

## CHARACTERIZATION OF HANFORD TANK WASTES CONTAINING FERROCYANIDES

J.M. Tingey, J.D. Matheson, S.G. McKinley, T.E. Jones, and K.H. Pool  
Pacific Northwest Laboratory\*  
Richland, Washington

### ABSTRACT

During the 1950's, radiocesium was scavenged from aqueous nitrate-containing wastes to obtain additional waste storage space at the Hanford site. The radiocesium was scavenged by adding sodium or potassium ferrocyanide and nickel sulfate to waste from the uranium recovery process. In this scavenging process, the cesium in the supernatant of this waste stream was precipitated as cesium nickel ferrocyanide. Excess sodium existed in this waste stream; therefore, the primary constituent of the precipitate from this process was sodium nickel ferrocyanide. After the radiocesium scavenging processes were completed and storage space was obtained, other waste types were added to those tanks which contained the ferrocyanide precipitates. These tanks have been declared an unreviewed safety question (USQ) because of potential thermal reactivity hazards associated with the ferrocyanide compounds and nitrate and nitrite. Hanford tanks with waste containing 1000 gram moles of ferrocyanide have been sampled. Extensive chemical, radiochemical, and physical characterization have been performed on these waste samples. The reactivity of these wastes were also studied using Differential Scanning Calorimetry (DSC) and Thermogravimetric analysis.

### INTRODUCTION

During the 1950s, radiocesium was scavenged from aqueous nitrate-containing wastes to obtain additional waste storage space at the Hanford site. The radiocesium was scavenged by adding sodium or potassium ferrocyanide and nickel sulfate to waste from the uranium recovery process. In this scavenging process, the cesium in the supernatant of this waste stream was precipitated as cesium nickel ferrocyanide  $[\text{NiCs}_2\text{Fe}(\text{CN})_6]$ . Excess sodium existed in this waste stream; therefore, the primary constituent of the precipitate from this process was sodium nickel ferrocyanide. Often strontium was also scavenged from the supernatant. By removing the cesium and strontium, the concentration of the long lived radioisotopes was sufficiently reduced in the supernate that the supernate could be transferred to cribs on the Hanford Site. The removal of the supernate provided the needed waste storage space in these underground tanks.

Currently, 17 storage tanks on the Hanford Site that are believed to contain >1000 gram moles (465 lb) of ferrocyanide compounds have been identified. Seven other tanks are classified as ferrocyanide-containing waste tanks, but contain <1000 gram moles of ferrocyanide compounds. These seven tanks are still included on the Hanford Watch List.

After the radiocesium scavenging processes were completed and storage space was obtained, other waste types were added to those tanks which contained the ferrocyanide precipitates. These tanks have been declared an unreviewed safety question (USQ) because of potential thermal reactivity hazards associated with the ferrocyanide compounds and nitrate and nitrite.

Cyanides are strong reductants and are known to react explosively with nitrates, nitrites, chromates, and other strong oxidants. The explosive behavior of cyanides with nitrates and nitrites has been reported for many years (1,2,3) and is the basis for an Austrian explosives patent. (4)

Since the mid 1980s, the potentially explosive reactions of ferrocyanides with nitrates and nitrites have been studied at the Pacific Northwest Laboratory (PNL) with both synthetic and actual tank wastes. (5,6,7,8) Hanford tanks with waste containing >1000 gram moles of ferrocyanide have been sampled. Extensive chemical, radiochemical, and physical characterization have been performed on these waste samples. The reactivity of these wastes was also studied using differential scanning calorimetry (DSC) and thermogravimetric analysis.

### EXPERIMENTAL APPROACH

Tank waste simulants were prepared following the cesium scavenging flowsheets used at Hanford in the 1950s. (9,10) Actual tank waste samples were retrieved from Tank 241-C-112 using a specially designed and equipped core-sampling truck. This core-sampling method is used to preserve waste stratification, collect samples within 3 in. of the bottom of the tank, minimize the radiation exposures and potential for releases of radioactive materials, and prevent any thermal or spark initiation of ferrocyanide reactions. The core-sampling truck obtains samples in samplers that are 19 in. in length and 7/8 in. in diameter with a volume of 190 mL. Each sample is identified as a segment, with the first sample obtained from the top of the tank. Successive 19-in. samples are obtained until the entire tank depth has been sampled. Two 19-in. segments were needed from Tank 241-C-112 to characterize the entire depth of the waste in this tank.

