor and not very interesting to plot. However, the sample scores (the relationships among the samples within a block of data) reveal important structures in the data and show how each sample's spectral response contributes to the X-block scores and how its concentration information contributes the Y-block factor scores. By plotting the factor scores in the X-block against the Y-block, we also reveal information about how the samples contribute to the relationship between the block.

Examples of these types of plots are shown in Figures 23 and 24 below for the first and second factors of the model.

Figure 23. First spectral response block factor scores plotted against the first moisture concentration factor scores for untreated IR data model. Solid line is the least squares relation between the factors in the two blocks. The "(m)" in the plot title says that this model was derived from mean centered data.

From the plot for the first factor, shown in Figure 23, one can clearly see that this factor is mainly describing the difference between those samples with high water content (samples 61-65, 66-70, and 71-75) and those with very low water content (samples 1-5 and 6-10). All the remaining samples have scores on both factors that are near zero indicating that this factor is not using their information in determining the relationship described by this factor. In other words, this first factor is mainly describing the gross changes between the spectral responses of samples with low water (below 10 wt%) content and those corresponding to high

water content samples (above 10 wt%) described above. Furthermore, it is mainly using the driest and the wettest samples to make the distinction. From this plot we could conclude that a 1-factor PLS model would be able to predict the difference between dry crust material and material with water contents above 15 wt%. However, such a model would not be very useful in predicting water concentrations between these two extremes. For long term monitoring situations, it may be sufficient to know if the water content of the crust is above or below a certain threshold. In this scenario, a very cheap IR sensing system could be devised -- provided that the moisture threshold criteria occurred somewhere near 15 wt% water.

Figure 24. Second spectral block factor scores versus the second concentration block factor scores.

The second factor of the PLS model describes the linear relationship between the samples with intermediate water concentrations and their respective FT-IR spectral responses. In this plot (shown in Figure 24) one can again see a clustering of samples with moisture above 10 wt% (samples 36-56) with high

positive scores on the X-block factor, samples with moisture from 5 to 7 wt% (samples 21-35) with intermediate negative scores on the X-block factor, and those samples with water concentration around 2.5 wt% (samples 11-20) with large negative score values on the X-block factor. It should be noted that those samples with very large scores on the first factor of the model (samples 1-10 and 66-75) have score values near, but not at, zero suggesting that there is additional information about these samples that were not described by the first factor that is being described by this second factor. Also notice that there remains considerable scatter off the regression line relating the factors in the two blocks. This indicates the "noise" level in the spectral responses that is not being modeled by the 2-factor PLS model. This noise is the portion of the spectral responses that is not modeled (i.e., the spectral residuals).

Finally, it is useful to look at the portion of the spectral response that is being included in the model. This is obtained by plotting the PLS model loadings as a function of wavenumber. The X-block loadings represent the variation in spectral response that is being used to model the relationship between the spectral domain and the concentration domain for each factor of the model. These loading plots are shown in Figures 25 and 26 for the first and second spectral block factors, respectively.

For the first factor, the spectral loadings plot, Figure 25, shows that almost all the wavelengths received the same loading, or weight, in the model. Therefore, this first factor can be assigned the interpretation of a baseline offset. However, the loadings do show some structure so that the "offset" is a multivariate correction that is different for different regions of the spectra rather than a simple univariate scaling or subtraction term. Notice that wavelengths below about 600 wavenumbers do not show significant loading values so the "offset" correction does not change that region of the FT-IR spectra much. Recall from the earlier discussion, that this first factor is mainly modeling the difference between the dry

and very wet samples (above 17 wt% water) and provide very little distinction among the samples with intermediate water concentration. Therefore, if one was only interested in predicting the difference between dry crust material and high water content (above ~15 wt%) material, one could monitor almost any of the wavelengths above 700 cm^{-1} with the most likely region being from 900 to 1500 cm^{-1} .

Figure 25. Spectral loadings for the first factor of the untreated IR data PLS model.

The second PLS model factor loadings in the spectral block are shown in Figure 26 below. This factor includes most of the structural information contained in the observed IR spectra including the multiple peaks between 1500 and 2400 cm^{-1} , the sharp peak at 2612 cm^{-1} , and the broad peak centered on 3000 cm^{-1} . Since these spectral features all have negative loadings, they are all correlated in their contribution to this model factor. This factor also includes the spectral regions at either end of the scan range (400 to 800 cm^{-1} and 3200 to 4000 cm^{-1}) with the

low wavenumber region inversely correlated to the structure peaks mentioned above and the higher wavenumber region of the spectra. Recall that this factor is what accounted for the PLS model's predictive ability for the intermediate water content samples. Therefore, if one wanted to select spectral regions for monitoring the intermediate water concentration, 3000 cm^{-1} and 600 cm^{-1} might be the best wavelengths.

