Use of Organic Functional Group Concentrations as a Means of Screening for Energetics

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June 1996

Prepared for Westinghouse Hanford Company
with the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest National Laboratory
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UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

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Available to DOE and DOE contractors from the
Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831;
prices available from (615) 576-8401.

Available to the public from the National Technical Information Service,
U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161

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Summary

One of the safety concerns associated with the waste tanks on the Hanford site is the presence of organics in a highly oxidizing environment that could potentially act as a fuel source to maintain a propagating reaction. To determine this risk, it is necessary to determine the amount of high enthalpy organics present in the tanks. Currently, the primary ways of obtaining this information are to either rely on tank-fill histories, which are often unreliable and do not account for waste-aging processes, or obtain samples from the tank and speciate the organics present through a series of analytical procedures. While organic speciation has been successful in providing very valuable information about organics present in the tanks and the waste aging processes that are occurring in general, it can be costly and time consuming for analyzing a large number of waste tanks.

Differential scanning calorimetry has previously been used to obtain heat of reaction measurements of Hanford tank waste samples. However, differential scanning calorimetry is shown here to inadequately measure calculated heats of reaction of simulant tank mixtures. For some organic compounds, such as sodium formate, the measured heat of reactions with sodium nitrate in simulant waste samples were approximately 50% of the calculated value. For other organic compounds, such as sodium laurate, the measured values were less than 5% of calculated values.

To minimize the cost of determining the safety of organic-containing waste tanks, we are developing a screening method to rapidly determine the relative enthalpy of organics, based on organic functional group determination. Fourier transform IR and Raman spectroscopy are used to detect C-H and COO⁻ content of simulant tank waste samples. The success of quantitation of these functional groups in a mixture will be presented. Once fully developed, this would provide an alternative or complement to DSC measurements for determining reaction enthalpies of tank waste samples.

Promising results from organic-functional-group determination by Fourier transform infrared and Raman spectroscopy of liquid and solid simulant waste samples were obtained in these preliminary development experiments. However, further development work is needed before implementing these techniques as a screening tool for rapid determination of organic functional groups for energy estimation.

Fourier transform infrared spectroscopy produced promising results for quantitating COO⁻ content in simulant waste-sample solutions. Calibration curves from integration over the COO⁻ stretching frequencies for six different organic components were very similar. For C-H content determination, linear calibration curves were also obtained by integrating over the C-H stretching frequencies for each of seven organic analytes tested. However, the extinction coefficients (slopes) were not identical and would add error to mixture analysis. The main discrepancy in C-H content determination was with formate analysis. Error from the presence of this compound would bias the energetic estimate high since it gives a higher than normal C-H response, even though formate is a low-enthalpy organic.

Fourier transform Raman spectroscopy was shown to be successful at semi-quantitating a variety of organics, such as ethylenediaminetetraacetic acid, N-(2-hydroxyethyl)ethylene-diaminetriacetic acid, citrate, acetate, and oxalate, in solutions that varied between 0.5% and 4% by mass organic in basic solution. Surface-enhanced Raman spectroscopy was also evaluated as a method for increasing sensitivity for solution analysis.

Fourier transform infrared spectroscopy of solid simulants gave mixed results for the C-H and COO⁻ content determination. While qualitative determination of these functional groups could be made in these organic containing simulants, high organic concentrations (e.g., > 4 moles C-H bonds per kg sample) and low moisture content (<10%) led to difficulties in quantitation. However, as a screening tool for determining high versus low organic functional group content, Fourier transform infrared spectroscopy could still be a viable technique.

Good correlation between Fourier transform Raman spectroscopy of the C-H functional group and organic content was obtained independent of the type of organic (formic acid or N-(2-hydroxyethyl)ethylenediaminetriacetic acid) and water content of the solid simulants. To obtain this correlation, normalization of the C-H peak area to an internal standard such as the nitrate peak had to be done. In contrast to the Fourier transform infrared spectroscopy results for the simulant solids samples, Fourier transform Raman spectroscopy results improved with decreasing water content of the sample due to the noncontact nature of the sampling.

Overall, the preliminary results presented here, suggest that indeed Fourier transform infrared and Raman spectroscopy would be useful screening tools for determination of C-H and COO⁻ organic content in tank waste samples analyzed in a hot cell environment. These techniques however, are not truly quantitative for this application and would be primarily used for identifying tanks of potential safety concern that would require further, more detailed confirmatory analysis by organic speciation techniques.

Glossary

ALARA	as low as reasonably achievable
ARC	accelerating rate calorimetry
ATR	attenuated total reflectance
C-C	carbon-carbon bond
C-H	carbon-hydrogen bond
C-O	carbon-oxygen bond
COO ⁻	carboxylate functional group
D2EHP	di-2-ethylhexyl phosphate
DBP	dibutyl phosphate
DSC	differential scanning calorimetry
DTA	differential thermal analyzer
ED3A	ethylenediaminetriacetic acid
EDDA	ethylenediaminediacetic acid
EDTA	ethylenediaminetetraacetic acid
FT	Fourier transform
HEDTA	N-(2-hydroxyethyl)ethylenediaminetriacetic acid
IDA	iminodiacetic acid
InGAs	indium gallium arsenide (detector)
IR	infrared
MCT	mercury cadmium telluride
NMR	nuclear magnetic resonance
NPH	normal paraffin hydrocarbon
NTA	nitrilotriacetic acid
PUREX	Plutonium Uranium Extraction
SERS	surface-enhanced Raman spectroscopy
TBP	tributyl phosphate
TGA	thermogravimetric analysis
TOC	total organic carbon
UV	ultraviolet
ΔH_f	enthalpy of formation

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1.0 Introduction

In the past few years, the organic species present in core and auger samples from Hanford waste tanks have been quantitatively determined quite successfully at Pacific Northwest National Laboratory^(a) (Campbell et al. 1994a, 1994b, 1994c). Complete organic speciation of select waste tanks has provided very important information about the identity of organics added to the tanks and the degradation products formed by thermal and radiolytic aging. This information has been used to determine the relative safety of specific waste tanks characterized and to predict the safety of other tanks expected to have similar organic content. While organic speciation may be necessary for characterizing some waste tanks, it is costly, time-consuming, and perhaps impractical for all of the 177 Hanford waste tanks.

The major concern with organics in the waste tanks is whether they represent a fuel source that could maintain a propagating reaction if triggered by an ignition source (Webb et al. 1995). In addition to the organics, some of Hanford's underground storage tanks for high-level radioactive wastes also contain significant amounts of nitrate and nitrite mixtures, which are strong oxidants. The chemical reactivity hazards of the organic, nitrate, and nitrite mixtures depend on the amount of energy that would be produced by a reaction between the organic and the nitrate or nitrite and the rate at which that energy is produced. In turn, the amount of energy produced and the rate at which it is produced depend on the nature or species of the organic, both the absolute and relative amounts of organic, nitrate, and nitrite in the stored waste, and the nature of the other constituents in the waste. These other constituents could reduce reactions as heat absorbers, diluents, or increase energetics as catalysts.

A screening strategy that would allow a quick assessment of a potential chemical reactivity hazard due to high-potential energetics within a tank could be a beneficial tool for decision makers. Traditionally, differential scanning calorimetry (DSC) has been used as an energetics screening method, but there is little evidence that this technique can reproducibly predict the energetics content of Hanford tank waste samples. Determining the presence of high-enthalpy organics was the primary focus of the screening tool for tank analysis conducted by PNNL. A theoretical relationship was found to exist between certain organic functional groups, such as C-H and COO⁻, and compound enthalpy. This information is the basis of a proposed rapid screening tool for determining specific organic functional groups that would indicate enthalpy, based on Fourier transform (FT) Raman and FT infrared (IR) spectroscopy.

Spectroscopic techniques such as IR and Raman are proven analytical methods for both qualitative and quantitative analysis of organic functional groups and have less safety and sensitivity problems than proton nuclear magnetic resonance (NMR) spectroscopy. Infrared spectroscopy has been shown to be very effective in identifying and quantitating nitroalkane materials in actual organic tank waste (Pool et al. 1994) and cyanide species in tanks containing ferrocyanide waste (Bryan et al. 1995).

This report describes the premise for developing a screening method for estimating reaction enthalpy of tank waste samples with FT-IR and FT-Raman spectroscopies. First, the theoretical basis for relating specific organic functional groups to sample reaction enthalpy will be described. To determine whether there was a precedence for quantitative determination of C-H or COO⁻ in

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heterogeneous solids, a brief literature search was conducted. Simultaneous to development of FT-IR and FT-Raman for organic functional group determination, studies with conventional energetics determinations (e.g., differential scanning calorimetry (DSC)) were employed as a way to tie the spectroscopic results to more traditional methods. These DSC studies were conducted on high nitrate and nitrite solutions spiked with organics of interest to determine whether there was an experimental link between organic functional group content and measured reaction enthalpy. Finally, results from preliminary development of FT-IR and FT-Raman for C-H and COO⁻ determination in simulant waste tank supernate and solid samples will be presented.

While the ultimate goal of this spectroscopic screening tool may be to adapt it to in-tank deployment for direct tank analysis, this project focused only on determining the feasibility of FT-IR and FT-Raman spectroscopy for determining organic functional groups in typical tank samples in a hot cell environment. Only brief discussion of the potential difficulties in adapting this to in-tank analysis will be provided in the conclusion.

2.0 Theoretical Approach

The current criteria for establishing that a waste is safe with respect to condensed-phase rapidly propagating reactions depend on inferring the nitrate reaction energies of the organics in the waste. This is currently done by assuming that the total organic carbon (TOC) content of a waste is sodium acetate, which has a reaction energy of -27 kJ/g-carbon (Webb et al. 1995). Table 2.1 shows the major organic compounds that were added to the tanks, as well as the many products of aging that have been identified in actual tank wastes (Webb et al. 1995; Campbell et al. 1994 b, c) or in waste simulants that have been subjected to accelerated aging via gamma radiolysis (Meisel et al. 1993; Camaioni et al. 1995) or thermolysis (Ashby et al. 1994; Delegard 1987). Table 2.1 also lists nitrate reaction energies (Burger 1995) and information relevant to the subsequent discussion. Clearly, there is great uncertainty in assuming the wastes are equivalent to sodium acetate in energy content. The actual compounds have widely varying reaction energies, ranging from -6.9 kJ/g carbon (-0.98 kJ/g) for sodium oxalate, a degradation product, to -42 kJ/g carbon (-4.3 kJ/g) for dodecane, a normal paraffinic hydrocarbon representative of the solvents used in the Plutonium Uranium Extraction (PUREX) process.

The theoretical or maximum energy release of an organic compound reacting with nitrate is calculated from the enthalpy of formation (ΔH_f) for the reactants and products, e.g.,

$$\Delta H_{\text{rxn}} = 6\Delta H_f(\text{Na}_2\text{CO}_3) + 4\Delta H_f(\text{CO}_2) + 6\Delta H_f(\text{H}_2\text{O}) + 5\Delta H_f(\text{N}_2) - 8\Delta H_f(\text{NaNO}_3) - \Delta H_f(\text{Na}_4\text{EDTA}) \quad (2.2)$$

where EDTA is ethylenediaminetetraacetic acid.

From Equation 2.2, it is clear that the energy released is governed by the stoichiometry of the reaction and the ΔH_f of the organic compound (or compounds in a mixture). Benson (1976) has shown that additivity principles can be used to estimate the ΔH_f of organic molecules. According to additivity rules, the various groups or chemical bonds in a molecule contribute to its ΔH_f additively (Benson 1976). Bond and group contributions are well established such that to estimate a compound's ΔH_f , the contributions made by the chemical bonds (bond additivity) or chemical groups (group additivities) in the molecule are summed (Benson 1976; Benson et al. 1969; Eigenmann et al. 1973). Additivity schemes are most often used to estimate the ΔH_f of compounds whose structures are known. However, the existence of bond/group additivities indicates that the energy content of a complex mixture of organics can be determined analytically without needing to speciate the mixture. The major groups or bonds present in the mixture need to be quantitated.

