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7. Abstract

This report summarizes the work completed in FY-95 in preparing an NIR moisture probe for early hot cell deployment. This work was completed by a team from WHC's Process Analytical Labs and Tank Technology Projects organizations and was funded by EM-50's Office of Technology Development and EM-30's Tank Waste Remediation Systems Programs.

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EXECUTIVE SUMMARY

This report summarizes the work completed in FY 1995 to prepare an NIR moisture probe for early hot cell deployment as part of a "fast-track", high priority activity. The moisture content of Hanford tank waste materials is a key parameter for a number of tank farm operation and remediation functions. The major driver for a hot cell moisture probe is that the current moisture sensing method, based on loss of weight, uses a very small sample volume that can be affected by particle size and sample morphology. In addition, during the handling time, prior to determining moisture content, the sub-samples can suffer loss of moisture (exacerbated by the high levels of air exchange in the hot cell). The NIR moisture probe does not require sample preparation and can be applied directly to a sample's surface. Moisture data can be obtained immediately after core extrusion from a more representative waste sample.

To facilitate this "fast-track" activity, a "Memorandum of Agreement" was signed by DOE-RL (both TWRS Characterization and Analytical Services), Westinghouse Hanford Company (Analytical Services), and the Tank Focus Area (Characterization) that identified a joint EM-50 and EM-30 commitment to support the development, installation/deployment, and test of an NIR moisture system in a 222-S WHC hot cell, by January 1996, as a routine operational system for use with tank waste materials.

The "fast-track" accelerated activities were completed for the task by a team from WHC's Process Analytical Lab and Tank Technology Projects organizations and was funded by EM-50's Office of Technology Development and EM-30's Tank Waste Remediation Systems Programs. A work plan was developed with the activities, milestones, deliverables, and task assignments to complete this FY 1995 "fast-track" work scope. The major "fast-track" accomplishments included:

- An FTIR NIR spectrometer system was installed in the 222-S hot cell facility for use in a hood and use in the 11A hot cell where tank cores are extruded and sub-sampled. A diffraction based system used for cold evaluations with simulants was identified as a back-up moisture measuring system.

- A new NIR probe was obtained from Axiom Inc., San Diego, CA, that had low sensitivity to lift-off and stray light, had a large 4-5 mm sample area, and a stainless steel housing/sapphire window for use with caustic, radioactive wastes. Measurements with simulants and real materials provided test data for probe comparisons (6 around 1 probe from WSRC, commercial NIR diffuse reflectance probe, and the Axiom probe) and NIR spectral data for calibration models that would extract moisture content from the spectral data.

- NIR spectra were recorded from simulant materials in the 0-35 wt% range (SY-101, BY-104, T-Plant Top and Bottom, U-Plant, and In-Farm simulants) and real tank materials with moisture contents in the 15-25 wt% range (material from tanks U-202:Cores 78 and 75, BX-103:Core 87, B-101:Core 90, and B-101:Core 90). Figure I-1 shows some of the simulant spectra, while Figure I-2 contains examples of the NIR spectra from real tank wastes.

- Two Go/No Go hot cell installation decision points were met using this NIR data:
  1. As indicted below in Figure I-3, the NIR system was shown to be able to quantitatively measure moisture concentration with an accuracy of 2.8 wt% (average error) and an error window of ±8.35 wt% (standard deviation). The average error represents the overall accuracy of the calibration model in predicting moisture content while the standard deviation (standard prediction error) provides the error bars or precision around the predicted value.

  2. The NIR spectral data provides an indication of relative moisture differences or changes (homogeneity) within tank waste samples.

Figure I-1: Simulant Spectra @20 wt% Moisture Range.

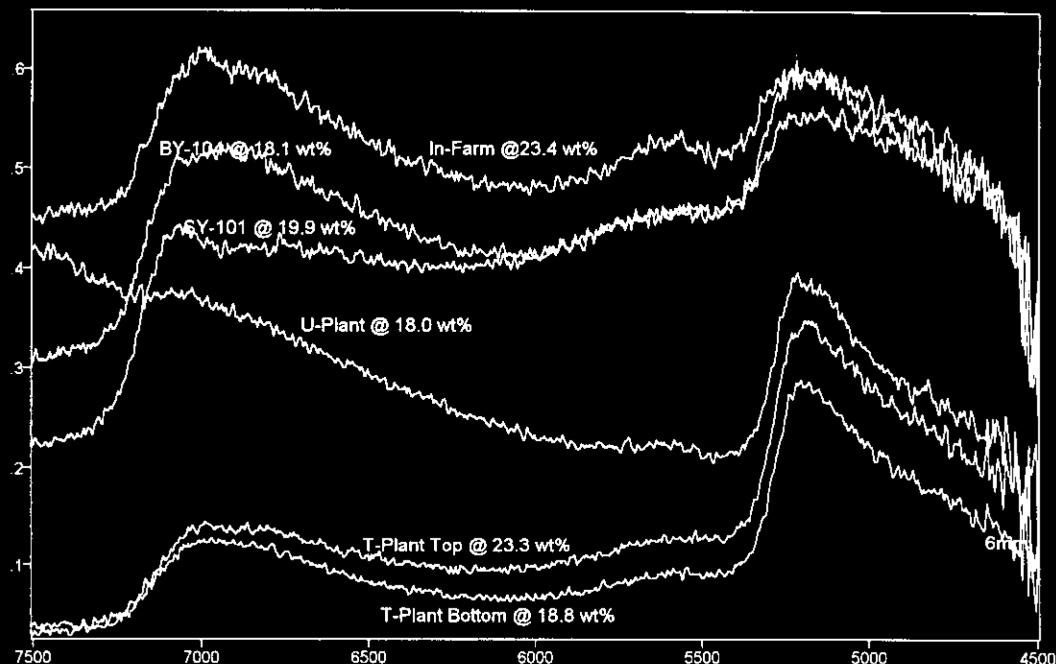


Figure I-2: U-202 Waste Sample @16.3 wt% Moisture.

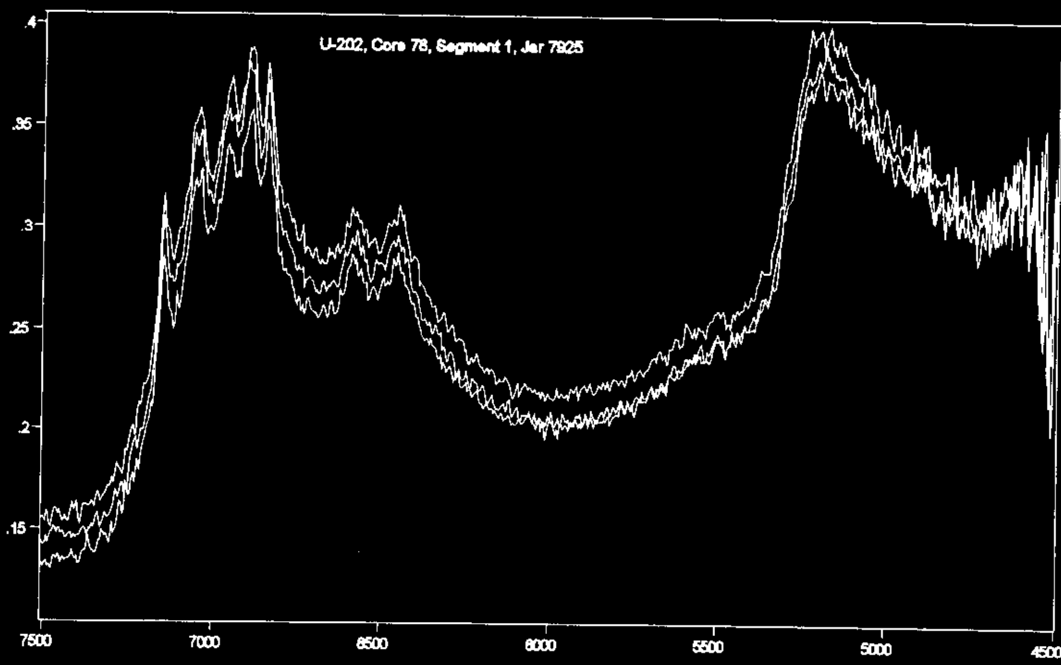
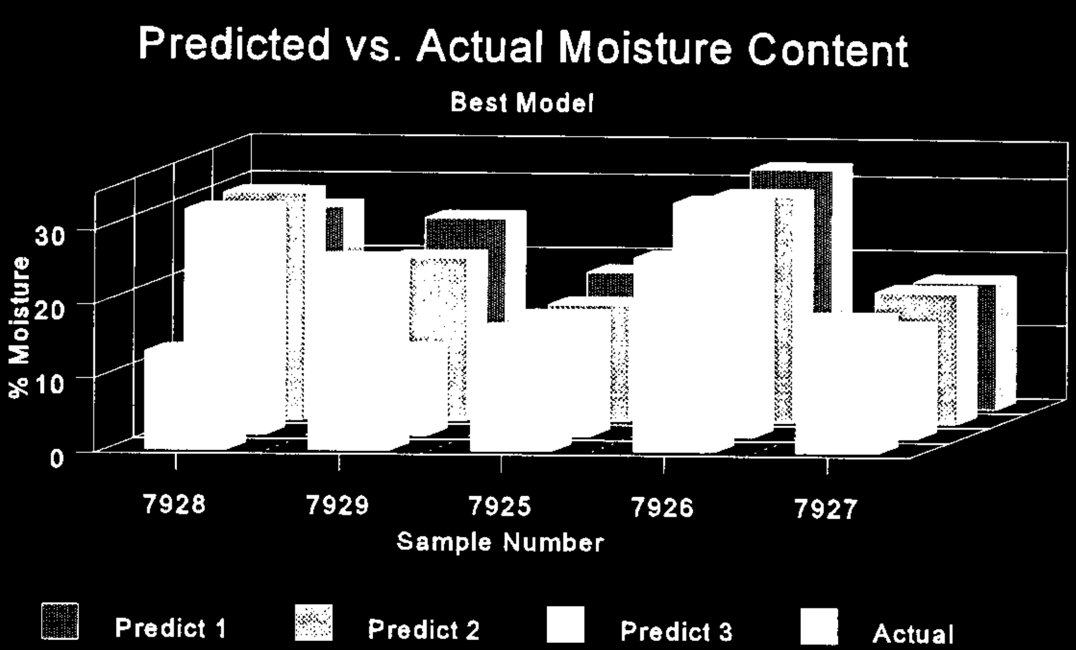


Figure I-3: Model Performance Using Real Waste Spectra.



CONCLUSION

A prototype hot cell NIR moisture probe is ready for hot cell deployment to sense moisture content and homogeneity in tank core, auger, and grab samples. The EM-50/EM-30 supported NIR fast-track plan was successful in accelerating the development of this system, in support of a January 1996, hot cell deployment milestone. This work needs to be continued in FY 1996.

ISSUES/FUTURE WORK

For long-term, routine operation, there a number of system issues that will need additional work in FY 1996:

Algorithm/Software Development: Work is needed to identify an optimum model and a method to incorporate new "standard" data into a model for use with unknown real waste samples. An algorithm is needed that allows homogeneity information to be easily generated from a number of NIR spectra. The FTIR system vendor is upgrading the spectroscopy system software package to a DOS environment (this will affect vendor support for the current software package). The current software package uses an unique operating system that is cumbersome to operate and can only be run using the spectrometer's computer system which causes a potential conflict between routine data acquisition and model development activities.

Routine Operation: A liquid nitrogen auto-filler will be required to support system operation on a routine basis. An auto-filler system has been procured, but resources will be needed to install the components in FY 1996. After some operational experience is obtained with the hot cell NIR system, technology transfer issues (system optimization, maintenance, backup, etc.) need to be re-assessed. Specifically, the current hot cell components, which include a long (30 meter) fiber optic cable, and the system interface/location in the hot cell, need to be examined. Backup components need to be identified and stocked to support a routine operation mode.

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1.0 INTRODUCTION

The moisture content of Hanford Site tank waste materials is a key parameter for a number of tank farm operation and remediation functions, including:

- Resolution of tank safety issues, especially for ferrocyanide and organic tanks
- Safe maintenance and operation of the Hanford waste tanks
- Support for retrieval, pretreatment, and immobilization of the tank waste materials, including on-line processing.

In FY 1995, a near-infrared (NIR) hot cell moisture probe was established as a high priority, "fast-track" implementation activity. A "Memorandum of Agreement" was signed by the U.S. Department of Energy, Richland Operations Office (DOE-RL), both Tank Waste Remediation Systems (TWRS) Characterization and Analytical Services, Westinghouse Hanford Company (WHC) Analytical Services, and the Tank Focus Area (TFA) Characterization that identified a joint EM-50 and EM-30 commitment to support the development, installation, deployment, and test of an NIR moisture system in Building 222-S hot cell by January 1996 as a routine operational system for use with tank waste materials (Quinn 1995).

