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FTIR Fiber Optic Methods for the Analysis of Hanford Site Waste

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FTIR FIBER OPTIC METHODS FOR THE ANALYSIS OF HANFORD SITE WASTE

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INTRODUCTION

Sampling and chemical characterization of mixed high-level waste stored in underground tanks at the Hanford Site is currently in progress. Waste tank safety concerns have provided impetus to analyze this waste. A major safety issue is the possibility of significant concentrations of fuel (ferrocyanide and/or organic compounds) in contact with oxidizers (nitrates and nitrites). It is postulated that under dry conditions and elevated temperatures, ferrocyanide- and/or organic-bearing wastes could undergo rapid exothermic reactions. To maintain the tanks in a safe condition, data are needed on the moisture and fuel concentrations in the waste.

Because of the highly radioactive nature of the waste, non-radioactive waste simulants mimicking actual waste are used to provide an initial basis for identifying realistic waste tank safety concerns. Emphasis has been placed on the use of new or existing Fourier transform infrared (FTIR)-based systems with potential for field or tank deployment to perform in situ remote waste characterization. Near-infrared diffuse reflectance and mid-infrared attenuated total reflectance fiber optic probes coupled to a Bio-Rad FTS 60A spectrometry system have been evaluated. The near-infrared diffuse reflectance fiber probe system has also been used for preliminary screening of the moisture content and chemical composition of actual Hanford Site waste tank waste core samples. The attributes of this method for analyzing actual radioactive waste are discussed.

EXPERIMENTAL PROCEDURES

PREPARATION OF WASTE SIMULANT MATERIAL

Simulated waste material was prepared from a non-radioactive "in-farm" feed solution by performing a ferrocyanide scavenging process used in the 1950s (Burns and Stedwell 1957). The feed solution composition was modified to include nitrite at a 1:3 mole ratio of nitrite to nitrate to account for radiolysis over the years of tank storage. The chemical composition of the feed solution used for this "in-farm" simulant preparation is shown in Table 1.

Table 1. Simulant Composition.

Constituent	Concentration, M
Na_2SO_4	0.23
Na_3PO_4	0.27
$NaNO_2$	1.5
$NaNO_3$	4.5
$CsNO_3$	0.00013

Note: No radionuclides

WASTE SLUDGE PREPARATION

Figure 1 displays a production flowsheet for ferrocyanide scavenging using the simulated waste feed in Table 1. The sludge preparation involves the following steps: 1) addition of $Na_4Fe(CN)_6$, $NiSO_4$, Na_2S, and $Ca(NO_3)_2$ to the simulated waste solution; 2) adjustment of the pH of the resulting mixture to 9.1 + 0.1; 3) agitation of the mixture to initiate formation of slurry/precipitate; 4) allowing the precipitate to settle; and 5) removal of the supernate from the sludge. A wet sludge with a consistency similar to peanut butter is produced. An aliquot of this sludge is taken for chemical characterization and examined "as received". An aliquot of the wet sludge is also smeared onto a specially fabricated sample holder, quickly frozen to prevent migration of soluble components of the waste to the sample surface, and allowed to dry in a freeze dryer at -50 °C for 6 hours.

INSTRUMENTATION

Optically opaque and highly absorbing materials such as wet sludges are not amenable to transmission infrared methods, and must be examined by reflection methods. Three reflection configurations in which an FTIR instrument can be interfaced with fiber optics for characterization include: 1) attenuated total reflectance (ATR); 2) diffuse reflectance (DR);

and 3) specular reflectance (SR). The fiber optic probe can be made either as a single fiber or as a bundle in a variety of fiber types, fiber lengths, and probe designs for reflection measurements.

The complete fiber optic system consists of an FTIR spectrometer, a fiber optic accessory, a fiber optic probe, and a detector. Two types of fiber optic probes were fabricated: 1) ATR single-fiber probes for the mid-infrared (MIR) and near-infrared (NIR) regions; and 2) DR and SR bifurcated bundle probes for the NIR region.

ATR Single-Fiber Probes. Evanescent field absorbance sensors (EFAS) operating on the ATR principle were made from silver halide (AgBr/Cl) fiber and a polymer-clad, low-OH silica fiber for the MIR and NIR fiber optic probes, respectively. The fiber for the NIR-EFAS probe consisted of a 400-μm outer diameter low-OH fused silica core, a 500-μm outer diameter polymer cladding, and a 600-μm outer diameter nylon jacket. The center 12 cm of the polymer-clad silica fiber was stripped of its jacket and cladding. For the MIR-EFAS, a 1000-μm unclad AgBr/Cl fiber was used. Each fiber probe was one meter long.

