Analysis of Underground Storage Tank Waste Simulants by Fourier Transform Infrared Photoacoustic Spectroscopy

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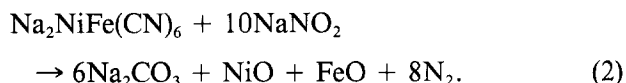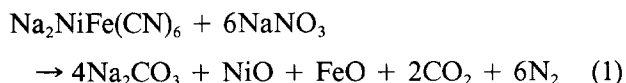
Underground storage tank waste sludge from nuclear fuel processes is difficult to analyze because of the extreme heterogeneity, chemical reactivity, and radioactivity of the waste. Conventional methods of analysis typically require extensive sample handling procedures either to thin the sample or to separate components prior to analysis. These procedures are time consuming, require radiation containment cells, and increase the risk of radiation exposure to lab personnel as a result of the extensive handling. In this paper a method utilizing Fourier transform infrared photoacoustic spectroscopy to analyze hazardous underground storage tank waste with a minimal amount of sample and sample handling is discussed. The method was developed with the use of waste tank simulants that were obtained from the Westinghouse Hanford Company. Emphasis was placed on the determination of disodium nickel ferrocyanide, sodium nitrate, and sodium nitrite because of the concern for the potential of exothermic reactions occurring between oxidizers and ferrocyanide-containing compounds. This method also allows for the analysis of other ions of interest in waste processes such as sodium sulfate. A simple sample preparation method is also discussed which uses freeze drying to remove water from the simulants while maintaining a uniform sample for analysis.

Index Headings: FT-IR/PAS; Photoacoustic spectroscopy; Environmental, waste and sludge analysis.

INTRODUCTION

Hazardous waste from nuclear fuel processing during the 1940s, as well as wastes from other types of operations, was collected and stored in underground storage tanks (USTs) located at the Westinghouse Hanford site in Richland, Washington. During the 1950s, in order to increase the amount of storage space and reduce the overall volume of waste, a scavenging process was implemented to remove radiocesium from the aqueous-nitrate portion of the waste in the USTs. In general, the scavenging processes involved the addition of sodium ferrocyanide and nickel sulfate to the liquid portion of the waste, precipitating the radiocesium out as cesium nickel ferrocyanide. However, with the huge excess of sodium that was present in the USTs, the primary constituent of the precipitate was disodium nickel ferrocyanide $[Na_2NiFe(CN)_6]$.

Ferrocyanide compounds are fairly stable by themselves. However, in the presence of oxidizers such as nitrates and nitrites, exothermic reactions can occur. Such reactions can result in uncontrollable increases in temperature and pressure in the tanks and potential release of high-level waste. Equations 1 and 2 below show the most energetic of the postulated reactions between disodium nickel ferrocyanide and sodium nitrate and nitrite.[1]

$$Na_2NiFe(CN)_6 + 6NaNO_3$$
$$\rightarrow 4Na_2CO_3 + NiO + FeO + 2CO_2 + 6N_2 \quad (1)$$

$$Na_2NiFe(CN)_6 + 10NaNO_2$$
$$\rightarrow 6Na_2CO_3 + NiO + FeO + 8N_2. \quad (2)$$