The tank waste samples were transferred to a shielded radiochemistry facility (PNL's High-Level Radiochemistry Facility that is also called the 325-A Hot-Cell Facility), which was designed to handle highly radioactive material. The samples were retrieved from the core sampler and processed as shown in Fig. 1. During this process the tank sample was subsampled every 4.75 in. along the core. These samples are called quarter segments, since four of these samples are taken from a 19-in. segment. These samples were then analyzed for

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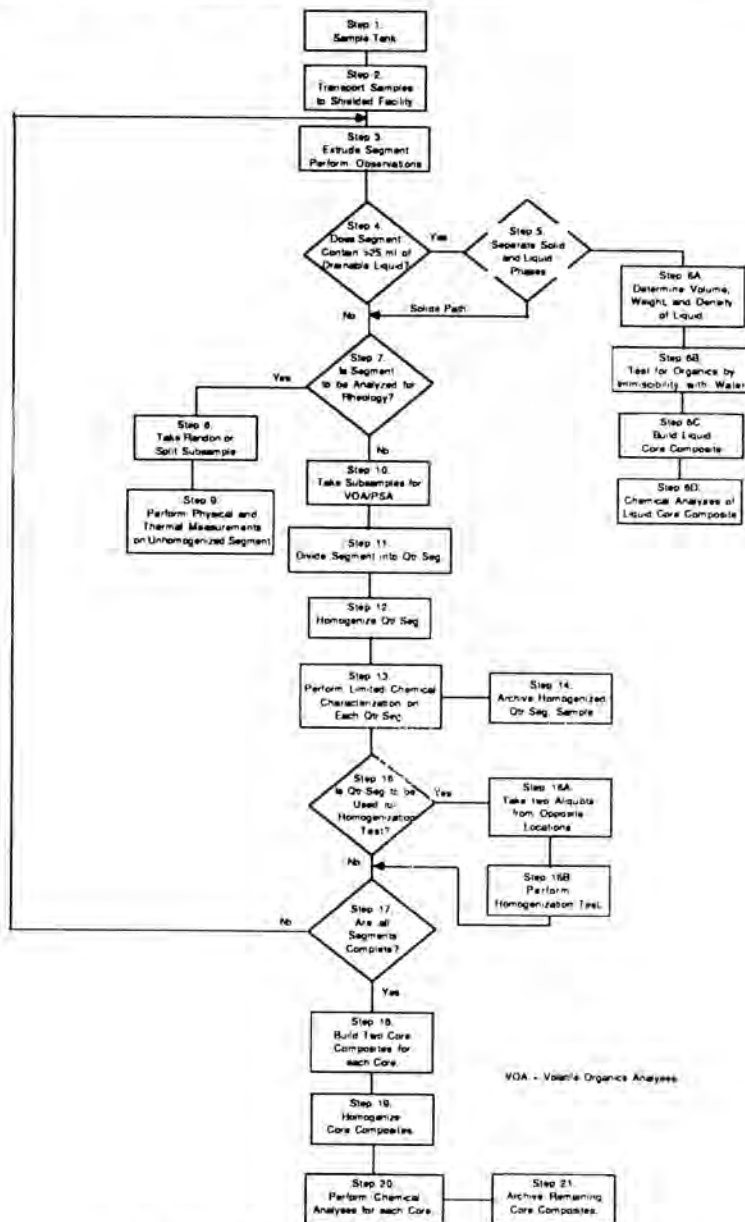


Fig. 1. Tank 241-C-112 core sample flowsheet.

chemical and radiochemical composition, physical properties, and thermal behavior. A composite of the entire core was also prepared that was analyzed more extensively than the quarter segments. The analyses performed on the quarter segments and core composite are given in Table I.

### ANALYSIS

Only a small portion of the data obtained from this characterization effort will be reported in this paper. The characterization data for this tank has been reported in three core data reports by S. G. McKinley et al. 1992.\* This report will deal primarily with the cyanide and carbon analyses, thermal analyses, and limited physical property measurements.