A sketch of the setup for both NIR and MIR EFAS single-fiber probe systems is depicted in Figure 2. Each EFAS system includes the following: 1) FTIR spectrometer with spectral range covering both the MIR and NIR regions; 2) a fiber positioner; 3) a stainless steel sampling trough; 4) a fiber coupler; and 5) a detector (mercury cadmium telluride [MCT] for MIR-EFAS, or InSb for NIR-EFAS). Only the sampling trough was located inside the laboratory hood while the other components of the system were external to the hood.

The beam emanating from the infrared source of the FTIR was focused onto the inlet of the single-fiber probe using the fiber positioner. The light was propagated along the 1-m fiber passing through the trough containing the waste sludge. Using the fiber coupler, the unabsorbed light was transmitted directly to the MCT detector for the MIR system or to the InSb detector via a 0.5-m silica fiber extension for the NIR system.

NIR Bifurcated Bundle-Fiber Probe. The probe has a common leg and is bifurcated into two legs (one connected to the infrared source and the other to the detector) joined together in a zip cord configuration. The common leg contains a center fiber (detector fiber) surrounded by six other fibers (light source fibers). Each fiber has a 400-μm-diameter very low-OH silica core, a 440-μm dope silica cladding, a 470-μm polyamide buffer, and a 700-μm polymer jacket. The polymer jacket was removed by immersion in acetone and stripped off using a wire stripper. The buffers of the common leg were molded together using an epoxy resin to form a bundle. The terminal of the common end was beveled toward the center fiber and then bonded to a 20-mil sapphire window using trimethoxychloropropyl silane.

The light from each source fiber exits the beveled surface, passes through the window, and then is refracted toward the center fiber. The light transmitted through the window is scattered by the sample, which may be in intimate contact with the window (diffuse reflectance mode) or about 1 mm away from the window (specular reflectance mode). The

scattered light is collected by the detector fiber and directed to the detector. The 5-m bifurcated silica bundle is connected to the NIR fiber optic accessory to interface with the FTIR spectrometer. Figure 3 displays the schematic diagram of the FTIR fiber optic system using the bifurcated bundle probe.

RESULTS AND DISCUSSION

ATR Single Fiber Probes. Figure 4 depicts a typical mid-infrared spectrum of a partially dried ferrocyanide-containing simulated waste ("in-farm") obtained by fiber optics in the ATR-evanescent field absorbance (ATR-EFAS) mode. The two very sharp bands at 3616 cm^{-1} and 3549 cm^{-1} superimposed on a broad peak around 3400 cm^{-1} and the band at 1620 cm^{-1} are assigned to the OH stretching and OH bending modes, respectively, from the waters of crystallization of $Na_2NiFe(CN)_6$ in the waste. The broad band at 3400 cm^{-1} is due to the OH stretch of liquid (free) water. The strong band at 2094 cm^{-1} is attributed to the $NiFe(CN)_6^{2-}$ moiety. The bands at 1788 cm^{-1}, 1363 cm^{-1}, and 833 cm^{-1} are due to the nitrate (NO_3^-) species. The other bands are not very well delineated from the background, so no definite band assignment is made.

Figure 5 presents spectra of the sludge in the near-infrared (NIR) region collected by a single fiber silica probe. Except for fiber artifacts (i.e., bands due to the polyamide polymer cladding of the silica core), distinct bands are discerned at 7005 cm^{-1}, 6784 cm^{-1}, 5215 cm^{-1}, and 4250 cm^{-1} in the partially dried sludge sample. The band at 4250 cm^{-1} is tentatively assigned to the first overtone of the CN^- stretch, while the 5215 cm^{-1} is the combination band between the OH stretching and OH bending modes. The band at 6784 cm^{-1} is a combination band consisting of the combination band at 5215 cm^{-1} and the OH bending mode. Finally, the grouping from 6800 cm^{-1} to 7150 cm^{-1} is mostly from the first overtone of the OH stretching vibrations.

NIR Bifurcated Fiber Probe. Figure 6 shows spectra of the wet sludge using the NIR bifurcated fiber probe. The top spectrum is that of the sample when the probe is touching the sludge (DR mode) while the spectrum at the bottom was obtained with the probe positioned at a distance of 1 mm above the sample (SR mode). It is interesting to note that there is no significant difference between the spectra obtained by these two configurations. Both spectra exhibit similar features characterized by the presence of broad OH stretching first overtone and OH combination bands.

Figure 7 shows the spectra of the dried sludge (freeze-dried at -50 °C for 6 hours) obtained by the two fiber-probe (DR and SR) modes. Freeze-drying apparently does not completely dehydrate the sludge, as indicated by the water bands at 7005 cm^{-1} and 5215 cm^{-1}. The presence of ferrocyanide is indicated by the band at 4250 cm^{-1}. It would be worth investigating whether the ratio of the intensity of the water band at 5215 cm^{-1} to that of the ferrocyanide band at 4250 cm^{-1} can be used as a practical indicator for simultaneous

screening of moisture and ferrocyanide concentrations. Perhaps the intensity ratio (intensity of 5215-cm^{-1} band:intensity of 3400-cm^{-1} band) can serve also as a monitor for free and bound water.