In order to safely treat and properly dispose of the waste in these tanks, the chemical composition must first be determined. Analysis by most conventional methods is difficult without extensive, costly, and time-consuming sample preparation because of the heterogeneity of the waste. Additionally, the presence of radioactivity requires that the tank samples be handled in elaborate containment cells (i.e., hot cells) and in minuscule amounts to reduce radiation exposure to workers. Several direct analytical methods [attenuated total reflectance (ATR), [2-3] Raman spectroscopy,[4] and X-ray diffraction[5]] and indirect methods [solution Fourier transform infrared (FT-IR) spectroscopy and ion chromatography[2]] have already been investigated. In this paper, a method is described for the quantitative determination of the infrared-active species in the tank wastes employing FT-IR photoacoustic spectroscopy (PAS). The method was developed with UST simulants prepared by the Westinghouse Hanford Company. PAS is used here as a direct analysis method for tank wastes because of its capability to optically interrogate small amounts of intractable materials which are fairly opaque. FT-IR/PAS has the advantage that little sample and little sample preparation are needed. Thinning or diluting the sample is not required as in other conventional spectroscopic methods. Signal generation in FT-IR/PAS results from the absorbed infrared radiation being converted into heat. The heat produces a thermal wave within the sample which travels to the surface and transfers to the surrounding gas in the PAS cell. This transfer causes a thermal expansion of the gas that results in an acoustic wave that is picked up by a microphone in the PAS cell. The photoacoustic signal is therefore largely dependent on the absorption coefficient of the sample as well as its thermal properties.[6] Consequently, all that is required to perform quantitative analysis is a sampling geometry that results in samples of constant volume and uniform composition.

Uniform samples for analysis were produced by freeze drying. Freeze drying prior to analysis removes interfering water and prevents the soluble components in the simulants from migrating. Migration of soluble components yields a nonuniform sample which makes analysis by PAS difficult because of artificial layering and variations in the thermal properties of the sample. Air- and oven-drying sample preparation methods were also investigated but showed evidence of the migration of si-

mulant components. The effect of component migration within the simulants is further examined in this paper by step-scan phase modulation.

EXPERIMENTAL

Samples for analysis were prepared by applying a small amount (approximately one milligram) of tank waste simulant to a specially designed sample disk which had a small cavity in it. This cavity allowed a small, reproducible volume of sample to be acquired. The simulant and sample disk were first placed in liquid nitrogen to quickly freeze the sample and then transferred to a freeze dryer to remove water, which would have resulted in spectral interferences and distortion due, in the latter case, to differences in the solid- vs. solution-phase spectra.

The freeze dryer used in these experiments was a programmable Fizons Model 350. The freeze dryer's sample compartment was quickly brought down to $-50°C$ and held there for 6 h. At this temperature, the crystalline water sublimes under vacuum. After the freeze-drying cycle was completed, the temperature was slowly ramped to ambient, and the sludge sample was removed and placed in a desiccator to await analysis. Samples that were freezed dried appeared very homogeneous under $40 \times$ magnification, whereas samples that were dried with air- and oven-drying protocols displayed numerous crystals on the surface under the microscope.

All data were collected on a Bio-Rad Digilab FTS-60A FT-IR spectrometer equipped with an MTEC Model 200 photoacoustic cell. Helium was used as the purge gas in the photoacoustic cell. Two hundred fifty-six scans were accumulated at 2.5 kHz at 8-cm^{-1} resolution. Sludge spectra were normalized against carbon black to account for spectral variations due to the infrared source and spectrometer.

Step-scan phase modulation studies were also performed on the FTS-60A. Data were collected at a mirror velocity of 25 Hz, phase-modulation frequency of 400 Hz, and phase modulation amplitude of two laser fringes.