In fact, not all the bonds or groups need to be determined. For the compounds in Table 2.1, reasonable correlations of reaction energies can be obtained from information such as C-H, carboxyl, and C-C contents. To illustrate, we calculated the reaction energies for tank waste organic compounds mixed with amounts of nitrate that yield stoichiometric, 4.5% TOC, and 1% TOC mixtures. Figure 2.1(a) plots these energies vs. the C-H bond content of the mixtures. Linear regression analysis of the data yields an r^2 of 0.932 and a standard error in the predicted reaction energy of -330 J/g. Plotting the reaction energies vs. carboxyl group content does not lead to a linear correlation (see Figure 2.1b). However, linear trends for the different TOC levels are observed. Multiple linear regression

Table 2.1. Theoretical Reaction Enthalpies for Organic Compounds and Probable Aging Products in Hanford Underground Tank Wastes

Organic Compound		TOC of Stoichiometric Mix (wt %)	$-\Delta H_{rxn}^{(a)}$ Stoichiometric Mix		$-\Delta H_{rxn}$ 4.5 Mass % ^(c) TOC
Name	Chemical Formula		<u>kJ/g Carbon</u>	<u>J/g of Mix</u>	<u>J/g of Mix</u>
Sodium glycolate	$NaC_2H_3O_3$	12.0	21	2500	930
Trisodium citrate	$Na_3C_6H_5O_7$	12.8	20	2600	900
Na_3HEDTA	$Na_3C_{10}H_{15}N_2O_7$	11.0	31	3400	1400
Na_4EDTA	$Na_4C_{10}H_{12}N_2O_8$	11.3	28	3150	1250
$Na_3ED3A^{(b)}$	$Na_3C_8H_{11}N_2O_6$	10.9	30	3200	1300
$Na_2EDDA^{(b)}$	$Na_2C_6H_{10}N_2O_4$	10.3	33	3400	1470
Na_3NTA	$Na_3C_6H_6NO_6$	11.7	24	2800	1100
$Na_2IDA^{(b)}$	$Na_2C_4H_5NO_4$	11.1	26	2900	1200
Sodium aminoacetate	$NaC_2H_4NO_2$	9.6	31	3000	1400
Sodium succinate	$Na_2C_4H_4O_4$	12.0	22.5	2700	1000
Sodium acetate	$NaCH_3O_2$	11.0	27	2970	1200
Sodium formate	$NaCHO_2$	11.8	14.6	1700	660
Sodium oxalate	$Na_2C_2O_4$	14.3	6.9	980	310
Tributyl phosphate	$C_{12}H_{27}PO_4$	9.7	41	4000	1860
Normal paraffin hydrocarbons (e.g., dodecane)	$C_{12}H_{26}$	10.1	42	4260	1900
4-Methyl-2-pentanone	$C_6H_{12}O$	10.6	42	4200	1800
Sodium dibutyl phosphate	$NaC_8H_{18}PO_4$	9.2	42	3800	1860
Sodium dodecanoate	$NaC_{12}H_{23}O_2$	10.4	40	4400	1700
Sodium butyrate	$NaC_4H_7O_2$	10.7	34	3600	1500

(a) Reaction enthalpy for a stoichiometric mixture of the organic compound and sodium nitrate, per gram of reactants (Burger 1995).

(b) Heats of formation of compounds estimated: $2\Delta H_f(Na_2EDDA) = \Delta H_f(Na_4EDTA) + \Delta H_f(\text{ethylenediamine})$; $2\Delta H_f(Na_3ED3A) = \Delta H_f(Na_4EDTA) + \Delta H_f(Na_2EDDA)$; $2\Delta H_f(Na_2IDA) = \Delta H_f(Na_3NTA) + \Delta H_f(\text{sodium aminoacetate})$.

(c) 4.5 wt% TOC as acetate = 1200 J/g which is criteria for organic safety.

EDDA = ethylenediaminediacetic acid
EDTA = ethylenediaminetetraacetic acid
ED3A = ethylenediaminetriacetic acid
HEDTA = N-(2-hydroxyethyl)ethylenediaminetriacetic acid
IDA = iminodiacetic acid
NTA = nitrilotriacetic acid

Figure 2.1. Correlations of Nitrate Reaction Enthalpies (ΔH_r) with Content of a) C-H Bonds and b) Carboxyl Groups. Data points are for reactions of compounds in Table 2.1 in stoichiometric, 4.5% TOC, and 1% TOC compound/nitrate mixtures.

with both TOC and COO^- content as independent variables yields a much improved correlation with $r^2=0.968$ (r^2 = correlation coefficient) and a standard error in the predicted reaction energy of ± 230 J/g. Figure 2.2a plots the predicted reaction energy vs. the experimental reaction energy. Figure 2.2b shows that using information about the C-H, carboxyl, and TOC content provides an even better correlation. Multiple linear regression analysis yields an r^2 of 0.985. Standard errors in the predicted reaction energy are ± 160 J/g. Clearly, these exercises show that fundamental relationships exist between organic molecular structure and energy content. Analytical methods capable of quantifying the major groups or chemical bonds present in tank wastes should yield reliable estimates of tank waste reaction energies.

Figure 2.2. Correlations of Predicted ΔH_r vs. ΔH_r for Compounds in Table 2.1 Reacting with Nitrate. Points are for stoichiometric, 4.5% TOC, and 1% TOC compound/nitrate mixtures. Predicted points are obtained from the multiple linear regression fit of ΔH_r vs. a) carboxyl content and TOC, b) C-H content, carboxyl content, and TOC. The degree to which points fall above or below the dashed lines is a measure of how good the fitted parameters are in reproducing the actual ΔH_r .

3.0 Literature Search

A short literature search was conducted to find precedence for spectroscopic quantitative determination of organic functional groups, namely C-H, C-O, and C-C, in complex solids. The strategy used for conducting the literature search consisted of searching databases available at the Hanford Technical Library and collecting and reviewing relevant journal articles. A summary of the results, including a bibliography of the references obtained, was documented in a Letter Report that can be found in Appendix A.

Briefly, several articles were identified that discussed the determination and quantitation of C-H content in relatively simple solutions. Powell et al. (1971) determined the quantitation capability of integrating over the C-H second overtone region in the near-infrared for solutions of various organics in carbon tetrachloride solutions from 0.01 to 0.10 M. Wexler (1968) determined that for pure compounds, the integrated intensities of the second overtone region in the near-infrared per C-H bond are nearly the same for most aliphatic, aromatic, and ethylenic bonds.

Another reference was found that examined 50 compounds for determining the correlation between the absorptivities of the methyl and methylene groups and the amount of functional groups present (Tosi and Pinto 1972). These authors found a linear relationship between absorptivity and chain length.

Near-infrared spectroscopy and chemometric learning algorithms were used to determine heat of formation, molecular weight, and number of methyl groups per molecule for hydrocarbon mixtures (Honings et al. 1985). Calibrations accurate to 1.2 kcal/mol for determining heats of formation, 1.5 g/mol for determining mean molecular weight, and 0.057 groups/molecule for methyl groups per molecule were obtained. Calibration sets of 42 samples and performance verification sets of 48 samples were used to develop each correlation. Extrapolation of this type of analysis to heterogeneous solid samples may be difficult due to the number of representative training-set samples required to develop correlations for near-infrared analyses.

Department of Energy reports, written by various laboratories, on Raman spectroscopy development for Hanford tank-waste characterization have been compiled. Considerable documentation exists to support the potential of Raman spectroscopy for tank waste characterization.

Preliminary design of in-tank probes have been proposed by Lawrence Livermore National Laboratory (Kyle 1994) in addition to some feasibility studies of two proposed methods. Kyle noted an observed effect of moisture content on the nitrate signal obtained by Raman spectroscopy. A decrease of 73% intensity was observed for the sodium nitrate peak when switching from dry sodium nitrate to 20 weight percent water sodium nitrate sample. Kyle proposed that this effect was due to the concomitant decrease in sample reflectivity as the moisture content increased.

A substantial progress report was prepared by Mann and Vickers (1994) on development of Raman spectroscopy for waste-tank characterization. Included were preliminary results from analysis of salt-cake simulants and waste-tank samples. Efforts were primarily aimed at analyzing for inorganic and ferrocyanide and ferrocyanide components. However, preliminary Raman spectra of organic compounds expected to be present in the waste tanks were also obtained. Fiber-optic-probe considerations and testing for potential in-tank deployment were discussed.

Other reports by Westinghouse Hanford Company addressed the issues of importance for potential deployment of Raman Spectroscopy for in-tank characterization or for hot-cell applications (Crawford et al. 1994; Lombardi et al. 1994; Lopez et al. 1995; Phillip 1994).

More details of the literature search and additional references can be found in Appendix A.

4.0 Correlation of Experimental and Theoretical Reaction Enthalpies for Organic Mixtures

Traditionally, energetics measurements of Hanford tank waste samples have been obtained by differential scanning calorimetry. Therefore, DSC was chosen to determine whether the same trend in organic functional group content and reaction enthalpy, presented in Section 2.0 for theoretical calculations, could be obtained experimentally. Presented here are attempts to correlate experimentally measured heats of reaction between select organics and sodium nitrate and/or nitrite with calculated theoretical reaction enthalpies.

4.1 Experimental

The DSC method measures enthalpy changes as the sample is heated at a known and constant rate. Power-compensated and heat flux DSCs are the two varieties currently available commercially. As Boerio-Goates and Callanah (1992) described, in heat-flux DSCs, which are similar to differential thermal analyzers (DTAs), the sample and a reference are heated by a single heating source, and the temperature difference between the two is brought out electronically as a differential power, but in the power-compensated DSC, the sample and reference samples are heated by individual heaters and monitored by individual thermocouples. Any temperature difference between the two heaters is used to control the power applied to either heater. If an endothermic reaction is observed by the instrument, additional power is supplied to the sample; if an exothermic reaction is observed, additional power is supplied to the reference heater. This differential power output necessary to maintain equal temperatures is correlated to reaction enthalpy.

A power-compensation DSC was used for these reaction enthalpy measurements. The DSC temperature was calibrated using the melting points of indium (156°C) and zinc (419°C); the indium was used to energy calibrate the instrument. The DSC analyses were performed at 5°C/min up to 450°C using an argon or nitrogen purge. The heat of reaction was measured between several organic salts and sodium nitrate, sodium nitrite, and an equimolar mix of sodium nitrate and sodium nitrite. The organic salts tested were the sodium salts of oxalate, formate, acetate, glycolate, glyoxalate, isobutyrate, succinate, tartrate, citrate, dodecanate (laurate), EDTA, HEDTA, and di-2-ethylhexyl phosphate (D2EHP).

To ensure that the DSC observed all of the reactions that were occurring, we performed supplemental qualitative analyses of each of the tested mixtures using simultaneous thermogravimetric analysis (TGA) and DTA coupled with infrared spectroscopic analysis of the thermally evolved gases. Simultaneous TGA and DTA measure and report mass changes and temperature differences between a sample and a reference as both are heated by a single furnace at a known and constant heating rate. Indium, tin, and lead were used to temperature calibrate this instrument. These analyses were performed at 5°C/min in an argon purge. The evolved gases were monitored using infrared spectroscopy.

In addition, because little exothermic activity was observed for the sodium laurate and sodium nitrate mixture, we used accelerating rate calorimetry (ARC) to determine if any exothermic reactions were occurring. The ARC was used in only one instance to determine if a reaction did or did not occur between sodium laurate and sodium nitrate. As described by Oscarson and Izatt (1992), the ARC is an adiabatic calorimeter that typically operates in a heat-wait-search mode; i.e., the instrument

heats the sample and its sealed sample container up to a user-specified temperature, waits for a brief period, monitors the temperature of the sample container, and compares it to the furnace temperature to determine if heat is being produced by the sample. If an exothermic reaction is observed (the instrument uses an operator selected self-heat rate criteria of typically 0.02 to 0.025°C/min to identify an exothermic reaction), the ARC maintains the temperature of the furnace at the sample's temperature, thus maintaining adiabatic conditions; the ARC typically is capable of tracking the sample's temperature up to 15°C/min.

4.2 Results

On a theoretical basis, the enthalpy resulting from the reactions of selected organics and nitrate and/or nitrite should depend on the amount of organic carbon, the amount of C-H bonds, or a combination of these with the amount of C-O bonds present in the mixture. To determine whether these salient characteristics of the organics correlate directly with the amount of energy that will be produced by the reaction of organics in Hanford wastes with sodium nitrate or nitrite, reaction enthalpies of select organics with sodium nitrate and sodium nitrite were measured with DSC and DTA. The simulant mixtures were made with 6 mass percent organic carbon and the remainder either sodium nitrate, sodium nitrite, or a mix of these to ensure that sufficient oxidant was present for complete reaction. The organics were chosen based on organics that are expected to be present in Hanford wastes either by direct addition or by aging with sodium nitrate and/or nitrite (Camaioni et al. 1995; Campbell et al. 1994b, c).

4.2.1 Measured Energetic for Sodium Nitrate Based Mixtures

The DSC and DTA measured reaction enthalpies at 6 mass percent organic carbon in sodium nitrate solution for the organics studied are compared to maximum theoretical reaction enthalpies predicted (Burger 1995) in Table 4.1. It is shown that the amount of heat produced or observed by the two instruments is a fraction of the maximum theoretical enthalpy. One possible explanation is that the reaction between the organics and the nitrate proceed, at least partially, by a less energetic reaction pathway than predicted by theory, which is consistent with previously obtained results (Scheele et al. 1995).