CONCLUSIONS

Based on the results, the near-infrared region is the region of choice for moisture determination in simulated waste. However, both NIR and MIR spectra must be collected to measure ferrocyanide species unambiguously and accurately. For ease of sample handling and cleanup, as well as the potential for field or waste tank deployment, the FTIR fiber optics system using diffuse/specular reflectance is preferred over the ATR method. More work, however, is needed to test whether the intensities of the combination band of water at 5215 cm^{-1} and the first overtone of the ferrocyanide band at 4250 cm^{-1} can be used to measure water and ferrocyanide simultaneously. There is a good probability that free and combined water can also be calculated from the water bands in the NIR and MIR spectral regions.

REFERENCES

Burns, R. E., and M. J. Stedwell, 1957, "Volume Reduction of Radioactive Waste by Carrier Precipitation," *Chemical Engineering Progress*, Vol. 53, p. 93.

Figure 1. Ferrocyanide Sludge Preparation Flowsheet.

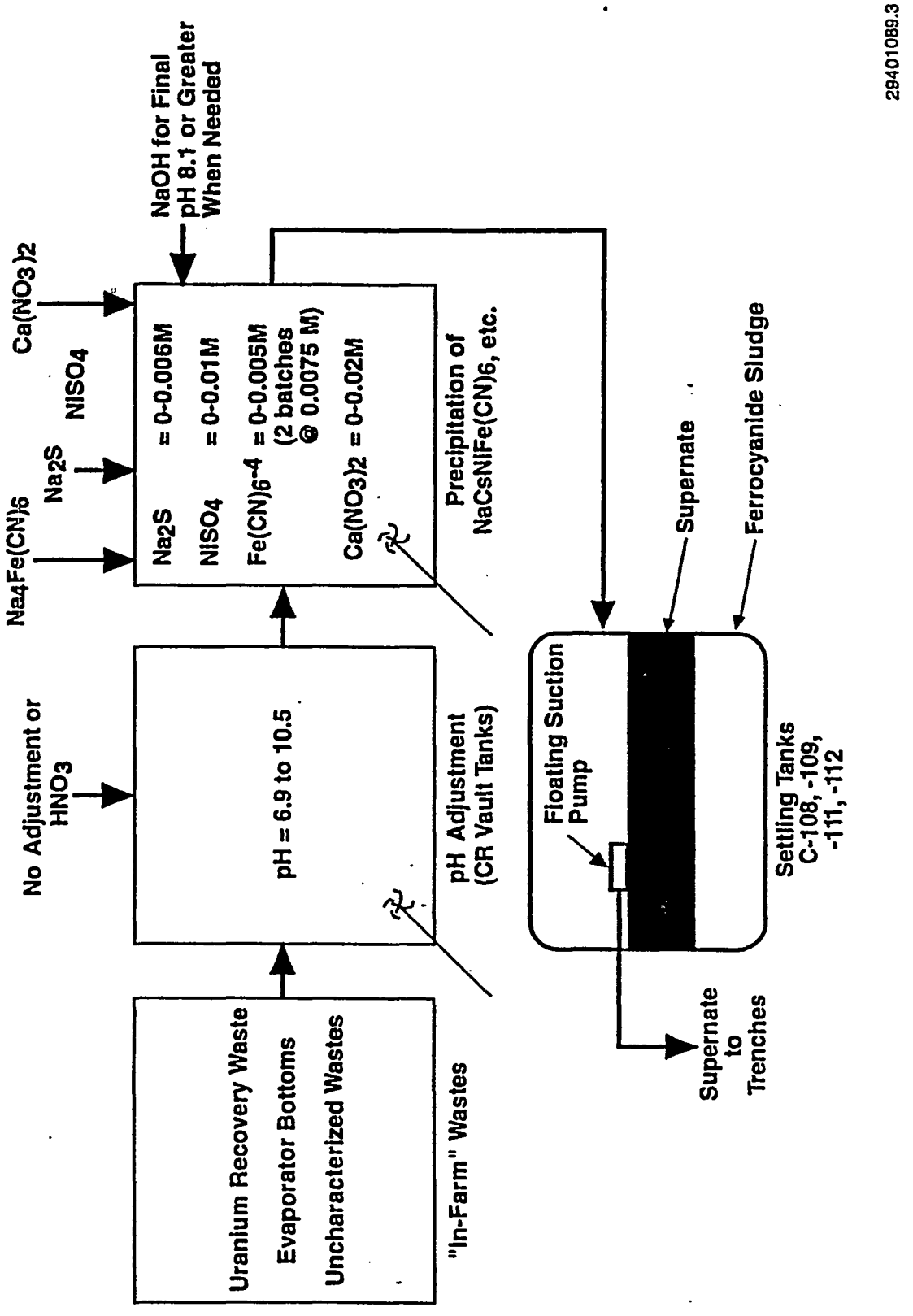

Figure 2. Evanescent Field Absorbance Sensor Setup.

