

**Ferrocyanide Safety Program
Cyanide Speciation Studies
FY 1994 Annual Report**

S. A. Bryan
K. H. Pool
S. L. Bryan
R. L. Sell
L. M. P. Thomas
B. D. Lerner

September 1994

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

Pacific Northwest Laboratory
Richland, Washington 99352

MASTER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Summary

This report summarizes Pacific Northwest Laboratory's FY 1994 progress toward developing and implementing methods to identify and quantify cyanide species in ferrocyanide tank waste. Currently, there are 24 high-level waste storage tanks at the U.S. Department of Energy's Hanford Site that have been placed on a Ferrocyanide Tank Watchlist because they contain an estimated 1000 g-moles or more of precipitated ferrocyanide. This amount of ferrocyanide is of concern, because the consequences of a potential explosion may exceed those reported previously in safety analyses.

To bound the safety concern, methods are needed to definitively measure and quantitate, to at least 0.1 wt%, the amount of ferrocyanides present within actual waste tanks. The target analyte concentration for cyanide in waste is approximately 0.1 to 15 wt% (as cyanide) in the original undiluted sample. After dissolution of the original sample and appropriate dilutions, the concentration range of interest in the analytical solutions can vary between 0.001 to 0.1 wt% (as cyanide).

In FY 1992 and 1993, two solution (wet) methods had been developed based on Fourier transform infrared (FTIR) spectroscopy and ion chromatography (IC); these methods were chosen for further development activities. The results of these activities are described below:

1. *Dissolution Methods for Ferrocyanide Materials.* Ferrocyanide flowsheet materials must be dissolved to obtain accurate quantitative analysis of the cyanide species within the waste. The merits of several methods of dissolution are discussed, as well as the logic for choosing a solvent based on ethylenediaminetetraacetic acid (EDTA) and ethylenediamine (en) in water.
2. *Influence of Chemical Additives on Cyanide Species Analysis.* Many inorganic and organic chemicals are known or suspected to be present within the ferrocyanide tank waste matrix; these chemicals could interfere with cyanide analysis. To determine the extent of interference, we prepared test solutions containing low concentrations of the analyte of interest [CN^- , $\text{Fe}(\text{CN})_6^{4-}$, and $\text{Fe}(\text{CN})_6^{3-}$] with conservatively high concentrations of the potential interfering additive. These solution concentrations were chosen to represent the "worst case" for analysis of each analyte. If interference was not observed for these solutions, then any analyte solution encountered from actual samples containing these components would not be expected to show interference. We also monitored the aging effect on cyanide species (during approximately a 2-month period) of the solutions containing chemical additives to assess shelf-life of analyte solutions before analysis.

For free cyanide and ferrocyanide analytes, interference was not observed with the additives tested. Nitrite was the only inorganic additive observed to interfere with the detection of the ferricyanide analyte by the quantitative conversion of the ferricyanide complex to ferrocyanide. Several organic additives also reacted with ferricyanide to produce the ferrocyanide complex. In all cases, the conversion was quantitative, and the total cyanide concentration was accurately determined.

3. *Test Procedure to Determine Cyanide Species from Ferrocyanide Flowsheet Materials.* A draft procedure is presented for determining major cyanide species [CN^- , $\text{Fe}(\text{CN})_6^{4-}$, and $\text{Fe}(\text{CN})_6^{3-}$] expected in samples from the Hanford ferrocyanide waste tanks. We have selected these analytes because they consist of most of the reasonable forms of cyanide possible resulting from the initial addition of ferrocyanide to the ferrocyanide waste tanks. The methods are based on FTIR and IC.

The overall detection limits for the relevant cyanide-containing species in the original undiluted waste are on the order of 0.1 wt% (as cyanide) for each method.

4. *Methods for Analyzing Flowsheet Materials.* Ferrocyanide flowsheet materials including various In-Farm and U-Plant simulated wastes, as well as sodium nickel ferrocyanide standard materials (WHC-3 and FECN-36), were analyzed by different methods. Cyanide analyses were performed by FTIR and IC methods, and by total cyanide analysis (distillation method). The analytical results are presented and compared by method. Excellent agreement was achieved between each method for all simulated wastes and standard materials.

In FY 1994, we continued the investigation of measuring the influence of chemical additives on the IC and FTIR analytical methods. The results of these activities are described below:

1. *Influence of Chemical Additives on Cyanide Species Analysis.* We found that for IC there is qualitative measurement of the ferricyanide and ferrocyanide with added organic interferents. Quantitative measurements for these cyanide complexes also were found with added inorganic interferents, with the exception of nitrate and nitrite ions. This problem is not associated with the ability of the IC system to separate the nitrate or nitrite ions from the ferricyanide and ferrocyanide species, but is due to the co-absorbance of these interfering ions with the cyanide complexes of interest. This problem is solved by the use of matrix-matched standards for the ferri- and ferrocyanide complexes.
2. *Influence of pH on Nitrite Reactivity with $Fe(CN)_6^{3-}$.* The reactivity of nitrite with ferricyanide to form ferrocyanide under analytical measurement conditions is of interest to this program, because the speciation and quantification of each of the cyanide complexes in solution depends on the relative stability of these complexes during analysis. It has been demonstrated earlier in this task that nitrite will reduce ferricyanide to form ferrocyanide quantitatively. The pH dependence of the reaction of ferricyanide with nitrite is of interest because, depending on conditions, this reaction may occur within the radioactive waste tank or during the required laboratory treatment steps prior to analysis. In solutions with pH 12, the conversion of ferricyanide to ferrocyanide was complete and quantitative. At lower pH levels (4 to 10) the conversion of ferricyanide to ferrocyanide was reduced. At these lower pH values, the formation of nitroprusside ($Fe(CN)_5NO^{2-}$) was observed. In all cases, a qualitative measurement of the cyanide species in solution was maintained.
3. *Location of FTIR Analytical System into Radiation Zone.* FTIR equipment was transferred and installed within a radiologically controlled laboratory. The detector and analytical cell used for the analysis of solution samples was mounted remotely from the main optical bench in order to allow placement of the detector into a radiologically controlled fume hood. This attachment was made through a light guide from the main optical bench into the remote sample compartment. The method detection limit (MDL) was measured for the system with the sample cell directly attached within the main optical bench (normal setup), and with the remote detector attached. The MDL for the direct attachment was 5.9 ppm (wt% cyanide) and for the remote attachment 7.4 ppm (wt% cyanide). This small difference between MDL values for the two attachment modes indicates that there is effectively no loss in quantitative limits by remote detector application.