Figure 26. Spectral loadings for the second factor of the raw FT-IR data PLS model.

Of course, one must remember that this factor was derived only after the information described by the first factor was removed from the calibration data set. The actual PLS model combines the information contained in both loading vectors to obtain a single regression vector to be used in prediction. The regression vector for the 2-factor PLS model of the raw spectra is shown in Figure 27. This vector, when multiplied by the spectral response for a new unknown

sample, will provide the PLS model estimate, or prediction, of the wt% water in the sample. The most important spectral regions for the prediction appear to be the region around 3000 cm^{-1} and the region between $500\text{--}700\text{ cm}^{-1}$. These two regions of the FT-IR spectra are inversely correlated to each other. The step-wise wavelength selection multiple linear regression (MLR) identified the two "best" wavelengths for prediction as 2914 cm^{-1} and 642 cm^{-1} with a standard error of estimation of 1.36 wt% water. These step-wise wavelength selection results were obtained using cross validation and are based on choosing the wavelengths that minimized the total prediction errors. These results are in good agreement with the PLS model results discussed above.

Figure 27. The regression vector for the 2-factor PLS model derived from the uncorrected FT-IR spectra and the wt% water concentration values.

Model Results Based on Baseline Correction Methods

In this next section we will present the results obtained when the various correction methods are applied to reduce the influence of the variable baseline offset on the PLS models. Recall from above, that the variable baseline offsets are mainly due to scattering effects related to surface roughness and throughput effects related to the sample's level relative to the focal point of the IR beam within the diffuse reflectance apparatus. Since none of these contributions are directly related to the water concentration within the sample (except the surface smoothness since the higher water content samples are actually more closely packed particles or slurries than the drier material), it seems logical that efforts to reduce the variation in the spectra due to the baseline offsets would lead to better calibration models. There have been a number of methods developed to attempt to correct for these types of baseline offsets within the diffuse reflectance community, both in the mid infrared and near infrared regions. In this study we investigated six commonly applied correction methods and evaluated their effectiveness in improving the calibration results. The methods studied included:

- Normalizing each spectra to the mean absorbance value for the spectra,
- Normalizing each spectra to its area (the sum of all absorbance values for the spectra),
- First and second derivative (with pre-smoothing) of each spectra individually,
- The Kubelka-Munk transform,
- Multiplicative Signal Correction (MSC)⁷ applied to each set of samples individually (i.e., the five replicate scans associated with each moisture level),
- MSC applied over all the samples in the calibration set.

The results of the correction methods are presented in Table 12 and briefly discussed below.

	Number of Factors in Model	Standard Error of Prediction	Slope of Regression (R^2)	Pearson's Correlation Statistic	Standard Error of Estimation
Raw Data	2	1.415	0.961	0.98	1.31
Mean Normalized	4	1.529	0.957	0.98	1.36
Area Normalized	3	1.710	0.944	0.97	1.55
First Derivative	3	1.297	0.968	0.98	1.18
Second Derivative	3	1.141	0.975	0.98	1.04
Kubelka Munk	4	1.319	0.968	0.98	1.18
MSC (each set)	3	1.192	0.972	0.98	1.09
MSC (combined)	4	19.67*	0.972	0.98	1.10

Table 12. The summary statistics for the PLS models derived from the FT-IR spectra after applying the different baseline correction methods to the spectral data. [* Note the SEP value is artificially high for this method since it is adjusted by the sample's leverage in the calibration model and there were a few samples with abnormally high leverage in this data. See discussion.]

In practice the derivative methods were implemented using the "GAP" derivative method⁸ preceded by moving window smoothing. In this study, we used a gap size of 5 cm^{-1} for the derivative and a smoothing window size of 21 cm^{-1} . The appropriate amount of smoothing required to achieve useful derivative spectra and the gap size for the derivative are adjustable parameters that could be optimized for the particular spectral responses encountered but this was not pursued in this study. After the derivatives were obtained, cross validation was

used to find the appropriate number of PLS model factors and the model was estimated. The PLS models derived from the derivative spectra performed better than the raw spectra's model with the second derivative model doing slightly better than the first derivative model (SEP values of 1.141 versus 1.297 wt% water, respectively). In both cases the first PLS factor accounted for about 90% of the spectral information and about 92% of the water concentration information. The remaining factors each described relatively minor amounts of information from both blocks to add corrections for the highest and lowest water concentration samples.

Of the two normalization steps, area normalization actually performed quite a bit worse than the raw data while the mean normalized spectra's model was only slightly worse than the raw data model. This is despite the fact that more factors were used in both of the normalized spectra models. It was interesting to note that both normalizations gave very similar PLS models. The fact that the mean normalized model outperformed the area normalized one is mainly due to the fact that an additional factor was suggested by the cross validation studies. For both models, the first factor described about 85% of the spectral information and about 88% of the water concentration information. As in the case for the derivative treatment, the remaining factors consisted of smaller corrections for the high and low water content samples.