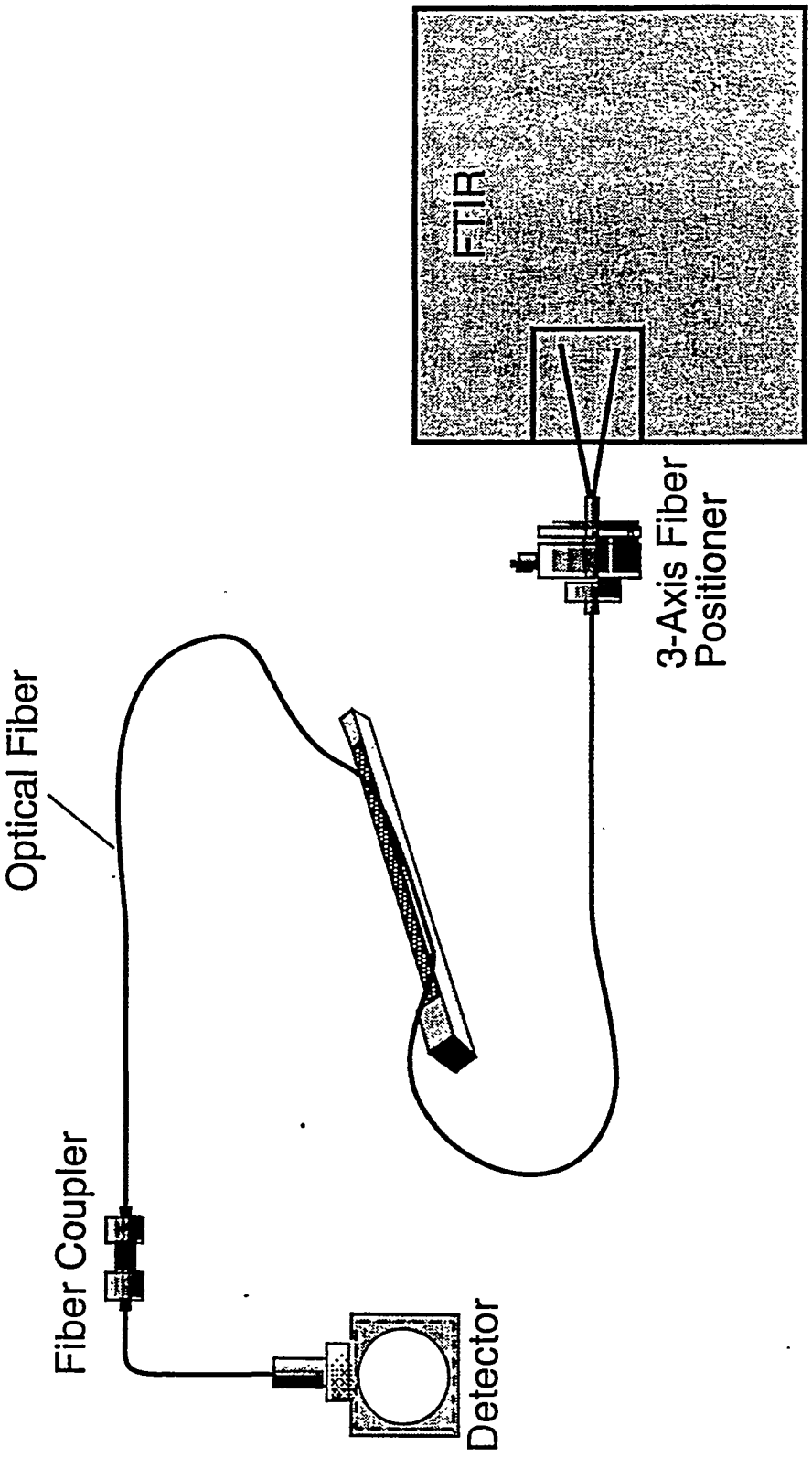

Figure 3. NIR-Fiber Optic System.