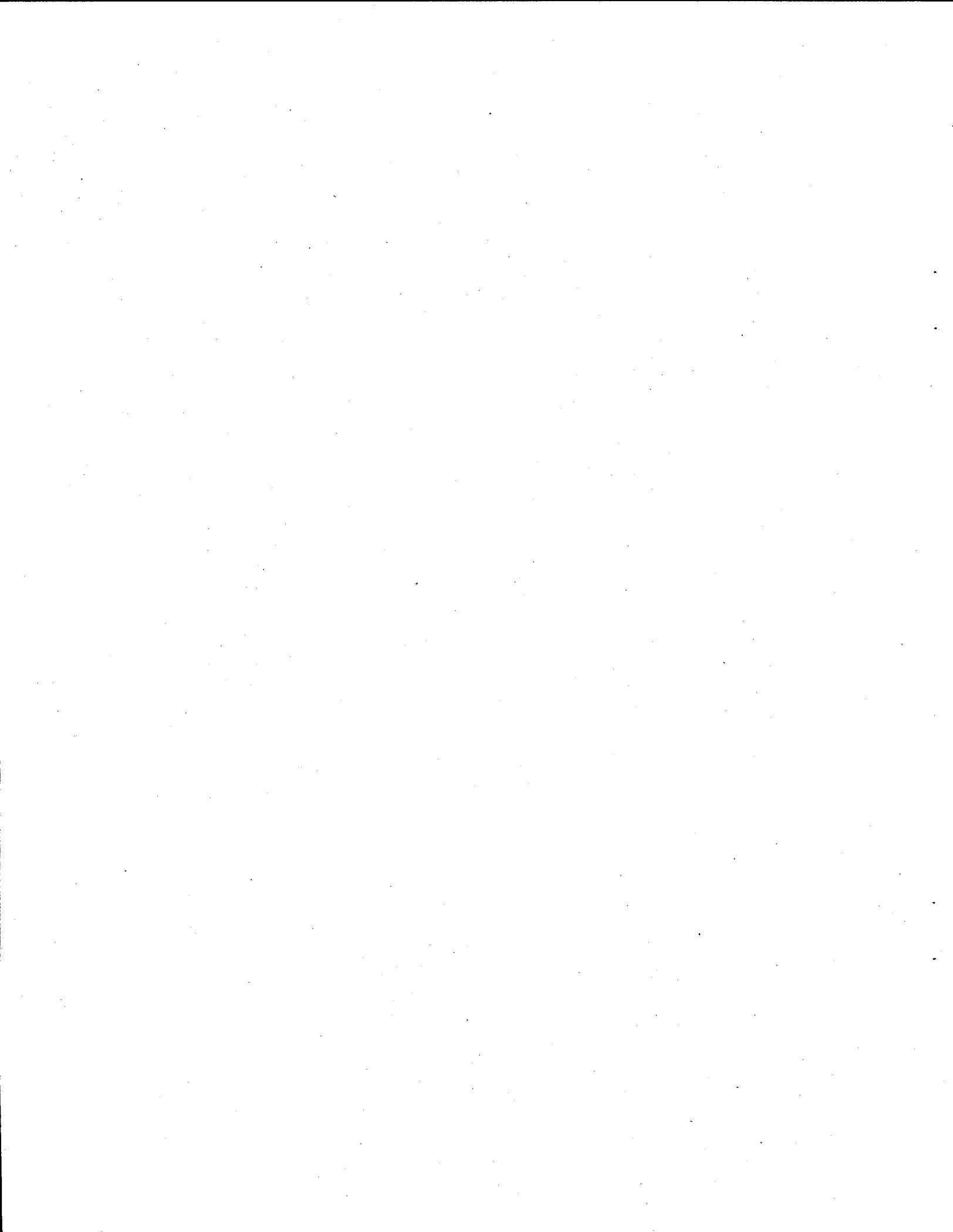
4. *Solid Analysis of Simulated Ferrocyanide Waste by FTIR.* Methods for reproducibly measuring solid samples for analytes of interest, with little or no sample preparation, has utility in many aspects of the ferrocyanide Tank Waste Safety Program. Limited work was performed on quantitative measurement of solid samples using FTIR techniques. Two methods were initially employed, attenuated total reflectance (ATR) and transmission mode using KBr pellets.

The ATR method showed problems with reproducibility between samples generated from different simulated waste preparations. This lack of reproducibility in the quantitative measurement was determined to be due to differences in surface characteristics between samples; the ATR method is a surface analytical method and changes in the surface properties of the analyte material cause major changes in the detected signal.

The transmission technique was demonstrated successfully for quantitative measurement of simulant samples. The transmission method uses light that passes through a homogenized sample to measure the quantity of the analyte species within the sample. Because the IR light penetrates the entire sample, the measurement is therefore a bulk property of the sample. Differences in surface properties of different samples have little or no effect on the transmission measurements.

Abbreviations List

ATR	attenuated total reflectance
DIW	deionized water
DOE	U.S. Department of Energy
DXRD	dynamic x-ray diffraction
EDTA	ethylenediaminetetraacetic acid
EIS	environmental impact statement
en	ethylenediamine
FTIR	Fourier transform infrared
FY	fiscal year
GAO	General Accounting Office
HEDTA	hydroxyethyl-ethylenediaminetriacetic acid
IC	ion chromatography
IDA	iminodiacetic acid
IR	infrared
MDL	method detection limit
NPH	normal paraffin hydrocarbon
NTA	nitrilotriacetic acid
PNL	Pacific Northwest Laboratory
SST	single-shell tank
TBP	tributylphosphate
USQ	unreviewed safety question



Contents

Summary	iii
Abbreviations List	vii
1.0 Introduction	1.1
2.0 Test Procedure to Determine Cyanide Species in Ferrocyanide Flowsheet Materials	2.1
3.0 Influence of Chemical Additives on Cyanide Species Analysis Using Ion Chromatography	3.1
3.1 Influence of Inorganic Additives on Ferrocyanide $[\text{Fe}(\text{CN})_6^{4-}]$ and Ferricyanide $[\text{Fe}(\text{CN})_6^{3-}]$ Analysis	3.3
3.2 Influence of Organic Chemical Additives on Ferrocyanide $[\text{Fe}(\text{CN})_6^{4-}]$ and Ferricyanide $[\text{Fe}(\text{CN})_6^{3-}]$ Analysis	3.4
4.0 Influence of pH on Nitrite Reactivity with Ferricyanide	4.1
4.1 Formation of $\text{Fe}(\text{CN})_5\text{NO}_2^-$ from $\text{Fe}(\text{CN})_6^{3-}$ and NO_2^- at Low pH	4.2
5.0 Implementation of FTIR Equipment into Radiologically Controlled Zone	5.1
5.1 Method Detection Limit (MDL) for Ferrocyanide Analysis Using Remote FTIR Compartment	5.1
6.0 Solids Analysis by FTIR	6.1
6.1 FTIR-ATR Technique	6.1
6.2 Transmission FTIR Technique	6.3
7.0 Status of Cyanide Speciation Studies	7.1
8.0 References	8.1

Figures

3.1	IC Chromatogram Showing Separation of Ferricyanide and Ferrocyanide Ions	3.2
3.2	Typical Ion Chromatogram Showing the Separation of Ferricyanide and Ferrocyanide	3.5
3.3	Concentration of Total Cyanide Species (Ferricyanide and Ferrocyanide) in Solution Originally Containing Ferricyanide 0.025 wt% (as cyanide) and Inorganic Additive	3.6
3.4	Concentration of Total Cyanide Species (Ferricyanide and Ferrocyanide) in Solution Originally Containing Ferrocyanide 0.025 wt% (as cyanide) and Inorganic Additive	3.7
3.5	Concentration of Cyanide Species in Solution Initially Containing Ferrocyanide and Organic Additive	3.8
3.6	Concentration of Cyanide Species in Solution Initially Containing Ferricyanide and Organic Additive	3.10
4.1	Ferricyanide ○, Ferrocyanide ▽, and Total Cyanide (Ferricyanide + Ferrocyanide) ■ of Various Solutions 23 Days After Preparation	4.1
4.2	Infrared Spectra of (a) Solution Initially Containing 20 wt% NaNO ₂ and Fe(CN) ₆ ³⁻ at pH 4, (b) Reference Solution of Na ₂ Fe(CN) ₅ NO, and (c) a Difference Spectrum of (a)-(b)	4.3
4.3	Infrared Absorbance vs. Concentration for Two Spectral Bands from Na ₂ Fe(CN) ₅ NO.	4.4
4.4	Ferricyanide ○, Ferrocyanide ▽, Fe(CN) ₅ NO ²⁻ ▲, and Total Cyanide ■ of Various Solutions 23 Days After Preparation	4.5
5.1	Photograph of FTIR with the Remote Detector Compartment Attached via an Optical Light Guide	5.2
6.1	Measured Normalized Absorbance Values for Various Ferrocyanide Simulated Wastes.	6.3
6.2	Extinction Coefficients for Various Ferrocyanide Simulated Waste from Transmission FTIR Measurements	6.5
6.3	Standard Addition Method for Solid Ferrocyanide Simulated Waste Samples Using Transmission FTIR Technique	6.6

Tables

3.1	List of Tested Inorganic and Organic Additives	3.1
3.2	Concentration of Total Cyanide as wt% Cyanide (Ferricyanide + Ferrocyanide) Measured in Inorganic-Containing Solutions.	3.4
3.3	Concentration of Total Cyanide as wt% Cyanide (Ferricyanide + Ferrocyanide) Measured in Inorganic-Containing Solutions.	3.5
3.4	Concentration of Ferricyanide, Ferrocyanide, and Total Iron-Cyanide (as ppm cyanide) Measured in Organic-Containing Solutions	3.9
5.1	Method Detection Limit for Ferrocyanide Using the Auxiliary Detection Compartment in Remote and Direct Connection with the FTIR Bench	5.3
6.1	Measured Normalized Absorbance Values for Various Ferrocyanide Simulated Wastes	6.2
6.2	Extinction Coefficients for Various Ferrocyanide Simulated Waste from Transmission FTIR Measurements.	6.4

1.0 Introduction

The research performed for this project is part of an effort that started in the mid-1980s to characterize the materials stored in the single-shell waste storage tanks (SSTs) at the U.S. Department of Energy (DOE) Hanford Site. Various radioactive wastes from defense operations have accumulated at the Hanford Site in underground waste tanks since the early 1940s.