Sodium nitrate and sodium nitrite were obtained from commercial sources and used without further purification. Stock solutions of these compounds were prepared with deionized water. Standard disodium nickel ferrocyanide and surrogate sludge samples were prepared and supplied by the Westinghouse Hanford Company. Nitrate and nitrite calibration standards were prepared by aliquoting the appropriate amount of standard from the stock solutions into a known amount of "washed" sludge simulant. "Washed" simulant was prepared by rinsing the soluble species (e.g., nitrate and nitrite ions) from the simulant matrix with deionized water. The samples were then thoroughly mixed by repeatedly cutting and folding with a spatula. The disodium nickel ferrocyanide, which is insoluble, was washed with deionized water prior to use. Disodium nickel ferrocyanide calibration standards were prepared by adding a known amount of the standard to a known amount of unwashed simulant. These samples were then also mixed by repeatedly cutting and folding with a spatula. Estimates of the measured limits of detection (LODs) were determined by taking three times the standard deviation of the intercept of the correlation plots divided by the slope.
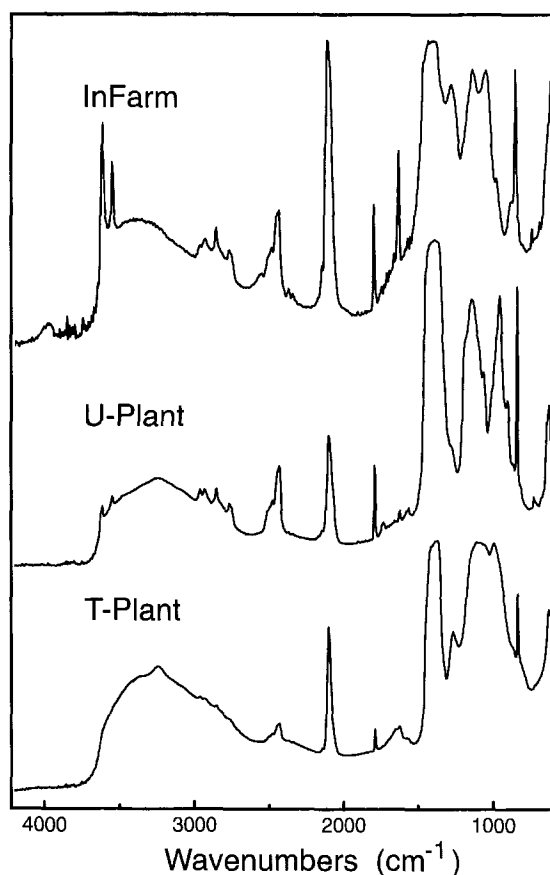

FIG. 1. Photoacoustic spectra of different underground storage tank waste simulants. The samples were prepared following the protocol described in the text. The names InFarm, U-Plant, and T-Plant indicate the different type of formulation process used to produce the simulant (see Ref. 7).

RESULTS AND DISCUSSION

Typical photoacoustic spectra of several tank waste simulants that were obtained following the outlined sample preparation protocol described above are shown in Fig. 1. Sharp absorption bands are observed that can be used for both qualitative and quantitative analysis. The simulated tank waste designations (i.e., InFarm, U-Plant, and T-Plant) distinguish between the different types of formulations that were used in the radiocesium scavenging processes.[7] The three formulations differ by the amount of certain components as exhibited by the varying intensities of several absorption bands in the photoacoustic spectra.