This report summarizes the work completed in FY 1995 in preparing an NIR moisture probe for early hot cell deployment. This work was completed by a team from WHC's Process Analytical Laboratory and Tank Technology Projects organizations and was funded by EM-50's Office of Technology Development and the WHC Ferrocyanide Safety Program as part of EM-30's TWRS Programs.

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2.0 TANK WASTE MOISTURE MEASUREMENT DRIVERS

The basic needs for the Hanford High Level Waste (HLW) tanks are defined by a "Data Quality Objective" (DQO) process which determines the data that are necessary to support safe operation of the tank farms and to allow the clean-up program to proceed with acceptable technical and programmatic risks and at a minimum cost. Moisture has been identified as one of the critical parameters that impacts the safety status of a waste tank containing organics and ferrocyanide materials (Postma et al. 1994). A tank with wastes that have moisture content greater than 17 wt% and an energetics content of less than 480 Joules per gram (J/g) on a dry weight basis (Babad et al. 1995) is considered safe.

The objective of this moisture sensor work is to provide a hot cell NIR probe for making moisture measurements (homogeneity and concentration) in tank waste cores and grab samples. The current thermogravimetric analysis (TGA) method, based on loss of weight, uses a very small sample volume that can be affected by particle size and sample morphology. In addition, during the handling time, prior to determining moisture content, the sub-samples can suffer loss of moisture (exacerbated by the high levels of air exchange in the hot cell). The NIR moisture probe does not require sample preparation and can be applied directly to a sample's surface. With an NIR hot cell moisture probe, moisture data can be obtained immediately after core extrusion and moisture data obtained from a more representative waste sample (larger sample sizes and a larger number of observations). This in situ hot cell probe can also be used to generate moisture profiles along the length of an extruded core.

Currently, very little information other than visual observation is available to the hot cell operator (the hot cell window provides, at best, a color distorted view of the sample). Many non-retractable decisions, relative to the analytical process, are made. A lack of advance information results in a full suite of procedural steps and chemical analysis to acquire sample data and assure data integrity. A hot cell NIR moisture probe will augment the flow of tank materials through the hot cell by reducing the time needed to make a moisture measurement and reducing the error induced by current handling and sampling limitations.

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3.0 FAST-TRACK ACCELERATED PLAN ACTIVITY SUMMARY

In FY 1995, four major activities were identified and completed in a "fast-track", accelerated task.

3.1 Develop Work Plan and Complete New Probe Procurement and NIR System Training

Work Plan/Team

A work plan was initially developed that described the activities, milestones, deliverables, and task assignments to complete the FY 1995 "fast-track" activities. A "fast-track" team was formed with WHC technical staff members from WHC's Remote Systems and Sensor Applications and Process Analytical Chemistry groups to coordinate these activities. The team met every two weeks.

Axiom Fiber Optic Probe

A new probe was procured from Axiom Inc., San Diego, CA. The objective of the new design was to reduce sensitivity to lift-off (probe distance from the sample) and increase the sample area being measured by the probe. The probe design attributes were to be low stray light effects, large sample area (4-5 mm), and a stainless steel housing sealed with a sapphire window for use with radioactive, caustic waste materials.

FTIR System Training

System training was completed at the BioRad. Fourier Transform Infrared (FTIR) spectrometer factory. The objective was to obtain an understanding of the FTIR's spectral data acquisition and numerical modeling packages (Partial Least Squares Fit and Principal Component Regression analysis).

3.2 Simulant/Archived Waste Measurements and Probe Testing

NIR Spectral Data Acquisition

Because is it was anticipated that there could be problems in cleaning the hot cell probe in situ, an early decision was made to use a non-contact probe design. The most common cleaning agent used in the hot cell is water. The issue is that with small samples there could be a significant bias added to a moisture reading if the probe was either wet or contained residual tank wastes.

Another issue that was investigated was the potential interference from the strong hot cell lights. Because of the optical attenuation of the hot cell's window, large high pressure sodium lamps are used to illuminate the hot cell interior. A non-contact probe with a space between the probe and sample could pick up a significant level of this light. However, tests in the cold mockup facility showed that there was no discernable impact on the performance of an NIR probe.

Collection Efficiency of Westinghouse Savannah River Company (WSRC) Probe

Tests were conducted a WSRC bevel-tipped probe with tank waste simulants. The lift-off distance was varied from 0 to 6 mm with spectra acquired at each point. These tests revealed that beyond a lift-off of 0-1 mm, the efficiency of the WSRC probe was very poor, thereby limiting its use as a non-contact probe.

Hood Testing of Axiom Probe

Tests were conducted using the Axiom probe with tank waste simulants. These tests showed a consistent signal strength when the probe to sample distance was varied from 3-7 mm. This signal consistency will allow hot cell operators to comfortably position the probe over the waste sample and produce good NIR spectral data from which moisture data can be extracted.

3.3 Decision Hold Point and Hot Cell Installation

Two application objectives were identified for a hot cell NIR moisture sensing system. These objectives were used as performance criteria to be met before completing the installation of the NIR system in the 222-S hot cell facility. The two criteria are:

1. The system must be able to quantitatively measure moisture concentration of a real tank waste to ±10% standard deviation (std.) at a moisture concentration level of 20 wt%. For an acceptable moisture performance, the NIR system must be able to predict moisture levels within ±10 wt% of the actual (TGA measured) value.

2. The NIR moisture probe system must be able to provide an indication of relative moisture differences or changes within tank waste samples for tank cores. The difference or change data would be used to generate moisture homogeneity profiles, particularly along the core axis. This application may be performed without the need for quantitative moisture readings and data from the NIR spectra.

Because of the "fast-track" nature of this project, a decision was made to pursue installation of the system in a hot cell hood concurrently with the work required to establish achievement of these two criteria. This hood is directly adjacent to the 11A hot cell, 222-S Hot Cell Laboratory., where tank waste cores are extruded and sub-sampled. The hot cell installation requires running the fiber optic through the hot cell wall with the spectrometer system placed on a cart near the wall adjacent to the 11A hot cell. Hot cell installation activities have been initiated and are expected to be completed in FY 1996.

NIR Data For Generating Moisture Homogeneity Profiles

NIR spectral data from ferrocyanide In-Farm flow sheet waste simulants (Jeppson and Wong 1993) were used to demonstrate the capability to sense moisture differences or changes in tank waste materials. A more detailed summary of this work is included in Appendix A. In this test, the homogeneity of NIR spectral data, recorded along the axis of a small vessel filled with In-Farm simulant, was shown to be consistent with expectations from In-Farm calibration samples and actual sample water content data measured from sub-samples with loss of weight methods. An isometric plot of spectra (probe spot size was about 4 mm in diameter) at 0.25 inch increments provided a viewing perspective of spectra that showed consistent moisture features for the 1.5 micron absorption band. These tests and the validation of the data with calibration samples and actual moisture data showed that the NIR moisture probe could provide an indication of relative moisture differences or changes in tank waste materials; the NIR moisture probe's performance met the second application objective of the *Decision Hold Point and Hot Cell Installation* milestone in the "Accelerated Schedule Workplan".

Quantitative Moisture Measurements

This work focussed on acquiring spectra, building calibration models, and predicting moisture concentrations for real waste materials. Five real waste samples were selected:

1) Tank U-202, Core 78, Segment 1, Jar 7925: This sample could be characterized as "Parmesan-cheese-like". The sample had large particle sizes, was yellowish in color, and had a moisture content of 16.3 wt% as determined by the TGA method.

2) Tank U-202, Core 75, Segment 2, Jar 7929: This sample could be characterized as "buttery". It appeared to be a very smooth dab of butter, yellow in color, and had a moisture content of 25.8 wt% (via TGA).

3) Tank BX-103, Core 87, Segment 2, Jar 7926: This sample looked like a dark olive clump of clay and had a moisture content of 26.3 wt% (via TGA).

4) Tank B-101, Core 90, Segment 2, Jar 7928: This sample was a brown, clayish sample that had an uncanny ability to slide along the vial wall. It had a moisture concentration of 13.3 wt% (via TGA).

5) Tank B-101, Core 90, Segment 1, Jar 7927: This sample was a brown, clayish sample with larger particles embedded in the material. It had a moisture content of 18.0 wt% (via TGA).

A number of PLS models were developed, based on the use of simulant samples spiked with known quantities of water. Water content was verified using loss of weight or thermogravimetric methods. The best model was able to predict moisture content with an accuracy of 2.8 wt% (average error) and an error window of ±8.35 % (standard deviation). The average error represents the overall accuracy of the calibration model in predicting moisture content while the standard deviation (standard prediction error) provides the error bars or precision around the predicted value.

These tests showed that the NIR moisture probe will provide quantitative moisture information in tank waste materials; the NIR moisture probe's performance met the first application objective of the *Decision Hold Point and Hot Cell Installation* milestone in the "Accelerated Schedule Workplan".

3.4 Develop Experience with Obtaining Data within the Hot Cell

This activity started with the initial operation of the NIR moisture system and the acquisition of spectra from simulant and real tank materials. It will continue through the January 1996 key milestone in conjunction with hot cell personnel. The objective is to provide support until operational personnel are fully comfortable with the operation of the NIR hot cell moisture probe. Activities that need additional attention that were not completed in FY 1995 include the development of a "turn-key" algorithm for processing (acquisition, display, processing, and archival) NIR spectral data. In addition, direct comparison of data from this technology to the previous weight loss method must continue until statistical confidence is established. Performance reliability must be documented.

4.0 NIR HOT CELL SPECTROMETER SYSTEMS

4.1 Bio-Rad FTIR System

An existing BioRad FTIR spectrometer was selected as the basic NIR spectrometer system. This selection considered several technical and programmatic aspects:

- A 1.0 to 2.0-μm (10,000 to 3,300-cm^{-1})spectral range that includes the 1.5 and 1.9-μm water absorption peaks. An imaging spectrometer with dispersive gratings has been ordered but will not be delivered until early in FY 1996.

- The FTIR system was already in the radiation zone of the laboratory and could be setup at a location convenient to handle the archive tank samples and simulant standards.

- The hot cell team was already knowledgeable about the operation of this system, with the exception of using the system's numerical modeling software options.
- The Polytec NIR system, procured to serve as the hot cell operations system, could not be delivered in time to complete the FY 1995 activities. Instead, the Bio-Rad system was deployed to the 11A hot cell for operations use.

The BioRad FTS 60A FTIR System was equipped with a Near-Infared (NIR) Kit with the following features:

- Spectral Range: 10,000 to 3,300 cm^{-1}
- Resolution: 0.5 cm^{-1}
- Beamsplitter: Quartz Substrate
- Source: Tungsten Halogen Lamp
- Detector: Indium Antimonide Liquid-Nitrogen Cooled

The BioRad FTS 60A spectrometer incorporates dynamic interferometer alignment in a high throughput 60° Michelson interferometer. The interferometer requires a 2-4 hour warm-up time to obtain optimal performance from the instrument. The need to have the system ready to acquire data with short notice from operations influenced the decision to keep the system powered continuously.

The associated Bio-Rad computer was equipped with a 68030 processor and a UNIX-similar operating system. The system is completely menu driven, including spectrometer alignment, wavelength calibration, data acquisition, data processing, and data analysis using either Principle Component Regression (PCR) or Partial Least Squares (PLS) algorithms.

Several accesories are necessary to prepare the Bio-Rad system for hot cell routine operations: a liquid nitrogen auto-filler and a 30-m fiber optic cable. Both were ordered earlier and the 30-m cable was delivered in September 1995. The liquid nitrogen auto-filler unit will ensure that detector is at its final operating temperature to support routine operations or operation on a short notice. The fiber optic cable contains 40 input and 40 output, 100um diameter optical fibers. The long cable length will allow the fiber optic probe to fully access all interior points in the 11A hot cell where archived samples are to be analyzed.

4.2 Polytec NIR System

An X-DAP-9 NIR spectrophotometer system was purchased from Polytec PI, Inc. for use with a fiber optic probe. This system, which uses an imaging spectrometer and detector array, covers an optical range of 800-1700 nm that includes the 1400-1500 nm water absorption over-tone band. This system is basically a "turn-key" system with a computer-based operating system. The major system components include:

- Stabilized tungsten lamp source and SMA-905 fiber optic interface.
- Imaging spectrometer with fixed position, ruled diffraction grating.
- Thermoelectrically cooled InGaAs diode array detector (1x256 pixels).
- Exposure control shutter.
- Computer control, data acquisition/processing system.