The Kubelka-Munk (K/S) transformation achieved a modest improvement in the predictive ability of the model over the model derived from the raw spectral responses. The formula for the Kubelka-Munk transformation is as follows:

$$\text{Kubelka-Munk} = \left[\frac{\left(1 - \left(\frac{\text{sample}}{\text{background}} \right) \right)^2}{2 \cdot \left(\frac{\text{sample}}{\text{background}} \right)} \right] \quad (1)$$

The PLS model based on the K/S spectra was dominated by the very high leverage attributed to spectra #8. In fact the fourth factor in this model only describes the relationship of sample #8 to the other samples. The first factor includes information from the high and low water content samples but the relatively little information from the intermediate water samples. The K/S transform was only partially able to correct for the baseline offset.

The MSC method attempts to correct for the baseline offset by regressing the observed spectra against their mean spectrum and then using the least squares coefficients to correct the individual spectra. Mathematically, the MSC correction can be represented by the following equations:

$$x_i = 1 \cdot a_i + \bar{x} \cdot b_i + e_i \quad (2)$$

where x_i represents spectrum i , $\bar{x}$ is the mean spectrum for the set of spectra, and a_i and b_i are parameters to be estimated by the least squares regression. Once a_i and b_i have been determined, the spectrum, x_i , can be corrected by the following equation:

$$x_{ik, \text{corrected}} = (x_{ik, \text{uncorrected}} - a_i) / b_i \quad (3)$$

where k represents the individual wavelengths of the spectrum i . The MSC technique was applied in two different ways to the FT-IR spectra collected in this study. In the first approach, we selected the five replicate spectra collected at

each water concentration experimental point and applied the MSC correction to each of the 15 sets of 5 spectra individually. When applied in this manner, the MSC should only correct for the variations in baseline offset due to variations in sample position and orientation within the IR beam. The results from this approach are labeled "MSC (each set)" in Table 12 above. This approach gave the second best model results that are actually quite close to the second derivative approach.

The second application of the MSC method was to apply the correction on the entire calibration data set. This is how MSC is usually applied. However, for this data set, the MSC correction introduces some artifacts when applied to the entire data set. Spectra #66 #67 and #71 are exaggerated relative to the other samples due to their unique negative absorbance with respect to the mean, or average, spectrum. As the mean spectrum needs to span both the high and low water spectral patterns, the multiplicative term, b_1 in Equation 3 above, goes negative for these samples. This leads to scaling up, rather than down, of the corrected spectra for these samples. We are currently investigating this phenomenon further. Consequently, these three samples dominate the PLS model with the first factor (which describes 90% of the corrected spectral information and 14% of the concentration profile information) is only modeling the difference between these three samples and all the others.

In general then, the second derivative treatment gave the best results for removing the baseline offsets while retaining the information needed to develop good calibration models. Fortunately, is also one of the easier correction methods to apply. The drawback to this correction approach is that the PLS loading plots are much more difficult to interpret when working with derivative spectra. Another potential drawback is the loss of resolution associated with the smoothing and derivative steps. With solid phase spectra this should not be much of a factor since the peaks tend to be broader anyway. The next best baseline offset

correction method proved to be the MSC of the individual sets of spectra. It should be noted that all the baseline offset correction methods allowed the cross validation studies to select one or more additional factors for inclusion into the PLS model relative to the raw spectra model. However, these additional factors were typically used to correct for nonlinear effects related to the change in spectral features occurring around 10 wt% water. These nonlinear corrections could not be detected in the uncorrected response data, probably due to the higher residual, or "noise" level, related to the baseline offsets. Figure 28 shows an example of this type of nonlinear structure that is clearly related to the difference between the high and low water concentration spectra. The spectra from #1 to #35 have increasing water from 0.6 wt% to 7.23 wt%, the remaining spectra (#35 to #75) have increasing water content above 10 wt%. Clearly there is a major nonlinear effect that the linear PLS must try to model.

Figure 28. Spectra scores on the third PLS factor of the Kubelka-Munk corrected spectra model.

Separate High and Low Water PLS Models

In the previous sections we pointed out that one of the problems with modeling the FT-IR spectra was the dramatic change in the spectral response between low water content samples (with wt% water below 10) and high water content samples (above 10 wt% water). In this section we will discuss two approaches to the problem. The first is to simply break the data set up into high and low water sets and then build a separate PLS model on each set. The advantage to this approach is that the PLS models should give better performance since they do not have to model both types of spectral responses. Since any of the PLS models discussed above are easily able to distinguish between the high and low water samples (usually using only the first factor) it should be relatively easy to have a screening model that covers the wide range of water concentration to predict the gross water content as either high or low. Based on the screening model prediction, one would then use the more detailed model that spans the predicted wt% water concentration in either the high or low wt% water range.