Compositional analysis of tank waste surrogates was performed by comparing the absorption bands of a simulant with those of pure compounds. This approach is illustrated in Fig. 2, which, for clarity, shows an expanded region of the photoacoustic spectra for a typical surrogate sample and several pure components. Nitrate ions present in the simulant are identified by absorption bands observed at 2433, 1789, 1400, and 837 cm^{-1}. Absorption bands at 2098, 1620, and 597 cm^{-1} are due to the nickel ferrocyanide ion. The absorption band at 1620 cm^{-1} is a result of the hydration of the disodium nickel ferrocyanide. This band provides a direct method for quantitation when the 2150-cm^{-1} absorption band is saturated. Sim-
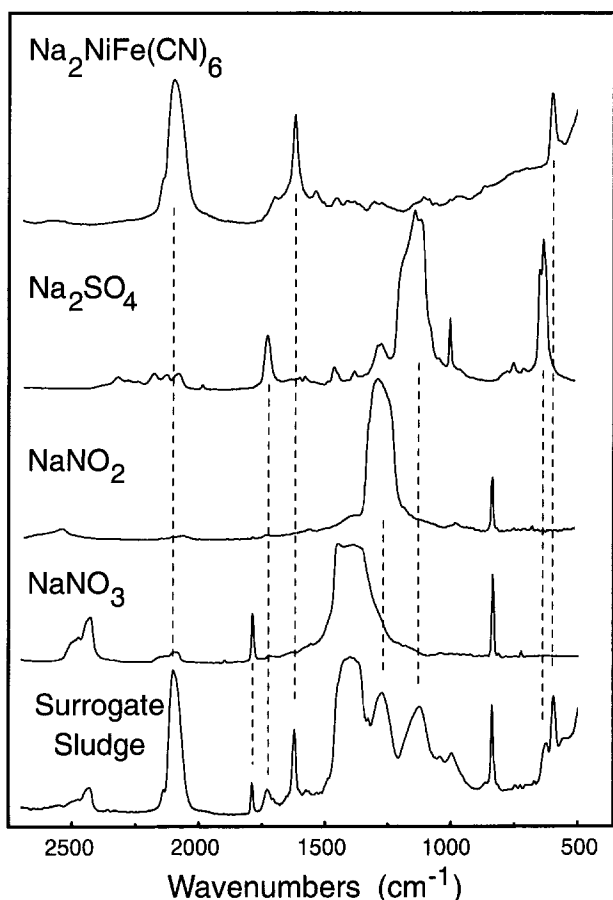
FIG. 2. Photoacoustic spectra of a tank waste surrogate and of several pure components which are present in the surrogate.
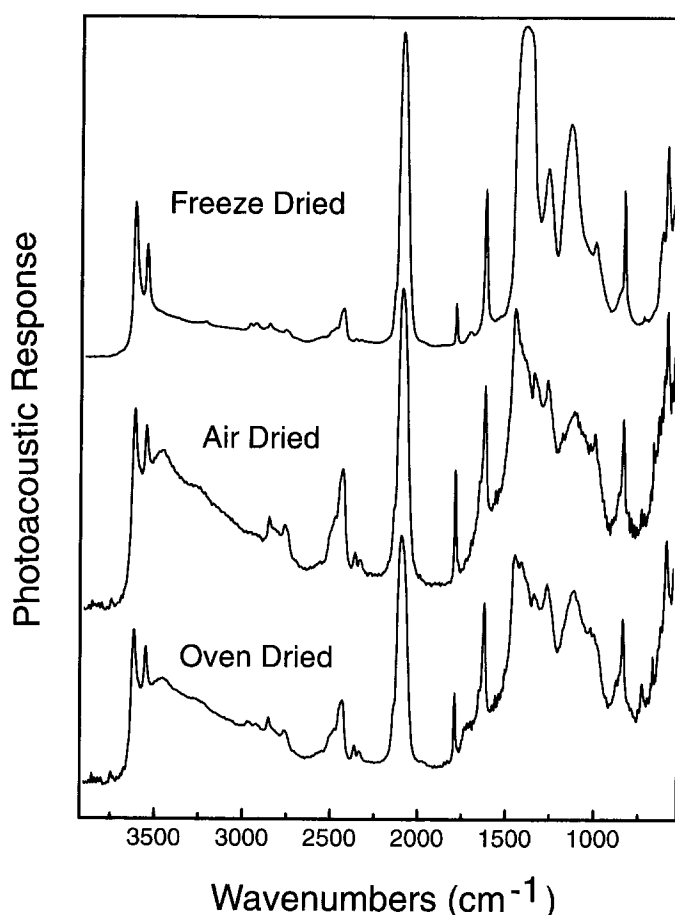

FIG. 3. Photoacoustic spectra of the same surrogate sample after the use of different drying protocols.

ilarly, nitrite ions can be identified by the strong absorption band centered at 1300 cm^{-1} and sulfate ions by the strong absorption bands centered at 1145 and 624 cm^{-1}.

Prior to quantitation, water present in the tank waste simulants had to be removed. As stated above, this was accomplished by taking a small portion of simulant and applying it to a specially designed sample stub which was then placed in a freeze dryer to sublime the water off. Tank waste simulants were also air and oven dried prior to analysis. However, only freeze drying the tank waste simulants yielded a reproducible, uniform sample for quantitative analysis. Under air- and oven-drying protocols, the water-soluble species (e.g., sodium nitrate and sodium nitrite) in the tank waste simulants tended to migrate during drying, making reproducibility and quantitative analysis difficult. The problem of migration was circumvented by quickly freezing the sample disk and simulant in liquid nitrogen to "lock" the soluble components in the solid matrix. The frozen sample was then placed in the freeze dryer to remove water prior to analysis.