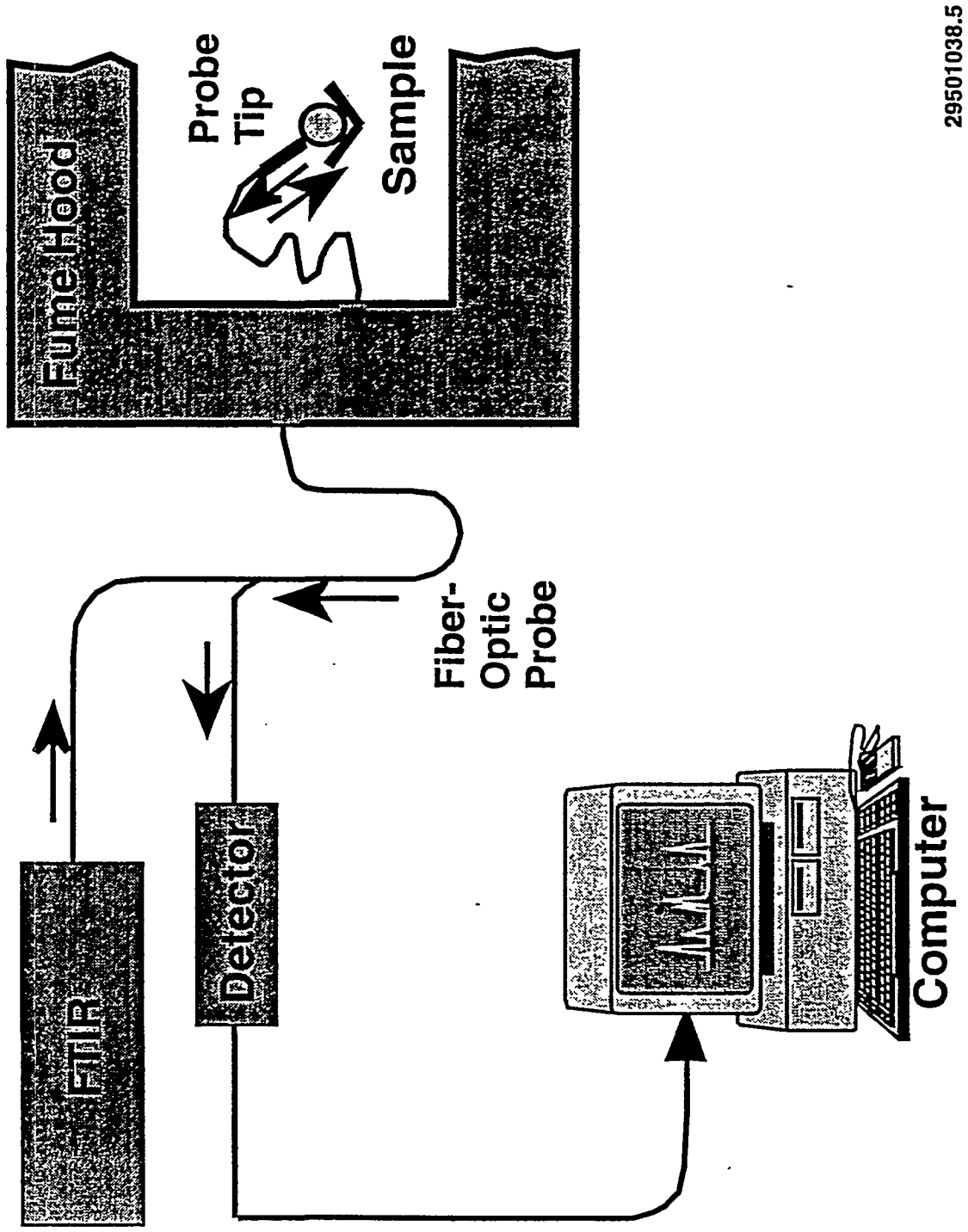

Figure 4. MIR Spectrum of Sludge on AgBr/Cl Fiber.