The best match to theoretical enthalpy measured by the DSC was for sodium formate (58%), the simplest organic, and the worst match obtained was for D2EHP, in which no reaction was observed even though theoretically it should be a more energetic reaction than sodium formate (see Table 4.1). Sodium laurate (dodecanate), another strongly aliphatic compound, was also relatively inert. This lack of observed energetic reaction was confirmed by ARC analysis.

In some cases, the DTA heat-flux device gave higher enthalpy yields than the power-compensation DSC instrument, but it did not consistently produce values significantly closer to theoretical values. By design and in its application to endothermic melting-point calibration standards, the power-compensation DSC provides more consistent results. A brief study and correlation of the measured responses of the DTA temperature calibration standards obtained since the instrument was acquired indicated that the response varied from day-to-day and depended on the temperature of the event; for 25 different standards measurements of enthalpy, the standard deviation was 12%, yielding a 95% confidence interval of $\pm 5\%$.

Table 4.1. Calculated and Measured Exothermic Reaction Enthalpies for Mixture of Sodium Nitrate and Selected Organics (6 wt% Organic Carbon)

Compound (Sodium Form)	Calculated $-\Delta H_{rx}$, J/g Sample	DSC Measured $-\Delta H_{rx}$, J/g Sample	% of Calculated	DTA Measured $-\Delta H_{rx}$, J/g Sample	% of Calculated
Formate	890	420	47	500	56
Oxalate	420	21	5.0	90	21
Glyoxalate	890	190	21	320	36
Glycolate	1200	180	15	420	35
Tartrate	1100	200	18	500	45
Citrate	1200	60	5.0	620	52
Acetate	1600	420	26	650	41
Succinate (a)	1600	160	10	270	17
EDTA	1700	(b)	-	460	27
HEDTA	1900	55	2.9	710	37
Isobutyrate	2000	180	9.0	210	10
D2EHP	2500	(c)	-	(c)	-
Laurate	2300	46	2.0	85	3.7

(a) 6.8 mass % organic carbon mixture.

(b) Complexity of reaction prevented calculation of measured enthalpy.

(c) No reaction observed.

A plot comparing the calculated maximum reaction enthalpy (ΔH_{rx}) predicted and DSC measured enthalpy for select organic compounds for 6 mass percent organic carbon in sodium nitrate mixtures is given in Figure 4.1. The organic compounds are organized in terms of increasing carbon content from left to right. Although a trend exists between calculated enthalpy and increasing carbon content in the organics (Figure 4.1), the trend is not observed with DSC experimental enthalpy values.

While a semi-empirical relationship was anticipated between certain organic functional group content and reaction enthalpy, no experimental relationship appears to exist for DSC-measured energetics. For example, Figure 2.1a shows a linear relationship between C-H content and calculated enthalpy. However, a similar plot (Figure 4.2) with experimentally determined enthalpies from DSC analysis shows no relationship between C-H content and experimentally determined enthalpy. Similarly, plotting C-O content and C=O content versus the DSC-measured energetics for 6 mass percent organic carbon mixtures of a series of organic compounds with sodium nitrate shows no significant correlation (Figures 4.3 and 4.4, respectively). However, it should be noted that the highest measured enthalpies were observed at higher C-O contents and the lowest were observed for the organics that contained the least amount of oxygen, i.e., the most aliphatic.

4.2.2 Measured Energetics for Sodium Nitrite Based Mixtures

Nitrite in the tanks largely came from the radiolysis of nitrate added during recovery of defense materials. As with nitrate, relationships should exist between the different characteristic organic components and the energy that would be released if a reaction were initiated in the waste.

Figure 4.1. Calculated and DSC Measured Enthalpy of Reaction of Selected Organic at 6 Mass Percent Organic Carbon in Sodium Nitrate

Figure 4.2. Effect of C-H Content in Mixtures of Selected Organics and Sodium Nitrate (6 Mass Percent Organic Carbon) on the DSC-Measured ΔH_{rxn}

Figure 4.3. Effect of C-O Content in 6 Mass Percent Organic Carbon Mixtures of Selected Organics and Sodium Nitrate on the DSC-Measured Energetics

Figure 4.4. Effect of C=O Content on the DSC-Measured Energetics for 6 Mass Percent Organic Carbon Mixtures of Selected Organics and Sodium Nitrate

Table 4.2 presents the DSC- and DTA-measured exothermic reaction enthalpies for the tested 6 mass percent organic carbon mixtures of selected organics and sodium nitrite. In addition, the predicted maximum theoretical reaction enthalpies as calculated by Burger (1995) are included for comparison. Similar results were obtained for DSC and DTA measurements of the sodium nitrite mixtures as for the sodium nitrate mixtures. Again, for the majority of the organics studied, less than half the calculated maximum reaction enthalpy is obtained experimentally by DSC or DTA analysis. A plot of the theoretically predicted and DSC-measured reaction enthalpies is provided in Figure 4.5 for visual comparison. Figures 4.6, 4.7, and 4.8 contain plots of C-H, C-O, or C=O content, respectively, with experimental DSC-measured reaction enthalpies. In contrast to predictions based on calculated reaction enthalpies, increased C-H content did not consistently result in increased heat production, as determined by DSC and DTA. Again, the more aliphatic organics produced the least heat.

4.2.3 Measured Energetics for Equimolar Sodium Nitrate and Nitrite Mixtures

The ratio of nitrates and nitrites depends largely on the radiation history of the waste, although it may be affected by other chemical factors. Because the two oxidants exhibit different reactivities and the possibility exists that interactions could occur, the ability to predict the energetics of organic-bearing wastes is important for the mixed-oxidant systems.

The DSC- and DTA-measured energetics for the 6 mass percent organic carbon as selected organics and equimolar sodium nitrate and sodium nitrite are presented in Table 4.3. The predicted theoretical maximum heats of reaction for both the sodium nitrate and sodium nitrite solutions are also provided in Table 4.3 for comparison. It is not possible to predict with our current understanding of the reaction mechanisms and associated kinetics which oxidant will predominate, and thus predict the theoretical heat of reaction for these mixtures. Mixed results were obtained

Table 4.2. Calculated and Measured Exothermic Reaction Enthalpies for Mixture of Sodium Nitrite and Selected Organics (6 Mass % Organic Carbon)

Compound (Sodium Form)	Calculated $-\Delta H_{rx}$, ^(a) J/g Sample	DSC Measured $-\Delta H_{rx}$, J/g Sample	% of Calculated	DTA Measured $-\Delta H_{rx}$, J/g Sample	% of Calculated
Formate	1100	540	49	420	38
Oxalate	530	93	18	240	45
Glyoxalate	1100	240	22	130	12
Glycolate	1600	410	26	770	48
Tartrate	1400	310	22	320	23
Citrate	1600	810 ^(b)	51	Not measured	-
Acetate	2100	230 ^(b)	11	Not measured	-
Succinate	2000	1400	70	730	37
EDTA	2100	170 ^(b)	8.0	Not measured	-
HEDTA	2400	(c)	-	Not measured	-
Isobutyrate	2600	800	31	590	23
D2EHP	3200	86	2.7	56	1.8
Laurate	3000	120	4.0	70	2.3

(a) Burger 1995.

(b) Scheele et al. 1995.

(c) Complexity of reaction prevented enthalpy measurement.

by the two different techniques where the DSC gave higher energetics results for some organics and the DTA gave higher results for other organics. However, all of the measured enthalpy values were well below those calculated with either sodium nitrate or sodium nitrite as the sole oxidant.

Comparison of the DSC-measured reaction enthalpies for different organics at 6 mass percent with sodium nitrate, sodium nitrite, or an equimolar mixture of the two oxidants is shown in Figure 4.9. In most cases, the measured enthalpy is higher for sodium nitrite as the sole oxidant. However, all these values are still significantly below those calculated (e.g., see Table 4.2).

In contrast to the trends between organic functional group content and calculated reaction enthalpy discussed in Section 2.0, no clear trend with DSC-obtained experimental reaction enthalpies and functional group content were obtained. This could be due to the complex decomposition reaction pathways of many of the organics studied. For example, it has been shown that ammonia is among the gases released during decomposition of organics such as sodium acetate and sodium HEDTA. (Scheele et al. 1995). This is direct evidence of different dissociation reaction pathways being followed by many of these organics of interest than predicted by calculated reaction enthalpies, where primarily nitrogen and nitrous oxide gases are expected (Burger 1995). Thus, different reaction pathways lead to discrepancy between experimental reaction enthalpies and calculated reaction enthalpies as obtained.

Figure 4.6. Effect of C-H Content in a 6 Mass % Organic Carbon Mixture of Selected Organics and Sodium Nitrite on the DSC-Measured ΔH_{rx}

Figure 4.7. Effect of C-O Content in a 6 Mass % Organic Carbon Mixture of Selected Organics and Sodium Nitrite on the DSC-Measured ΔH_{rx}

Figure 4.8. Effect of C=O Content in 6 Mass % Organic Carbon Mixtures of Selected Organics and Sodium Nitrite on the DSC-Measured ΔH_{rx}

Table 4.3. Calculated and Measured Exothermic Reaction Enthalpies for Mixtures of Equimolar Sodium Nitrate and Sodium Nitrite with Selected Organics (6 Mass % Organic Carbon)

Compound (Sodium Form)	Calculated for Nitrate $-\Delta H_{rx}^{(a)}$, J/g Mix	Calculated for Nitrite $-\Delta H_{rx}^{(a)}$, J/g Mix	DSC Measured $-\Delta H_{rx}^{(a)}$ J/g Mix	DTA Measured $-\Delta H_{rx}$, J/g Mix
Formate	890	1100	320	580
Oxalate	420	530	210	250
Glyoxalate	890	1100	270	240
Glycolate	1200	1600	370	570
Tartrate	1100	1400	250	450
Citrate	1000	1600	220 ^(b)	Not measured
Acetate	1600	2100	380 ^(b)	Not measured
Succinate ^(c)	1600	2000	920	700
EDTA	1700	2100	150 ^(b)	Not measured
HEDTA	1900	2400	120 ^(b)	Not measured
Isobutyrate	2000	2600	490	590
D2EHP	2500	3200	100	65
Laurate	2300	3000	54	130

(a) Burger 1995

(b) Scheele et al. 1995

(c) Succinate analyzed at 6.5 Mass % Organic Carbon.

Figure 4.9. Comparison of DSC-Measured Reaction Enthalpies for Selected Organic Compounds (6 Mass %) with Sodium Nitrate, Sodium Nitrite, or an Equimolar Mixture of the Two as the Oxidant

In summary, the DSC- and DTA-measured reaction enthalpies were significantly lower than theoretical calculations predicted, in most cases well below 50%. In addition, the expected relationships between the C-H, C-O, and C=O content of these mixtures of organics with sodium nitrate and/or sodium nitrite and the DSC-measured reaction enthalpies were not observed. This suggests that either the calculated values need to be adjusted to more closely simulate what can be measured or that more understanding of the reactions taking place in these mixtures during DSC or DTA measurement is needed for predicting safety from an energetics standpoint.

5.0 Development of FT-IR and FT-Raman for Organic Analysis in Liquid and Solid Simulants

Preliminary spectroscopic technique development efforts focused on determining the ability to perform FT-IR and FT-Raman analysis of heterogeneous solid or liquid samples resembling Hanford tank waste with minimal sample preparation, such as dilution or homogenization. Issues addressing implementing these techniques for in-tank analysis, such as using fiber optic cables and remote sampling probes, were beyond the scope of this project. The experiments discussed here were geared towards eventual tank waste sample analysis in a hot-cell environment and not *in situ* applications directly. The results of the preliminary feasibility studies with simulant solid and liquid tank waste samples are discussed below.

5.1 Experimental

5.1.1 Preparation of Liquid Simulants

The homogeneous liquid simulant SY1-SIM-93B (Table 5.1) was chosen to represent the basic inorganic matrix for the organic solutions. The simulant was prepared following the recipe developed by Bryan and Pederson (1994). A stock solution of each organic of interest was prepared by dissolving the salt of the organic into portions of the stock SY1-SIM-93B solutions. A stock solution of each organic was prepared by dissolving the organic salt in the inorganic simulant to a targeted 20 mass percent organic; however, solubility precluded reaching this target for several of the organics. The stock solutions were diluted to prepare 5 to 6 standards covering the concentration range 0.2 to 15 mass percent organic. For later data analysis, the sample concentrations were calculated on the basis of mole C-H bonds per kg total solution. The organics studied include sodium formate, sodium succinate, sodium glycolate, sodium citrate, IDA, Na₃HEDTA, Na₄EDTA, sodium acetate, and sodium isobutyrate.