During the 1950s, additional tank storage space was required to support the defense mission. Hanford Site scientists developed two procedures to obtain this additional storage volume within a short time period without constructing additional storage tanks. One procedure involved the use of evaporators to concentrate the waste by removing water. The second procedure involved developing precipitation processes for scavenging radiocesium and other soluble radionuclides from tank waste liquids. The scavenging processes used sodium and potassium ferrocyanide and nickel sulfate to precipitate radioactive cesium from solutions containing nitrates and nitrites. Radioactive strontium and cobalt were scavenged from some of the solutions using calcium or strontium nitrate and sodium sulfide, respectively. After allowing the radioactive precipitates to settle, the decontaminated solutions were pumped to disposal cribs, thereby providing additional tank storage volume. Later, some of the tanks were found to be leaking; pumpable liquids were removed from these tanks, leaving behind a wet solid (sludge) residue containing the ferrocyanide precipitates (Burger et al. 1991). In implementing this process, approximately 140 metric tons of ferrocyanide, [calculated as $\text{Fe}(\text{CN})_6^{4-}$], was added to waste that was later routed to 24 large (750,000 to 1,000,000 gallon) underground SSTs.

The explosive nature of ferrocyanides in the presence of oxidizers has been known for decades, but the conditions under which impure mixtures containing nitrates and nitrites can undergo propagating reactions have not been thoroughly studied. At the Hanford Site, the potential reactivity of mixtures of ferrocyanides, nitrates, and nitrites was first recognized when the radiocesium scavenging process using ferrocyanide was investigated for application to radioactive wastes produced by the next generation processing technology. The investigation found that cesium zinc ferrocyanide and nitrate exploded when heated (Hepworth et al. 1957). In the laboratory, mixtures of ferrocyanide and oxidizing materials, such as nitrates and nitrites, have been shown to undergo energetic reactions when heated to high temperatures (above 270°C) or exposed to an electrical spark of sufficient energy to heat the mixture. Because the scavenging process precipitated ferrocyanide from solutions containing nitrate and nitrite, an intimate mixture of ferrocyanides and nitrates and/or nitrites is likely to exist in some regions of the ferrocyanide tanks.

Efforts have been underway since the mid-1980s to evaluate the potential for ferrocyanide reactions in Hanford Site SSTs (Burger 1984; Burger and Scheele 1988). The 1987 Environmental Impact Statement (EIS), *Final Environmental Impact Statement, Disposal of Hanford Defense High-Level Transuranic and Tank Waste, Hanford Site, Richland, Washington* (DOE 1987), included an environmental impact analysis of potential explosions involving ferrocyanide-nitrate mixtures. The EIS postulated that an explosion could occur during mechanical retrieval of saltcake or sludge from a ferrocyanide waste tank. The EIS concluded that this worst-case accident could create enough energy to release radioactive material to the atmosphere through ventilation openings, exposing persons offsite to a short-term radiation dose of approximately 200 mrem. A General Accounting Office (GAO) study (Peach 1990) postulated a greater worst-case accident, with independently calculated doses of one to two orders of magnitude greater than postulated in the DOE EIS. Uncertainties regarding the safety

envelope of the Hanford Site ferrocyanide waste tanks led to the declaration of the ferrocyanide unreviewed safety question (USQ) in October 1990.

Despite the fact that the measured temperatures in these tanks continue to drop ($3^{\circ}\text{C}/\text{year}$) and the highest temperature currently recorded is 56.7°C (Hanlon 1991), there has been a good deal of speculation as to the possibility of "hot spots" forming in the tanks due to radiolytic heating. In order to address these concerns, a number of studies have been conducted by Westinghouse Hanford Company (WHC), Pacific Northwest Laboratory (PNL),^(a) and others in an effort to identify the reactions that occur, and to quantify the magnitude of the energy released during reactions (Burger 1984; Burger and Scheele 1988, 1990; Scheele et al. 1991, 1992; Scheele and Cady 1989; Hallen et al. 1991). Although these studies have yielded many insights, the specific reactions have yet to be identified, and the prevailing reaction rates have yet to be quantified.

Toward resolving the USQ, the Ferrocyanide Safety Program was implemented. This program is composed of four principal components. The first component, tank monitoring, involves developing, deploying, and maintaining instrumentation for continuous monitoring of the tank contents. The second program component, modeling and analyzing existing tank data, allows predictive calculations of, for example, the existence of hot spots within the waste or concentrations of gases within the tank dome space. Ferrocyanide waste characterization using actual tank samples is the third program component. This activity focuses on the chemical analysis of gas space, surface samples, and core samples from the ferrocyanide tanks. The fourth program component is research and development. This activity's objective is to understand the potentially hazardous reactions of precipitated ferrocyanides and their aging products within SST ferrocyanide waste.

This report focuses on activities for the third component of the Ferrocyanide Safety Program, characterization of ferrocyanide waste. The contents of this report are arranged in order of the requirements to analyze ferrocyanide species. Following the introduction, Section 2.0 presents experimental methods and the draft test procedure developed by this task for analyzing cyanide complexes. Section 3.0 discusses the influences of inorganic and organic chemical additives on cyanide species analysis by ion chromatography (IC). Section 4.0 discusses the influence of pH on the reactivity of ferricyanide. Section 5.0 presents the information regarding the relocation and implementation of the Fourier transform infrared (FTIR) spectroscopy equipment into a radio-controlled zone. Section 6.0 discusses the analysis of simulated ferrocyanide waste samples by two solid methods, attenuated total reflectance (ATR) and transmission FTIR. Section 7.0 contains a reference list.

(a) Operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

2.0 Test Procedure to Determine Cyanide Species in Ferrocyanide Flowsheet Materials

This section contains a draft test procedure for determining cyanide species from ferrocyanide flowsheet materials. This procedure will be used to identify concentrations of major cyanide species [CN^- , $\text{Fe}(\text{CN})_6^{4-}$, and $\text{Fe}(\text{CN})_6^{3-}$] expected in samples from the Hanford ferrocyanide waste tanks. These analytes were selected because they consist of most of the reasonable forms of cyanide possible, resulting from the initial addition of ferrocyanide to the ferrocyanide waste tanks. The methods are based on FTIR and IC. The overall detection limits for the relevant cyanide-containing species in the original undiluted waste are on the order of 0.1 wt% (as cyanide) for each method.

Title of Procedure

Determination of Free Cyanide and Cyanoferrate Species by FTIR and Reversed Phase IC Techniques

Applicability

This procedure provides methods for determining major cyanide-containing species [$\text{Fe}(\text{CN})_6^{3-}$, $\text{Fe}(\text{CN})_6^{4-}$, $\text{Fe}(\text{CN})_5\text{NO}^{2-}$, and CN^-] expected in samples from the ferrocyanide waste tanks. The overall detection limits for the relevant cyanide-containing species are on the order of 0.1 wt% each.

Definitions

DIW	Deionized water
batch	A group of samples of similar matrix processed at the same time
SST	Single-shell tank

Responsible Staff

- Cognizant scientist
- Analyst/technician

Procedure

Equipment and Materials

- Analytical four-place balance
- FTIR spectrometer
- ATR circle cell, constructed with fluorocarbon wetted parts
- Plastic syringes (5 or 10 mL)
- Syringe filters
- Magnetic stirrer and disposable stir bars
- Scintillation vials with plastic insert caps

- High-performance liquid chromatograph system (HPLC) including high-pressure pump; eluant reservoirs; "reversed phase" column, with UV-vis or suppressed conductivity detector; and appropriate data display

Reagents

Sample Pretreatment Solution: 5% ethylenediaminetetraacetic acid (EDTA) or HY + 5% ethylenediamine (en).

Weigh 5.0 ± 0.1 g acid-form EDTA into 100-mL volumetric flask. Add ~60 mL DIW followed by 5.0 ± 0.1 g en. Swirl to mix and dissolve solids. Adjust volume to mark with DIW. Store this solution in a labeled poly bottle.