Table 13 shows the PLS model statistics for separate models built with the uncorrected spectra for samples 1-7 (spectra 1-35) which cover the range of 0.6 to 7.2 wt% water (the LOW model) and for samples 8-15 (spectra 36-75) which cover the range of 10.4 to 22.2 wt% water (the HIGH model). Notice that the model errors for the LOW model are much better than we obtained for any of the spectral correction methods. Of course, the spectral corrections could be applied to this spectral calibration data as well with the expected reduction in the prediction errors. For the HIGH model however, the improvements are not quite so good in going from the full range model to the limited moisture range model. While the prediction errors are still about as good as the best baseline offset correction methods, and better than the raw data, the improvements were not as dramatic as we obtained for the LOW model.

	Number of Factors in Model	Standard Error of Prediction	Slope of Regression (R ²)	Pearson's Correlation Statistic	Standard Error of Estimation
Raw Data	2	1.415	0.961	0.98	1.31
LOW Model	3	0.412	0.978	0.99	0.34
HIGH Model	3	1.328	0.891	0.94	1.10

Table 13. The summary statistics for the two PLS models derived from the FT-IR spectra in either the low wt% water or the high wt% water ranges.

The last method we investigated was Locally Weighted Regression^{9,10} (LWR) as a means to deal with the nonlinear difference in the spectral response between the high and low water content samples. In LWR, each unknown sample is calibrated for individually by selecting the spectral responses, and concentrations, from the calibration set that are most similar to the spectra of the unknown sample and using those "similar" samples to build a local model for predicting the unknown's concentration. During the model development stage this process can be simulated by using cross validation to find appropriate model parameters and obtain estimates of the method's performance for unknown samples. Before we can proceed with a discussion of the model building step we need to establish a method for selecting samples that are "similar" to our unknown sample's spectral response.

The Singular Value Decomposition (SVD) is a well-established numerical method for decomposing any matrix of data into its component basis vectors. The basic equation for the SVD is as follows:

$$\mathbf{X} = \mathbf{U} \cdot \mathbf{S} \cdot \mathbf{V}^T \quad (4)$$

where X is our matrix of calibration set spectra with each sample's spectrum arranged as a row of X and each column of X is the response at a particular wavelength over all the calibration set samples. The U matrix, called the left singular vectors, is a collection of orthogonal vectors, each of length m where m equals the number of rows in X , which describe the covariation among the rows of X . U has k columns where k is equal to the rank of X . The columns of U are strictly analogous to the score vectors from the PLS model and can be interpreted in the same way. The matrix S is a k by k square matrix whose diagonal elements are called the singular values of X and whose off diagonal elements are all zero. The singular values describe the relative magnitude of the left and right singular vectors. Recalling back to our PLS model, the singular values are related to how much variance in X is described by the individual u and v singular vectors. The matrix V , called the right singular vectors, is a collection of k orthogonal vectors, like U , except that the V vectors have a length n where n is equal to the number of wavelengths, or columns, in X and describe the covariation among the columns in X . The superscript T on the V matrix merely indicates the transpose of the matrix. The V vectors are again strictly analogous to the loading vectors of the PLS model.

The important point about this discussion is that either the U or V matrices contain all the information present in X . Therefore, one convenient method for determining if a sample's spectrum is similar to the calibration set spectra is to convert the spectrum into a set of score values and compare the new sample's scores to the scores from the calibration set spectra. The scores for the new sample are calculated by:

$$u_{new} = x_{new} \cdot V \quad (5)$$

where u_{new} is a 1 by k vector of score values for the new sample. The distance of the new sample's spectrum to all the calibration set spectra is then calculated by computing its Euclidean distance to the calibration spectra in the score space defined by U as follows:

$$\begin{aligned} U &= U \cdot S; & z_j &= u_j - u_{new} \\ d_j &= \sqrt{(z_j \cdot z_j^T)} \end{aligned} \tag{6}$$

where u_j is the row of U containing the scores for the calibration set sample j and d_j is then the Euclidean distance of the new sample to sample j in the score space. Once we have the distances of the new sample to all the calibration set samples, we simply pick some number of calibration samples to form the model based on their minimal distance from our new sample. This is the *local* part of locally weighted regression.