5.1.2 Preparation of Solid Simulants

The inorganic portion of the solid simulants was prepared as described in Section 5.1.1 for the organic solutions (Table 5.1). A stock solution of sodium formate and Na₃HEDTA, was prepared by dissolving the organic into the SY1-SIM-93B simulant to prepare each target concentration. The target organic concentrations were between 2.5 and 10% TOC. The stock solution was then split into three containers and dried in an oven at 60°C to approximately 10, 20, and 30% by weight H₂O.

The final concentrations of organic and water content are presented in Table 5.2. Aliquots of a representative series of these samples were provided to Westinghouse Hanford Company for confirmatory spectroscopic studies in their laboratories.

Table 5.1. Composition of SY1-SIM-93B Waste Simulant

<u>Molecular Formula</u>	<u>Component</u>	<u>Mass Percent</u>
Na ₂ CO ₃	Sodium Carbonate	1.75
Al(NO ₃) ₃ • 9 H ₂ O	Aluminum Nitrate	13.29
NaNO ₃	Sodium Nitrate	2.80
NaNO ₂	Sodium Nitrite	11.37
NaOH	Sodium Hydroxide	11.21
H ₂ O	Water	59.58

Table 5.2. Final Concentrations of Organic and Water Content for the Solid Simulants

<u>Organic</u>	<u>Percent TOC, Dry Weight</u>	<u>Percent TOC, Wet Weight</u>	<u>Mole C-H/kg Sample</u>	<u>Mole COO⁻/kg Sample</u>	<u>Percent Water</u>
HEDTA	1.3	1.0	1.3	0.27	19
HEDTA	2.4	2.0	2.4	0.51	17
HEDTA	4.0	3.2	4.0	0.85	20
HEDTA	6.9	5.2	7.9	1.7	26
HEDTA	10.0	7.6	10.6	2.3	22
Formate	0.75	0.54	0.46	0.46	28
Formate	2.3	1.6	1.7	1.7	30
Formate	3.9	3.0	2.8	2.8	21
Formate	7.3	4.9	5.3	5.3	33
Formate	10.0	7.0	8.9	8.9	31
HEDTA	1.3	0.85	1.0	0.22	35
HEDTA	4.0	3.2	3.9	0.84	19
HEDTA	10.0	8.2	11.3	2.43	18
Formate	0.75	0.50	0.42	0.42	34
Formate	3.9	3.2	3.0	3.0	19
Formate	7.3	5.5	5.9	5.9	25
Formate	10.0	8.4	10.7	10.7	17
HEDTA	1.3	0.95	1.1	0.24	27
HEDTA	2.4	2.0	2.5	0.50	15
HEDTA	4.0	3.4	4.2	0.90	17
HEDTA	6.9	5.8	7.5	1.6	13
HEDTA	10.0	8.9	12.4	2.7	11
Formate	0.75	0.61	0.52	0.52	19
Formate	3.9	3.6	3.3	3.3	9.7
Formate	10.0	9.0	11.4	11.4	9.5
93B Simulant	—	—	—	—	29
93B Simulant	—	—	—	—	19
93B Simulant	—	—	—	—	2

5.1.3 Fourier Transform Infrared Spectroscopic Measurements

The FT-IR spectra were collected on a Nicolet 800 spectrometer equipped with a NaBr beam splitter and mercury cadmium telluride (MCT)/A range (5800 to 720 cm^{-1}) liquid-nitrogen-cooled detector. The spectra of the liquid samples were collected using a liquid flow-through ZnSe attenuated total reflectance (ATR) cell. The spectra of the solids samples were collected using a ZnSe and Ge ATR throughplate. The 30 and 20% moisture samples have enough liquid to make good contact with the crystal without using pressure; however, for the 10% moisture samples a pressure plate was used to ensure better contact. The experimental parameters, such as number of scans, resolution, and cell size were evaluated to determine the optimal operating conditions. Final parameters used for the liquid sample analyses were a small volume cell (0.4 mL) with 100 scans (approximately 30 to 60 seconds) and 4-nm resolution. The background was collected with the SY1-SIM-93B inorganic portion present in the cell, using the same parameters as reported for the samples. For solid sample analyses, the final parameters were 100 scans, 2-nm resolution with an aperture of 10.0, a gain of 1.0, and total acquisition time for each spectrum of 1.45 minutes. The background was collected as the empty throughplate for each acquisition. Separate spectra were obtained with the dried SY1-SIM-93B simulant and later subtracted from the sample spectra to remove the contribution of the simulant. The sample spectra were background subtracted and then integrated over the region of interest: approximately 3000 to 2700 cm^{-1} for the C-H stretching region and 1700 to 1400 cm^{-1} for the COO^- stretching region.

5.1.4 Fourier Transform Raman Spectroscopic Measurements

All Raman spectra were collected on a Nicolet model 950 Fourier transform Raman spectrometer equipped with an indium gallium arsenide (InGAs) detector. The FT Raman differs from other Raman instruments in that the excitation source is a near IR laser operating at $1.06\text{ }\mu\text{m}$. Because of the weakness of the Raman signal at this excitation frequency, an interferometer is used to collect as much of the signal as possible. It should be noted that although other excitation frequencies are being used for Raman tank waste work, the independence of the overall Raman effect with respect to excitation frequency means that this work is applicable to other projects.

A 180° sampling configuration was used for characterizing the liquid samples. In this configuration, the Raman-scattered radiation is emerging along the same axis as the excitation beam. This configuration is generally considered superior for Raman characterization of liquid samples. The C-H region of interest is between 3100 and 2500 cm^{-1} . A single relatively sharp peak for nitrate is observed around 1070 cm^{-1} and is used as an internal standard. The analysis time for liquid samples was approximately 15 minutes.

For the solids analysis, the samples were analyzed directly through the glass sample vial, minimizing sample handling. A 180° sampling configuration was used for characterizing the solid samples. The analysis time used for these preliminary studies of solid samples was approximately 1 hour.

In the Raman effect, when monochromatic light illuminates a sample, two processes can occur. The first is Rayleigh scatter, which is elastically scattered radiation and thus contains no molecular structural information. The second is Raman scatter, which is monochromatic light being changed in frequency by the motion of the various bonds. Raman scatter therefore contains information about the molecular structure. More germane to this project is the use of Raman as a semi-quantitative tool

as opposed to a qualitative tool. An understanding of this is necessary to fully comprehend the benefits and difficulties of applying Raman as a semi-quantitative method.

A generalized diagram of the processes that occur when the Raman light source illuminates the sample is shown in Figure 5.1.

Figure 5.1. Processes That Occur During Raman Scatter

When the illuminating beam (typically a laser) impinges on the sample, the light is both scattered throughout the sample and partially reflected. The amount of light reflected at the air/sample interface will depend on two factors: the difference in refractive index between the sample and atmosphere and the angle of sample illumination. The angle of illumination is nominally perpendicular to the surface. Particle morphology, however, may cause this to change radically from this level. After the light enters the sample, the volume of sample illuminated depends on scattering, which is related to particle size distribution and the transparency of the sample to the illuminating light wavelength. A small portion of the radiation is then Raman shifted. The Raman-shifted radiation must exit the sample and enter the collection optics. The amount of Raman-shifted light that reaches the collection optics also depends on a number of factors. Raman-scattered radiation radiates in a spherical fashion. Thus, only a small fraction of the total Raman-shifted radiation will be directed towards the collection optics. Raman-shifted light that is directed towards the collection optics may also be attenuated by the absorption of radiation by other sample components and reflective losses at the air-sample interface.

Overall, the observed intensity of the radiation, which is used to determine the concentration of a given component, will vary according to these factors. These may or may not be controllable when working with real samples. Ideally, all analyses should be done as a liquid, which will minimize the difficulties caused by matrices that change from sample to sample. Alternatively, it may be possible to change the wavelength of radiation being used to illuminate the sample to one that is less affected by elements of the sample matrix (the ability to change excitation wavelengths while retaining much of the information is a unique aspect of Raman spectroscopy). Finally, it may be possible to use the Rayleigh radiation, which is unshifted laser radiation that is scattered from the sample, to provide a correction factor to the sample matrix effects. The last possibility has not been evaluated for the sample conditions used here.

5.2 Results

5.2.1 Fourier Transform Infrared Spectroscopy of Liquid Simulants

Fourier transform infrared spectra were obtained for all organics being studied. Problems occurred with the analysis of acetate and isobutyrate. Acetate showed no C-H signal (probably covered by the large O-H stretch inherent to aqueous solutions), and isobutyrate decomposed in solution in less than 1 day.

The infrared spectra of each of the organic solutions prepared in SY1-SIM-93B have similar diagnostic peaks. The O-H stretching region is characterized by a strongly absorbing peak centered at approximately 3150 cm^{-1} . This peak is caused by NaOH and H_2O in the SY1-SIM-93B simulant and shifts slightly due to changes in sample pH. The C-H stretching region begins on the downward slope of this O-H stretch around 3000 cm^{-1} . Although the C-H peaks appear on the edge of the O-H peak, the C-H peak can be readily isolated and integrated. The COO^- region shows two distinctive peaks around 1650 cm^{-1} and 1450 cm^{-1} representing the antisymmetric (1650 to 1450 cm^{-1}) and symmetric (1450 to 1360 cm^{-1}) stretches of the COO^- moiety. Figure 5.2 shows the FT-IR spectra of the C-H and COO^- regions of HEDTA in solution to illustrate the observed spectra. Integration of the C-H and COO^- regions of each spectra results in excellent linear correlations between the C-H and COO^- peak area and concentration. Figure 5.3 shows the standard curves of the C-H region for each of the organic samples measured, and Figure 5.4 shows the standard curves of the COO^- peaks for each of the organics. As can be seen in Table 5.3, the slopes for the COO^- region for each of the organic samples are quite similar. This indicates that the extinction coefficients of the COO^- group for each organic is similar. The chemical environment of the COO^- moiety is very similar for all of the organics measured. Since each of the organic samples measured has a similar slope, a single curve can be chosen to represent the calibration of COO^- in solution to determine the concentration of COO^- from an unknown sample. By comparing the percent difference of each of the slopes, the error in quantitation of COO^- can be estimated. As shown in Table 5.3, the choice of a mid-range slope value for glycolate as a representative curve introduces less than 20% total error in the quantitation of COO^- . Using the glycolate slope as the representative curve for each of the organic species will result in the COO^- estimate being approximately 20% low for citrate and succinate and approximately 10% high for EDTA, HEDTA, and formate.

The quantitation of C-H in an unknown sample cannot be determined in the same manner as the COO^- , since the slopes of the C-H standard curves, shown in Table 5.4, vary from one another considerably more. This variation indicates that the extinction coefficients of the C-H groups for some of the organics are not similar. This can easily be explained when the structure and chemical environment of the organic samples are compared. Figure 5.5 shows the structures of the organics being discussed here. The formate C-H group has sp^2 hybridization, whereas all of the other C-H functional groups in the other organics studied have sp^3 hybridization. This difference in hybridization explains why the slope for formate is significantly different than the other organics.

The remaining organics have C-H groups that can be divided into three types of environments. The ethylene group of HEDTA and EDTA is bound by two amines. The methylene group of HEDTA, EDTA, and IDA is bound by an amine and COO^- . The C-H functional group of glycolate, succinate, and citrate is bound by either one or two COO^- . The different substituent groups affect the spectrum of the C-H groups in two ways: 1) the wavelength region of the C-H group is shifted to higher or lower energy depending upon the substituent group, and 2) as the substituent group changes, the environment of the C-H group changes so the extinction coefficient will change slightly.

Figure 5.2. FT-IR Spectrum of C-H and Carboxylate Region for HEDTA in SY1-SIM-93B Simulated Waste

Figure 5.3. Comparison of C-H Response for Organics Present in SY1-SIM-93B Waste Simulant

Figure 5.4. Comparison of COO⁻ Response for Organics Present in SY1-SIM-93B Waste Simulant

Table 5.3. A Comparison of the Magnitude of the Slope for the COO⁻ Standard Curves

<u>Organic Sample</u>	<u>Observed Slope</u>	<u>Error^(a) of COO⁻ Quantitation (%)</u>
Citrate	43.02	16 (low)
Formate	33.60	10 (high)
Glycolate	37.19	0
Succinate	44.23	20 (low)
HEDTA	35.19	5 (high)
EDTA	34.46	7 (high)

(a) Error resulting from using the glycolate slope as the representative curve for quantitation of COO⁻ for all of the organic species.