The acquisition of this system was based on earlier work with an NIR system that was developed for moisture sensing with tank materials by WSRC. The WSRC system was successfully used to demonstrate that calibration models using the 1400-1500-nm water absorption band could be used to extract moisture data from NIR spectra. The decision to purchase this commercial Polytec system was based on significant software and hardware deficiencies with the WSRC system. A more detailed description of this NIR work is included in Reich (1995).

The computer system contained both data acquisition and data processing software packages for:

- Acquiring spectral data from the diode array detector
- Process spectra (base-line, smoothing, and truncation operations)
- Construction of calibration models from calibration data,
- Extraction of moisture data from calibration models.

The 256 element array and 800-1700 nm range provides a basic resolution of about 3.5 nm/pixel. This was more than adequate to produce good moisture prediction performances with numerical analysis models.

The spectrometer in the Polytec unit uses the direct output from a single optical fiber; there are no windows or beam shaping lenses or other components in the system. This simplicity provides a high input efficiency and allows spectra to be obtained with exposure times under 1 second. This interface, however, limits the system to probes with a single input optical fiber (i.e. the WSRC and Polytec probes described below). It may be possible to modify this interface for a larger number of optial fibers.

Although this system includes modeling software to perform either PLS and PCR numerical modeling, an off-line software package (GRAMS/386[1]) was used to evaluate modeling parameters and moisture prediction with the spectra generated with this system. The Polytec spectral processing software was limited in the number of functions it can perform and, after models are constructed, it still requires an operator to implement the transport of data between the basic acquisition and processing software packages and the modeling software. The GRAMS package has a much wider menu of spectral processing options and a much richer PLS model analysis capability.

An extended wavelength (1000-2000 nm) Polytec X-DAP-10 is currently on order for deployment as a routine hot cell moisture measuring system, early in FY 1996. This will allow the use of the water absorption band at 1800-1900 nm as well as the 1400-1500 nm band for moisture content measurements. The early development work indicated that the upper band was more sensitive with low moisture concentrations while the lower band was more sensitive with high moisture concentrations (Veltcamp 1995). However, the interfacing with this system to the hot cell probe needs to be examined.

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[1] GRAMS/386 is a registered trademark of Galactic Industries.

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5.0 FIBER OPTIC NIR SYSTEM PROBES

The quality of the NIR moisture data is dependent on the performance of the fiber optic probe as well as a number of other system parameters. Several NIR probes were evaluated with simulant and real tank materials. The basic issues with the NIR probes included:

- Sensitivity to hot cell background light.
- Optical sensitivity/efficiency
- Sensitivity to lift-off (probe to sample) distance
- Compatibility with hot cell interfaces, such as handling with a manipulator and remote cleaning,

Three candidate fiber optic probes were considered for the hot cell NIR moisture sensing system:

1. WSRC 6 around 1, conical tip, sapphire window.
2. Polytec, diffuse reflectance probe.
3. Axiom, multiple fiber probe.

The WSRC probe was the earliest probe acquired by WHC and was used as the reference probe in the assessment of the other two probes.

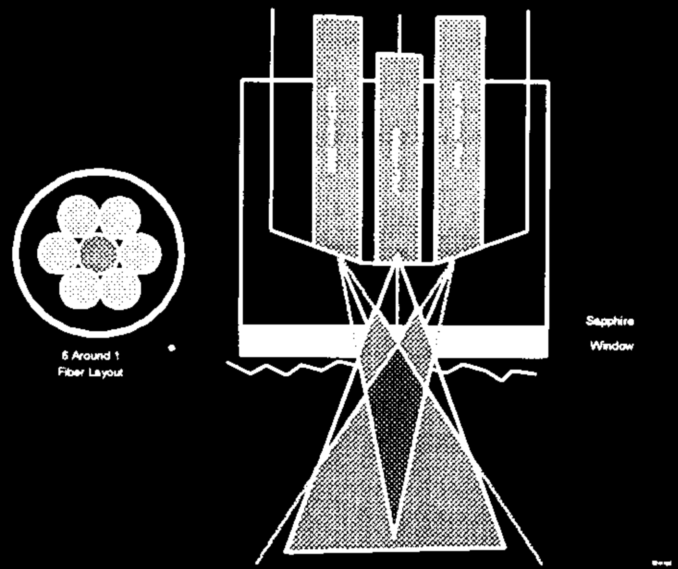
5.1 Probe Descriptions

Lopez et al. (1995) and Reich et al. (1995) contain a more complete description of the WSRC 6 around 1 and Polytec probes than presented below.

5.1.1 WSRC 6 around 1, Conical Tip, Sapphire Window Probe

The WSRC probe was designed and furnished as part of an NIR moisture sensor system from WSRC. As indicated in Figure 1, the fibers are laid out in a 6 around 1 pattern with the "6 around" fibers terminated on a cone shaped surface and the central "1" fiber terminated on a small flat. The "6 around" fibers carry optical light to the sample while the central single fiber collects the diffusely scattered/reflected sample light. This probe uses 400-μm diameter, stepped-index silica (core and cladding) radiation resistant fibers which are commercially available. The fibers have a numerical aperture of approximately 0.22 (NA/0.22) which produces a 30 degree expanding cone of light from the fibers. This cone of light controls or determines the spot size of the probe. The cone shape tips the optical axis of the "6 around" fibers toward the center of the probe as shown in Figure 1. This causes the optical patterns to cross as noted by the shaded areas. The smaller area shows the volume where all fibers cross with each other as well as with the central fiber. The larger shaded region shows the volume where the central fiber optical pattern crosses with any one of the 6 around fibers. This crossed pattern produces a plane where the area of crossing with all fibers has a maximum diameter. This cross-over plane is where a diffusely reflecting sample will produce an optimum NIR signal from a sample. The NA (0.22) of the fibers and angle of the cone produces a probe spot size of approximately 0.8 mm diameter.

Figure 1. Westinghouse Savannah River Co. Near-Infrared Fiber Optic Probe for Moisture Sensing with Tank Wastes.



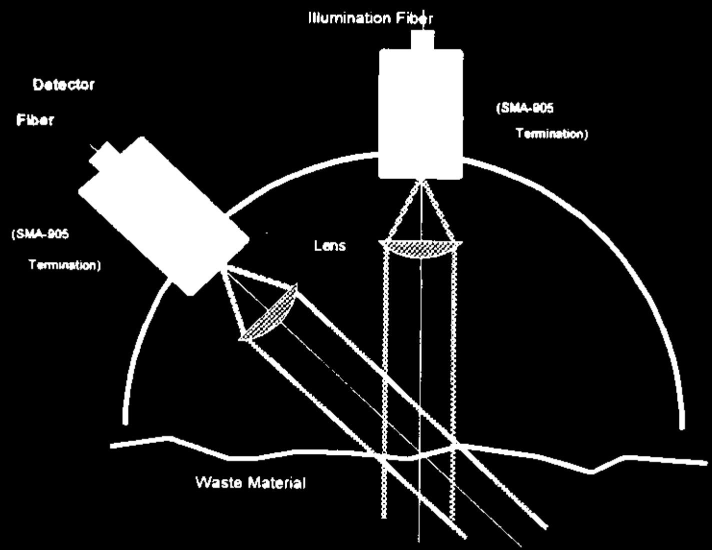
The WSRC probe was designed to be used as a contact or a "mash" probe where the probe window would be placed in direct contact with the sample material. The position of the optical window was adjusted so that the window's outer surface was outside of this optimum cross-over plane as indicated in Figure 1. As will be shown below, this probe design is very sensitive to the lift-off distance when the probe is used as a non-contact probe. The probe's optical sensitivity is very good when it is used as a contact or immersion probe with solids and liquids.

5.1.2 Polytec, Diffuse Reflectance Probe

The Polytec diffuse reflectance probe is a commercially available optical fiber probe head originally designed for diffuse reflectance spectrometer measurements using the backscatter from solid, non-transparent samples. As shown in Figure 2, the probe consists of two small optical components (consisting of a holder, lens, and SMA-905 fiber optic connector) mounted at 45 degrees to each other. Their optical axes cross at the plane of the hemispherical mount (1 inch radius). A single fiber cable, terminated with an SMA-905 connector is attached to each optical component. The lenses can be adjusted to produce a converging or diverging beam from a single, large diameter optical fiber. The fiber optic cables used with this probe were 400-μm diameter, stepped-index silica (core and cladding), radiation resistant commercially available optical fibers. The lenses were adjusted to produce expanding beams which had a 4-5 mm diameter spot size at the cross-over plane (mouth of the 1 inch radius hemispherical mount).

Although this probe design does not appear to be exceedingly efficient in collecting diffuse scattered light, it was sensitive enough to produce good NIR spectra when coupled to an imaging spectrometer (fixed grating) with an InGaAs, charge-coupled detector (CCD) array. This was the probe configuration used to obtain the NIR data from the In-Farm settling vessel, discussed below. The spectrum recording times were less than 1 second/spectrum which produced a

Figure 2. Diffuse Reflectance Fiber Optic Probe for Near-Infrared Moisture Measurements with Tank Wastes.



spectrum with a signal level in the upper 75% of the CCD's range and had good signal-to-noise features from the tank waste simulants that were tested.

5.1.3 Axiom, Multiple Fiber Probe

The Axiom multiple fiber probe contains a more complex optical system as shown in Figures 3 through 6. As shown in Figure 3, the Axiom probe's optics consit of an input, multiple fiber, fiber optical cable (80 fibers), input lens, reflective cylinder, output lens, and some stops not shown on these figures. The probe's outer housing, indicated by the larger outer cylinder in Figure 3, was stainless steel with a sapphire window attached to the end of the housing. The fiber cable furnished with this probe was custom designed and consists of a random distribution of 40 illuminating and 40 detecting fibers mounted in an SMA-905 connector housing. The fibers are 100-µm diameter, stepped-index silica (core and cladding), radiation resistant, commercially available fibers.

The two lenses, an input lens and an output lens, are arranged in a telocentric design with the image and object positions located at the lens' focal lengths. For the input lens this produces a series of collimated beams, one from each illumination fiber. The beams from the off-axis fibers produce light at an angle to the probe axis (Figures 4 and 5), and reflect off the inner surface of the reflective cylinder which is centered on the probe axis. The output lens collects this light and creates an image of the input fiber optic cable's surface about 6 mm from the sapphire window. Both the output lens and the sapphire window are tipped (10-15 degrees), as indicated in Figure 6, to reduce the level of stray light being reflected directly back into the fiber optic from their surfaces. The input lens also contains a small central spot, not shown, to reduce its stray light reflections.

Figure 3. Optical Components in the Axiom Diffuse Reflectance Fiber Optic Probe.

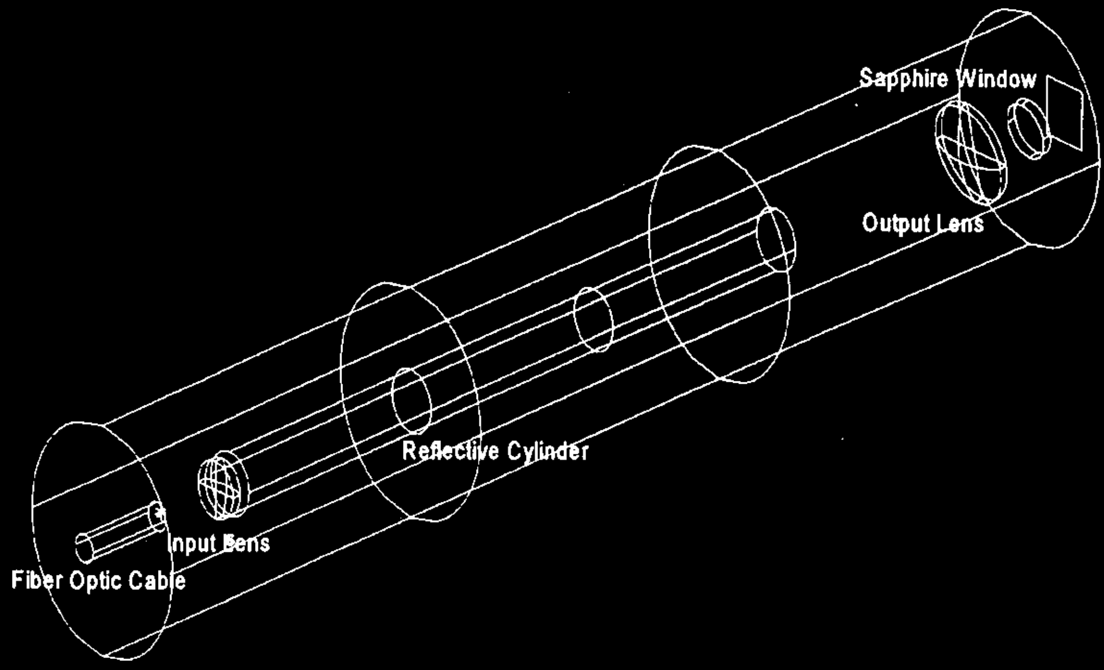


Figure 4. Ray-Trace Showing the Path of Light from an Off-Center Fiber Optic.