0.01 M NaOH:

Dissolve $0.40 (\pm 0.01)$ g NaOH pellets in 1.0 ± 0.05 L of DIW.

Chromatography Eluant:

32.5 vol% acetonitrile, 2 mM tetrabutylammonium hydroxide, 0.6 mM Na_2CO_3 .

Stock Standard Solutions:

KCN, $\text{K}_3\text{Fe}(\text{CN})_6$, $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$ or $\text{K}_4\text{Fe}(\text{CN})_6$, and $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$ dissolved in 0.01 N NaOH. Each stock standard solution should be approximately 1 wt% of cyanide and stored away from light in a laboratory refrigerator.

Sample Pretreatment

Weigh 1 g of sample (± 0.001 g) into a labeled scintillation vial. Add a disposable magnetic stir bar. Weigh 10 g pretreatment solution (± 0.01 g) into the vial. Stir for at least one-half hour to ensure complete dissolution of alkali metal-nickel-cyanoferrate compounds.

Sample Analyses

FTIR:

Warm up the instrument according to manufacturer's recommendation. Set the wave number display window to cover the 2200 to 1900 cm^{-1} region at a resolution of 8 cm^{-1} or higher while instrument is warming up and stabilizing. Prepare working calibration standards. Dilute stock standard solutions (described above) with sample pretreatment solution by weight. Prepare at least 4 calibration standards (1 of these may be a blank) that encompass the expected sample concentration range.

Inject the standards sequentially into the ATR cell using a plastic syringe (5 or 10 mL) and in-line disposable syringe filter (if necessary). Develop the FTIR interferogram and record its transform for each standard. In a like manner, inject samples and spiked samples. Record all FTIR interferograms for later peak position identification and peak height (or area) determinations.

IC:

Warm up the instrument and allow it to stabilize for approximately one-half hour. If suppressed conductivity detection is used, make sure suppressor regenerate flow is adequate to reduce background conductivity to less than 10 $\mu\text{S}/\text{cm}$. Prepare matrix-matched calibration of $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Fe}(\text{CN})_6^{3-}$ and standards as described previously. Add solid CaCO_3 (~0.05 g/mL) to each calibration standard and sequentially load instrument sample loop (100 μL) by injection of each standard through 0.45- μm syringe filter. In a like manner, inject samples and spiked samples. Record chromatographic peak areas (or peak heights) for later data analysis.

Calculations - Data Analysis

For either FTIR or IC data, prepare a calibration curve by plotting instrument response (peak area or peak height) versus concentration of standard for each analyte. Analyte concentrations in unknown samples and spiked samples are found by relating observed instrument responses to the calibration curve and multiplying by appropriate dilution factors, if any.

Spike recoveries (% Recovery) are calculated from:

$$\% \text{ Recovery} = \frac{\text{wt. analyte found in spiked sample} - \text{wt. analyte found in sample alone}}{\text{wt. analyte spike added}} \times 100$$

Quality Control

Each analytical session (batch processed) shall include as a minimum: 1 method blank, 1 spiked sample, and 1 spiked blank (or control sample). For samples analyzed in support of SST characterization, duplicate analyses shall be performed for each. The control sample and spiking material should be prepared from available, well-characterized materials such as $\text{Na}_2\text{NiFe}(\text{CN})_6$, In-Farm simulated waste, $\text{K}_3\text{Fe}(\text{CN})_6$, KCN, and/or $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$.

Spike recoveries or control sample recoveries outside the 85 to 115% range render suspect all results for the analytical session. The cognizant scientist shall investigate the situation and modify the procedure, if necessary, to restore observed recoveries to the acceptable range.

Records

Records pertaining to application of this procedure shall be managed and maintained according to QA Plan MCS-033.

References

Bryan, S. A., K. H. Pool, L. L. Burger, C. D. Carlson, N. J. Hess, J. D. Matheson, J. L. Ryan, R. D. Scheele, and J. M. Tingey. 1993. *Ferrocyanide Safety Project, Task 3.5 Cyanide Species Analytical Methods Development, FY 1992 Annual Report*. PNL-8399, Pacific Northwest Laboratory, Richland, Washington.

Bryan, S. A., K. H. Pool, S. L. Bryan, R. L. Sell, and L. M. P. Thomas. 1993. *Ferrocyanide Safety Program Cyanide Speciation Studies FY 1993 Report*. PNL-8887, Pacific Northwest Laboratory, Richland, Washington.

Nicolet Instrument Corporation Operation manuals.

Dionex Instrument Corporation Operation manual.

3.0 Influence of Chemical Additives on Cyanide Species Analysis Using Ion Chromatography

Dissolved ferrocyanide waste and simulated waste contain an array of chemical species that may interfere with the analytical solution methods used to quantify cyanide complexes. To assess the impact of the suspected interferent species, we systematically measured cyanide complexes of interest with and without the additives. Table 3.1 lists the suspected interfering species we have tested to date. The species concentrations were chosen based on ferrocyanide and SST simulated waste flowsheets (U-Plant and In-Farm).

Work has centered on the IC method of analysis to assess the influence of potential interferences on cyanide species detection. In the following sections we show the results of interferent tests from ferrocyanide waste simulants containing potential organic and inorganic interferents.

Figure 3.1 shows an IC chromatogram for the separation of ferricyanide $[\text{Fe}(\text{CN})_6^{3-}]$ and ferrocyanide $[\text{Fe}(\text{CN})_6^{4-}]$, with each at the 50-ppm concentration level. This chromatogram demonstrates that these ions can be spatially separated by retention time as well as resolved by their characteristic absorbancies in the UV-vis spectrum. The solvent used in this experiment is the complexant pretreatment solution developed by Bryan et al. (1993b). This example chromatogram shows the potential for using this method to speciate the various complexes of cyanide at low concentrations.

Table 3.1. List of Tested Inorganic and Organic Additives

Inorganic Additives	Organic Additives
Na_2SO_4	Sodium citrate
Na_2CO_3	Sodium acetate
Na_3PO_4	Sodium formate
NaCl	Normal paraffin hydrocarbon (NPH) (saturated)
NaNO_2	Sodium oxalate
Na_2CrO_4	Hydroxyethyl-ethylenediaminetriacetic acid (HEDTA)
NaF	Tributylphosphate (TBP) (saturated)
NaNO_3	Glycerin
NaAlO_2	Ethylenediaminetetraacetic acid (EDTA)
	Sodium glycolate
	Iminodiacetic acid (IDA)
	Glycine
	Nitrilotriacetic acid (NTA)
	N-butanol
	Ethylenediamine (en)