Table 5.4. Identification of the C-H Wavelength Region and the Calibration Slopes for Various Organic Samples

<u>Organic</u>	<u>Wavelength Region of C-H Groups (cm⁻¹)</u>	<u>Slope</u>
Citrate	3000 to 2880	0.23
Formate	2880 to 2660	1.6
Glycolate	2980 to 2800	0.43
Succinate	3000 to 2880	0.22
EDTA	2990 to 2760	0.37
HEDTA	3000 to 2790	0.55
IDA	3000 to 2780	0.37

Based on the above structural argument, the following organics can be grouped together: HEDTA, EDTA, and IDA should behave similarly, succinate, citrate, and glycolate should behave similarly, and formate should be significantly different from both groups. As shown in Table 5.4, this expectation is corroborated by both the spectra and the slope of the standard curves, with a few exceptions. The spectra and the slope of glycolate is more similar to that of HEDTA and EDTA rather than its structural equivalents succinate and citrate. Also, the spectrum of IDA is more similar to succinate and citrate than HEDTA and EDTA, but the slope is more similar to HEDTA and EDTA. Figures 5.6 and 5.7 illustrate that in an unknown sample, the wavelength region and peak shape of the observed C-H peak will allow an accurate determination of the correct type of organic present. Note that both Figures 5.6 and 5.7 contain the spectra of 8% IDA. This is to illustrate that although the peak shape of the IDA would seem to indicate that IDA should be grouped with citrate and succinate, the wavelength region definitely does not fit that grouping, but rather it fits the grouping with EDTA, HEDTA, and glycolate. This grouping is expected for IDA, based on structural arguments, and is borne out from both the slope of the IDA calibration curve and the wavelength region of the C-H peak.

Since the organic samples basically fall into two groupings (with formate by itself), a standard curve can be chosen for each group and used to determine the concentration of C-H present in

HEDTA

N-(2 Hydroxyethyl)ethylenediamine
triaceticacid, trisodium salt

EDTA

Ethylenediamine tetra aceticacid,
tetrasodium salt

IDA

Iminodiaceticacid, sodium salt

Sodium Glycolate

Sodium Succinate

Sodium Formate

Sodium Citrate

Figure 5.5. Structures of the Organics Containing Different Functional Groups Being Tested by FT-IR Spectroscopy

Figure 5.6. Comparison of FT-IR C-H Stretching Peak Shape and Wavelength to Illustrate the Ease of Grouping Types of Organics for Quantitation. The organics are mass percent spiked into the SY1-SIM-93B simulant.

Figure 5.7. Comparison of FT-IR C-H Stretching Peak Shape and Wavelength to Illustrate the Utility of Grouping Types of Organics for Quantitation. The organics are mass percent spiked into SY1-SIM-93B simulant.

unknown samples. Table 5.5 identifies the grouping, the standard curve, and the error associated with the slopes of each curve. By comparing the percent difference of each of the slopes, the error in quantitation of C-H can be determined. As shown in Table 5.5, the choice of a mid-range slope value as a representative curve for each grouping introduces less than a 30% total error in the quantitation of total C-H. Using the glycolate curve as the reference curve for HEDTA, EDTA, IDA, and glycolate will result in the C-H estimate being approximately 27% low for HEDTA and approximately 16% high for EDTA and IDA. Using the succinate curve to represent both succinate and citrate will result in the citrate C-H estimate being approximately 8% low. One important consideration is that even though the C-H in formate has a greater response than the C-H in other organics, the quantitative C-H amount would be a conservative estimate of energy content since formate gives a high C-H response, but represents low enthalpy content.

Table 5.5. Proposed Grouping of Organics for Quantitation of Unknown Samples. The error calculated using the reference slope versus the single element slope is reported.

<u>Organic</u>	<u>Grouping (reference curve is underlined)</u>	<u>Error(a) for Quantitation of Total C-H Concentration</u>
Citrate	Citrate, <u>Succinate</u>	8%
Formate	<u>Formate</u>	0%
Glycolate	HEDTA, EDTA, IDA, <u>Glycolate</u>	0%
Succinate	Citrate, <u>Succinate</u>	0%
EDTA	HEDTA, EDTA, IDA, <u>Glycolate</u>	16%
HEDTA	HEDTA, EDTA, IDA, <u>Glycolate</u>	27%
IDA	HEDTA, EDTA, IDA, <u>Glycolate</u>	15%

(a) The errors were estimated from using either succinate, formate, or glycolate as the reference curve as indicated in the grouping column.

5.2.2 Fourier Transform Raman Spectroscopy of Liquid Simulants

The objective of this study was to characterize liquid samples by FT-Raman spectroscopy for their organic content. This is actually more difficult than characterizing solids for this near-IR Raman system because of the large water IR overtone band superimposed on the Stokes-shifted part of the spectrum. The minimum detectable limit for a sample in a water matrix would be approximately 1% (weight-to-weight [w/w]). This minimum detectable level can, in theory, be improved by using surface-enhanced Raman spectroscopy (SERS), which will be discussed in more detail. It might be possible to avoid this water interference for liquid samples by using a Raman system at a different wavelength, such as the visible region.

For this test, sodium acetate, citric acid, EDTA, HEDTA, and oxalic acid were dissolved in 2 M NaOH at concentrations of 0.5%, 1%, 2%, and 4% on a w/w basis. An aliquot of each sample was then placed in an NMR tube for placement in the Raman laser beam. Spectra were collected for about 15 minutes at a resolution of 4 cm⁻¹. The NaOH solution did not contribute any peaks to the spectrum other than the broad water peaks. For purposes of comparison, Figure 5.8 shows the spectra of the NaOH versus the SY1-SIM-93B liquid matrix. The laser power used for each data acquisition is included in this and all subsequent figures as "x" W, where W is Watts.

Figure 5.8. Comparison of the FT-Raman Spectra of Sodium Hydroxide and the Liquid SY1-SIM-93B Simulant Tank Matrix

Example FT-Raman spectra of the organics used in this study are shown in Figure 5.9. All spectra shown are at the 4% w/w concentration level. As can be seen, the spectra all have a peak in the C-H stretching range (1500 to 1300 cm^{-1}), although the oxalic spectrum is very weak. The baseline corrected area of this peak was integrated and plotted versus concentration to determine if a useful correlation existed. Initial attempts were taken with the spectra at 4 cm^{-1} resolution. The results were not, however, particularly linear. To reduce the noise, the spectra were deresolved by transforming them to 16 cm^{-1} resolution. This reduction in resolution suppressed the noise without severely affecting the spectral feature. The results are shown graphically in Figure 5.10. It is readily apparent that concentrations down to 0.5% w/w can be characterized using this technique. It is doubtful that levels below this concentration can be characterized, however, as indicated by the intercepts of the response lines for the target analytes.

Nevertheless, it may be necessary to characterize samples that are lower in concentration than 0.5% w/w. Currently, it is possible to increase the Raman scatter from a sample by using the SERS. In the SERS technique, the target analyte is added to a solution or surface that contains dispersed particles of unoxidized metal. In practice, silver is used, although gold and copper have been used as well. Signal enhancement occurs through direct interaction of the silver with a pi-bond structure or through an indirect electromagnetic interaction. The Raman response of a signal can be increased by SERS by several orders of magnitude. To date, SERS has been applied primarily to aromatic or similar extended pi-bonded target analytes. There have been indications in the literature, however, that SERS can also enhance the signal of sigma bonds as well. For this reason, the use of SERS to enhance the signal of the target analytes used in this study was examined.

The silver SERS substrate was prepared according to the procedure of Lee and Meisel (1982): silver nitrate is reduced in solution using citrate. The sample is prepared by adding an aliquot of the silver to an aliquot of sample and waiting for 12 to 24 hours. For purposes of this work, a 1-mL aliquot of each of the 0.5% w/w acids was added to a 1-mL aliquot of the SERS solution. This allows a direct assessment of the SERS enhancement.

The spectra of several of the SERS-enhanced samples versus the original spectra for acetate, EDTA, and HEDTA are shown in Figures 5.11, 5.12, and 5.13, respectively. The only apparent peak due to SERS activity is at approximately 600 cm^{-1} . This corresponds to an in-plane stretching of the carbonyl group of carboxylic acid, which has much greater intensity than the non-SERS sample.

The SERS spectrum of EDTA was collected earlier in this study. Curiously, this spectrum showed two features in addition to the carboxylic acid feature noted above. The first of these features was at approximately 1500 cm^{-1} , while the second was located at 1200 cm^{-1} . To determine the origin of these peaks, which were presumed to be from one of the CH_2 groups in EDTA, the SERS spectrum of d_4 -EDTA was collected. The d_4 -EDTA used substituted deuteriums for the hydrogens on the ethylene bridge, and so it would be expected that either the bands would be shifted or else be unaffected. Both bands shifted, suggesting that the bridge ethylene protons were the source of the observed spectral features. The presence of these two spectral features has proven difficult to reproduce, however, as indicated by the current EDTA SERS spectrum where the features are completely absent. One reason may be that making the silver particles consistently is difficult, and a feature of the particles in the first preparation was absent in the subsequent preparations. Alternatively, the solution may have had a feature that affected the SERS results; for example, SERS is known to be sensitive to solution ionic strength.

Figure 5.9.

Comparison of the FT-Raman Spectra of Oxalic Acid, Sodium HEDTA, Sodium Acetate, Citric Acid, and Sodium EDTA

Figure 5.10. FT-Raman Response of the C-H Region Versus Concentration in Liquid

Overall, the results using Raman spectroscopy for characterizing liquid tank waste had varying degrees of success. One difficulty that needs to be addressed is the sample matrix, which either reduces reproducibility or decreases sensitivity. This is not to say that Raman cannot be applied to this problem. Raman can be used to readily characterize the components of a sample. At the least, Raman can identify the functional groups present in a sample, which can act to guide further analytical work. Further development and research with the specific types of organics and sample matrix expected in tank waste should allow for fine-tuning of this screening tool. More reproducible silver dispersions could be made by controlling the reaction conditions. Organic components could be concentrated by using a suitable membrane. Such a membrane could contain the necessary silver particles as well. Finally, differences in matrices could be largely quantitated by using an elastic light scattering technique like Rayleigh scatter to provide a correction factor for quantitation.

Figure 5.11. Comparison of FT-Raman Spectroscopy (top) and Surface-Enhanced Raman Spectroscopy (bottom) of Sodium Acetate

Figure 5.12. Comparison of FT-Raman Spectroscopy (top) and Surface-Enhanced Raman Spectroscopy (bottom) of EDTA

Figure 5.13. Comparison of FT-Raman Spectroscopy (top) and Surface-Enhanced Raman Spectroscopy (bottom) of Sodium Acetate

5.2.3 Fourier Transform Infrared Spectroscopic Measurements of Solid Simulants

The infrared spectra of each of the two organic solids prepared in SY1-SIM-93B have similar diagnostic peaks. Figure 5.14 shows the FT-IR solid spectra of the C-H region for formate and HEDTA. The O-H stretching region is characterized by a strongly absorbing peak centered at approximately 3400 cm^{-1} . This peak is caused by the presence of NaOH and H_2O in the SY1-SIM-93B simulant. The C-H stretching region begins on the downward slope of this O-H stretch around 3000 cm^{-1} . Although the C-H peaks appear on the edge of the O-H peak, the C-H peak can be readily isolated and integrated (Figure 5.15). Unlike the liquid spectra, where the organic C-H peaks were more strongly absorbing than the O-H peak at high concentrations of organic, in the solids samples, the O-H peak was always more intense than the organic C-H peak. The COO^- region shows two peaks around 1600 cm^{-1} and 1400 cm^{-1} , representing the antisymmetric (1650 to 1450 cm^{-1}) and symmetric (1450 to 1360 cm^{-1}) stretches of the COO^- moiety. A nitrate peak also exists in this region and overlaps the symmetric COO^- peak as shown in Figure 5.16. Figures 5.17 and 5.18 show the standard curve of the C-H and COO^- region for formate and HEDTA. The curves show only one set of moisture data for each of the organic samples. As can be seen in these figures, the correlation between peak area and concentration is not linear for the solid samples. The lines have been drawn to illustrate the shape of the curves and have no inherent meaning. Although the concentration is reported as mole of C-H bonds per kilogram of solvent to better correlate the spectra with energy values, one point is marked on each of the curves in Figures 5.17 and 5.18 to point out where the organic concentration is approximately 3% TOC. Currently, 3% TOC is the screening limit required to evaluate the energetics of the tanks (Babad and Turner 1993).

The response of formate is not the same as that for HEDTA in either the C-H or COO^- standard curves. This was not unexpected, based on the solution organic FT-IR results. However, the magnitude of the difference between HEDTA and formate may be larger than that observed in the liquid work. Additional organic samples should be evaluated in the solid matrix to determine if the FT-IR responses will be clustered together as with the liquid FT-IR results.