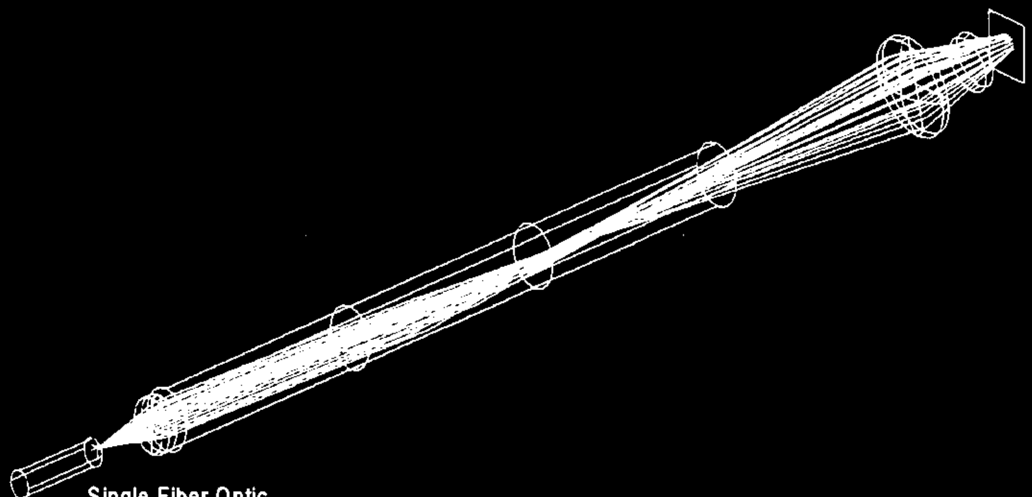
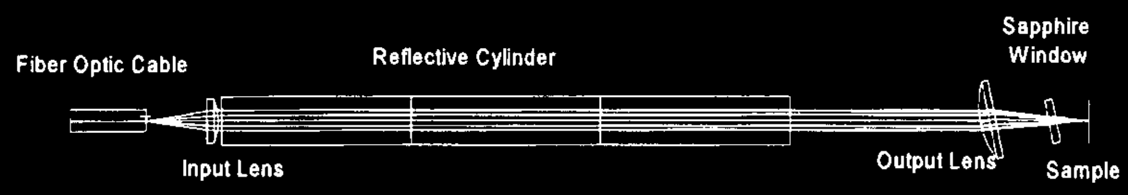


Figure 5. Top-View of the Axiom Probe Showing a Ray-Trace for a Single Off-Center Optical Fiber.

Figure 6. Side-View of the Axiom Probe Showing the "Tipped" Output Lens and Sapphire Window and a Ray-Trace for a Single Fiber Centered on the Probe Axis.

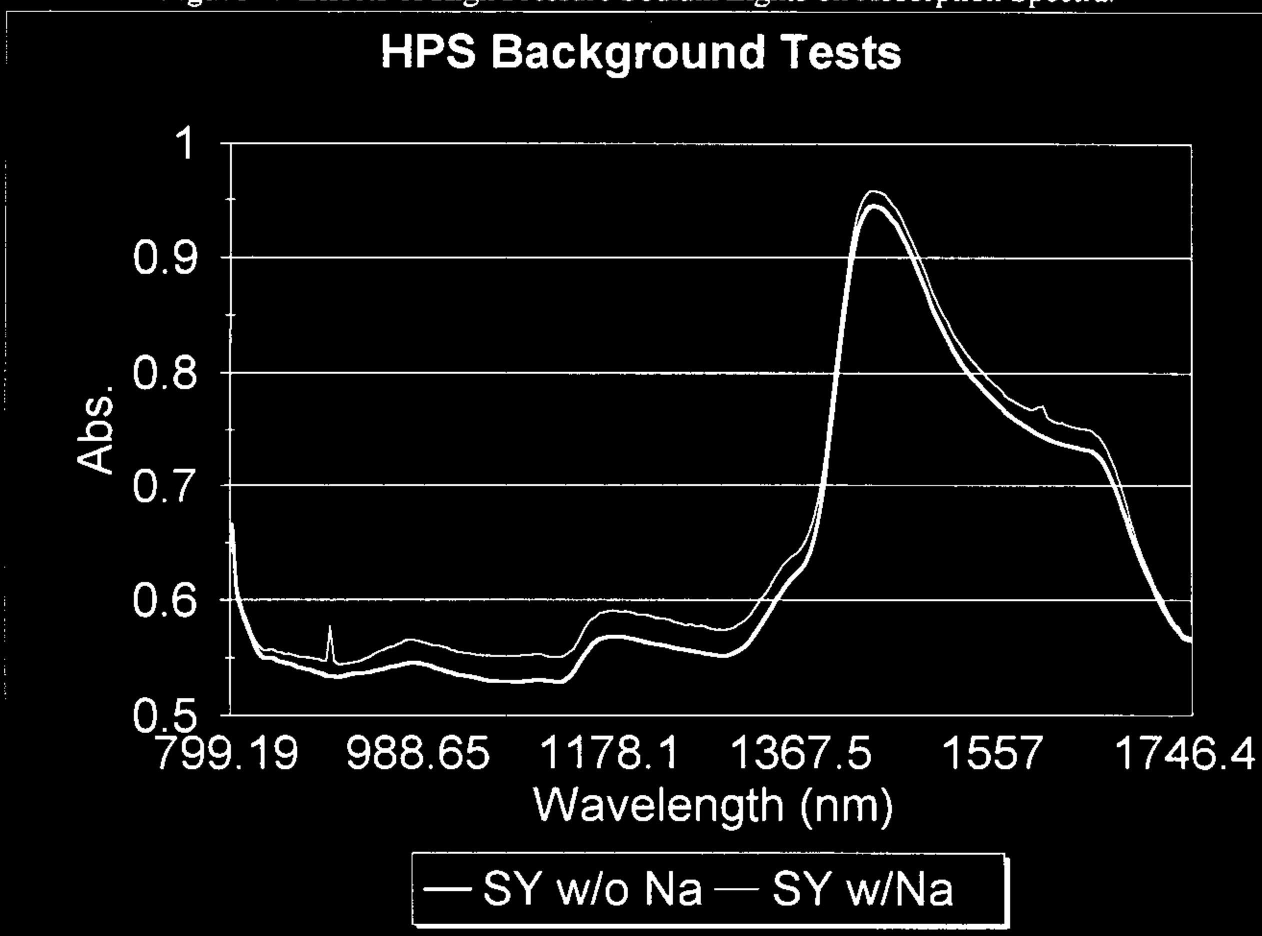


5.2 Background Lighting Effects

The non-contact nature of the Axiom probe raised some early concern over potential interferences caused by the strong hot cell lights. Because of the attenuation of the protective lead window, large high pressure sodium lamps (40,000 lumens) are used to illuminate the interior of the hot cell.

Background lighting effects were investigated using the Polytec (dispersive grating with fixed CCD detector array) system in the Hanford 305 Building cold test facility. A high pressure sodium lamp (40,000 lumens) was used to simulate hot cell lighting intensity and acquire spectra in the 800 to 1700 nm range. Test results showed that the sodium lines should not interfere significantly with the absorption spectra (see Figure 7). In addition, in the hot cell application, any residual sodium features will be acquired as part of the background signal and will be removed (ratioed out) from the waste sample spectra.

Figure 7. Effects of High Pressure Sodium Lights on Absorption Spectra.



5.3 Lift-Off Sensitivity

The numerical models used to extract moisture data from the NIR spectra use all of the spectral features, including the amplitude information, to derive their moisture prediction values. The lift-off related intensity variation is one of the parameters that affects the performance of a moisture prediction model.

All fiber optic probes experience some intensity changes (although it may be small) related to the distance between the probe and the sample. There is an incentive to eliminate as many variations as possible in order to maximize the moisture prediction performance, including any lift-off caused intensity variation. With the NIR moisture probes, optical fibers (and in some cases, lens-forming optics) illuminate a sample and collect the sample-reflected/scattered light that contains the NIR moisture information. The distance between the probe and the sample (lift-off) basically affects the optical efficiency of the probe. This may be due to a lift-off related change in the size of the sample illumination spot size, a lift-off dependent collection efficiency (solid angle or effective f/number change when lift-off is varied), or both of these.

Data from a contact or "mash" probe can be used to demonstrate the effects of lift-off on the NIR spectrum. A contact probe is designed to be most efficient when the probe is in contact with the sample, as shown in Figure 8. This figure shows the performance of the WSRC contact probe as the lift-off distance is varied (0 mm meaning the probe is in contact with the sample). As the probe is "lifted" from the sample, the signal level decreases while the apparent noise level increases. The decrease in the signal-to-noise ratioof the spectra as the probe is moved away from the sample translates into a poorer PLS/PCR prediction of moisture content.

The Axiom probe performed very well as a non-contact probe. Testing showed that it is relatively insensitive to lift-off variations. Figure 9 shows the probe's signal variation from a potassium bromide sample as the probe lift-off position is varied. These results indicate that the Axiom probe will collect a nearly constant spectrum from a sample over a 3 to7-mm probe-to-sample distance. This should allow hot cell operators, using the hot cells remote manipulators, to position the probe over the sample material and obtain a constant spectral response.

Figure 8. T-Plant Bottom Simulant at 20 wt% Moisture.

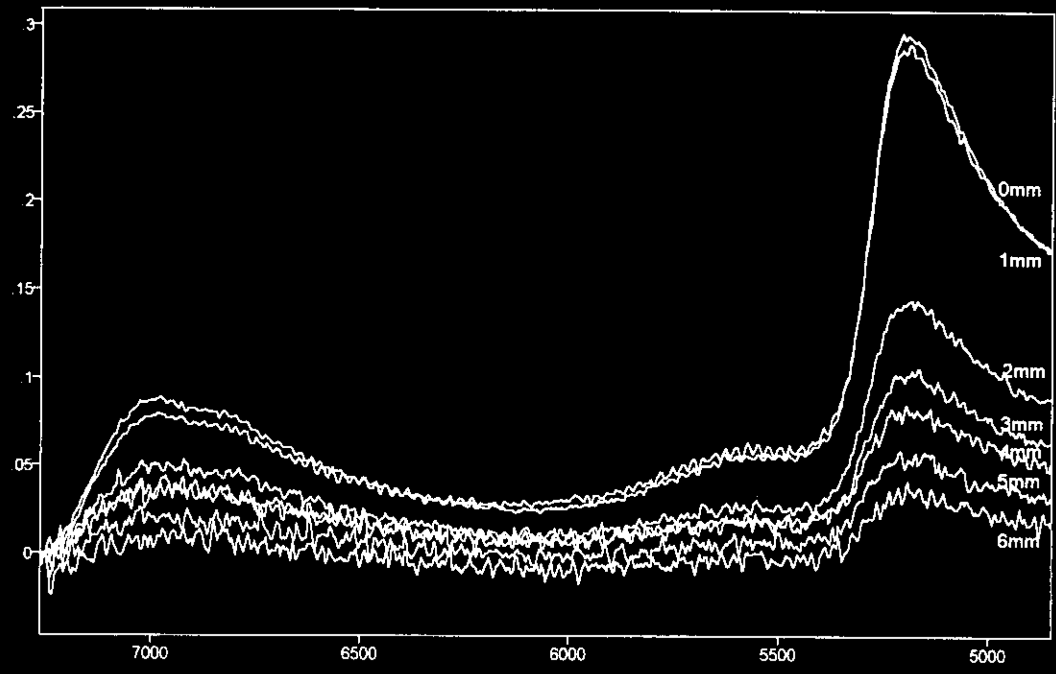
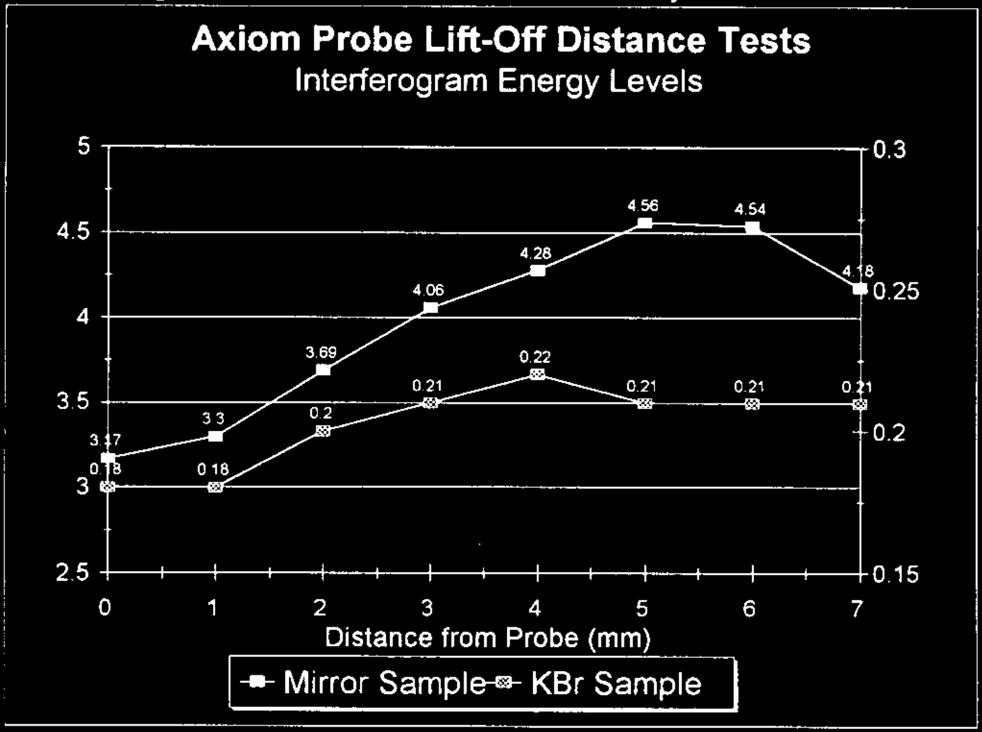