Total cyanide analyses were performed using a microdistillation method that was modified for use in shielded radiochemistry facilities. The sample was dissolved with a solution 0.17 M in EDTA and 0.83 M in ethylenediamine. The dissolved sample was then distilled with a  $\text{H}_2\text{SO}_4/\text{MgSO}_4$  releasing solution and a NaOH trap solution. The distillation was performed at 125°C. The distillate was then analyzed for cyanide using an argentometric titration. The total cyanide analyses method is effective for tank waste samples where the concentration of total cyanide is greater than approximately 0.1 wt%. The detection limit for this procedure is approximately 20  $\mu\text{g}$  cyanide.

Carbon analyses including total carbon, total organic carbon, and total inorganic carbon was performed using a hot

\* S. G. McKinley, L. R. Greenwood, E. W. Hoppe, J. M. Tingey, and M. W. Urie. "Single Shell tank Waste Characterization Project and Safety Analysis Project Core 34 Data Report (Tank 241-C-112)." Letter Report to Westinghouse Hanford Company, Richland, Washington (1992).

**TABLE I**  
Analyses Performed on Tank 241-C-112 Core Samples

Quarter Segment Level Analyses			
Direct	Fusion/Dissolution	Water Leach	
Total Organic Carbon	GEA	Anions by Ion Chromatography	
DSC	<sup>90</sup> Sr	Cyanide	
STG	ICP		
Cyanide			
Wt% Water			
Core Composite Analyses			
Direct	Fusion/Dissolution	Acid Digestion	Water Leach
Carbon Analyses	ICP	ICP	ICP
Mercury	Total Alpha	Se	GEA
pH	Total Beta	Sb	pH
Cyanide	GEA	As	Cr <sup>6+</sup>
Wt% Water	U	GEA	Ammonia
DSC	<sup>99</sup> Tc		Total Alpha
TGA	<sup>90</sup> Sr		Total Beta
Semi-VOA	<sup>79</sup> Se		GEA
VOA	<sup>59/63</sup> Ni		<sup>3</sup> H
TOX/EOX	Pu Isotopics		
<sup>14</sup> C	U Isotopics		
Rheology	AEA		
Particle Size			

persulfate method. The samples were acidified with heated sulfuric acid converting the inorganic carbon to CO<sub>2</sub>. The CO<sub>2</sub> was swept to a coulometry detector with an O<sub>2</sub> carrier gas. The organic carbon was then converted to CO<sub>2</sub> with potassium persulfate and a silver catalyst. The CO<sub>2</sub> was measured in the same manner as used to determine the inorganic carbon. The total carbon was calculated as the sum of the inorganic and organic carbon concentrations or was measured directly by initially adding the heated sulfuric acid, potassium persulfate, and silver catalyst to the sample in a one-step process. With this method both the inorganic and organic carbon in the sample were oxidized to CO<sub>2</sub>.

Scanning thermogravimetry (STG) and DSC were performed on the homogenized quarter segments and the core composite sample. These two thermal analysis techniques are useful in determining the thermal stability or reactivity of a material. DSC measures heat released or absorbed while the temperature of the sample is increased at a constant rate. STG measures the mass of a sample while the temperature of the sample is increased at a constant rate. Both methods can be modified to measure isothermal changes in the material.

DSC is often used to measure thermal decomposition temperatures, heats of reaction, reaction temperatures, melting points, and solid-solid transition temperatures. STG is used to measure thermal decomposition temperatures, water contents, and reaction temperatures. The two methods often provide complimentary information.

The calibration of the differential scanning calorimeter and the thermogravimetric analyzer were checked before running these samples. An indium standard was run on the calorimeter to check the temperature and enthalpy calibra-

tions. The balance calibration of the thermogravimetric analyzer was checked with a 100-mg standard weight, and the temperature calibration of the analyzer was checked with alumel and perkalloy curie point magnetic transition standards. The temperature and enthalpy calibration checks were all within 2°C and 0.2 J/gm of their reported values, and the balance calibration was within 0.01 mg.

## RESULTS

The concentrations of nitrate, nitrite, total organic carbon, and free cyanide of samples from all three core samples taken from Tank 241-C-112 (cores 34, 35, and 36) are given in Table II. The activities of <sup>137</sup>Cs and <sup>90</sup>Sr from these same samples are also reported in Table II. These compounds are the key to understanding the reactivity of the materials in these tanks. Each of these core samples was obtained from a different position in the tank.