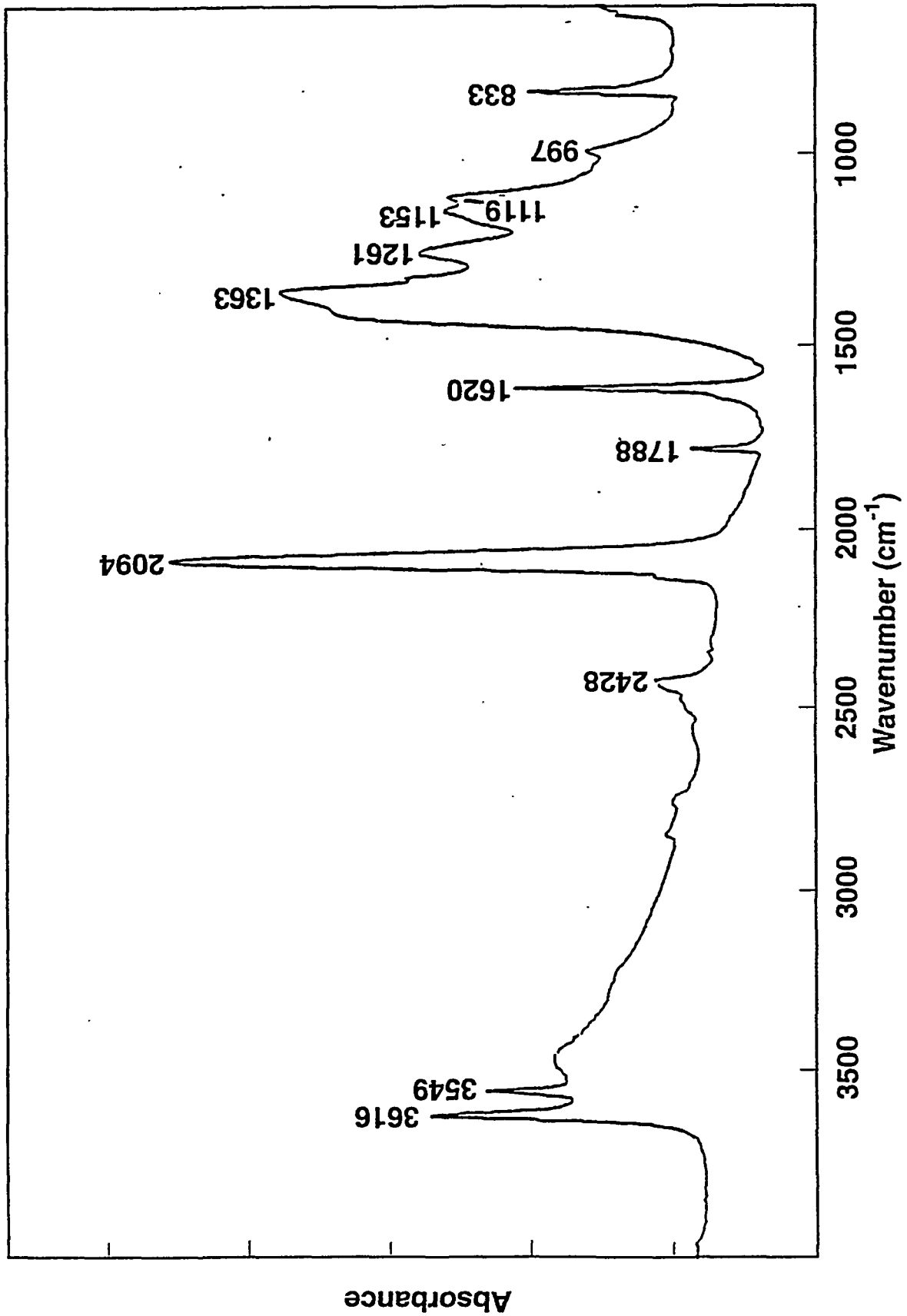

Figure 5. NIR Spectra of Sludge.