Figure 9. Axiom Probe Lift-Off Sensitivity Test Results.



6.0 CALIBRATION MODELS

A primary focus of the NIR fast track activity was to develop a reliable method to extract calibrated moisture data from NIR spectra of real tank wastes. The strategy employed to achieve this objective was to use calibration models, developed from tank simulant spectra, to predict moisture contents from spectra obtained using real tank waste samples.

In general, the goal of developing a calibration model is to create an equation which, when applied to spectra of unknown moisture concentrations, will accurately predict the moisture content of the sample. In order to calculate these equations, a set of "standards" are required which reflect the composition of the "unknowns" as closely as possible, and have known moisture contents. These standards must span the expected range of moisture concentrations expected in the unknowns, have a similar composition, and be measured under the same conditions (sampling method, pathlength, instrument, etc.) as the unknowns. This set of spectra and the known quantities of moisture in each individual sample form a training set or calibration set from which the calibration equations are built. The unknown samples are then measured in the same manner on the same instrument and the equations are used to "predict" the concentration of moisture in each unknown. The steps required to execute this strategy are identified as follows:

1) Acquire NIR spectra from simulant moisture standards and obtain actual moisture data.
2) Develop PLS/PCR-based calibration models using the simulant standards. (A summary description of the PLS/PCR model theory is included in Appendix B).
3) Use these models to test/demonstrate the feasibility of extracting moisture content data from the NIR spectra of the real tank wastes.

Initially, model development focused on accurately determining moisture content using samples in the range of 0-25 wt%. This was based on the tank safety driver that tanks with wastes that have a moisture content greater than 17 wt% and an energetic content of less than 480 J/g on a dry weight basis are consdered to be safe (Babad et al. 1995). Simulant standards were prepared by "spiking" dry simulant materials with known quantities of water in the 0-25wt% range. However, to provide a useful and beneficial system for the hot cell operations, particularly when sludge samples are being analyzed, models need to be developed to predict higher moisture concentrations as well (up to 60 wt%). Therefore, moisture standards were also created in the 20-35 wt% range.

Simulant material was spooned from the sample vial in order to fill a 10 mm wide by 3 mm deep sample planchet. Using a vertical translation stage accurate to within 0.01 mm, the Axiom probe was set at approximately 6 mm from the probe window to the sample surface. The Bio-Rad system was set to acquire spectra at 20 kHz and 256 coadds (for each wavelength channel, a sum of the levels from a number, 256 in this case, of individual spectrum). To obtain the actual moisture content, each sample was weighed, placed in a laboratory oven set to approximately 110°C and allowed to dry out at least 24 hours, and then weighed again. The weight of the sample before and after drying is the moisture content lost by the sample.

In the 20-35 wt% range, the growth of the 1.5 μm water absorption peak dominates the spectrum. As summarized in the table below, models developed using a moisture range of 0-25 wt%, where the growth of the 1.9 μm peak dominates most spectra, achieved a lower prediction error (as measured by the standard deviation) than models developed using the 0-35 wt% data set.

Table 1. Comparison of PCR and PLS models generated with NIR spectra.

Model Description	PCR Standard Deviation (Factors[a])	PLS Standard Deviation (Factors)
Smoothed[b] Data Set, Mean-Centered[b], 0-25 wt%	1.89 (8)	1.57 (9)
Raw Data Set, Mean-Centered, 0-25 wt%	1.92 (10)	1.75 (7)
Raw Data Set Shifted @ 7500 cm^{-1} to a value of 0.0, Mean-Centered, 0-25 wt%	1.90 (10)	1.77 (6)
Multi-Point Baseline Corrected[b], Mean-Centered, 0-25 wt%	2.10 (9)	1.91 (7)
Smoothed and Multi-Point Baseline Corrected, Mean-Centered, 0-25 wt%	2.00 (4)	2.01 (4)
Raw Data Shifted @ 7500 cm^{-1} to a value of 0.0, 0-35 wt%		3.35 (9)
Smoothed Data Set, Mean-Centered, 0-35 wt%		3.63 (9)
Raw Data Set, Mean-Centered, 0-35 wt%		3.63 (8)
Raw Data Set, Mean-Centered, 0-25 wt% Including "Original" Spectra at High Moisture Content[c]	4.16 (18)	4.09 (7)
Multi-Point Baseline Corrected, Mean-Centered, 0-25 wt% Including "Original" Spectra at High Moisture Content	10.49 (3)	

a Factors: The number of mathematical components used to model the spectra.

b Several data pre-processing steps were explored:
Mean-Centering: Subtracting the average spectrum from every spectrum in the data set. The average moisture value is also subtracted from each sample concentration.
Multi-Point Baseline Correction: A user-defined baseline is developed and subtracted from each individual spectrum.
Smoothed: A 19-point moving average is applied across each individual spectrum.

c Simulant standards initially developed ranged from 0-25 wt% but also included a high moisture content sample termed "Original".

Figures 10 through 14 contain plots of spectra obtained from real waste samples. The spectra and moisture content of these samples were obtained in the same manner discussed above for the simulant materials.

Six PLS models were used to predict moisture contents from the real waste sample spectra. Appendix C contains the actual data generated by the models and Figure 15 provides a graphical representation of the best model's performance.

The best model was able to predict moisture content with an accuracy of 2.8 wt% (average error) and an error window of ±8.35 wt% (standard deviation). The average error represents the overall accuracy of the calibration model in predicting moisture content while the standard deviation (standard prediction error) provides the error bars or precision around the predicted value.

In general, this PLS model was able to predict moisture content very well for most samples. The model did not predict the B-101 Jar 7928 (Figure 13) sample very well and this may be because the spectral intensity of the peaks are much larger than anticipated. Figure 16 contains simulant spectra in the 20 wt% region. Most simulant spectra experience an intensity of approximately 0.15 absorption units in the 7000 cm^{-1} range. Compared to the B-101 sample with an intensity of 0.3 absorption units, it is not surprising that the model predicted a higher moisture content than expected. The model also had trouble predicting one of the U-202, Jar 7929 spectra (Figure 14). A closer look at these spectra reveal offset changes that may be caused by particle size effects.

Overall, the model performed very well. Work needs to continue in the development of better models and to specifically include the real waste data in the model training sets. This should provide a better model for predicting moisture in real wastes whose spectra may differ from the simulant standards. The real tank wastes specifically contain spectral features in the 6250-7250 cm^{-1} range that do not appear in any of the simulants. Any significant spectral feature differences will have an adverse effect on the ability of a simulant-based model to predict moisture in the real wastes.

Figure 10. Tank 241-U-202 Waste Sample @16.3 wt% Moisture.

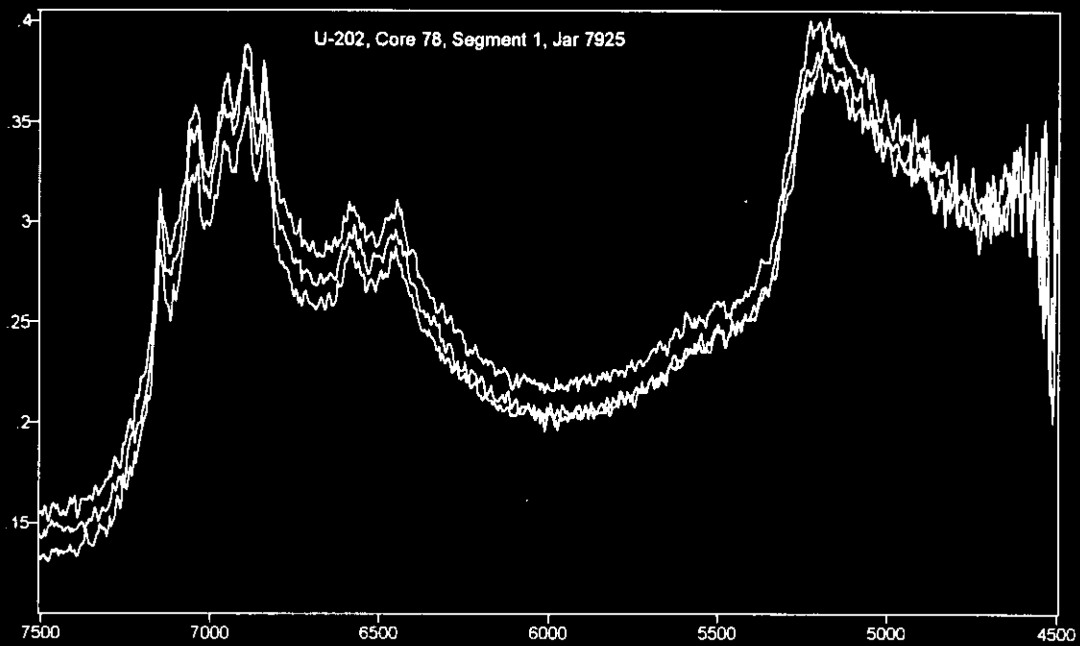


Figure 11. Tank 241-BX-103 Waste Sample @26.3 wt% Moisture.

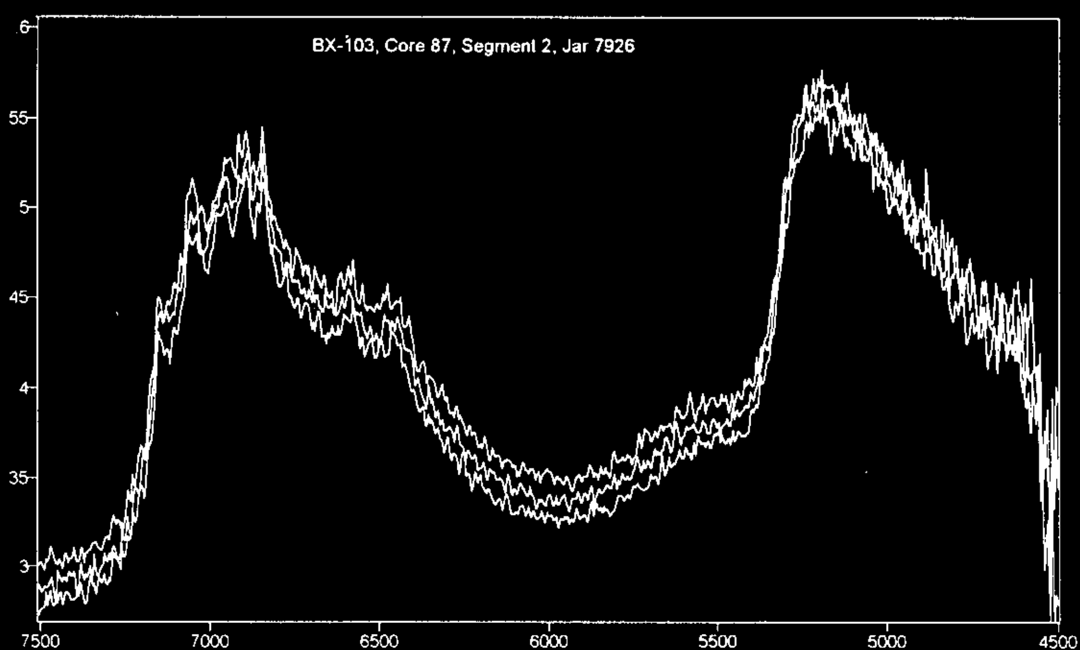


Figure 12. Tank 241-B-101 Waste Sample @18.0 wt% Moisture.