Anion analysis indicated that the primary anions of those measured (fluoride, chloride, nitrite, nitrate, sulfate, phosphate, and free cyanide) in Tank 241-C-112 were nitrate and nitrite. A significant amount of phosphate was also observed, but the concentration of phosphate (approximately 1.8 wt%) was significantly smaller than nitrite or nitrate. The ratio of these anions to the ferrocyanide present is much larger than the stoichiometric ratio required for total oxidation of the ferrocyanide (6 moles of nitrate or 10 moles of nitrite per mole of ferrocyanide).

The measurement of total organic carbon provides some insight into the amount of cyanide that may be present in the sample. Carbon analyses using combustion methods tend to give more reproducible cyanide analysis than does the hot

TABLE II  
Results of Chemical Analyses

Sample <sup>(a)</sup>	Concentration (wt%)				Activity (uCi/g)	
	Nitrate	Nitrite	Cyanide <sup>(b)</sup>	TOC	<sup>137</sup> Cs	<sup>90</sup> Sr
C34-1D	7.9	6.0	0.19	0.24	240	1310
-2B	7.0	5.4	0.16	0.20	610	4860
-2C	6.5	4.9	0.14	0.10	800	1140
-2D	6.0	4.6	0.12	0.15	510	2510
Composite	7.2	5.5	0.16			3510
C35-2D	4.4	3.5	0.08	0.26	700	3210
C36-1C	6.2	4.8	0.11	0.82	410	400
-1D	6.7	5.1	0.12	0.49	1240	15
-2A	6.6	4.9	0.12	0.39	880	19
-2B	4.3	3.0	0.07	0.27	530	71
-2C	4.6	3.2	0.08	0.29	100	144
-2D	5.1	3.5	0.09	0.23	35	199
Composite	5.6	4.1	0.10	0.31		507

a) The samples are labeled by core and quarter segment. The core is indicated by C and the core number following the C. The number after the hyphen is the segment number with the higher number being closer to the bottom. The letter is the quarter segment with A being the top 4.75 in. and D being the bottom 4.75 in.

b) Free Cyanide

persulfate method. Analysis of simulated ferrocyanide-containing wastes by combustion at 700°C (total organic carbon) or at 1000°C (total carbon) give cyanide recoveries between 90% and 105%. The recoveries observed with the hot persulfate method for carbon analyses were between 55% and 60%. Therefore, the concentration measured for total organic carbon by combustion and hot persulfate methods provides an approximation for the concentration of cyanide present as ferro- and ferri-cyanide complexes. The mean concentration of organic carbon in the tank as measured by the hot persulfate method is 0.3 wt%. If all of the measured organic carbon concentration was in the form of cyanide, the cyanide concentration would be between 0.7 wt% and 1.2 wt% (assuming a 55% recovery of cyanide).

The data in Table II indicate that the measured total organic carbon concentration decreases as one approaches the bottom of the tank. Limited data on the nickel concentration in the tank also indicates a significant decrease in the nickel concentration near the bottom of the tank. The thermal analysis data from core 36 also indicates that the ferrocyanide concentration at the bottom of the tank is substantially lower than near the surface of the waste. This trend in ferrocyanide concentration is particularly obvious for core 36 where the measured total organic carbon concentration and <sup>137</sup>Cs activity decrease near the bottom of the tank.

The concentration of free cyanide (approximately 0.1%) in the tank, as shown in Table II, is significantly lower than the ferrocyanide concentration estimated from the total organic carbon measurements, but is still substantial in these tank wastes.

Water leach data on these samples indicate that only a minimal amount of the iron, nickel, and cesium present in the tank samples is soluble. The fact that the cesium is not soluble indicates most of the cesium in these solids is complexed. It is

expected that this cesium is complexed in the form of cesium nickel ferrocyanide.

Total cyanide analysis was performed on a single sample obtained from this tank (quarter segment 2D from core 34) due to the developmental nature of this method and the limited amount of sample available. Five aliquots from this sample were analyzed using the ethylenediamine/EDTA dissolution and microdistillation method. The total cyanide present in this sample was  $0.45 \pm 0.06$  wt%. This concentration compares well with the measured organic carbon concentration for this quarter segment (0.15 wt% as carbon or 0.33 wt% as cyanide with no correction for percent recovery). The total organic carbon of this sample was also measured using the combustion method at 1000°C. The carbon concentration obtained from this measurement was  $1.12 \pm 0.16$  wt% carbon or 2.5 wt% cyanide if all the carbon was cyanide.