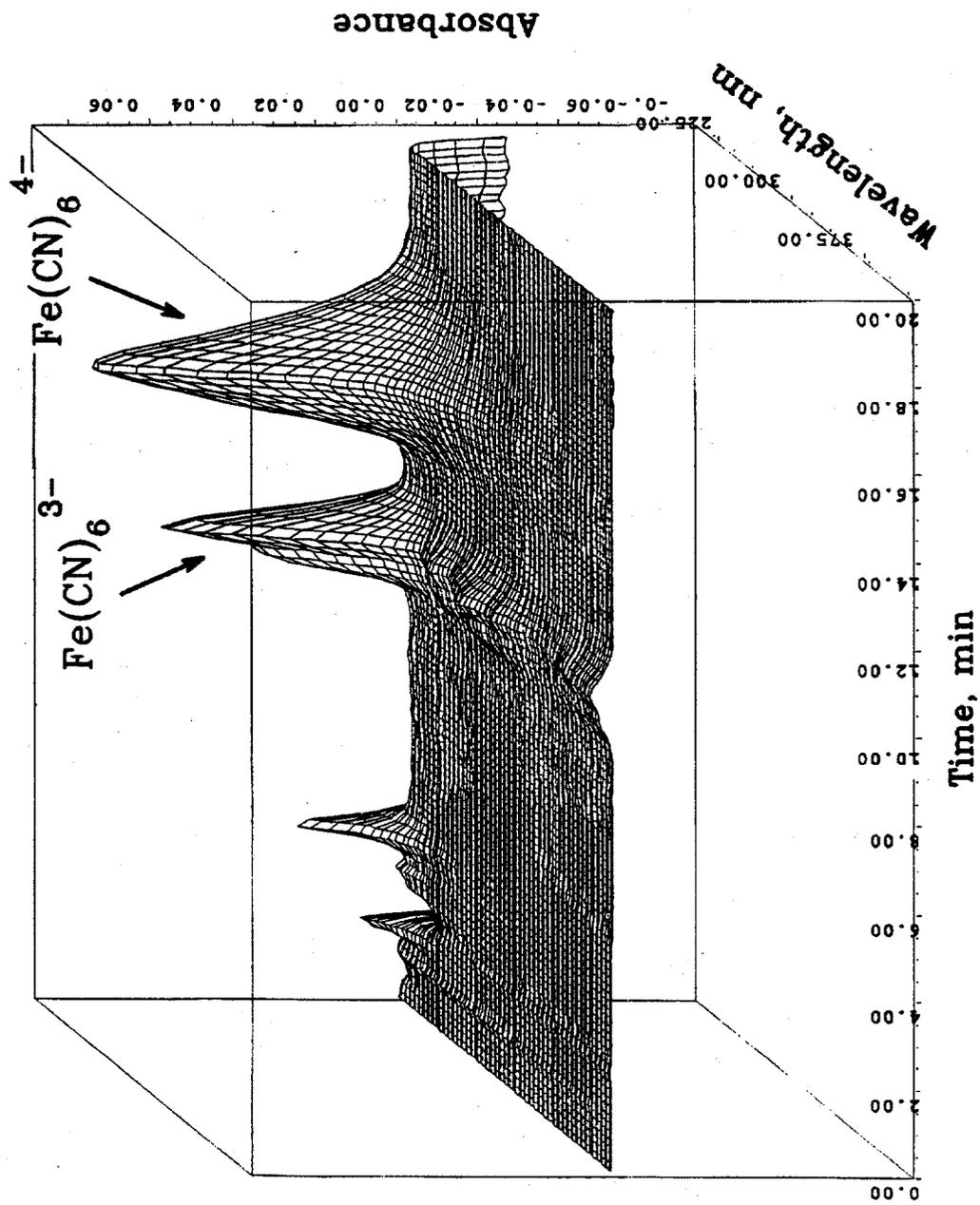


Figure 3.1. IC Chromatogram Showing Separation of Ferricyanide and Ferrocyanide Ions. The concentration of each ion is 50 ppm, the detector is a UV-vis diode-array.

The lowest detection limit is being sought in order to allow for dilution of tank waste samples during the dissolution process prior to analysis. The dilution factor for a tank waste sample is dependent in part on the concentration of the cyanide species present, but also on the activity of the radionuclides within the sample. By achieving the best detection limit possible, we are able to demonstrate two important goals: 1) a best lower-bound quantitation limit, and 2) attention to ALARA concerns and minimizing personnel exposure.

3.1 Influence of Inorganic Additives on Ferrocyanide $[\text{Fe}(\text{CN})_6^{4-}]$ and Ferricyanide $[\text{Fe}(\text{CN})_6^{3-}]$ Analysis

Ferrocyanide simulants containing potential inorganic interferents have been prepared and analyzed by IC. Solutions containing 250 ppm (0.025 wt% as cyanide) ferrocyanide $[\text{Fe}(\text{CN})_6^{4-}]$ and ferricyanide $[\text{Fe}(\text{CN})_6^{3-}]$, with various amounts of inorganic interferent concentrations were analyzed using the HPLC system with the photo-diode array detector system described previously.

The results of this test are summarized in Tables 3.2 and 3.3 for ferricyanide and ferrocyanide, respectively. A typical ion chromatogram output is shown in Figure 3.2. The retention time for elution of the ferricyanide ion is 11.2 min; the retention time for the elution of ferrocyanide ion is 15.8 min. The total amount of cyanide (sum of ferricyanide and ferrocyanide) analyzed by IC is shown in the tables. The data in the tables are presented in Figures 3.3 and 3.4, respectively.

As can be seen from the tables and figures, the measured concentration of the cyanide in each solution is essentially the concentration of cyanide complex added initially to each solution, with the exception of the nitrite and nitrate solutions. For the analysis of both the ferricyanide and ferrocyanide, the solutions containing nitrite and nitrate show low analyzed cyanide complex.

Although there is a redox interconversion between the ferricyanide to ferrocyanide with added nitrite, we know from earlier work (Bryan et al. 1993a) that the total cyanide concentration is not changed by the addition of nitrite or nitrate. Therefore, the lower analyzed concentration of ferricyanide and ferrocyanide within the IC is due to interference with the detection of the iron-cyanide complexes in the presence of nitrite and nitrate. We believe the source of the error stems from the same cause, the absorbance of the nitrite and nitrate ions within the UV-vis detector is coincident with the absorbance of the ferri- and ferrocyanide complexes. We believe this interference can be eliminated by using matrix matched standard solutions containing the same concentration of nitrite and nitrate as the samples solutions. This avenue is currently under investigation.

Table 3.2. Concentration of Total Cyanide as wt% Cyanide (Ferricyanide + Ferrocyanide) Measured in Inorganic-Containing Solutions. Solutions initially contained 250 ppm ferricyanide and various inorganic additives.

Sample Number	Matrix	Total Cyanide Concentration (ppm) (ferricyanide + ferrocyanide)
0	standard	229
1	0.5% Na ₂ SO ₄	262
1	0.5% Na ₂ SO ₄	237
2	2.5% Na ₂ CO ₃	272
2	2.5% Na ₂ CO ₃	220
3	2.7% Na ₃ PO ₄	242
3	2.7% Na ₃ PO ₄	261
4	5.0% NaCl	275
4	5.0% NaCl	242
5	20.0% NaNO ₂	79
5	20.0% NaNO ₂	68
6	1.5% Na ₂ CrO ₄	331
6	1.5% Na ₂ CrO ₄	252
7	0.5% NaF	293
7	0.5% NaF	237
8	15.0% NaNO ₃	110
8	15.0% NaNO ₃	48
9	2.5% NaAlO ₂	288
9	2.5% NaAlO ₂	249

3.2 Influence of Organic Chemical Additives on Ferrocyanide [Fe(CN)₆⁴⁻] and Ferricyanide [Fe(CN)₆³⁻] Analysis

Ferrocyanide simulants containing potential organic interferents have been prepared and analyzed by IC. Solutions containing ferrocyanide at 250 ppm (0.025 wt% as cyanide) concentration with

Table 3.3. Concentration of Total Cyanide as wt% Cyanide (Ferricyanide + Ferrocyanide) Measured in Inorganic-Containing Solutions. Solutions initially contained 250 ppm ferrocyanide and various inorganic additives.

Sample Number	Matrix	Total Cyanide Concentration (ppm) (ferricyanide + ferrocyanide)
0	standard	258
1	0.5% Na ₂ SO ₄	228
1	0.5% Na ₂ SO ₄	260
2	2.5% Na ₂ CO ₃	232
2	2.5% Na ₂ CO ₃	254
3	2.7% Na ₃ PO ₄	234
3	2.7% Na ₃ PO ₄	239
4	5.0% NaCl	241
4	5.0% NaCl	228
5	20.0% NaNO ₂	114
5	20.0% NaNO ₂	134
6	1.5% Na ₂ CrO ₄	230
6	1.5% Na ₂ CrO ₄	237
7	0.5% NaF	232
7	0.5% NaF	240
8	15.0% NaNO ₃	74
8	15.0% NaNO ₃	89
9	2.5% NaAlO ₂	232
9	2.5% NaAlO ₂	242

2.5 wt% organic interferent concentration were analyzed using HPLC with the photo-diode array detector system described previously. The results of this test are shown in Figure 3.5.

The solutions analyzed and displayed in Figure 3.5 were prepared 8 months prior to analysis. This early preparation was done to determine the stability of the ferrocyanide analyte with respect to the potential organic interferent. As can be seen from the figure, the concentration of the cyanide complex in each solution does not change to a very large degree over this relatively long period of time. The variability between analyses of the same sample is reasonable considering the age of these solutions.