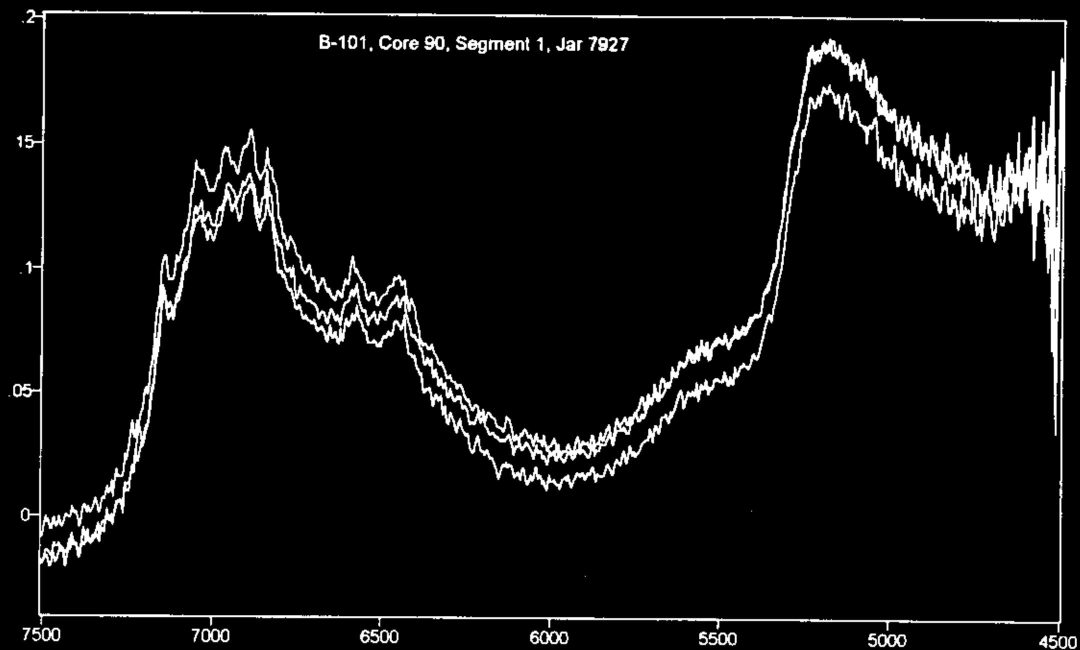


Figure 13. Tank 241-B-101 Waste Sample @13.3 wt% Moisture.

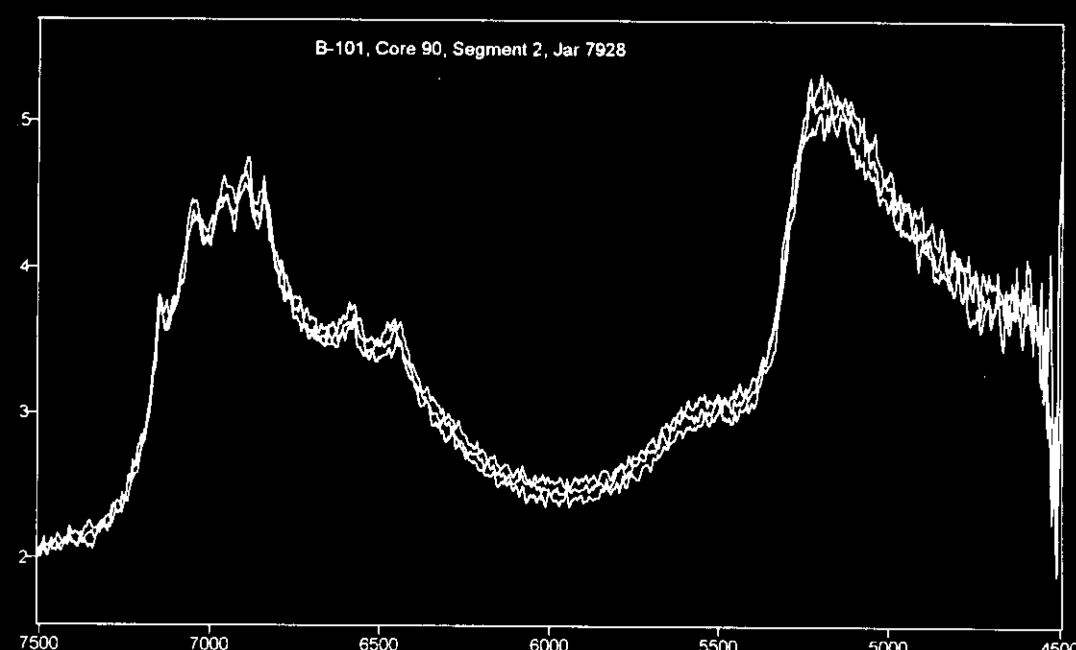


Figure 14. Tank 241-U-202 Waste Sample @25.8 wt% Moisture.

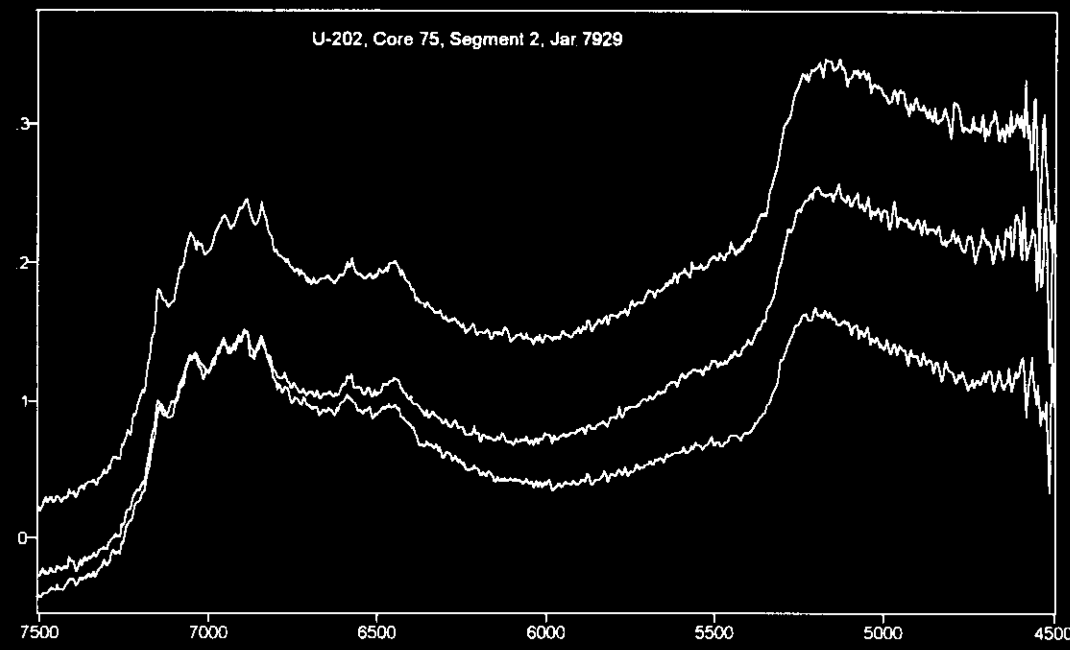


Figure 15. Model Performance Using Real Waste Spectra.

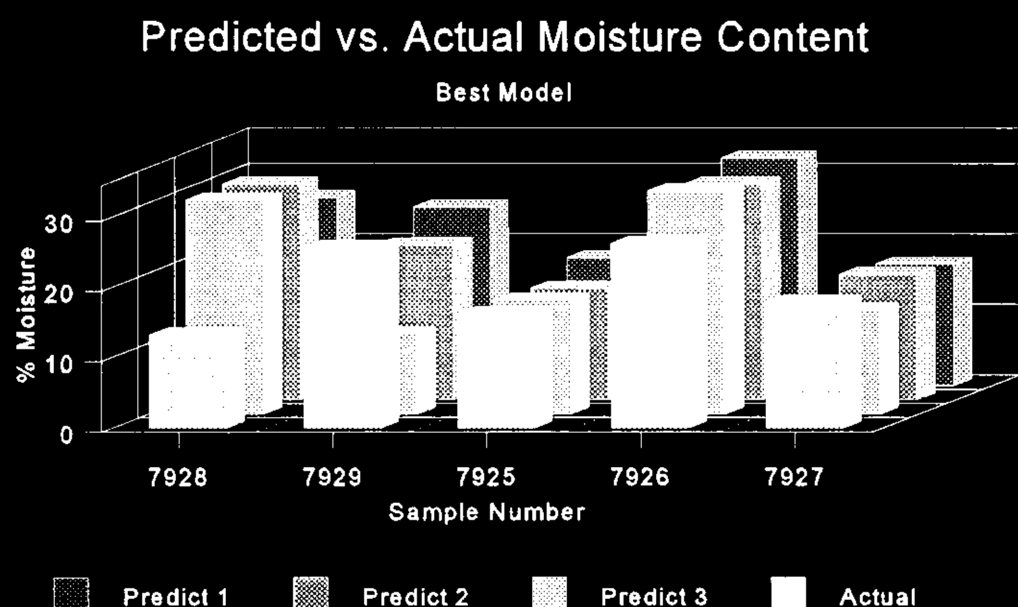
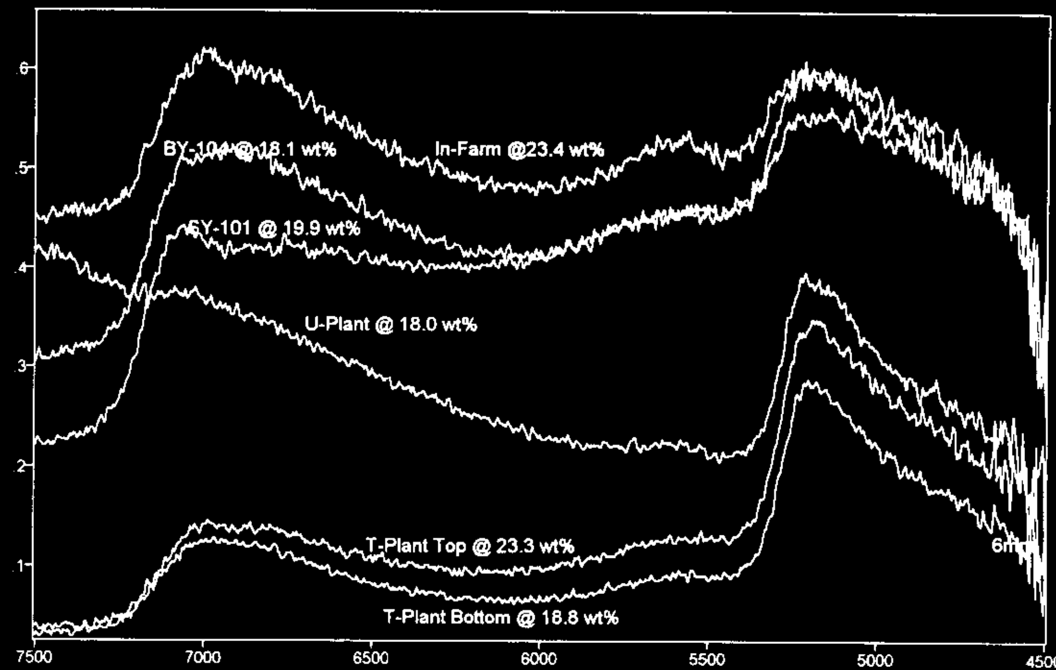


Figure 16. Simulant Spectra @20 wt% Moisture Range.



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7.0 CONCLUSIONS

A prototype NIR moisture probe has been setup and is ready for hot cell deployment to sense moisture content and homogeneity in tank core and auger samples. The EM-50/EM-30 supported NIR fast-track plan was successful in accelerating the development of this system, in support of a January 1996 hot cell deployment milestone. This work is continuing in FY 1996.

NIR data from simulant and real tank wastes demonstrated that the NIR moisture system meets two key performance related Go/No Go decision points:

1. The NIR moisture probe can quantitatively measure moisture concentration of a real tank waste with an average error of 2.8 wt% with a error window of ±8.35 wt%. This performance was demonstrated with spectral data from five real waste samples with moistures ranging from 13.3 to 26.3 wt%.