The photoacoustic spectra of a tank waste simulant after different drying protocols are shown in Fig. 3. The photoacoustic spectra of simulants that were either air or oven dried indicate that, during the drying process, water-soluble components within the surrogate migrate. This behavior is illustrated by comparing the relative ratios of the nitrate-ion (2433 and 1789 cm^{-1}) and nickel ferro-

cyanide-ion (2098 and 1620 cm^{-1}) absorption bands. For the air- and the oven-dried simulants, the amount of nitrate appears to increase, indicating that the nitrate ions are migrating toward the sample surface during drying. Further evidence of nitrate migration can also be obtained by visual examination with a microscope of the simulant surface after application of the different drying protocols (Fig. 4). Crystals or ridges appear on the surface for simulants that were either air and oven dried, whereas the freeze-dried simulant shows a uniformly porous surface. The appearance of crystals indicates that nonuniform samples are produced by air- and oven-drying protocols.

The lack of uniformity can be further investigated by step-scan phase modulation studies. The theory of step-scan phase modulation will not be covered because of its complexity, but in general this method allows one to determine whether the generation of the photoacoustic signal is from the surface or from the bulk of the sample, as a result of a phase difference.[8] Thermal diffusion through the sample causes the phase difference (i.e., time lag) between signal generation from the surface and the bulk of the sample. Signals that are generated from the surface of the sample will reach the microphone in the photoacoustic cell quicker than those signals that are generated deeper in the sample. As stated previously, the photoacoustic signal is dependent on the thermal properties of the sample. Thermal properties determine the effective diffusion length or sampling depth within the sample. In
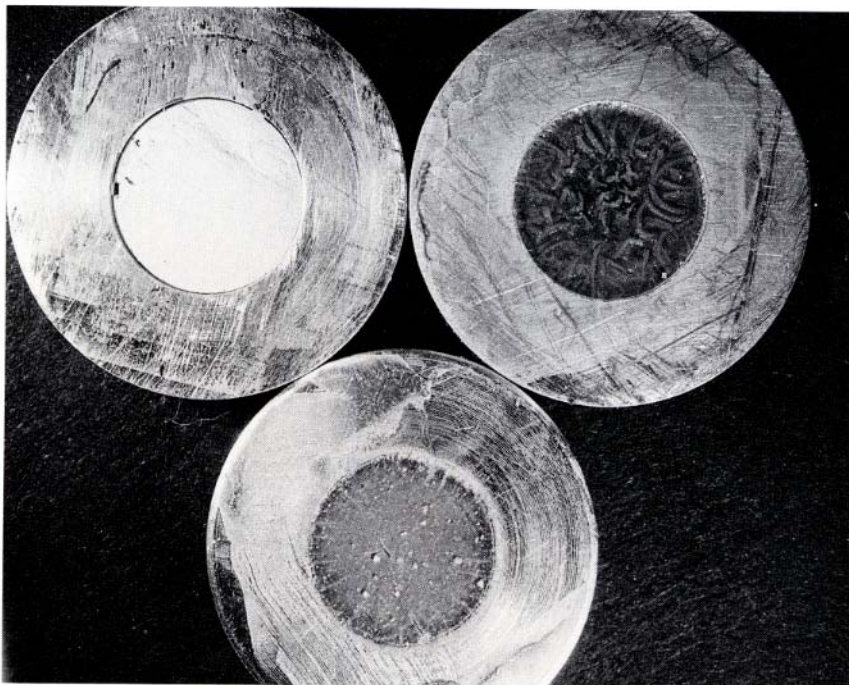
FIG. 4. Photograph of a sludge simulant in a sample disk after the use of different drying protocols. The diameter of the sample disk is 1 cm. Clockwise from top left: freeze-dried, oven-dried, and air-dried samples. The air- and oven-dried samples show nonuniform surfaces with crystals and ridges, whereas the freeze-dried sample shows an amorphous surface.