The last wrinkle is that if we pick 10 calibration set samples to form our model, we want to weight those samples with the smallest distance to our unknown higher than the samples that are further away (and thus less similar). This is the *weighting* part of locally weighted regression. This weighting is accomplished as follows:

$$a = d_j/d_f; \quad w_j = (1 - a^3)^3 \tag{7}$$

where d_j is the distance of sample j to the unknown and d_f is the distance of the final, or furthest, calibration set sample used in the model development from the unknown. The weights for each of the chosen calibration set samples, w_j , are collected into a weight vector W . Now we are ready for the *regression* part of locally weighted regression by building the model:

$$Wy = Wxb \quad (8)$$

which we solve as

$$b = [X^T \cdot W^2 \cdot X]^{-1} \cdot X^T \cdot W^2 \cdot y \quad (9)$$

where now X refers to the selected calibration set sample's score vectors, W is the diagonal matrix of weights and y is the vector of wt% water concentrations for the selected samples from the calibration set. Equation 9 is really just a weighted Principal Component Regression (PCR) with a subset of the full calibration set. The preceding discussion omitted some details about scaling and preprocessing so the interested reader should consult the literature before attempting to implement the algorithm outlined above. A one and a half page MATLAB script is available from the Author on request.

In generating a LWR model there are two parameters that must be established. The first is the order, or rank, of the SVD decomposition. The second is the number of samples from the full calibration set to use in generating the local model. Both of these parameters can be determined using the techniques of cross validation described earlier. For the uncorrected FT-IR spectral data, it was found that a six-factor model employing 30% of the calibration set samples gave the best results (paying attention to the dangers of overfitting). The results of the model are given in Table 14 and plotted in Figure 29. The LWR results are the best we were able to produce for the IR spectra and are in the same range (in terms of expected errors in predicting moisture) as the NIR results described above. By restricting the model to include only those samples with similar spectra, the LWR model can automatically account for the sharp nonlinear response change in the spectra and correct for the variable baseline offsets much better than the PLS models built on the full data set. While the LWR modeling is inherently more complicated than PLS or other modeling methods, the actual computation time

for model estimation and for prediction is only slightly longer than the more traditional methods. It should be noted that the LWR method described above is based on determining "similar" samples in the spectral response space. Under development are LWR methods which define "locality" in both the spectral and concentration spaces. Preliminary results suggest that this modification will improve the LWR method. We should also mention that the LWR method could also be applied to the visible spectral data to improve the predictive model in that spectral domain. For the NIR data, the PLS model was a single factor linear model so no improvement is expected by applying LWR to that data.

	Number of Factors in Model	Standard Error of Prediction	Slope of Regression (R^2)	Pearson's Correlation Statistic	Standard Error of Estimation
Raw Data	2	1.415	0.961	0.98	1.31
LWR Model	6	0.680	0.989	0.99	0.677

Table 14. The summary statistics for the LWR model based on a local region consisting of thirty percent of the samples from the FT-IR spectra calibration data set (no baseline offset correction).

Figure 29. Actual versus predicted wt% water for the uncorrected FT-IR spectra using locally weighted regression. Note that the largest prediction errors occur at the crossover point in the spectral response change around 10 wt% water.

Conclusions

In this study we have concentrated on answering the question related to the feasibility of moisture prediction using spectral information. The approach we took was the use of prepared surrogate waste samples with a range of moisture levels and spectral information obtained in the visible, near-infrared, and mid-infrared regions combined with multivariate calibration methods. Since this preliminary study was aimed at establishing the feasibility of the approach, many aspects of experimental design were chosen to eliminate factors that could complicate the moisture calibration. Variations due to compositional makeup of the crust material, particle size effects, and experimental setup could all affect the prediction of moisture from the spectral measurements. These effects will be

more fully explored in the next phase of the work. Even so, there were many interesting observations to come out of this study. Based on the results obtained so far, it is anticipated that moisture can be determined from optical reflectance measurements made on the crust material.

Since different spectral regions were studied in this phase of the project, one can make some general observations as to the relative merits of each spectral region with regard to moisture monitoring. The initial studies show that the NIR spectral region is better suited to moisture calibration than either the VIS or IR regions. For the NIR region the standard error of estimation is roughly half a weight percent for water while for the VIS spectral region it is about three times larger and for the IR region the results are somewhere in between (depending on the preprocessing used). The standard errors of prediction, based on cross validation results, are in good agreement with these values indicating that the PLS models are not overfitting the data. As a further check, the predicted value for the moisture content of the bulk simulant was predicted to be 9.37 wt% using the NIR model and the gravimetric determination obtained by drying was 9.63 wt%. The NIR models were also better suited to predicting the low, or zero, water concentration samples than the VIS model. The IR models required more extensive spectral preprocessing to achieve reasonable results. Finally, the NIR spectral model was a simpler model that did not require additional factors to account for nonlinear and interference corrections required by the VIS and IR models.