2. Spectral data from the NIR moisture probe provide a reliable indication of relative moisture differences or changes (homogeneity) within tank waste samples.

These tests and the validation of the data with calibration samples and actual moisture data support the continuation of the work to deploy this system in the hot cell as a routine moisture scanning system.

The system development work in FY 1995 addressed a number of issues:

- The hot cell system will initially use an FTIR spectroscopy system; a diffraction grating based NIR system will be maintained as a backup system.

- A non-contact probe, from a commercial vendor, will be used that eliminates cleaning and cross-contamination issues with a contact or "mash" probe that makes material contact. The probe demonstrated a minimum sensitivity to lift-off (sample to probe distance) variations.

- Interference or background light from hot cell sodium lamps is not an issue in obtaining reliable NIR spectral data for extracting moisture data.

- The FTIR software data acquisition, data processing, and modeling packages will be used to implement algorithms for extracting moisture data from the NIR spectra.

- A calibration algorithm, which applies truncation, smoothing, baseline correction operations on the NIR spectra, provided optimum performance with PLS based numerical models.

Issues/Future Work:

For long-term, routine operation there a number of system issues that will need additional work in FY 1996:

Algorithm Development: As more data are taken from the core samples, the models must be updated in order to more reliably predict moisture from tanks which exhibit abnormal spectral features. Work is needed to identify an optimum model and a method to incorporate new "standard" data into a model for use with unknown real waste samples. An algorithm is needed that allows homogeneity information to be easily generated from a number of NIR spectra.

Software: The FTIR system vendor is upgrading the spectroscopy system software package to a DOS environment (this will affect vendor support for the current software package). The current software package uses an unique operating system that is cumbersome to operate and can only be run using the spectrometer's computer system causes a potential conflict between routine data acquisition, processing and archiving operations.

LN_2 Auto-Filler: A liquid nitrogen auto-filler will be required to support the system on a routine basis. An auto-filler system has been procured, but resources will be needed to install the new detector and auto-filler system in FY 1996.

Routine Operation - Backup Components: After some operational experience is obtained with the hot cell NIR system, system optimization, maintenance and backup, issues need to be re-assessed. The current hot cell components, which include a long (30 meter) fiber optic cable, and the system interface/location in the hot cell specifically need to be examined. Backup components will be identified and stocked to support a routine operation mode.

8.0 REFERENCES

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APPENDIX A:
Status Report of Part 2: Decision Hold Point and Hot Cell Installation Key Go/ No Go Decision

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APPENDIX A: Status Report of Part 2: Decision Hold Point and Hot Cell Installation Key Go/ No Go Decision

INTRODUCTION:

This decision/hold point milestone is part of an accelerated work plan for this "fast-track" activity that supports a key January 1996 NIR hot cell probe milestone.

Part 2: Provide an indication of relative moisture differences or changes within tank waste samples. For tank cores, the difference or change data would be used to generate moisture homogeneity profiles, particularly along the core axis. This application may be performed without the need for quantitative moisture readings/data from the NIR spectra.

The data presented shows that the NIR probe being developed for hot cell deployment meets part 2. of this milestone.

BACKGROUND:

The key issue in Part 2 of this decision/hold point is a moisture probe which obtains NIR spectra from tank wastes/simulants that are:

a. sensitive to waste/simulant moisture content.
b. can indicate relative moisture differences and changes in the waste.

Tank waste moisture homogeneity data will help provide a level of confidence that alliquots taken from waste samples in a hot cell have moisture content that is representative of the whole tank sample being examined. The probe must be minimally affected by sample-to-probe interfaces, such as lift-off, and waste matrix properties, such as particle size and surface irregularities.

NIR MOISTURE PROBE DATA:

a.) Acquisition of Moisture Dependent NIR Spectra:

Figure A-1 shows a series of NIR spectra of In-Farm simulant samples; these spectra demonstrate that an NIR based moisture probe does respond to varying water content. These In-Farm simulant samples were prepared by drying the simulant for approximately 24 hours at 110 C°, grinding and dividing into sub-samples, and then spiking each sub-sample with a different amount of water. After the water was added, the samples were stirred to mix the water into each sample. The NIR were then recorded. The moisture values were then also obtained for each sample by using loss of weight or a thermogravometric method: weighing each sub-sample, drying at 110 C°, and weighing each sub-sample after drying. The water content is the difference between the two weights.

The raw spectra originally had a base-line (Y-axis) offset from the variations in optical scattering between the samples. Each spectrum was individually baseline or Y-axis shifted until the amplitude at the 1300 nm wavelength point was at 0. This did not change the spectral shape or relative amplitude, but it does make it easier to see the moisture dependent spectral changes.

The spectra in Figure A-1 show an increase in the 1350-1650-nm absorption band that is related to the water content. The vertical axis or Y-axis is absorbance and the horizontal or X-axis is wavelength. Theses data clearly show progressive absorption changes that are proportional to the moisture concentration.

b.) Relative Moisture Difference/Change Indicator:

To demonstrate the ability of the NIR probe to sense moisture differences or changes, spectral measurements were obtained through the wall of a clear cylindrical vessel (4" diameter by approximately 7.75" long) that was filled with an In-Farm simulant. Figure A-2 shows the vessel and the scan positions along the vessel axis. The vessel was originally fabricated as part of an In-Farm particulate settling study. It was conjectured that since the vessel had been settling for over two years, there should be a moisture gradient from top to bottom in the In-Farm simulant.

Visually, the In-Farm material appears to be light or sky blue in color. The simulant directly against the vessel wall appeared to be fairly consistent with some voids and cracks from material shrinkage. Some parts of the vessel wall had unknown discolorations. These were avoided, for the most part, in acquiring NIR spectral data.

The Polytec, diffuse reflectance probe in a modified housing was used to record the NIR data directly through the vessels clear 0.25-inch thick wall (clear polyethylene material). The probe spot size was about 4 mm in diameter.

NIR spectra were recorded at 0.25-inch increments along the axis of the vessel, starting about 0.5 inches inward from the vessel end-caps (a scan length of about 6.75-inches), as indicated in Figure A-2. Three spectra were recorded and averaged at each axial position (the vessel was turned so that spectral data were obtained from three different 4 to 5-mm spots at each axial position). Although the In-Farm material had settled about 2-inches (leaving a solid column height of approximately 5-inches), there was enough material adhering to this part of the vessel's wall to still get a good NIR spectral response. Two independent scans were obtained at 90 degrees to each other, picking a fairly clear wall area with a minimum of scratches and imperfections.

Figure A-3 shows the array of NIR spectra recorded, after a baseline or Y-axis shift was applied to each spectra, similar to the calibration data above (the whole spectrum was shifted vertically until the 1300-nm wavelength point was at 0). The band at 1150 to1250-nm is the C-H stretch overtone of the vessel wall material and is not related to the In-Farm simulant chemical constituents or to moisture.

In comparison with the spectral changes in the In-Farm simulant data, shown previously in Figure A-1, the Figure A-3 spectral changes are small. This would indicate that the moisture is fairly constant along the vessel axis. In addition, the moisture content of the upper 2-inches of the vessel (the settled region) also show similar NIR spectra and subsequently similar moisture concentrations. In the 1350 to 1650-nm water absorption band, the spectra appear fairly constant with no top to bottom moisture change as originally anticipated. Small variations in individual spectrum are visible, but there are no trends, such as that shown in Figure A-1 from moisture variations. The small localized variations in the spectra are attributed to localized changes in optical scattering from voids and cracks that appeared in the In-Farm material and wall imperfections (scratched, bubbles, and etc.).

To show the potential small differences between the vessel spectra, the spectrum at the 6.71-inch position, which was at the bottom of the vessel, was used as a reference and all other spectra subtracted from this reference. This enhances spectral differences and reduces common spectral features to zero. An over-lay of these differences along with the 6.71-inch reference is shown in Figure A-4. Notice that the 1150 to 1250-nm absorption band from the vessel wall is not visible. This shows a fairly constant optical performance by the fiber optic probe and the NIR spectrometer system. The interpretation of this figure is that in the 1350 to 1650-nm band, any spectral residue above the "0" line indicates a spectrum with less moisture than the 6.71-inch reference spectrum, while features below the "0" line indicate a spectrum with higher water absorption than the 6.71-inch reference spectrum.

The absence of differences or changes from the top to the bottom of the vessel spectra indicate that there is no moisture gradient in the vessel.

CONCLUSION:

The spectral data from the In-Farm vessel and calibration standards show that the NIR moisture probe can provide an indication of relative moisture differences or changes in tank waste materials. These data show that the NIR moisture probe's performance meets Part 2 of the *Decision Hold Point and Hot Cell Installation* milestone in the "Accelerated Schedule Workplan" to deploy an NIR probe for moisture screening of waste tank core samples.

Figure A-1. Isometric View of Base-Line Adjusted In-Farm Simulant Calibration Spectra.

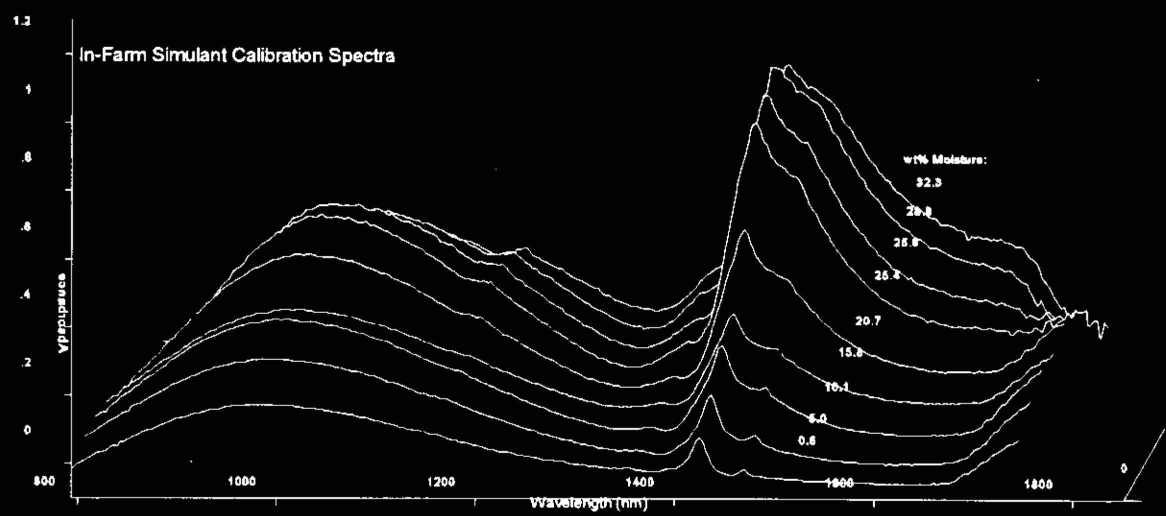


Figure A-2. Clear-Walled Vessel Filled With In-Farm Simulant Showing the Scan Positions Used to Obtain NIR Moisture Data Through the Vessel Wall.

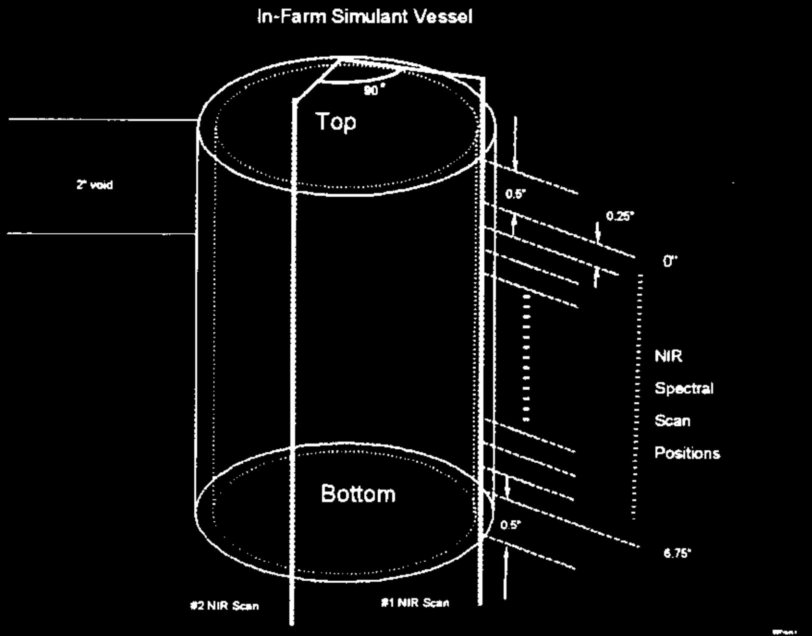


Figure A-3. Isometric View of In-Farm Vessel NIR Spectra. The Isometric Z-Axis Shows the Probe Positions Along the Vessel Axis.