The effect of moisture content on the quantitation of C-H and COO^- was examined by comparing the response of each moisture sample set. As can be seen in Figures 5.19 and 5.20, when the moisture content is above 10%, the C-H responses are similar for formate and HEDTA and COO^- responses are very similar for formate and HEDTA. However, at a moisture content of 10%, the response deviates considerably. This is because of poor contact of the solid sample with the ATR crystal. This is especially clear when examining the C-H response for the HEDTA 10% moisture curve shown in Figure 5.20. As the HEDTA concentration increases beyond 4 moles C-H bonds per kilogram of sample, the curve flattens out and even drops slightly, indicating that the significantly greater C-H concentration in the sample produced no additional response. This could only be caused by poor contact of the sample with the crystal, as is typically encountered when using ATR crystals for solids analysis. It should be noted that ATR may not be the best method for IR analysis of solid samples. However, its ease of adaptation to hot-cell work made it attractive as a first attempt for these analyses to develop a hot-cell application. Raman spectroscopy may prove to be more amenable to analysis of the solid samples, which will be discussed next.

Figure 5.14. FT-IR Spectrum of C-H Region for Solid Samples of Formate and HEDTA in SY1-SIM-93B Simulated Waste

Figure 5.15. Baseline Corrected Spectra Showing C-H Region of HEDTA and Formate

Figure 5.16. FT-IR Spectrum of Carboxylate Region for Solid Samples of Formate and HEDTA in SY1-SIM-93B Simulated Waste

Figure 5.17. Comparison of HEDTA and Formate C-H Region for Solid Sample in SY1-SIM-93B

Figure 5.18. Comparison of Formate and HEDTA COO⁻ Region for Solid Samples in SY1-SIM-93B

Figure 5.19. Effect of Water on C-H Region of Formate Solid Samples in SY1-SIM-93B

Figure 5.20. Effect of Water on C-H Region of HEDTA Solid Samples in SY1-SIM-93B

5.2.4 Fourier Transform Raman Spectroscopic Measurements of Solid Simulants

An attempt was made to apply Raman as a rapid method for screening of solid waste tank samples for organic carbon. A matrix composed of the major components of SY1-SIM-93B tank waste simulant was used as the model for this study; the actual composition of this material is shown in Table 5.1 of this report. The Raman spectrum of dry SY1-SIM-93B tank matrix is shown in Figure 5.21. As can be seen, the dry SY1-SIM-93B tank matrix spectrum has only a few features. The major spectral features are due to nitrate and nitrite. The same solid samples, spiked with either sodium formate or sodium HEDTA, that were prepared for the FT-IR solids work were used for these Raman studies.

Two calculation methods were used to quantify the organic content based on the FT-Raman data. In the first method, a direct measure of the C-H content was found by calculating the baseline corrected area of the region between 3100 cm^{-1} and 2600 cm^{-1} . This spectral area was selected because of its known spectral correlation with C-H stretches. This wide integrated area is required because of the differences in the location of the various C-H stretches. This is illustrated in Figure 5.22, which shows the Raman spectrum between 3100 to 2600 cm^{-1} of stock solid samples of sodium HEDTA, sodium formate, sodium EDTA, and sodium citrate.

It was also recognized that the various samples may have different laser radiation penetration depths and returning Raman scatter. These differences would be detrimental to any quantitative work. Nominally, an internal standard should be included to correct for these effects. Since all samples used the same SY1-SIM-93B simulant, the nitrate band at 1050 cm^{-1} was selected to serve as an internal standard. The nitrate peak was represented as the integrated area between 1150 and 950 cm^{-1} . The results are presented in Table 5.6. The calculated TOC numbers are based on the dry weight of the organic and inorganic solids. The amount of water present lowers the weight percent TOC by approximately 2 to 3%. Comparing the formate and HEDTA results in Table 5.6 using a weight basis is not entirely accurate, since there would be a greater number of moles of formate than HEDTA. Increasing the number of moles increases the number of molecules that can Raman scatter, and thus, it is expected that on a pure weight basis, a greater response should occur for the formate than the HEDTA. The moles C-H per kilogram sample was calculated as follows. The number of C-H groups per molecule was determined (two C-H groups per CH_2 unit, etc.). The weight percentage these C-H groups contribute to the molecule was calculated. This percentage was then applied to the actual weight of material added. The number of moles of C-H was then calculated by dividing by the weight of one mole of C-H. The number of moles of C-H was then divided by the total sample weight including the water contribution. Table 5.6 also includes integrated areas of the C-H and nitrate spectral peaks, and the ratio of the C-H peak versus the nitrate peak areas.

Several observations should be mentioned. Most notable is the inconsistency in the nitrate peak results. All of the samples were prepared from the same SY1-SIM-93B stock solution and were treated in a consistent manner. It would therefore be expected that factors like particle size and distribution would be consistent from sample to sample. The nitrate band should either be constant or vary in a consistent manner with, for instance, the water content, which could affect the illuminating laser penetration depth. However, inspection of the bands (shown in Figure 5.23) indicates that a difference in the band shape occurs with water and organic content. It is interesting to

Figure 5.21. FT-Raman Spectrum of Dry SY1-SIM-93B Simulant Tank Matrix

Figure 5.22. FT-Raman Spectra of the C-H Stretching Region for Sodium HEDTA, Sodium Formate, Sodium EDTA, and Sodium Citrate

Table 5.6. FT-Raman Results of Formate and HEDTA Spiked into SY1-SIM-93B Simulant Dried to Solids

<u>Organic</u>	<u>% TOC</u> <u>Calculated</u>	<u>Moles C-H per</u> <u>kg Sample</u>	<u>% Water</u>	<u>C-H Region</u> <u>Area</u>	<u>NO₃⁻ Region</u> <u>Area</u>	<u>C-H/NO₃⁻</u> <u>Ratio</u>
Formate	2.3	2.11	14	5.2	102	0.05
		1.7	30	9.6	110	0.08
HEDTA	2.3	2.5	15	13.3	121.6	0.11
		1.37	16.7	21.1	137.5	0.15
Formate	4.0	3.49	9.7	59.6	196.4	0.30
		3.45	19.2	36.7	170.4	0.22
		3.32	20.4	23.5	145.6	0.16
HEDTA	4.0	2.34	16.9	62.9	186.0	0.11
		2.19	18.8	18.6	138.6	0.13
		2.22	20.1	19.1	169.3	0.11
Formate	7.0	5.9	25	26.8	93.3	0.29
		5.35	33.3	30.6	92	0.33
HEDTA	7.0	4.2	13	51.4	82.8	0.62
		7.9	26	48.3	107.1	0.45
Formate	10.0	8.73	9.4	424.5	212.6	2.0
		9.15	17.4	109.2	64.3	1.7
		7.68	30.7	81.1	47.8	1.7
HEDTA	10.0	6.21	10.9	224.2	179.3	1.24
		5.67	18.2	169.4	168.3	1.0
		10.6	22	107.8	106.1	1.0

note that this occurs only with the HEDTA samples and not with the formate, which implies that the HEDTA has a band with an intensity that varies with water content.

Figure 5.24 is a graph of the C-H area only with percent TOC. As can be seen from the graph, only a weak trend exists between the observed C-H band areas and the percent TOC. Indeed, the scatter of the results is such that no clear distinction exists between the 2, 4, and 7% TOC levels. It is not until 10% TOC is reached that a clear discrimination occurs. Excluded from the graph are the 10% formate and HEDTA TOC values with low sample water content. In both cases, the values for both the C-H region and the nitrate bands are much higher than the other samples at the same TOC level. This suggests that a critical combination of water and organic material greatly affects the sample particle morphology. This combination of high organic content and low water content represents a potentially flammable situation, however, and thus should be considered as a positive result.

It is desirable to decrease the scatter in the data to increase the sensitivity of the results to changes in TOC. One method evaluated was to use nitrate as an internal standard. An internal standard should correct for changes in the penetration depth of the Raman laser and any loss of Raman scatter radiation. A graph of TOC versus the C-H peak area/nitrate peak area is shown in Figure 5.25. In addition, the ratio of the moles of C-H per kg of sample versus the C-H/nitrate band ratios is shown in Figure 5.26. In both of these cases where the C-H peak area is normalized, there is a distinct trend in FT-Raman response with increasing organic C-H content of the sample.

Figure 5.23. Difference in the Nitrate Peak Observed by FT-Raman as a Function of the Sample Water Content or Organic Concentration (HEDTA)

Figure 5.24. Plot of the C-H Region Area from FT-Raman Versus TOC for Sodium Formate or Sodium HEDTA spiked into SY1-SIM-93B Simulant

Figure 5.25. Plot of the Normalized C-H Region Area from FT-Raman Versus TOC from Sodium Formate or Sodium HEDTA Spiked into SY1-SIM-93B Simulant at Various Water Concentrations

Figure 5.26. Plot of the Normalized C-H Region Area from FT-Raman Versus Moles C-H per kg Sample for Sodium Formate and Sodium HEDTA Spiked with SY1-SIM-93B Simulant at Various Water Concentrations

We also evaluated the sampling precision. The laser beam, approximately 1 mm in diameter, illuminates a sample that is approximately 2 cm in diameter and 1 cm high. Small sample inhomogeneities are certainly possible. This was characterized by taking several spectra in slightly different locations from two samples: the 4% TOC/20% water formate sample and the 10% TOC/11% water HEDTA sample. It was found that the C-H/NO₃ ratio varied by 27% for the formate and 19% for the HEDTA. This approximate variability was mirrored by each TOC group.

Overall, the results from this experiment are mixed. A definite trend exists between the C-H content and the spectral response. This trend becomes the most predictable when using moles C-H versus kilogram of sample ratioed against the nitrate content to characterize the sample's organic content. The trends for the formate and HEDTA are not convergent at higher organic loadings, however. This is due partly to differences in the C-H Raman response for formate and HEDTA, which is to be expected. It is also apparent that the formate and HEDTA response is essentially flat for the lower organic concentrations, which may be due to differences in sample preparation. The 2.3% and 7% TOC samples were prepared separately from the 4% and 10% TOC samples. Although the samples used the same SY1-SIM-93B stock solution, the measured nitrate peak areas differ by approximately 50% between the 4% and 10% TOC group and the 2.3% and 7% TOC group (see Table 5.6). Slight changes in the sample preparation (particularly the evaporation step) grossly affected the optical properties of the sample. This impact must be considered when extending this method to actual waste tank samples where the matrix is extremely uncontrolled. It may be possible to correct for differences in actual samples by, for instance, characterizing a component in the waste that is known to have a narrow band in the spectrum (the nitrate for example). Once this is known, then a correction factor may be applied to the results. Alternatively, this waste correction factor may also be found by characterizing the optical properties of the waste by using the Rayleigh scatter.

6.0 Conclusions

Preliminary results from the Fourier transform infrared and Raman spectroscopy studies suggest that spectroscopic determination of functional groups will be a good indicator of enthalpy content. For example, FT-IR analysis of liquid simulant samples showed that COO^- content could be quantitated within 20% relative error for different organics and C-H content within 30% relative error. Again, since the goal of this analytical method is to provide a screening tool to determine relative enthalpy content of tank waste samples in a hot-cell and not complete quantitation, these preliminary results are well within the range of a useful screening tool. Additional work on testing mixtures of organics and testing actual tank waste samples that have been speciated for comparison should be completed for final testing of this method. A summary of the key findings of these two spectroscopic techniques is provided.

FT-Raman Spectroscopy

- Non-linear but predictable trend of C-H response over the range of 2 - 8 moles C-H bond/kg sample. Little variation due to water content of the solid samples was observed.
- Linear C-H response for liquid samples down to a level of 0.5% w/w was obtained. However, there was some difference in response for different organic compounds.
- Initially may need more development than FT-IR for liquid samples and hot-cell applications, but is more amenable in the long term for solid samples and in-tank analysis with fiber optic probes.

FT-Infrared Spectroscopy

- Solution response for mole carboxylate/kg solution was linear for all organics tested. The maximum COO^- error was 20%.
- Solution response for C-H was linear for all organics tested. The quantitation of C-H was broken into three distinct wavelength regions in the spectrum. Quantitation errors using these three regions resulted in a maximum error of 27%.
- Solid response for carboxylate and C-H was non-linear, but quantifiable. Quantitation errors are possible for TOC levels greater than 4% COO^- because almost all of the light is absorbed by the sample.
- Moisture content did not affect quantitation of COO^- or C-H of solids unless the samples contained less than 10% total water. This is due to poor contact of the sample with the crystal. This can likely be resolved by adding a slight amount of liquid to the sample to ensure good contact during analysis.
- Quantitation of COO^- and C-H is excellent for solution work; however, solution work requires sample preparation. Quantitation of COO^- and C-H for solids works well; however, solid analysis may require minimal treatment of the sample if the moisture level is too low (i.e., addition of small quantity of water to facilitate crystal contact).