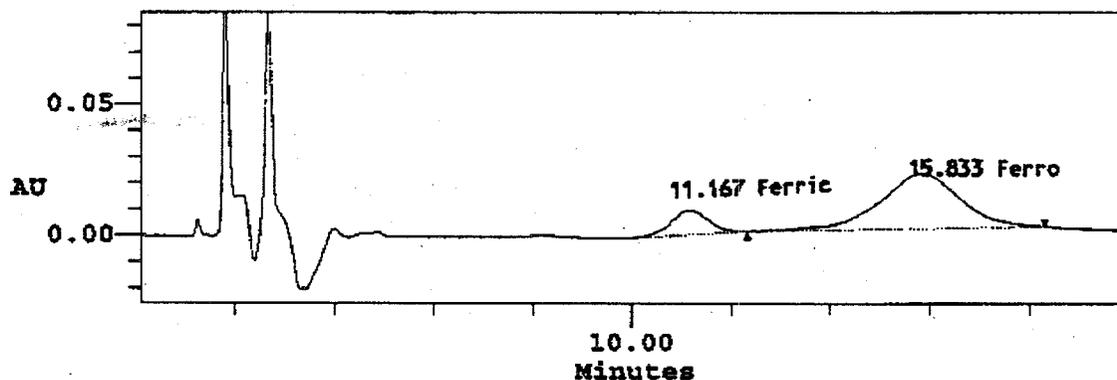
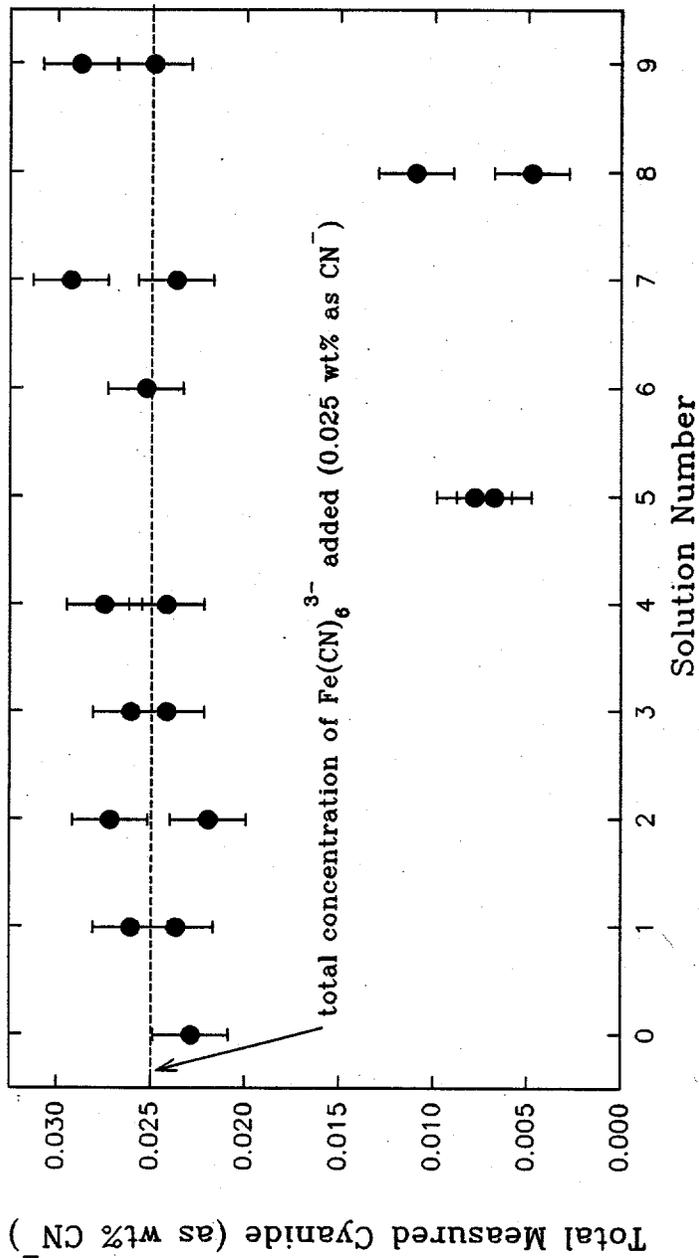


Figure 3.2. Typical Ion Chromatogram Showing the Separation of Ferricyanide and Ferrocyanide. This analyte solution contained 2.7 wt% sodium phosphate.

Solutions containing 250 ppm (0.025 wt% as cyanide) ferricyanide $[\text{Fe}(\text{CN})_6^{3-}]$ with 2.5 wt% organic interferent concentration were analyzed using HPLC with the photo-diode array detector system described previously. These solutions were prepared 8 months prior to analysis in order to assess the effect of aging on the cyanide analysis. The results of this test are summarized in Table 3.4 for ferricyanide. The total of ferricyanide and ferrocyanide analyzed by IC is displayed in Figure 3.6 and discussed below.

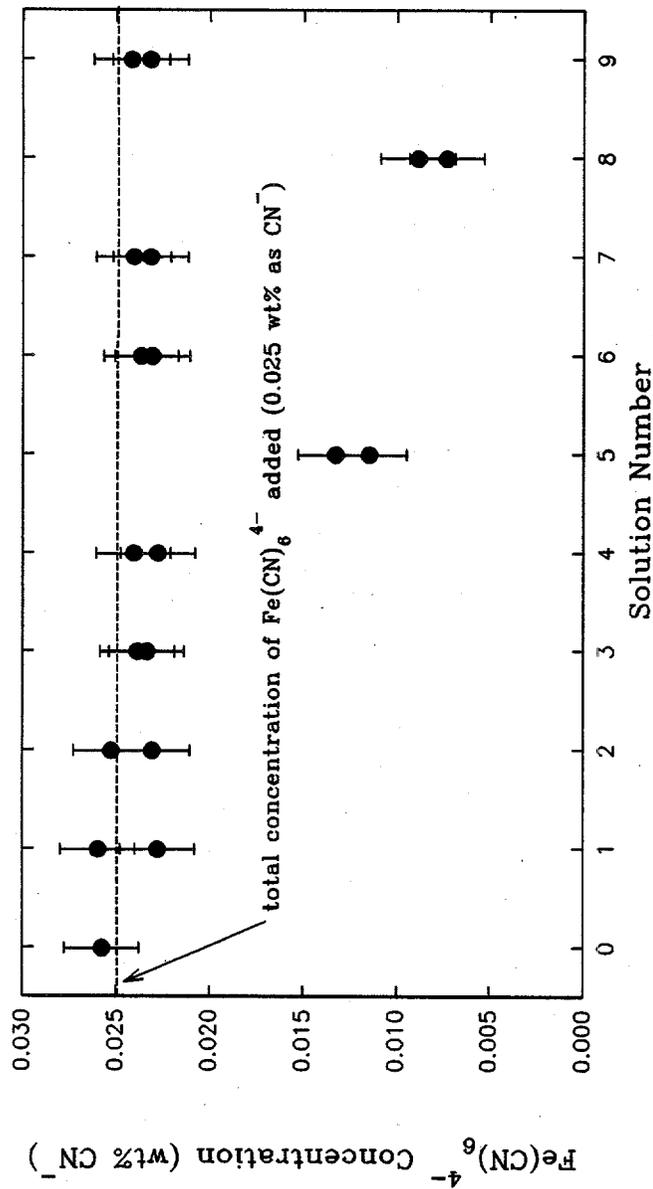
As can be seen from the figure, the concentration of the cyanide complex in each solution does not change to a very large degree over this relatively long period of time. The variability between analyses of the same sample is reasonable considering the age of these solutions.



all solutions initially contained $\text{Fe}(\text{CN})_6^{3-}$ (0.025 wt% as CN^-) with listed additive

- | | | |
|--|--------------------------------------|-----------------------------|
| 0. 0.025 wt% $\text{Fe}(\text{CN})_6^{3-}$ (blank) | 4. 5.0 wt% NaCl | 7. 0.5 wt% NaF |
| 1. 0.5 wt% Na_2SO_4 | 5. 20.0 wt% NaNO_2 | 8. 15.0 wt% NaNO_3 |
| 2. 2.5 wt% Na_2CO_3 | 6. 1.5 wt% Na_2CrO_4 | 9. 2.5 wt% NaAlO_2 |
| 3. 2.7 wt% Na_3PO_4 | | |