nonphase modulation experiments, each wavenumber, σ, modulates at its own frequency ($f = v\sigma$, where v is the interferometer's optical path difference mirror velocity) and thus probes different diffusion lengths or sample depths, making phase difference interpretation complicated. This approach differs from step-scan phase-modulation experiments, where a single modulation frequency is applied over the entire spectral range to generate the photoacoustic signal. Therefore, all the wavenumbers probe the same effective diffusion length. Applying a single modulation frequency is accomplished by "dithering" the mirror of the spectrometer at a set rate or modulation frequency around each point. The resultant signal is then fed into a lock-in amplifier which amplifies the signal at each point in the interferogram and facilitates extraction of phase information.

Phase modulation data can be presented by plotting the absorption band intensity of the analyte of interest as a function of phase angle. Figure 5a shows the peak amplitude of the 1789-cm^{-1} nitrate-ion absorption band as a function of phase angle for the simulant dried by the three different methods. The relative intensities have been scaled to simplify interpretation. The maximum intensity for the air- and oven-dried samples occurs at a phase angle of approximately 135° and that of the freeze-dried simulant has its maximum intensity at a phase angle of approximately 153°. The amplitudes of the air- and oven-dried samples appear to be "leading" that of the homogeneous freeze-dried sample, indicating that the majority of the nitrate-ion signal is being generated at the surface of these samples. The amplitude of the freeze-dried sample comes at a later phase angle, implying that there is an artificial layering of components within the air- and oven-dried samples. For comparison, Fig. 5b shows the absorption band intensity of the 2098-cm^{-1} nickel fer-
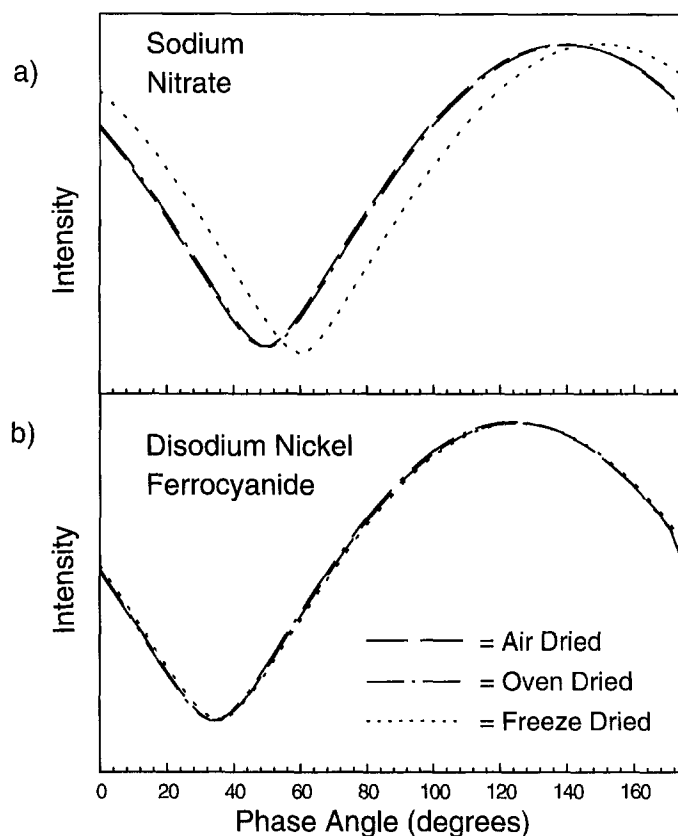