- Remote analysis systems are in use currently by industry; however, sensitivity and other problems may be encountered with deployment to remote tank analysis.
- For solids analysis, attenuated total reflectance may not be the best method. It was chosen because of its ease for implementation into the hot cell working environment.

The complementary nature of infrared and Raman spectroscopy was apparent for the solid and liquid simulant waste samples studied. There may be some possible ways to correct for the changes in tank matrix that would otherwise interfere with results. For Raman, the Rayleigh line (elastically scattered radiation) could, in theory, be used to partially correct for the matrix effects. Similarly for FT-IR, the 2200 cm^{-1} region of the spectrum, where no distinct features are present, could be used to correct for scattering due to the tank matrix. Additional work on testing mixtures of organics and testing actual tank waste samples that have been speciated for comparison should be completed for final testing of this method.

However, DSC-obtained experimental reaction enthalpies for selected organics typically found in Hanford tank waste are significantly lower than theoretically calculated reaction enthalpies (Burger 1995) and do not show clear trends with C-H and COO^- content. This is most likely due to the complex nature of the reactions occurring as suggested by the discrepancy with calculated reaction enthalpies and the detection of gases such as ammonia during DSC analysis. Fourier transform IR and Raman may help supplement the information obtained by DSC analysis to provide a better estimate of tank safety from an energetics standpoint.

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Meisel D, CD Jonah, S Kapoor, MS Matheson and MC Sauer Jr. 1993. *Radiolytic and Radiolytically Induced Generation of Gases from Synthetic Wastes*, ANL-93/43, Argonne National Laboratory, Argonne, Illinois.

Oscarson JL, and RM Izatt. 1992. "Calorimetry." In: *Physical Methods of Chemistry*, eds. BW Rossiter and RC Baetzold. John Wiley & Sons, New York, pp. 573-620.

Pool KH, RR Adey, DL Baldwin, RM Bean, SA Bryan, IE Burgeson, MC Burt, JA Campbell, NG Colton, LC Cronk, SA Clauss, SK Fadeff, SA Homi, FV Hoopes, EW Hoppe, TY Hosaka, GS Klinger, BD Lerner, RB Lucke, GM Mong, JK Rau, DE Rinehart, LM Robbins, GA. Ross, DR Sanders, RW Sanders, RL Sell, MJ Steele, RT Steele, SR Strebin, SW Thomson, JM Tingey, and JJ Wagner. 1994. *Waste Tank Organic Safety Project: Analysis of Liquid Samples from Hanford Waste Tank 241-C-103*. PNL-9403. Pacific Northwest Laboratory, Richland, Washington.

Scheele RD, JL Sobolik, RL Sell, and LL Burger. 1995. *Organic Tank Safety Project: Preliminary Results of Energetics and Thermal Behavior Studies of Model Organic Nitrate and/or Nitrite Mixtures and a Simulated Organic Waste*, PNL-10213, Pacific Northwest Laboratory, Richland, Washington.

Webb AB, JL Stewart, DA Turner, MG Plys, B Malinovic, JM Grigsby, DM Camaioni, PG Heasler, WD Samuels, and JJ Toth. 1995. *Preliminary Safety Criteria for Organic Watch List Tanks at the Hanford Site*. WHC-SD-WM-SARR-033, Rev. 0, Westinghouse Hanford Company. Richland, Washington.

Appendix A

Letter Report

Literature Search in Support of Feasibility Study of Raman and Infrared Spectroscopic Detection of Organics in Heterogeneous Solids

Letter Report

Literature Search in Support of Feasibility Study of Raman and Infrared
Spectroscopic Detection of Organics in Heterogeneous Solids

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December 1995

Prepared for Westinghouse Hanford Company
under a Related Services Agreement
with the U.S. Department of Energy
Contract DE-AC06-76RLO 1830

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Richland, Washington

INTRODUCTION

This literature search was conducted in support of the feasibility study of Raman and infrared spectroscopy for in situ determination of organic functional groups present in Hanford tank waste. The feasibility studies were initiated simultaneously with the literature search. The main goal of the brief literature search was to find precedence for spectroscopic quantitative determination of organic functional groups, namely C-H, C-O, and C-C, in complex solids. The ultimate goal of the experimental feasibility studies is to be able to analyze directly in the waste tanks for organic functional groups to eliminate the need for costly tank sampling, transfer of radioactive waste-tank samples to the laboratory, and manipulation of these samples before analysis. The strategy of the literature search is presented below in addition to two bibliographies: references collected and reviewed and references not collected due to time constraints for obtaining articles from interlibrary loan (included in the appendices). Summaries of some of the key references obtained are provided.

STRATEGY

1. Read Analytical Chemistry Journal Fundamental Reviews 1990, 1992, and 1994 for references in the Infrared Spectroscopy and Raman Spectroscopy sections.
2. Search CD-ROM databases in the Hanford Technical Library for specific keywords in a variety of combinations.
 - Databases: chemistry citations, pollution and toxicology (PollTox), national technical information service (NTIS), chemistry abstracts, and DOE energy science reports.
 - Keywords: organics, in situ, spectroscopy, quantitation, hydrocarbon, remote analysis
3. Author searches on the CD-ROM databases from key authors found in subject searches.

From these searches, a total of 40 references were identified and collected for further review, and a total of 15 references were identified but have not been obtained at the time of this report because they had to be ordered through inter-library loan or document retrieval. Some of the most promising articles/books from this list have been requested and should be received in the near future. A bibliography of the references that either were obtained or are readily available at the Hanford Technical Library is provided in Appendix A, and the bibliography of the references that are not readily available but which may be of interest to order is provided in Appendix B.

SUMMARY

Two articles were found that discuss the quantitation of total C-H content in pure organic compounds and in simple solutions by integration of the intensity measurements of the C-H overtone region in the near-infrared (Wexler 1968; Powell et al. 1971). Wexler determined that for pure compounds, the integrated intensities of the second overtone region per C-H bond are nearly the same for most aliphatic, aromatic, and ethylenic bonds. Certain methyl branching would cause a lowering of the integrated intensity and alicyclic rings would cause an increase in intensity. In addition, it was noted

that electron withdrawing groups such as nitro, nitrile, nitrate, and sulfoxide would also cause a lowering of intensity of the C-H measurement.

Powell et al. (1971) determined the quantitation capability of integrating over the C-H second overtone region in the near-infrared for solutions of various organics in carbon tetrachloride solutions from 0.01 to 0.10 M. From these studies, it was determined that the analysis of a mixture containing all of the compounds investigated would have a maximum error of 17%. This error is due to the variability in the response/intensity of different C-H bonds found in the organics studied, which included alkanes, alkenes, cycloalkanes, and branched hydrocarbons. Each specific organic gave a linear calibration curve of intensity of the C-H overtone region to concentration.

Neither of these research groups applied this C-H determination method to complex solutions or solids. However, if there is no interference from other bonds in the near-infrared region of the C-H overtones, it should be feasible. A table of the wavelength regions and absorptivities of functional groups observed in the near-infrared region was found in Polesello and Giangiacomo (1983). This information is included in Table 1.

Another reference was found that examined 50 compounds for determining the correlation between the absorptivities of the methyl and methylene groups and the amount of functional groups present (Tosi and Pinto 1972). They found a linear relationship between absorptivity and chain length.

Near-infrared spectroscopy and chemometric learning algorithms were used to determine heat of formation, molecular weight, and number of methyl groups per molecule for hydrocarbon mixtures (Honings et al. 1985). Calibrations accurate to 1.2 kcal/mol for determining heats of formation, 1.5 g/mol for determining mean molecular weight, and 0.057 groups/molecule for methyl groups per molecule were obtained. A table containing the wavelengths and weighing coefficients used to spectrophotometrically determine the heat of formation, mean molecular weight, and methyl groups per molecule for a series of hydrocarbon mixtures is given. Calibration sets of 42 samples and performance verification sets of 48 samples were used to develop each correlation. Extrapolation of this type of analysis to heterogeneous solid samples may be difficult due to the number of representative training-set samples required to develop correlations for near-infrared analyses.

Attempts to find references to the organic sensors used by the oil industry for down-hole analysis were unsuccessful. This may be in part due to the databases searched and the journals that are readily available in the Hanford Technical Library.

Many references of hydrocarbon analysis in soils and groundwater were identified and have been ordered through inter-library loan services, but were not available in time for inclusion in this letter report.

HANFORD TANK WASTE SPECIFIC REFERENCES

Finally, DOE reports, written by various laboratories, on Raman spectroscopy development for Hanford tank-waste characterization have been compiled. Considerable documentation exists on supporting the potential of Raman spectroscopy for tank waste characterization.

Preliminary design of in-tank probes have been proposed by Lawrence Livermore National Laboratory (Kyle 1994) in addition to some feasibility studies of two proposed methods. Kyle noted an observed effect of moisture content on the nitrate signal obtained by Raman spectroscopy. A

decrease of 73% intensity was observed for the sodium nitrate peak when switching from dry sodium nitrate to 20 weight percent water sodium nitrate sample. Kyle proposed that this effect was due to the concomitant decrease in sample reflectivity as the moisture content increased.

A substantial progress report was prepared by Mann and Vickers (1994) on development of Raman spectroscopy for waste-tank characterization. Included were preliminary results from analysis of salt-cake simulants and waste-tank samples. Efforts were primarily aimed at analyzing for inorganic and ferricyanide and ferrocyanide components. However, preliminary Raman spectra of organic compounds expected to be present in the waste tanks were also obtained. Fiber-optic-probe considerations and testing for potential in-tank deployment were discussed.

Jones et al. (1992) proposed the use of photoacoustic spectroscopy (PAS) and transient infrared spectroscopy (TIRS) for on-site infrared analysis with little or no sample preparation. Both of these techniques are being tested for analysis of radioactive materials, and TIRS is being tested for analysis of solids and viscous liquids. Photoacoustic spectroscopy is a sensitive technique for the analysis of small gaseous samples. A beam of infrared light is pulsed into the sample cell. If the sample gas absorbs the light, the gas is heated by the energy pulses, and its temperature is altered. These temperature modulations create pressure fluctuations that are monitored as sound waves by an external microphone.

Transient infrared spectroscopy is a method designed to analyze solids and viscous liquids moving along a process line (Jones et al. 1992). It is being developed to monitor waste content in the encapsulation matrix to determine if the appropriate ratio of waste to polyethylene is maintained. This is one potential pretreatment technique for Hanford radioactive waste minimization. Applicability of this technique to in situ analysis of tank waste for organics is not readily feasible.

Other reports by Westinghouse Hanford Company addressed the issues of importance for potential deployment of Raman Spectroscopy for in-tank characterization or for hot-cell applications (Crawford et al. 1994; Lombardi et al. 1994; Lopez et al. 1995; Phillip 1994).

CONCLUSION

Only limited references, with the exception of DOE reports from a variety of laboratories dealing specifically with Hanford tank-waste analysis, had any direct relation to providing information on the capability of determining C-H content in solids and sludges by infrared and Raman spectroscopy.

Table 1. Spectra-Structure Correlations and Average Molar Absorptivity Data for Near-Infrared Region

	Microns																						
	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9	3.0	3.1	
>NH amine																							
Aromatic						-0.5														-20			
Aliphatic	-					-0.5															-1		
NH ₂ amide					0.7	-0.7				3	0.5	-0.5						100		-100			
>NH amide						-1.3					-0.5									-100			
$\begin{array}{c} \text{H} \\ \diagup \\ \text{N} \\ \diagdown \\ 4 \end{array}$ anilide						-0.7					0.9	-0.3								-100			
>NH imide	-					-															-		
-NH ₂ hydrazine	-					0.5	-0.5				-										-		
-OH alcohol						-2					(-)								-50				
-OH hydroperoxide																							
Aromatic					1	-1					-1.3								30		30		
Aliphatic					-2						-0.8										80		
-OH phenol																							
Free						-3					-									-200			
Intramolecularly bonded																					Variable		
-OH carboxylic acid						-														-10	-100		
-OH glycol																							
1.2																		50		50			
1.3																		20		50	20-100		
1.4																		50		80	5-40		
OH water						-0.7				-1.2								30		-7			
=NOH oxime						-														-200			
HCHO (possible hydrate)																							
-SH											-0.05												
PH										-0.2													
C=O																					-3		
-C=N										-0.1													

Polisello, A. and R. Giangiacomo. 1983. "Application of Near IR Spectrophotometry to the Non-Destructive Analysis of Foods: A Review of Experimental Results." *CRC Critical Reviews in Food Science and Nutrition*, 18:203-230.