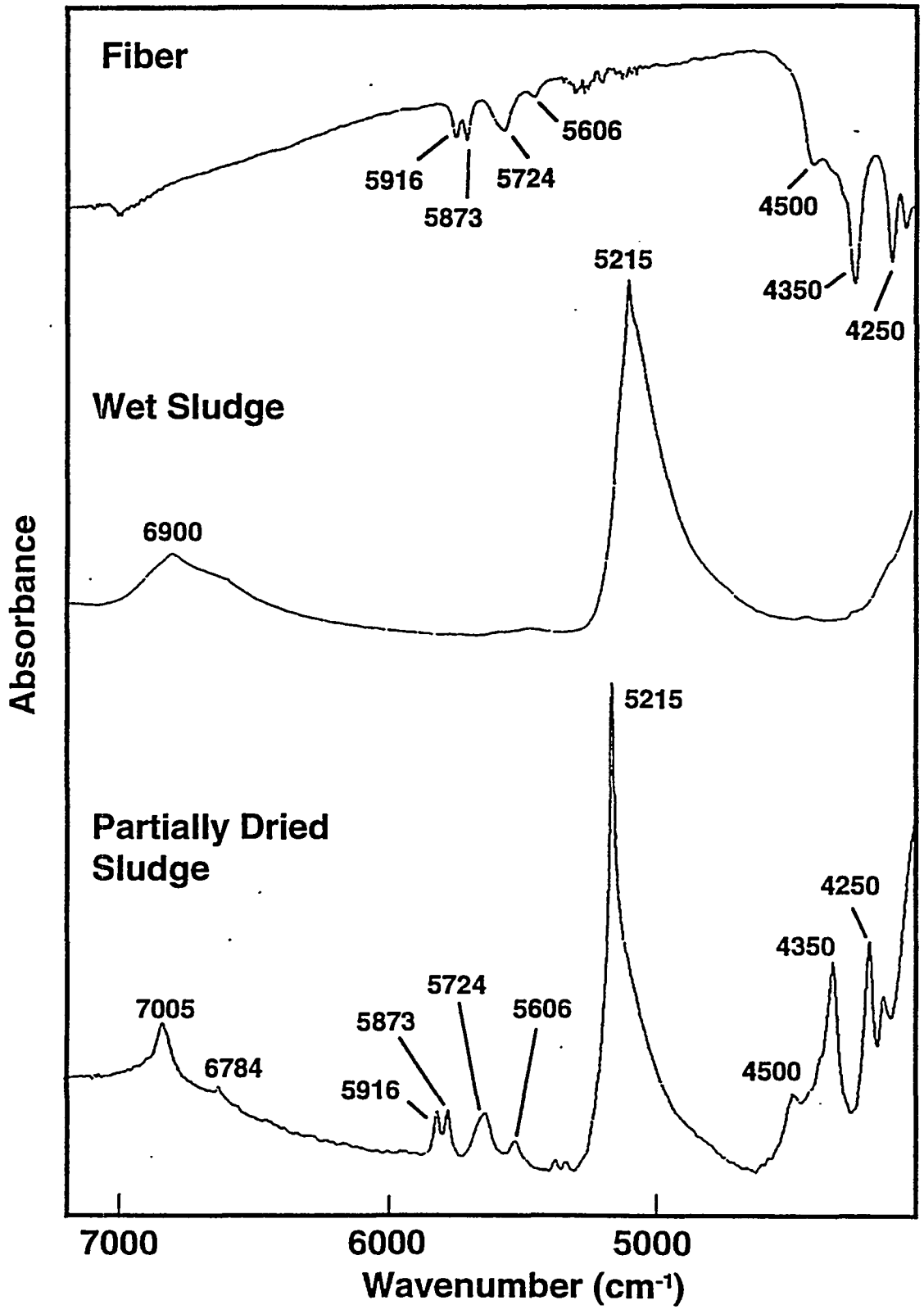

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Figure 6. NIR Spectra of Wet Sludge.