While the visible spectra models were not able to achieve the same level of performance as the other spectral regions, the results obtained may prove to be more than adequate. It is not clear that moisture monitoring in the tanks needs to be better than a few wt% water, and the visible model can certainly achieve that. A visible light sensing system has some attractive aspects in terms of low cost and simplicity. For remote observation, existing video or photographic

techniques could be modified to obtain spectral information needed to determine the water content. One potential problem that was not addressed in this phase of the study is the presence of the very white leachate often found on the crust surface. Since we were working with a bulk crust surrogate, the effect of this leachate layer on the moisture calibrations was not investigated in this study.

For the mid-infrared (IR) studies, perhaps most interesting aspect is the marked change that occurs in the measured IR diffuse reflectance spectra over a very narrow water concentration range. This complicated the calibration for the IR spectra and limited the performance of the linear calibration approaches. As was mentioned in the result section, this could prove to be a valuable phenomenon if it proves to be reproducible in the tank crust environment. The potential exists to develop a very simple type of IR sensor that would be able to verify moisture above or below this threshold. It is also interesting that the LWR model could develop very good predictive models even with this nonlinear response change. In fact the LWR model was the best model for the IR spectra even though none of the pre-processing methods to remove scatter effects were required. Presumably, combining the preprocessing with the LWR calibration could improve the IR results even more.

While the IR results are very promising, there are also some inherent drawbacks to the IR technology as a remote sensing system. First and perhaps most important, the IR radiation will have a very limited effective interaction path with the solid crust material. Therefore, changes in the compositional makeup of the crust material, particle size effects, and experimental setup will all complicate the prediction of moisture from the IR spectral measurements. Of course the other spectral regions are also affected by these parameters albeit not as stringently. Also one has to consider the cost of instrumentation, ease of use and calibration, and suitability to the monitoring environment all of which are slightly against the IR technology. On the other hand, the NIR region has the advantages of more

light interaction with the surface and sub-surface material, simpler calibration procedures, and potentially more accessible and cheaper hardware required for remote sensing or fiber optic sensing.

It should be noted that for the simple experimental design implemented for these tests, the full spectrum calibration model presented here is not required. Although not reported here, similar results were also obtained using a two, or three, wavelength multiple linear regression models for the VIS and NIR spectral data. The wavelength selection methods did not perform as well for the IR data due mainly to the more complicated response of the spectra to different moisture levels. Both the reduced wavelength and full spectrum calibration methods have their own relative merits. The full spectrum method has the added advantages of increased diagnostic information, ability to handle more complex relationships, and increased robustness gained through signal averaging. The reduced wavelength methods yield models that can be directly transferred to discrete element optical sensors that may be better suited to the type of remote on-line application being envisioned for the waste tank monitoring. The final choice for which method gets applied will depend more on the complexity of the spectra and other sensing constraints for in-tank monitoring than on the inherent strengths or weaknesses of the different approaches.

On the basis of the available results from the Phase 1 studies, we recommend that the further development work for the moisture monitoring effort concentrate on the NIR spectral region. Our results show that NIR gave very good predictive models. The NIR region also has many advantages for working in the tank environment that make it the most likely candidate for successful implementation as an on-line monitoring method.

References

- 1 . J.E. Meacham, H. Babad, and H. Toffe, "Moisture Monitoring of Ferrocyanide Tanks: An Evaluation of Methods and Tools", *WHC-EP-0658*, Westinghouse Hanford Company, Richland, Washington, 1993.
- 2 . The Mathworks, Inc., 540 Prime Place Way, Natick MA.
- 3 . P. Geladi and B.R. Kowalski, "Partial Least Squares Regression: A Tutorial", *Anal. Chim. Acta*, 185, 1-17 (1986).
- 4 . A. Lorber, L.W. Wangen and B.R. Kowalski, "A Theoretical Foundation for the PLS Algorithm", *J. Chemom.*, 1, 19-31 (1987).
- 5 . H. Martens and T. Naes, "Multivariate Calibration", John Wiley & Sons, UK, 1989.
- 6 . S. Chatterjee and A.S. Hadi, "Influential Observations, High Leverage Points, and Outliers in Linear Regression", *Statist. Sci.* (with discussion), 1, 379-416, 1986.
- 7 . P. Geladi, D. MacDougall and H. Martens, *Appl. Spectrosc.* 39, 491 (1985).
- 8 . K.H. Norris, "Extracting Information from Spectrophotometric Curves Predicting Chemical Composition from Visible and NIR Spectra", proceedings from the IUFOST Symposium, Oslo, Norway, 1982.
- 9 . W. Cleveland and S. Devlin, "Locally Weighted Regression: An Approach to Regression Analysis by Local Fitting", *J. Am. Stat. Ass.*, 83, 596 (1988).
- 10 . T. Naes and T. Isaksson, "Locally Weighted Regression in Diffuse Near-Infrared Transmittance Spectroscopy", *Appl. Spectrosc.*, 46, 34 (1992).