Table 2. Spectra-Structure Correlations and Average Molar Absorptivity Data for Near-Infrared Region

	Microns																					
	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9	3.0	3.1
Terminal =CH ₂ Vinylxy (-OCH=CH ₂) Other		—		—	—0.02		—0.3	—0.3				—0.2	—0.2	—0.5								
Terminal —CH—CH ₂ O		—		—			—0.2						—1.2									
Terminal —CH—CH ₂ CH ₂				—			—						—									
Terminal =CH	—					—1.0																
C18—CH=CH	—											—0.15									—50
—		—			—					—	—			—						
—CH ₃			—0.02	—				—0.1						—0.3								
>CH ₂		—0.02	—	—				—0.1						—0.25								
\C—H		—		—				—														
—CH aromatic				—0.1			—0.1															
—CH aldehydic													—0.5									
—CH (formic)												—1.0										
—NH ₂ amine																						
Aromatic	—0.04			0.2	—1.4						—1.5								30	—	—30	
Aliphatic	—				—0.5						—0.7								1	—5	—2	

References Collected and Reviewed

Aldridge, P. K., J. J. Kelly, J. B. Callis and D. H. Burns. 1993. "Noninvasive Monitoring of Bulk Polymerization Using Short-Wavelength Near-Infrared Spectroscopy." *Anal. Chem.* **65**, 3581-3585.

Discusses use of near-infrared spectroscopy for in situ process monitoring of polymer formation. The present conversion of methyl methacrylate to monomer to poly (methyl methacrylate) is monitored by observing loss of the vinyl CH's (converted to methylene CH's).

Angel, S. M., T. J. Kulp and T. M. Vess. 1992. "Remote-Raman Spectroscopy at Intermediate Ranges Using Low-Power CW Lasers." *Appl. Spectrosc.* **46**, 1085-1091.

Development of portable Raman system for spectral measurements of remotely located samples up to 20 m away. Application of the system includes monitoring organic and inorganic compounds at toxic waste sites. Discusses instrumentation and optics. Considerations for long range measurements. Effects of sampling distance on observed signals were addressed with minimal emphasis on data interpretation and specific functional group identification.

Asher, S. A. 1993. "UV Resonance Raman Spectroscopy for Analytical, Physical, and Biophysical Chemistry." *Anal. Chem.* **65**, 59A-66A.

Good primer on Raman scattering. Part I of this two-part article deals with instrumentation, phenomenology, and fundamental applications of Resonance Raman spectroscopy.

Brown, T. L. 1958. "Infrared Intensities and Molecular Structure." *Chem. Rev.* **58**, 581-609.

Review of relationship between infrared intensities and structure.

Chan, K., H. Ito and H. Inaba. 1984. "Remote Sensing System for Near-Infrared Differential Absorption of CH₄ Gas using Low-Loss Optical Fiber Link." *Appl. Opt.* **23**, 3415-3420.

Discusses an all-optical remote sensing system for detection of methane gas by monitoring the C-H overtone region in the near-infrared region. Attempts to push the distance for remote operation to 20-km fiber-optic probes were proceeding.

Chong, C. K., C. Shen, Y. Fong, J. Zhu, F. X. Yan, S. Brush, C. K. Mann and T. J. Vickers. 1992. "Raman Spectroscopy with a Fiber optic Probe." *Vib. Spectrosc.* **3**, 35-45.

Discusses general use of fiber-optic probes for remote analysis.

Ciurezak, E. W. 1995. "Near-IR Spectroscopy." *Today's Chemist at Work.* 31-36.

Good overview of near-infrared spectroscopy.

Crawford, B. A., F. L. Kohlasch, J. R. Jewett and D. A. Dodd. 1994. "Assessment of Argon Ion Laser Dispersive Raman Spectroscopy for Hot Cell Applications." WHC-SD-WM-RPT-098. Westinghouse Hanford Company, Richland, Washington.

Recommendations for continued development of Raman spectroscopy for ultimate tank waste characterization analysis. Suggest the use of nitrate as an internal standard for quantitation purposes. Also recommend that a 750 nm laser Raman system or a Fourier transform Raman system should be used to avoid silica interference that heavily plagued the argon-ion laser based instrument used.

Francis, S. A. 1950. "Absolute Intensities of Characteristic Infra-Red Absorption Bands of Aliphatic Hydrocarbons." *J. Chem. Phys.* 18, 861-864.

Gerrard, D. L. and J. Birnie. 1992. "Raman Spectroscopy." *Anal. Chem.* 64, 502R-513R.

Major review of Raman spectroscopy advances over a two-year period with numerous references.

Gerrard, D. L. 1994. "Raman Spectroscopy." *Anal. Chem.* 66, 547R-557R.

Major review of Raman spectroscopy advances over a two-year period with numerous references.

Hibbard, R. R. and A. P. Cleaves. 1949. "Carbon-Hydrogen Groups in Hydrocarbons: Characterization by 1.10- to 1.25-Micron Infrared Absorption." *Anal. Chem.* 21, 486-492.

Honings, D. E., T. B. Hirschfeld, and G. M. Hieftje. 1985. "Near-Infrared Determination of Several Physical properties of Hydrocarbons." *Anal. Chem.* 57, 443-445.

Near-infrared spectroscopy and chemometric learning algorithms are used to determine heat of formation, molecular weight, and number of methyl groups per molecule for hydrocarbon mixtures.

Jones, R. W., S. Ochiai and J. F. McClelland. 1992. "On-Site Infrared Analyses for Complex Systems." IS-M-723 or Conf-920791-8. Ames Laboratory, Ames, IA.

Discusses use of photoacoustic spectroscopy (PAS) and transient infrared spectroscopy (TIRS) for on-site infrared analysis with little or no sample preparation. Both of these techniques are being tested for analysis of radioactive materials and TIRS is being tested for analysis of solids and viscous liquids. Photoacoustic spectroscopy is a sensitive technique for the analysis of small gaseous samples. A beam of infrared light is pulsed into the sample cell. If the sample gas absorbs the light, the gas is heated by the energy pulses, and its temperature is altered. These temperature modulations create pressure fluctuations which are monitored as sound waves by an external microphone.

Transient infrared spectroscopy is a method designed to analyze solids and viscous liquids moving along a process line. It is being developed to monitor waste content in the encapsulation matrix to determine if the appropriate ratio of waste to polyethylene is maintained. This is one potential pretreatment technique for Hanford radioactive waste minimization. Applicability of this technique to in situ analysis of tank waste for organics is not readily feasible.

Kelly, J. J., C. H. Barlow, T. M. Jinguji and J. B. Callis. 1989. "Prediction of Gasoline Octane Numbers from Near-Infrared Spectral Features in the Range 660-1215 nm." *Anal. Chem.* **61**, 313-320.

Used near-infrared spectroscopy to predict the quality parameters of gasoline. A relationship does exist between chemical structure, as identified by near-infrared spectral features, and fuel performance as determined by octane number. Numerous test samples were required to set up the correlation and multivariate analysis. The absorptivities of the overtones or combinations of carbon-hydrogen stretching vibrations observed in the near-infrared spectroscopic region are largely independent of the remainder of the molecule but are dependent on the concentration of the absorbing group.

Kelly, J. J. and J. B. Callis. 1990. "Nondestructive Analytical Procedure for Simultaneous Estimation of the Major Classes of Hydrocarbon Constituents of Finished Gasolines." *Anal. Chem.* **62**, 1444-1451.

Near-infrared spectroscopy is used to estimate the major classes of hydrocarbons in gasolines. Training sets of well characterized samples are required to successfully set up the method.

Koglin, E. and M. J. Schwuger. 1992. "In Situ Analysis of Adsorbed Molecules by Microsurface-enhanced Raman Scattering." *Faraday Discuss.* **94**, 213-220.

Use of surface-enhanced Raman spectroscopy for in situ study of liquid/solid interfaces. Efforts focus on obtaining information from very small sample sizes for spots down to one micrometer and from dilute solutions.

Krska, R., K. Taga and R. Kellner. 1993. "New IR Fiber-Optic Chemical Sensor for In Situ Measurements of Chlorinated Hydrocarbons in Water." *Appl. Spectrosc.* **47**, 1484-1487.

Use polyethylene coated silver halide fibers as fiber-optic sensors for chlorinated hydrocarbons in water. Good quantitation was achieved for relatively simple solutions.

Kyle, K. R. 1994a. "Test Report for Remote vs. Contact Raman Spectroscopy." UCRL-ID-116643. Lawrence Livermore National Laboratory, Livermore, CA.

Compares two possible sampling systems for in-tank Raman analysis.

Kyle, K. R. 1994b. "Conceptual Design of a Raman Probe for Inclusion in the In-Tank Cone Penetrometer." UCRL-ID-118926. Lawrence Livermore National Laboratory, Livermore, CA.

Lombardi, D. R., C. Wang, B. Sun, A. W. Fountain, III, T. J. Vickers, C. K. Mann, J. G. Douglas, F. L. Kohlasch and F. R. Reich. 1994. "Quantitative and Qualitative Analysis of Some Inorganic Compounds by Raman Spectroscopy." WHC-SA-2098-FP. Westinghouse Hanford Company, Richland, Washington.

Lopez, T., F. R. Reich and J. G. Douglas. 1995. "Summary of FY 1994 Raman Spectroscopy Technology Cold Test Activities." WHC-SD-WM-RPT-116, Rev. 0. Westinghouse Hanford Company, Richland, Washington.

Mann, C. K., T. J. Vickers and J. D. Womack. 1987. "Detection and Determination of Minor Components in Nominally Pure Solids by Raman Spectroscopy." *Appl. Spectrosc.* **41**, 1324-1329.

Discusses difficulties in determining minor impurities in relatively pure colorless solids. Sulfanilic acid and sulfanilamide could be detected as impurities down to 0.5% level with Raman spectroscopy. Different methods for quantification based on cross-correlation of the spectrum or least-squares fitting were compared. Quantification by least-squares fitting without first subtracting out the large background feature was unsatisfactory. Cross-correlation, however, is useful when the analyte is found in the presence of a constant background (such as perhaps nitrate in tank waste).

Mann, C. K. and T. J. Vickers. 1994. "Detection and Quantitative Analysis of Ferrocyanide and Ferricyanide: FY 93 Florida State University Raman Spectroscopy Report." WHC-SD-TD-RPT-010. Westinghouse Hanford Company, Richland, Washington.

Large progress report from Florida State University Raman Spectroscopy development for waste tank characterization. Included are preliminary attempts at Raman analysis of salt cake simulants and waste tank samples. Raman analysis of organic components expected to be present in waste is also addressed. Fiber optic probe considerations and testing for potential in tank deployment were discussed.

McClure, W. F. 1994. "Near-Infrared Spectroscopy The Giant is Running Strong." *Anal. Chem.* **66**, 43A-53A.

Historical development of near-infrared spectroscopy instrumentation.

Mizaikoff, B., R. Gobel, R. Krska, K. Taga, R. Kellner, M. Tacke and A. Katzir. 1995. "Infrared Fiberoptic Chemical Sensors with Reactive Surface-Coatings." *Sensors and Actuators B-Chemical*. **29**, 58-63.

Noble, D. 1995. "Illuminating Near-IR." *Anal. Chem.* **735A**-740A.

Brief overview of near-infrared spectroscopy instrumentation available.

Parker, S. F., N. Conroy and V. Patel. 1991. "Some Consequences of the Fourier Transform in Fourier Transform Raman Spectroscopy." *Spectrochim. Acta Part A*. **49A**, 657-666.

Highlights the advantages and disadvantages of FT Raman spectroscopy compared to traditional dispersive Raman instrumentation.

Philipp, B. L. 1994. "Environmental Requirements for Hanford Deployable Cone Penetrometer Raman Spectroscopy Fiber Optic Probes." WHC-SD-TD-RPT-008. Westinghouse Hanford Company, Richland, Washington.

Describes the potential environment a Raman spectroscopy instrument and fiber-optic probe could be exposed to for in situ analysis of Hanford tank waste.

Polesello, A. and R. Giangiacomo. 1983. "Application of Near Infrared Spectrophotometry to the Nondestructive Analysis of Foods: A Review of Experimental Results." *CRC Critical Reviews in Food Science and Nutrition*. **18**, 203-230.

Contains table of near-infrared functional group wavelengths and molar absorptivities.

Powell, D. L., B. J. Darland and T. R. Williams. 1971. "The Determination of Total C-H by Near Infrared Analysis." *Anal. Lett.* 4, 479-483.

Integrated intensity over the first overtone of the C-H stretch region in the near-infrared spectral region to quantitate total hydrogen bonded to carbon. For simple mixtures in solution, an accuracy of 10% was obtained.

Putzig, C. L., M. A. Leugers, M. L. McKelvy, G. E. Mitchell, R. A. Nyquist, R. R. Papenfuss and L. Yurga. 1992. "Infrared Spectrometry." *Anal. Chem.* 64, 270R-302R.

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