Two simulated ferrocyanide-containing wastes of known concentrations were also analyzed by this method. The analysis of these simulated wastes indicated that this method produces cyanide recoveries between 90% and 96%. When the core sample was spiked with these simulated ferrocyanide wastes and a potassium ferrocyanide of known concentration, the percent recoveries were between 83% and 96%. These recoveries indicate that the total cyanide concentration in this sample may be biased 15% to 20% low.

The DSC and STG analyses were performed in duplicate on each of the samples obtained from Tank 241-C-112. In the DSC scans and STG thermograms of these samples, several transitions were observed. The temperature range, onset temperature, and enthalpy for each of these transitions is given in Table III.

Many ferro- and ferri-cyanide compounds as well as simulated ferrocyanide-containing waste samples have also been analyzed by these thermal techniques. The results from these nonradioactive samples indicate that the oxidation of ferro-

TABLE III  
Differential Scanning Calorimetric Data for Tank 241-C-112

Sample	Transition 1			Transition 2			Transition 3		
	Range	Onset	Enthalpy	Range	Onset	Enthalpy	Range	Onset	Enthalpy
C34-2B	30-240	30	847	260-300	276	-12	300-400	349	30
C34-2C	30-240	30	795	260-300	267	-13	300-400	360	13
C34-2D	33-240	33	930	260-300	289	-17	300-400	347	13
C34 Comp	34-240	34	734	260-300	276	-11	300-400	357	10
C35-2D	34-195	34	780	225-290	230	-12	This transition not quantifiable		
C36-1C	34-240	34	1070	260-300	267	-11	300-380	301	31
C36-1D	32-230	32	1310	260-310	277	-16	This transition not quantifiable		
C36-2A	30-230	30	1110	277-300	280	-10	300-400	305	35
C36-2B	33-235	30	870	260-325	298	-9	325-400	330	28
C36-2C	32-240	32	830	This transition not quantifiable			305-407	320	36
C36-2D	34-172	34	1056	This transition not quantifiable			300-395	328	45
C36 Comp	34-240	34	890	270-325	288	-19	This transition not quantifiable		

and ferri-cyanide by nitrite and/or nitrate is a complex series of reactions. (7) An example of the DSC scan and STG thermograms of these materials is given in Fig. 2.

The first transition observed in the samples from Tank 241-C-112 is an endotherm that begins at the lower temperature limit of the analysis (30°C) and is essentially complete by about 240°C. This transition can be divided into at least three transitions, but these transitions are not always resolvable. The most likely reactions occurring in this region (30° to 240°C) are the release of bulk and interstitial water and waters of dehydration. The majority of energy and weight loss in this region occurs between 30° and 170°C. The enthalpy and weight loss associated with this transition is exhibited much larger than the other transitions. This is due to the large amount of water associated with these waste samples.

An exothermic transition is observed over the temperature range from 290° to 350°C with an average onset temperature of about 290°C. The enthalpy of this transition is approximately -12 J/g of sample. This enthalpy is small compared to the enthalpy for the first transition ( $\approx 1000$  J/g of sample).

The final transition is observed over a temperature range from 300° to 400°C. This transition is endothermic with an enthalpy of approximately 30 J/g. The onset temperature for this transition ranges from 300° to 330°C.

Similar behavior has been observed in previous thermal analysis studies of  $\text{Cs}_2\text{NiFe}(\text{CN})_6$  and  $\text{Na}_2\text{NiFe}(\text{CN})_6$ . These previous studies were performed on crushed dried material; therefore, the water loss endotherm was not as large as was observed in the C-112 core samples. The concentration of the  $\text{Cs}_2\text{NiFe}(\text{CN})_6$  and  $\text{Na}_2\text{NiFe}(\text{CN})_6$  was also much higher in the previous studies, so the weight changes and enthalpies observed were much greater. The small enthalpies for the ferrocyanide transitions are indicative of low concentrations of ferrocyanide. This data supports the conclusions drawn from the chemical and radiochemical analyses. As can be seen in Table III, the thermal behavior of quarter segments 1C, 1D, 2A, 2B, and the composite from core 36 are very similar; but exothermic behavior is not observed in quarter segments 2C

and 2D. This supports the chemical data that indicated the ferrocyanide content decreases significantly near the bottom of the tank.