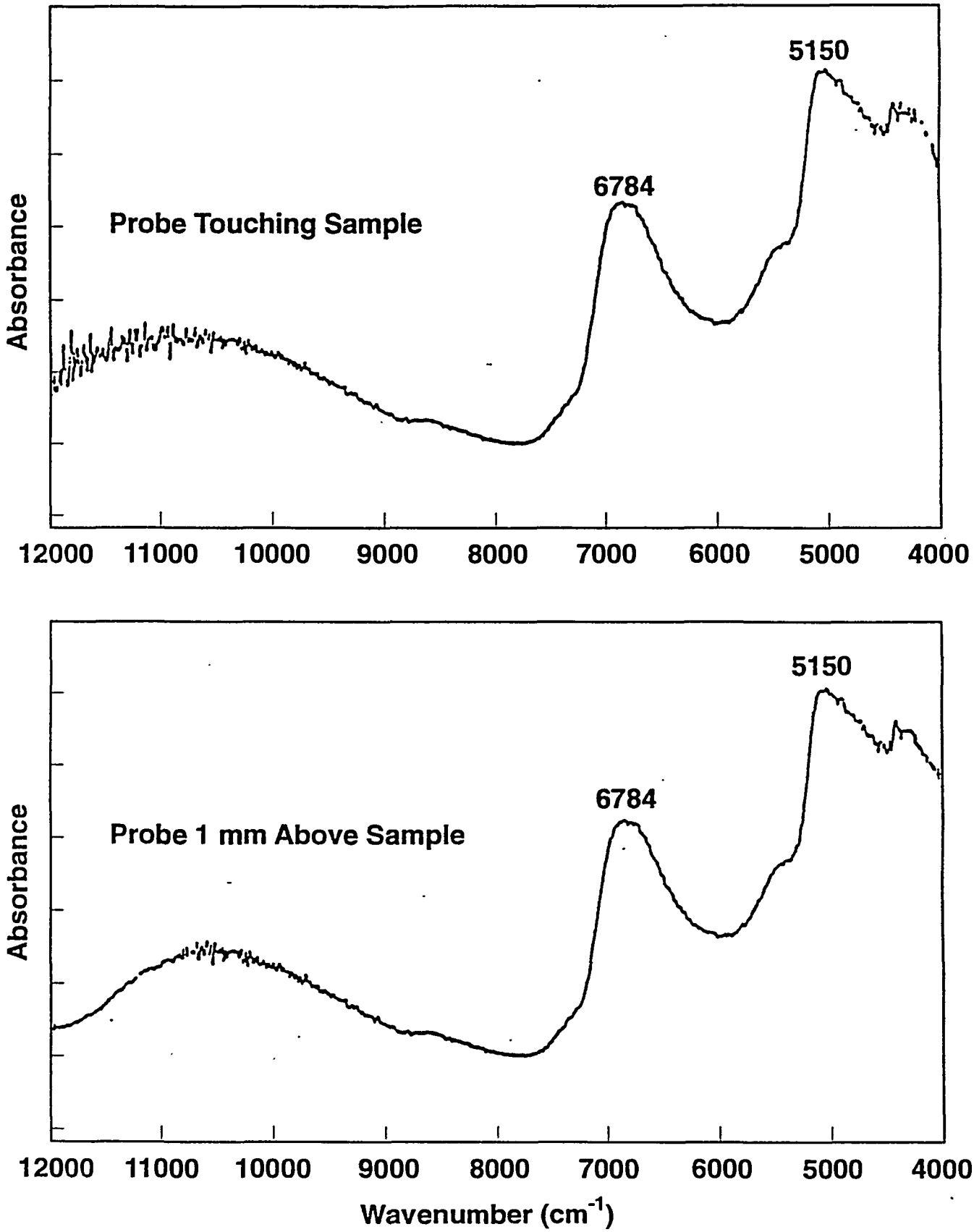
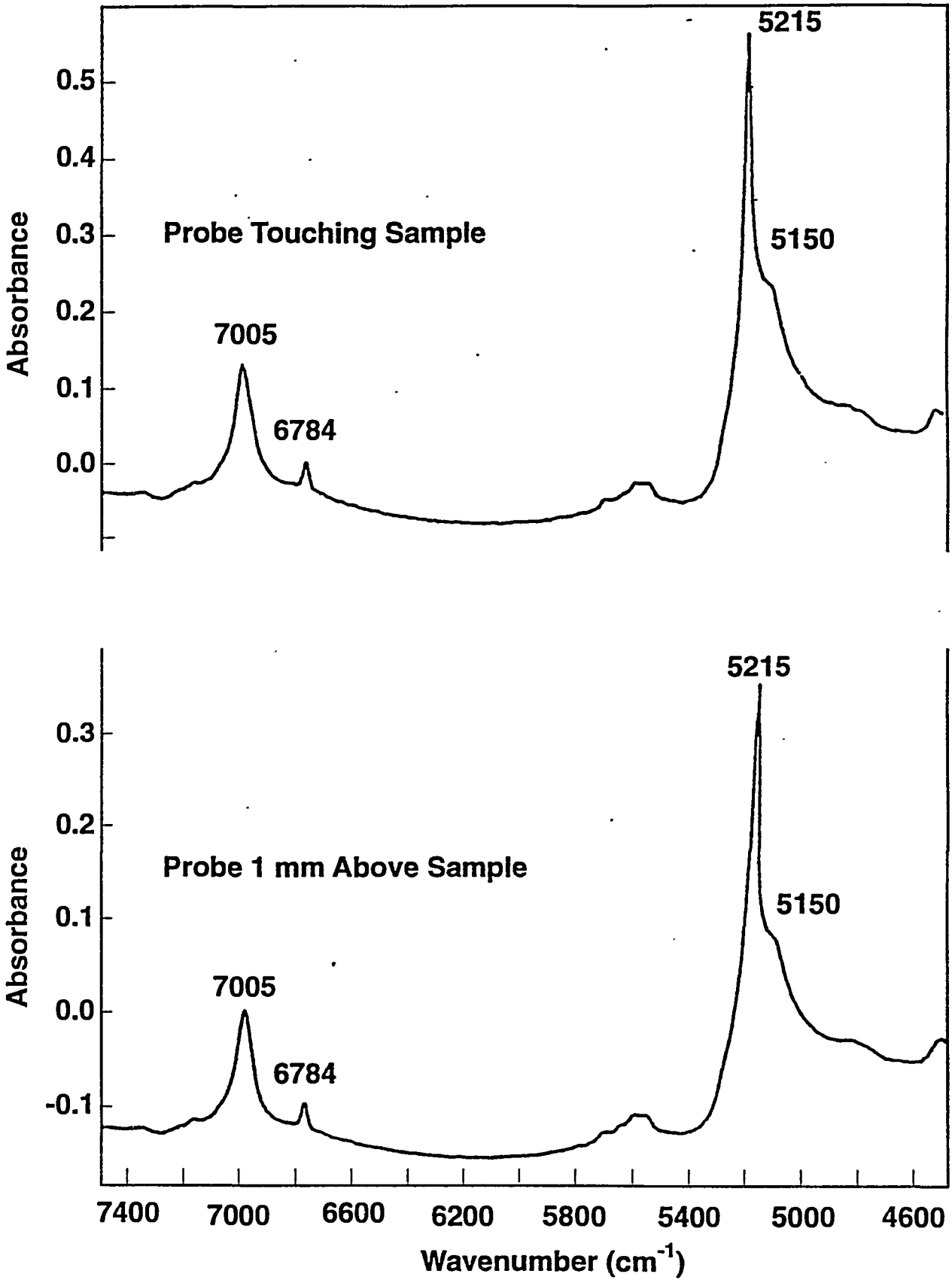


Figure 7. NIR Spectra of Freeze-Dried Sludge.



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