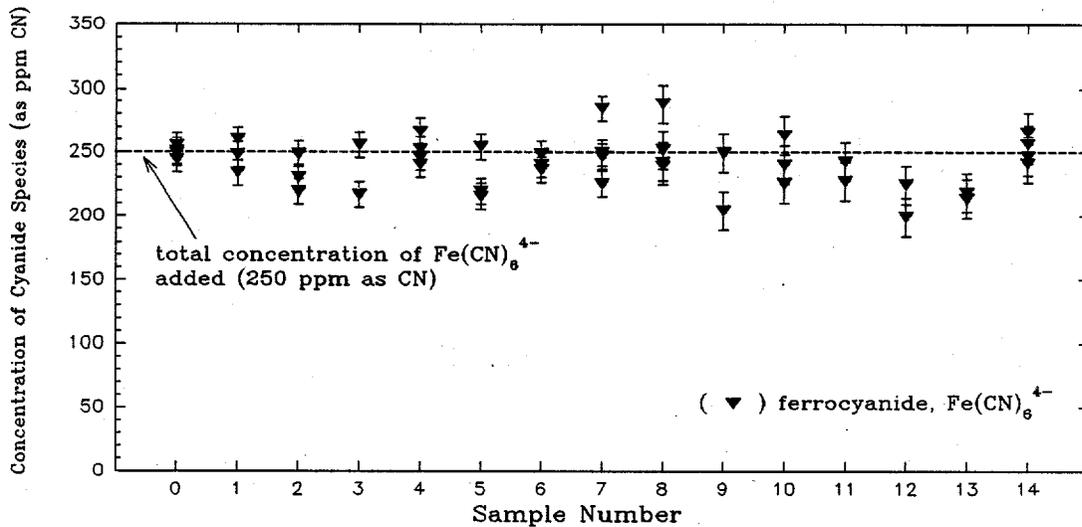
Figure 3.3. Concentration of Total Cyanide Species (Ferricyanide and Ferrocyanide) in Solution Originally Containing Ferricyanide 0.025 wt% (as cyanide) and Inorganic Additive.



all solutions initially contained $\text{Fe}(\text{CN})_6^{4-}$ (0.025 wt% as CN^-) with listed additive

- | | | |
|--|--------------------------------------|-----------------------------|
| 0. 0.025 wt% $\text{Fe}(\text{CN})_6^{4-}$ (blank) | 4. 5.0 wt% NaCl | 7. 0.5 wt% NaF |
| 1. 0.5 wt% Na_2SO_4 | 5. 20.0 wt% NaNO_2 | 8. 15.0 wt% NaNO_3 |
| 2. 2.5 wt% Na_2CO_3 | 6. 1.5 wt% Na_2CrO_4 | 9. 2.5 wt% NaAlO_2 |
| 3. 2.7 wt% Na_3PO_4 | | |

Figure 3.4. Concentration of Total Cyanide Species (Ferricyanide and Ferrocyanide) in Solution Originally Containing Ferrocyanide 0.025 wt% (as cyanide) and Inorganic Additive.



all solutions initially contained 250 ppm $\text{Fe}(\text{CN})_6^{4-}$ and 2.5 wt% organic additive

- | | | |
|--|----------------------|---------------|
| 0. $\text{Fe}(\text{CN})_6^{4-}$ (250 ppm, CN) | 6. HEDTA | 12. glycine |
| 1. sodium citrate | 7. TBP | 13. NTA |
| 2. sodium acetate | 8. glycerin | 14. n-butanol |
| 3. sodium formate | 9. EDTA | |
| 4. NPH | 10. sodium glycolate | |
| 5. sodium oxalate | 11. IDA | |

Figure 3.5. Concentration of Cyanide Species in Solution Initially Containing Ferrocyanide and Organic Additive. These solutions were analyzed by IC. The solutions were allowed to age 8 months prior to analysis.

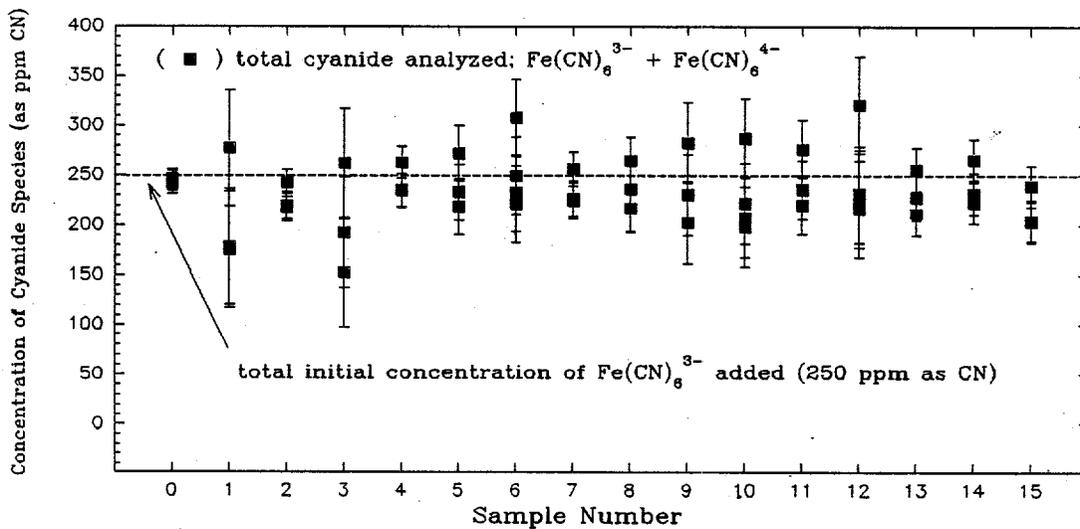
Table 3.4. Concentration of Ferricyanide, Ferrocyanide, and Total Iron-Cyanide (as ppm cyanide) Measured in Organic-Containing Solutions. Solutions initially contained 250 ppm ferricyanide and 2.5 wt% organic additive.

Sample	Matrix	Concentration (ppm)		
		Ferricyanide	Ferrocyanide	Total
0	standard	205.2	39.3	244.5
0	standard	223.5	522.6	246.2
0	standard	217.9	23.8	241.7
1	Na citrate	109.5	168.1	277.6
1	Na citrate	93.8	84.6	178.4
1	Na citrate	84.5	591.0	5175.6
2	Na acetate	85.8	156.4	242.2
2	Na acetate	116.6	103	219.6
2	Na acetate	101.15	116.95	218.1
3	Na formate	116.7	145.2	261.9
3	Na formate	116.7	35.9	152.6
3	Na formate	93.5	599	192.6
4	NPH	242.7	20.4	263.1
4	NPH	202.3	32.3	234.6
4	NPH	210.4	24.5	234.9
5	Na oxalate	DL*	272	272
5	Na oxalate	DL	233	233
5	Na oxalate	DL	218.5	218.5
6	HEDTA	2.7	5305.0	5307.8
6	HEDTA	DL	221.35	221.4
6	HEDTA	DL	249.55	249.6
6	HEDTA	DL	232.35	232.4
7	TBP	226.7	29.55	256.3
7	TBP	189.8	534.8	224.7
7	TBP	190.6	36.2	226.8
8	glycerine	71.7	192.85	264.6
8	glycerine	71.35	164.6	236
8	glycerine	58.3	158.85	217.2
9	EDTA	DL	282.65	282.7
9	EDTA	DL	230.5	230.5

Table 3.4. (contd)

Sample	Matrix	Concentration (ppm)		Total
		Ferricyanide	Ferrocyanide	
9	EDTA	DL	202.45	202.5
10	Na glycolate	32.2	255	287.2
10	Na glycolate	22.2	185.55	207.8
10	Na glycolate	22.75	199.15	221.9
10	Na glycolate	221	76.5	198.5
11	IDA	DL	276.3	276.3
11	IDA	DL	235.65	235.7
11	IDA	DL	219.95	220
12	glycine	DL	321	321
12	glycine	22.2	204.4	226.6
12	glycine	DL	230.9	230.9
12	glycine	DL	216.35	216.4
13	NTA	DL	255.9	255.9
13	NTA	DL	227.6	227.6
13	NTA	DL	211.9	211.9
14	n-butanol	119.25	146.35	265.6
14	n-butanol	103.65	118.65	222.3
14	n-butanol	103.65	118.65	222.3
14	n-butanol	111	120.5	231.5
15	ethylenediamine	DL	239.3	239.3
15	ethylenediamine	DL	203.4	203.4
15	ethylenediamine	DL	204.6	204.6

* DL = less than detection limit



all solutions initially contained 250 ppm $\text{Fe}(\text{CN})_6^{3-}$ and 2.5 wt% organic additive

- | | | |
|--|----------------------|---------------------|
| 0. $\text{Fe}(\text{CN})_6^{3-}$ (250 ppm, CN) | 6. HEDTA | 12. glycine |
| 1. sodium citrate | 7. TBP | 13. NTA |
| 2. sodium acetate | 8. glycerin | 14. n-butanol |
| 3. sodium formate | 9. EDTA | 15. ethylenediamine |
| 4. NPH | 10. sodium glycolate | |
| 5. sodium oxalate | 11. IDA | |

Figure 3.6. Concentration of Cyanide Species in Solution Initially Containing Ferricyanide and Organic Additive. These solutions were analyzed by IC. The solutions were allowed to age 8 months prior to analysis.