FIG. 5. Plot of maximum absorption intensity as a function of phase angle for the 1789-cm^{-1} absorption band of sodium nitrate (a) and the 2098-cm^{-1} absorption band of disodium nickel ferrocyanide (b). The phase angle is also a function of the absorption coefficient of a particular band, which accounts for the difference in phase maxima between sodium nitrate (135°) and disodium nickel ferrocyanide (123°). In general, the absorption band with the larger absorption coefficient will maximize at an earlier phase angle.
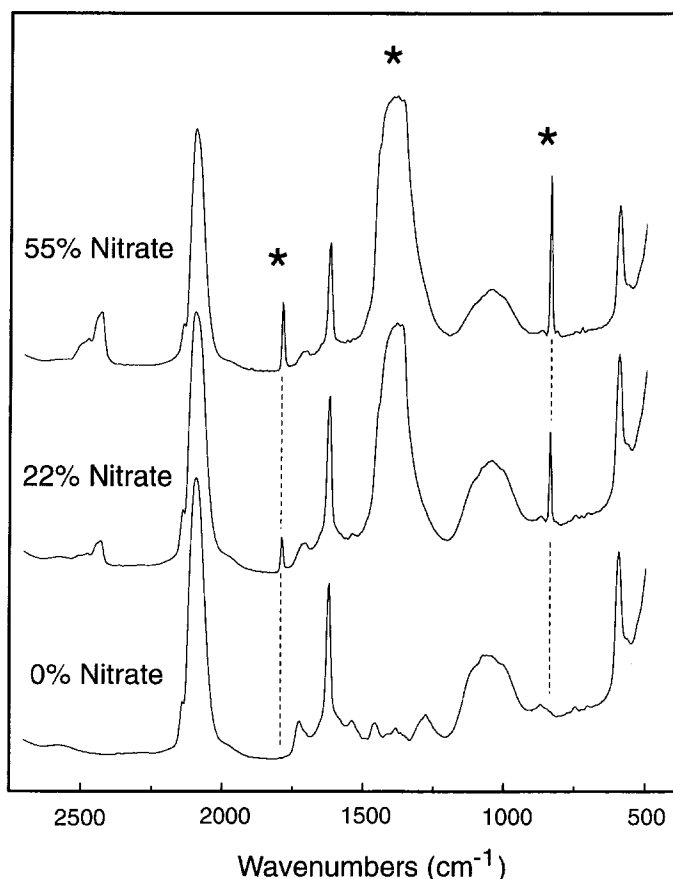
FIG. 6. Photoacoustic spectra of a "washed" simulant containing known amounts of sodium nitrate. The absorption bands due to the presence of sodium nitrate are marked with asterisks. The absorption bands at 2098, 1620, and 597 cm^{-1} are due to disodium nickel ferrocyanide.

FIG. 7. (a) Calibration plot obtained for sodium nitrate. This plot was obtained by plotting the peak height of the 1789-cm^{-1} band (see Fig. 6) as a function of nitrate. The nitrate absorption band was normalized by ratioing against the disodium nickel ferrocyanide absorption band (1620 cm^{-1}). Regression coefficient (r^2) = 0.996 (LOD = 2.8%). (b) Correlation plot obtained for standard additions of disodium nickel ferrocyanide. Regression coefficient (r^2) = 0.985 (LOD = 3.6%).

rocyanide ion as a function of phase angle for the simulant dried three different ways. Again, the relative intensities have been scaled for clarity. Disodium nickel ferrocyanide is an insoluble sludge component; therefore it is not expected to migrate during drying. As we can see, there is virtually no difference in phase angle (maximum intensity at approximately 123°) between the three samples, indicating that the insoluble nickel ferrocyanide ion remains fairly uniformly dispersed throughout the sample and does not migrate during any of the drying processes employed. Similar interpretations can be obtained from monitoring other absorption bands.