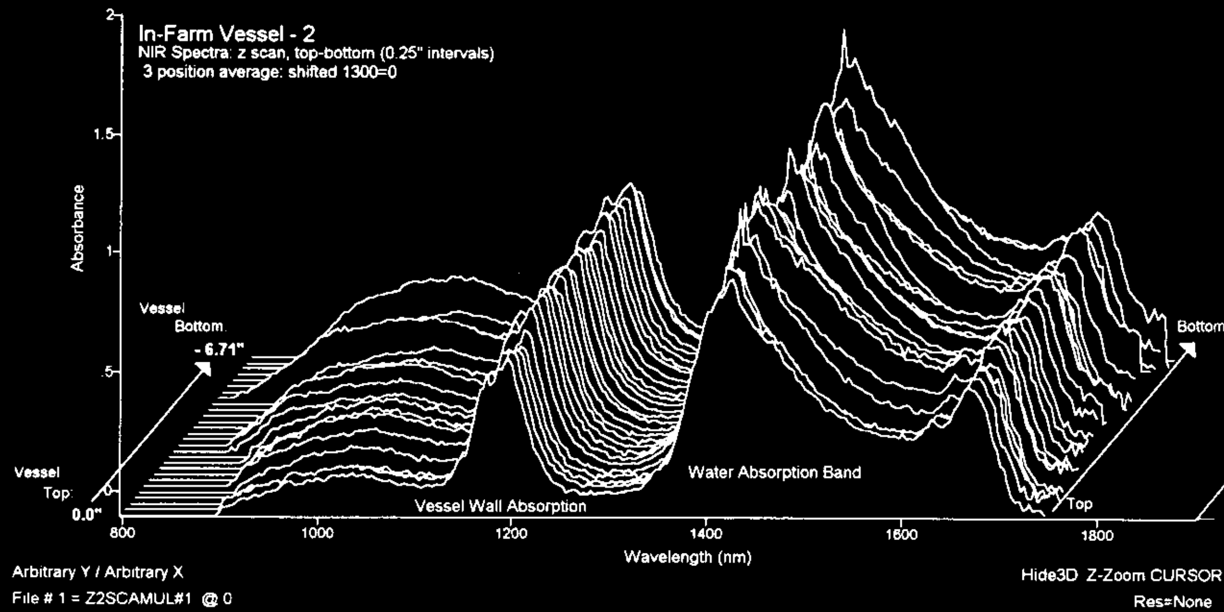
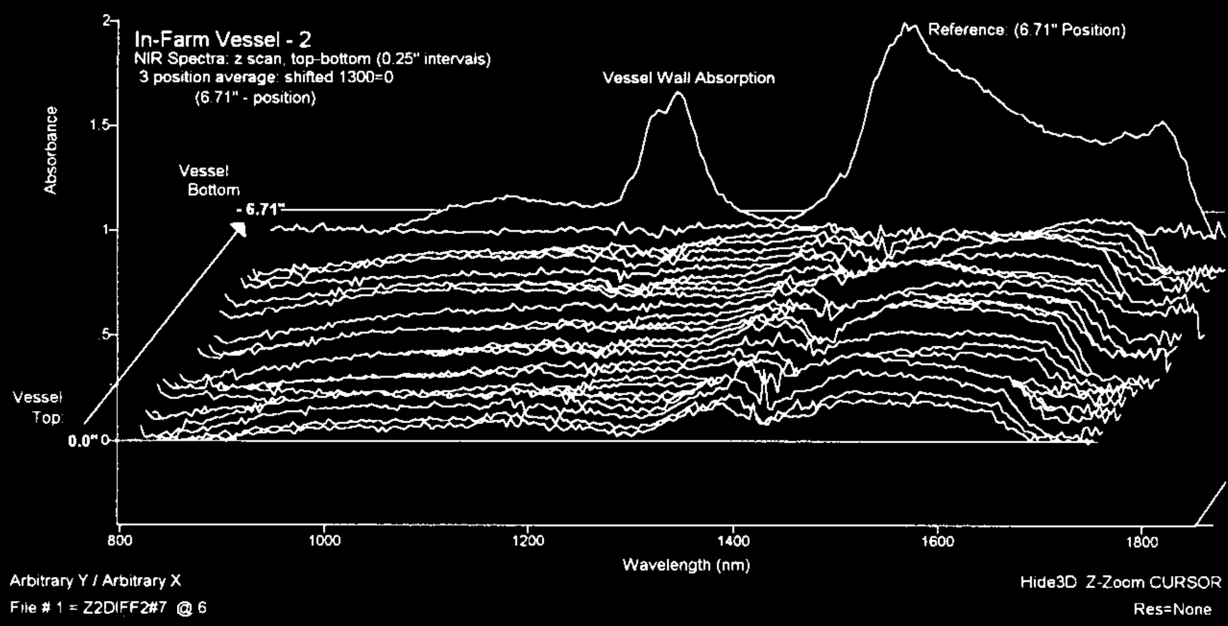


Figure A-4. Isometric View of Difference Spectra. The Isometric, Z-Axis is the Probe Position Along the Vessel Axis.



APPENDIX B:
Principal Component Regression and Partial Least Squares Theory

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APPENDIX B: Principal Component Regression and Partial Least Squares Theory

Inverse Beer's Law Model:
The inverse Beer's law model describes the moisture concentration as a linear function of **n** samples of the absorbance spectrum **a**:

$$c = \sum_v a_v q_v + c_0 \qquad (1)$$

where $\mathbf{q}_v$ is a vector of coefficients and $\mathbf{c}_0$ are constants which must be determined by a calibration procedure.

A calibration experiment is run in which spectra are collected for **m** calibration samples. The resulting set of spectra can be represented by a matrix **A** with **m** rows and **n** columns representing **m** spectra with **n** wavelength points. The **m** samples are also analyzed for moisture content, resulting in a matrix **C** with **m** rows and one column. The calibration must be completed by solving for the matrix **Q**:

$$C = A\,Q \qquad (2)$$

In this equation, in order to eliminate the $\mathbf{c}_0$ constants from Equation (1), the **C** matrix and the **A** matrix are "centered" by subtracting the column means (average column values) from the columns of **C** and **A**, respectively.

Principal Component Regression:
The PCR solution for matrix **Q** can be computed by decomposing the matrix into the product of three matrices:

$$A = U\,S\,V^T \qquad (3)$$

The rows of matrix $\mathbf{V}^T$ represent the principal components of the calibration spectra, and the rows of matrix **U** represent the "factor loadings" or "principal coordinates of the spectra in matrix **A**. The principal coordinates represent the linear combinations of the principal components which form the original matrix **A**.

The singular values, **S**, represent the relative importance of the principal components in the construction of matrix **A**. The principal components associated with small singular values are most sensitive to noise. These principal components are unreliable for use in predicting component concentrations. In applying principal component analysis to determining moisture content, the principal components associated with the larger singular values should correlate with the changes in moisture, and the PC's corresponding to small singular values represent random variation and should be ignored.

Partial Least Squares:
Like PCR, the PLS algorithm is based on Equation (2), the "inverse Beer's Law." However, where PCR decomposes the **A** matrix to determine the optimum calibration coefficients, PLS decomposes the **C** matrix as well.

In PLS analysis, **A** matrix is decomposed into the product of a **r** by **n** matrix **T** of latent variables and an **m** by **r** matrix **B** of loading factors:

$$A = T B + E$$

where **E** represents the residual error in fitting matrix **A** to **r** latent variables.

Similarly, matrix **C** is decomposed into an **m** by **r** matrix **U** of latent variables and a **p** by **r** matrix **P** of loading factors:

$$C = U P + F$$

where **F** represents the residual error in fitting matrix **C** to **r** latent variables.

In PLS analysis, the two matrices, **T** and **U**, are calculated such that both the **E** and **F** matrices are "small" and the correlation of **U** with **T** is maximized. The correlation of **U** and **T** represent the potential advantage of PLS over PCR since the first **r** latent variables of the **A** matrix will be more likely to present the variation in the **C** matrix in comparison with the first **r** principal components, which are calculated without reference to the **C** matrix.

APPENDIX C:
Calibration Model Performance Using Real Waste Spectra

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APPENDIX C: Calibration Model Performance Using Real Waste Spectra

Sample	Model Description					
	Smoothed, Mean-Centered 0-25wt% Simulant Data Set Using 9-Factor PLS Model			Smoothed, Mean-Centered 0-35wt% Simulant Data Set Using 10-Factor PLS Model		
	Predicted	Actual	Error	Predicted	Actual	Error
U-202, 7925	46	16.3	29.7	18.09	16.3	1.79
	46.93	16.3	30.63	15.78	16.3	-0.52
	44.29	16.3	27.99	16.21	16.3	-0.09
BX-103, 7926	52.37	26.3	26.07	32.24	26.3	5.94
	50.22	26.3	23.92	30.66	26.3	4.36
	53.18	26.3	26.88	31.69	26.3	5.39
B-101, 7927	32.67	18	14.67	17.19	18	-0.81
	29.36	18	11.36	17.74	18	-0.26
	30.15	18	12.15	14.85	18	-3.15
B-101, 7928	54.06	13.3	40.76	26.7	13.3	13.4
	54.78	13.3	41.48	30.66	13.3	17.36
	55.92	13.3	42.62	30.44	13.3	17.14
U-202, 7929	26.91	25.8	1.11	11.47	25.8	-14.33
	30.88	25.8	5.08	21.98	25.8	-3.82
	37.99	25.8	12.19	25.35	25.8	-0.45
	Average Error		23.1	Average Error		2.79
	Standard Prediction Error		13.2	Standard Prediction Error		8.35

	Raw, Mean-Centered 0-25wt% Simulant Data Set, Using 7-Factor PLS Model			Raw, Mean-Centered 0-35wt% Simulant Data Set, Using 9-Factor PLS Model		
	Predicted	Actual	Error	Predicted	Actual	Error
U-202, 7925	21.64	16.3	5.34	34.78	16.3	18.48
	20.41	16.3	4.11	32.27	16.3	15.97
	18.44	16.3	2.14	31.49	16.3	15.19
BX-103, 7926	33.95	26.3	7.65	44.29	26.3	17.99
	32.4	26.3	6.1	43.87	26.3	17.57
	33.41	26.3	7.11	47.08	26.3	20.78
B-101, 7927	17.11	18	-0.89	26.92	18	8.92
	16.17	18	-1.83	25.57	18	7.57
	14.99	18	-3.01	24.1	18	6.1
B-101, 7928	32.9	13.3	19.6	41.08	13.3	27.78
	34.6	13.3	21.3	41.85	13.3	28.55
	33.58	13.3	20.28	40.35	13.3	27.05
U-202, 7929	15.57	25.8	-10.23	21.31	25.8	-4.49
	14.81	25.8	-10.99	30.75	25.8	4.95
	18.54	25.8	-7.26	35.67	25.8	9.87
	Average Error		3.96	Average Error		14.8
	Standard Prediction Error		10.4	Standard Prediction Error		9.38

	Raw, Mean-Centered, 0-25% Simulant Data Set with 7500cm^{-1} Shifted to 0.0 Using a 9-Factor PLS Model			Raw, Mean-Centered, 0-35% Simulant Data Set with 7500cm^{-1} Shifted to 0.0 Using a 9-Factor PLS Model		
	Predicted	Actual	Error	Predicted	Actual	Error
U-202, 7925	24.53	16.3	8.23	30.37	16.3	14.07
	24.11	16.3	7.81	26.98	16.3	10.68
	22.11	16.3	5.81	24.85	16.3	8.55
BX-103, 7926	36.26	26.3	9.96	41.12	26.3	14.82
	34.32	26.3	8.02	42.22	26.3	15.92
	36.1	26.3	9.8	42.87	26.3	16.57
B-101, 7927	18.89	18	0.89	27.67	18	9.67
	17.66	18	-0.34	27.91	18	9.91
	16.87	18	-1.13	25.34	18	7.34
B-101, 7928	35.12	13.3	21.82	41.34	13.3	28.04
	37.62	13.3	24.32	39.6	13.3	26.3
	36.7	13.3	23.4	36.49	13.3	23.19
U-202, 7929	16.61	25.8	-9.19	23.73	25.8	-2.07
	17.15	25.8	-8.65	29.19	25.8	3.39
	21.32	25.8	-4.48	32.14	25.8	6.34
	Average Error		6.42	Average Error		12.8
	Standard Prediction Error		10.7	Standard Prediction Error		8.34

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