Appendix A. PLS Calibration

In this appendix we will describe the Partial Least Squares (PLS) method used in the modeling study. PLS is a multivariate regression method used to develop predictive models that describe the relationship between two or more blocks, or sources, of data. In this study the two blocks of data consist of the measured spectral responses (which we will call the X-block) and the weight percent water values (which we will call the Y-block). The PLS method works by constructing latent, or pseudo, variables in each block that describe the important multivariate information within the individual blocks and the correlated information between the two blocks. Conceptually, PLS is closely related to the Principal Component Analysis (PCA) and Principal Component Regression (PCR) methods and these will be briefly described to provide the background needed to understand the PLS algorithm.

In PCA, the goal is to describe the multivariate structure present in data from a single source or block. This is accomplished by decomposing the original data matrix, X , into a summation of orthogonal rank one matrices. The component sub-matrices of X can further be decomposed as the outer product of two vectors, often called the score (t) and loading (p) vectors for historical reasons. This decomposition is shown mathematically in the following equation

$$X = X_1 + X_2 + \dots + X_n = t_1 p_1^T + t_2 p_2^T + \dots + t_n p_n^T = \sum_{i=1}^n t_i p_i^T \quad (10)$$

where n is the maximum dimensionality, or rank, of X and is equal to the smaller of the row or column dimension in X . Note: in this report, matrices are denoted as bold upper case letters, vectors are column vectors and are denoted as bold lower case letters, scalars are represented as non-bold lower case letters, and the superscript T represents the transpose of a matrix or vector.

Typically, the decomposition is performed such that the first sub-matrix describes the greatest amount of variance, or information, about X and each successive sub-matrix describes a lesser amount of variance that is independent of, or orthogonal to, the preceding sub-matrices. Frequently in multivariate data, the pseudo-rank of a matrix is significantly less than its dimensionality due to correlation among the rows and/or columns of the matrix. As a consequence, the first few sub-matrices (or score and loading vector pairs) may contain most of the relevant information while the remaining sub-matrices contain mostly random variance (i.e., noise) or non-interesting minor variance. Therefore, the decomposition is usually performed as shown in the following equation

$$X = \sum_{i=1}^k t_i p_i^T + E = TP^T + E \quad (11)$$

where k is then chosen such that the relevant information is described by the score and loading vectors while the uninteresting variance and most of the noise remains in the error, or residual, matrix E . There exists several statistics and procedures for determining the pseudo-rank, k , of a matrix. One of the most common tests involves cross validation where part of the data in X is removed, the decomposition is performed on the remaining data, and then the missing data is re-estimated from the score/loading pairs. The number of score/loading pairs (often simply called factors) that produces the lowest errors in re-estimating the missing data is selected as the pseudo-rank, k , of the matrix. The cross validation is often performed many times with different data being removed each time to develop statistical confidence in the optimal value for k .

For each factor of the model, the score vector, t , describes the correlation's and covariance among the rows of X and the loading vector, p , describes the covariance and correlation among the columns of X . Each of the score and loading vectors is simply a particular linear combination of the original measurement samples or variables, respectively, that describes a multivariate

structure in the original data. Collectively, the score and loading matrices, T and P, each describes all of the relevant information in X segregated into an orthogonal row and column space. The advantages of such a decomposition are that 1) the original data in X, with its complex multivariate correlation's, can be represented by the independent axes of the score or loading space to obtain a simplified representation of the structure in the data and 2) by selecting the appropriate number of factors, one can effectively separate the relevant information in X from the "noise".

The preceding PCA discussion dealt with the case where one only has a single block, or source, of data. In the present study we are dealing with two sources of data, the spectral responses and the water concentration. In this case we are interested in describing the multivariate relationships between the two sources. One approach to this problem would be to perform separate PCA decompositions on the two blocks of data as shown in Equation 12 below.

$$\begin{aligned} \mathbf{X} &= \mathbf{T}_x \mathbf{P}_x^T + \mathbf{E}_x \\ \mathbf{Y} &= \mathbf{T}_y \mathbf{P}_y^T + \mathbf{E}_y; \quad \text{or for a single } \mathbf{y} \text{ vector} : \mathbf{t}_y = \mathbf{y} \end{aligned} \quad (12)$$

Once the preceding decompositions have been performed, one could simply utilize the score matrices $\mathbf{T}_x$ and $\mathbf{t}_y$ as replacements for X and Y and perform the standard multiple linear regression (MLR) to obtain the regression equation relating the two blocks as shown in the next two equations.

$$\begin{aligned} \mathbf{Y} &= \mathbf{X}^T \mathbf{b} \\ \mathbf{T}_y &= \mathbf{T}_x^T \mathbf{b}; \quad \text{for a single } \mathbf{y} \text{ vector} : \mathbf{y} = \mathbf{T}_x^T \mathbf{b} \end{aligned} \quad (13)$$