To demonstrate that the photoacoustic response from the simulants is linear and can be applied to quantitative analysis, we analyzed several of the simulants by standard addition procedures. Figure 6 shows example photoacoustic spectra of a "washed" simulant that contains various known amounts of nitrate ion. The sharp absorption bands at 1789 and 837 cm^{-1} as well as the broad features at 1400 and 2433 cm^{-1} are due to nitrate ions. As the concentration of nitrate increases, so does the intensity of the various nitrate absorption bands. A plot of the normalized nitrate absorption band at 1789 cm^{-1} as a function of nitrate concentration (weight %) is shown in Fig. 7a. Normalization was accomplished by ratioing the nitrate-ion band intensity against the nickel ferrocyanide band at 1620 cm^{-1}. The photoacoustic response is
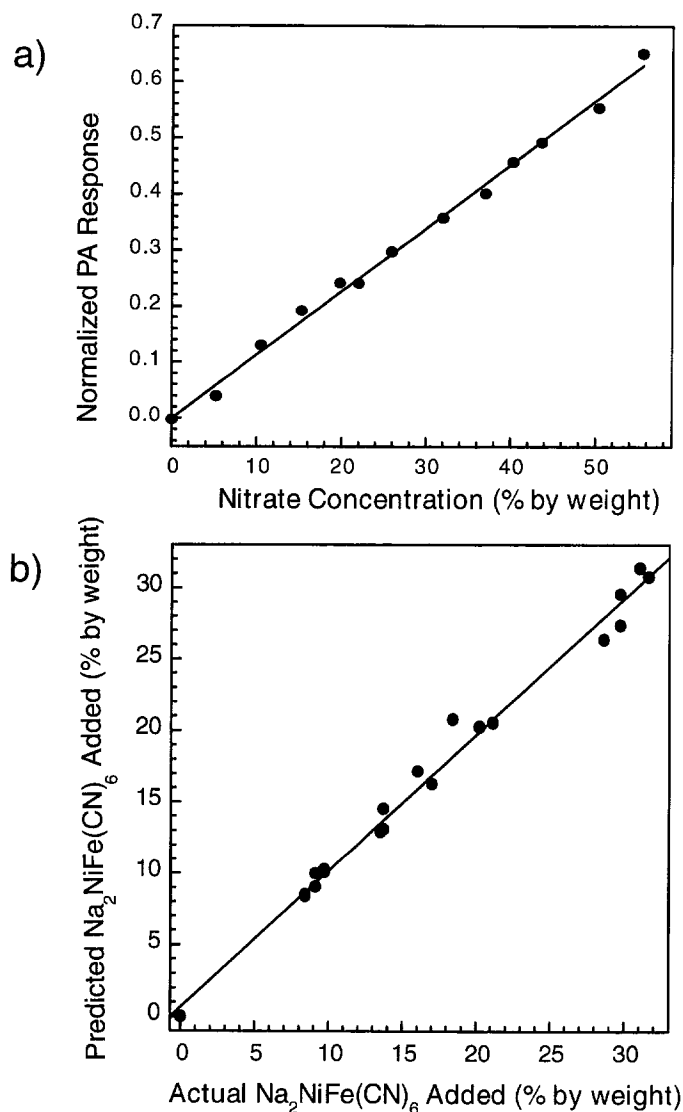
linear with a regression coefficient (r^2) of 0.996 for a concentration range of 0 to 54% nitrate by weight. Similar correlations were also obtained for other species such as sodium nitrite (r^2 = 0.994) and sodium sulfate (r^2 = 0.991) by adding known amounts of standard to "washed" simulants.

The correlation plot of known amounts of standard disodium nickel ferrocyanide added to an unwashed sludge simulant containing the nickel ferrocyanide ion is shown in Fig. 7b. The correlation that is obtained is again fairly linear, with a regression coefficient of 0.985. Although the correlation is not as good as that obtained for nitrate, nitrite, and sulfate, it still is adequate enough to perform quantitative analysis. The lower correlation coefficient is due to the scatter in the data points. The scatter arises because of the difficulties that were encountered in sample preparation.

CONCLUSION

Fourier transform infrared photoacoustic spectroscopy has been shown to be viable for the analysis of underground storage tank waste surrogates for nitrate and nickel ferrocyanide within the concentration range of interest. Extending the FT-IR/PAS method to actual UST wastes provides benefits, such as reducing worker exposure to the chemical activity and radioactivity of the tank wastes by requiring minimal amounts of sample for analysis and practically no sample handling. The method is also rapid and can be used as a mapping technique for sample cores that are taken from the USTs, which will assist remediation activities by quickly identifying the various layers within the USTs.

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