The weight percent change observed by STG over the temperature ranges from 30° to 500°C is reported in Table IV. The weight loss observed over the temperature range of the first endothermic transition is a measure of the water associated with these samples. The weight loss associated with this transition ranges from 40% to 60%, indicating that these tank waste samples contain a significant amount of water. This percent water significantly increases the safety of this tank.

A small weight loss (6%) is observed over the next transition region. This weight loss is due to both dehydration and the ferrocyanide reactions. Similar weight losses were also observed in simulated ferrocyanide-containing waste materials.

A small weight gain is observed in some of the quarter segments from both cores 34 and 36, while other samples exhibited no weight change or a small weight gain. Both weight gains and weight losses were also observed in the simulated ferrocyanide containing waste materials.

## CONCLUSIONS

The data obtained from the characterization of waste from Tank 241-C-112 indicate that the concentration of ferrocyanide in this tank is low (< 2.5 wt% cyanide). The data also indicate the ferrocyanide is not homogeneously distributed throughout the tank, and it appears that a heel containing low concentrations of ferrocyanide may exist in this tank. Significant water (40% to 60 wt%) is present in this tank, which increases the safety of the ferrocyanide material in this tank.

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**TABLE IV**  
Scanning Thermogravimetric Data for Tank 241-C-112  
Weight Loss (%)

Sample	Transition 1	Transition 2	Transition 3
C34-2B	52	5.4	-0.6
C34-2C	45	4.0	-0.3
C34-2D	33	6.3	0
C34-Composite	35	6.1	-0.6
C35-2D	42	6.0	0
C36-1C	46	8.9	-0.3
C36-1D	52	2.0	-0.2
C36-2A	52	1.9	-0.2
C36-2B	38	3.1	-0.1
C36-2C	41		
C36-2D	47	3.5	0.3
C36-Comp	44	2.9	0.3

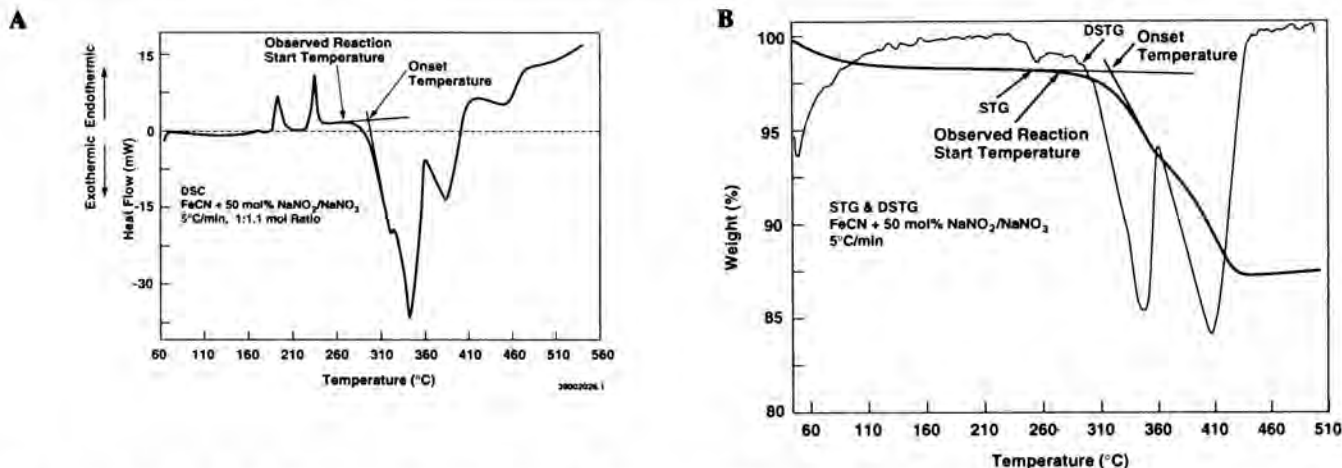


Fig. 2. Thermal Analysis of a Ferrocyanide with 50 mol% Nitrate and Nitrite. Plot a) is a DSC scan, and plot b) is the STG thermogram.

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