Solving for the vector of regression coefficients, b, involves taking the generalized inverse of $\mathbf{T}_x$ (since $\mathbf{T}_x$ is full rank with orthogonal columns this inversion presents no numerical problems) as follows.

$$\hat{\mathbf{b}} = (\mathbf{T}_x^T \mathbf{T}_x)^{-1} \mathbf{T}_x^T \mathbf{T}_y; \quad \text{for a single } \mathbf{y} \text{ vector} : \hat{\mathbf{b}} = (\mathbf{T}_x^T \mathbf{T}_x)^{-1} \mathbf{T}_x^T \mathbf{y} \quad (14)$$

Equations 13 and 14 above represent the PCR method. There are two problems with this approach. First, in doing the PCA decomposition the number of factors, k , to retain in the PCA models is based only on the information contained in each separate block. It is possible that important structure relating the two blocks of data may not be included in the model if it is minor relative to the variance within each block. The second problem is that even if the information describing the relationship between the two sources is included in the PCA model, it may be "spread" over two or more factors requiring a more complex PCR model.

The PLS method attempts to address these two limitations of the PCR approach by calculating factors within each block that are both descriptive of the major within block variance (like PCA) and descriptive of the correlation between the blocks (like MLR). PLS accomplishes these goals by decomposing both blocks simultaneously using an iterative algorithm and sharing information between the two blocks in performing the decompositions. The PLS algorithm proceeds as follows.

- 1) First estimate a score vector, $\mathbf{u}$, for the Y-block using the first column of the Y-block:

$$\mathbf{u} = \frac{\mathbf{y}_1}{\|\mathbf{u}^T \mathbf{u}\|} \quad (15)$$

where $\|\mathbf{u}^T \mathbf{u}\|$ is the Euclidean norm of $\mathbf{u}$.

- 2) Calculate the X-block weight vector, $\mathbf{w}$, using the estimated Y-block score vector $\mathbf{u}$.

$$\mathbf{w} = \frac{\mathbf{X}^T \mathbf{u}}{\|\mathbf{w}^T \mathbf{w}\|} \quad (16)$$

- 3) Calculate the X-block score vector, $\mathbf{t}$.

$$\mathbf{t} = \mathbf{X}\mathbf{p} \quad (17)$$

Note: if there is only one Y-block variable, then there are no further iterations and the algorithm goes to Step 6.

- 4) Calculate the Y-block loading vector, $\mathbf{q}$, using the X-block score vector, $\mathbf{t}$.

$$\mathbf{q} = \frac{\mathbf{Y}^T \mathbf{t}}{\|\mathbf{q}^T \mathbf{q}\|} \quad (18)$$

- 5) Calculate a new score vector, $\mathbf{u}$, for the Y-block.

$$\mathbf{u} = \mathbf{Y}\mathbf{q} \quad (19)$$

At this point check are made for convergence. If the algorithm has converged, then proceed to Step 6, otherwise go back up to Step 2 with the new $\mathbf{u}$ vector.

- 6) Calculate the X-block loading vector, $\mathbf{p}$, and re-scale the results.

$$\begin{aligned} \mathbf{p} &= \frac{\mathbf{X}^T \mathbf{t}}{\|\mathbf{t}^T \mathbf{t}\|} \\ \mathbf{t} &= \mathbf{t} \|\mathbf{p}^T \mathbf{p}\| \\ \mathbf{p} &= \frac{\mathbf{p}}{\|\mathbf{p}^T \mathbf{p}\|} \end{aligned} \quad (20)$$

- 7) Calculate the inner relationship, b .

$$b = \frac{\mathbf{u}\mathbf{t}}{\|\mathbf{t}^T\mathbf{t}\|} \quad (21)$$

- 8) Subtract the variance described by this factor from the X-block and the Y-block.

$$\begin{aligned} \mathbf{X} &= \mathbf{X} - \mathbf{t}\mathbf{p}^T \\ \mathbf{Y} &= \mathbf{Y} - \mathbf{t}\mathbf{b}\mathbf{q}^T \end{aligned} \quad (22)$$

- 9) If the next factor is to be calculated, substitute the X and Y calculated in Step 8 and loop back up to Step 1. Otherwise, the X and Y calculated in Step 8 become the residual matrices for the X-block and the Y-block, respectively.

Once the algorithm has calculated the desired number of factors, the regression coefficient vector, $\mathbf{b}$, can be estimated as follows:

$$\mathbf{B} = \mathbf{W}(\mathbf{P}^T\mathbf{W})^{-1}\mathbf{Q}; \quad \text{for a single } \mathbf{y} \text{ vector : } \mathbf{b} = \mathbf{W}(\mathbf{P}^T\mathbf{W})^{-1}\mathbf{y} \quad (23)$$

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