4.0 Influence of pH on Nitrite Reactivity with Ferricyanide

The reactivity of nitrite with ferricyanide to form ferrocyanide under analytical measurement conditions is of interest to this program because the speciation and quantification of each of the cyanide complexes in solution depends on the relative stability of these complexes during analysis. It has been demonstrated earlier in this task that nitrite will reduce ferricyanide to form ferrocyanide quantitatively. The pH dependence of the reaction of ferricyanide with nitrite is of interest because, depending on conditions, this reaction may occur within the radioactive waste tank or during the required laboratory treatment steps prior to analysis. The reaction of ferricyanide with nitrite under various pH conditions is shown in Figure 4.1 corresponding to 23 days of reaction time after preparation. The cyanide concentrations were measured by the FTIR method (Bryan et al. 1993).

Each solution was prepared with the same concentration of ferricyanide (0.12 wt% as cyanide) and 20 wt% NaNO_2 , with the pH of each adjusted to the desired level by the addition of HNO_3 or NaOH as needed. Aliquots of each solution were analyzed for all cyanide species present. Ferricyanide $[\text{Fe}(\text{CN})_6^{3-}]$ and ferrocyanide $[\text{Fe}(\text{CN})_6^{4-}]$ complexes the predominant cyanide species observed in solution. However, closer scrutiny of solutions at low pH values revealed that other iron-cyanide

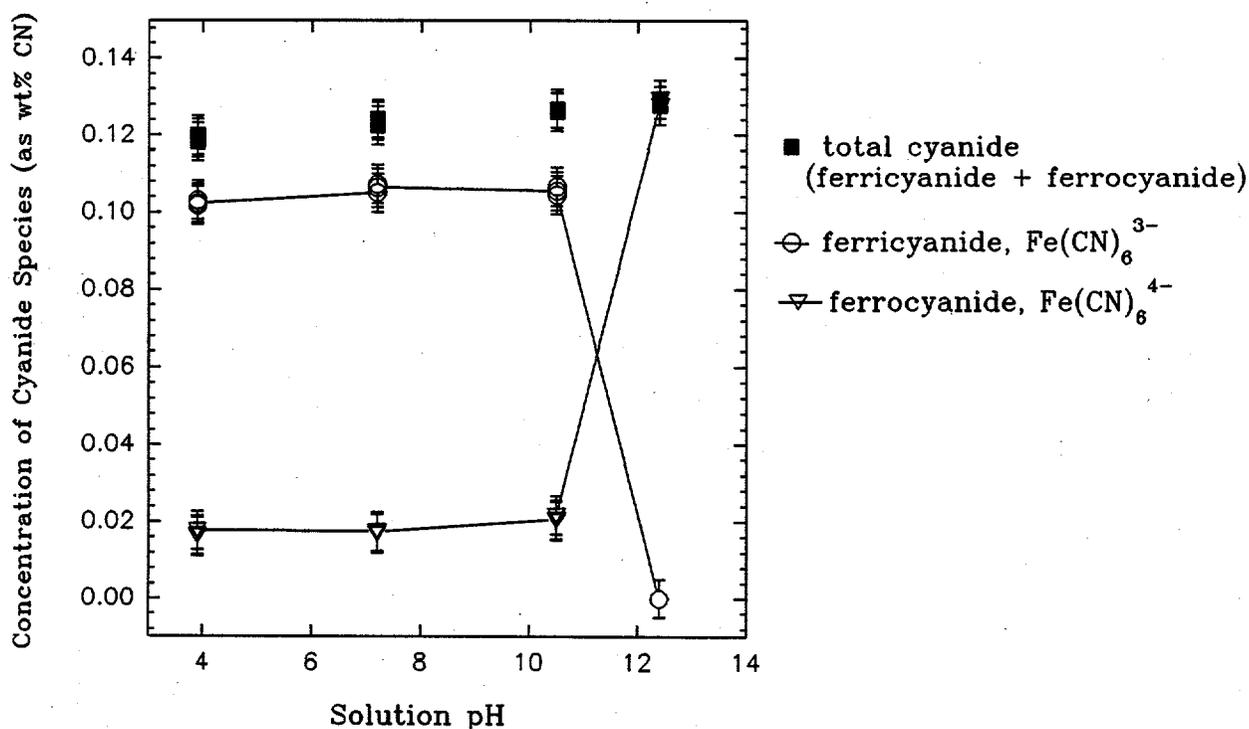


Figure 4.1. Ferricyanide \circ , Ferrocyanide ∇ , and Total Cyanide (Ferricyanide + Ferrocyanide) \blacksquare of Various Solutions 23 Days After Preparation. These solutions initially contained 20 wt% nitrite and 0.12 wt ferricyanide.

products have formed. As can be seen in Figure 4.1, there is a bias at low pH solutions to have a lower total cyanide concentration. This can be explained by other complexes of cyanide being formed within this solution at low pH.

4.1 Formation of $\text{Fe}(\text{CN})_5\text{NO}^{2-}$ from $\text{Fe}(\text{CN})_6^{3-}$ and NO_2^- at Low pH

Figure 4.2 shows the IR spectrum of a pH 4 solution initially containing 20 wt% NaNO_3 and 0.12 wt% $\text{Fe}(\text{CN})_6^{3-}$ after 26 days of aging. This spectrum shows the parent ferricyanide complex as well as the reduced ferrocyanide complex. There is, however, a third cyanide-containing component within this solution. We have identified this species as the nitroso-pentacyano-iron complex $\text{Fe}(\text{CN})_5\text{NO}^{2-}$ based on the location and relative absorbance of the IR bands in the solution spectrum and the possible products expected in a low pH nitrite solution, and rationalized that a nitroso adduct of iron could be formed. Figure 4.2(b) shows the solution spectrum of $2\text{Na}_2\text{Fe}(\text{CN})_5\text{NO}$ for comparison with the peaks found in spectrum 4.2(a). The spectral lines and relative intensities in 4.2(b) are a good match for the compound found in Figure 4.2(a). Figure 4.2(c) shows the "difference spectrum" of the subtraction of an arbitrary fraction of spectrum 4.2(b) from spectrum 4.2(a). The level baseline obtained from this operation is further confirmation that these spectra are of the same compound, and that the new compound formed in solution with 20 wt% NaNO_3 and 0.12 wt% $\text{Fe}(\text{CN})_6^{3-}$ at pH 4 is $\text{Fe}(\text{CN})_5\text{NO}^{2-}$.

This data, taken after a 3-week period following solution preparation, indicates this reaction is not extremely fast, but certainly fast enough to occur on the time scale of tank waste aging time-frames.

In order to account for the quantity of ferricyanide converted to the $\text{Fe}(\text{CN})_5\text{NO}^{2-}$, we can employ Beers Law analysis of the absorbance bands for the nitroso complex. Figure 4.3 shows the Beers Law relationship between absorbance and concentration for the 1935 cm^{-1} and 2141 cm^{-1} bands associated with the respective $\text{N}=\text{O}$ and $\text{C}\equiv\text{N}$ stretching motions in $\text{Fe}(\text{CN})_5\text{NO}^{2-}$. We used both bands as a means to quantitate the $\text{Fe}(\text{CN})_5\text{NO}^{2-}$ concentration in solutions containing this species.

Figure 4.4 contains the same data depicted in Figure 4.1, and also contains the $\text{Fe}(\text{CN})_5\text{NO}^{2-}$ concentrations and corrected total cyanide concentration allowing for the added iron-nitroso complex. The total cyanide concentration measured for each solution at the various pH values is now approximately at the original concentration when the solutions were prepared. Figure 4.4 shows that there is a gradual decrease in the amount of nitroso complex formed from pH 4 to pH 12. There is essentially no nitroso complex formed at pH 12.

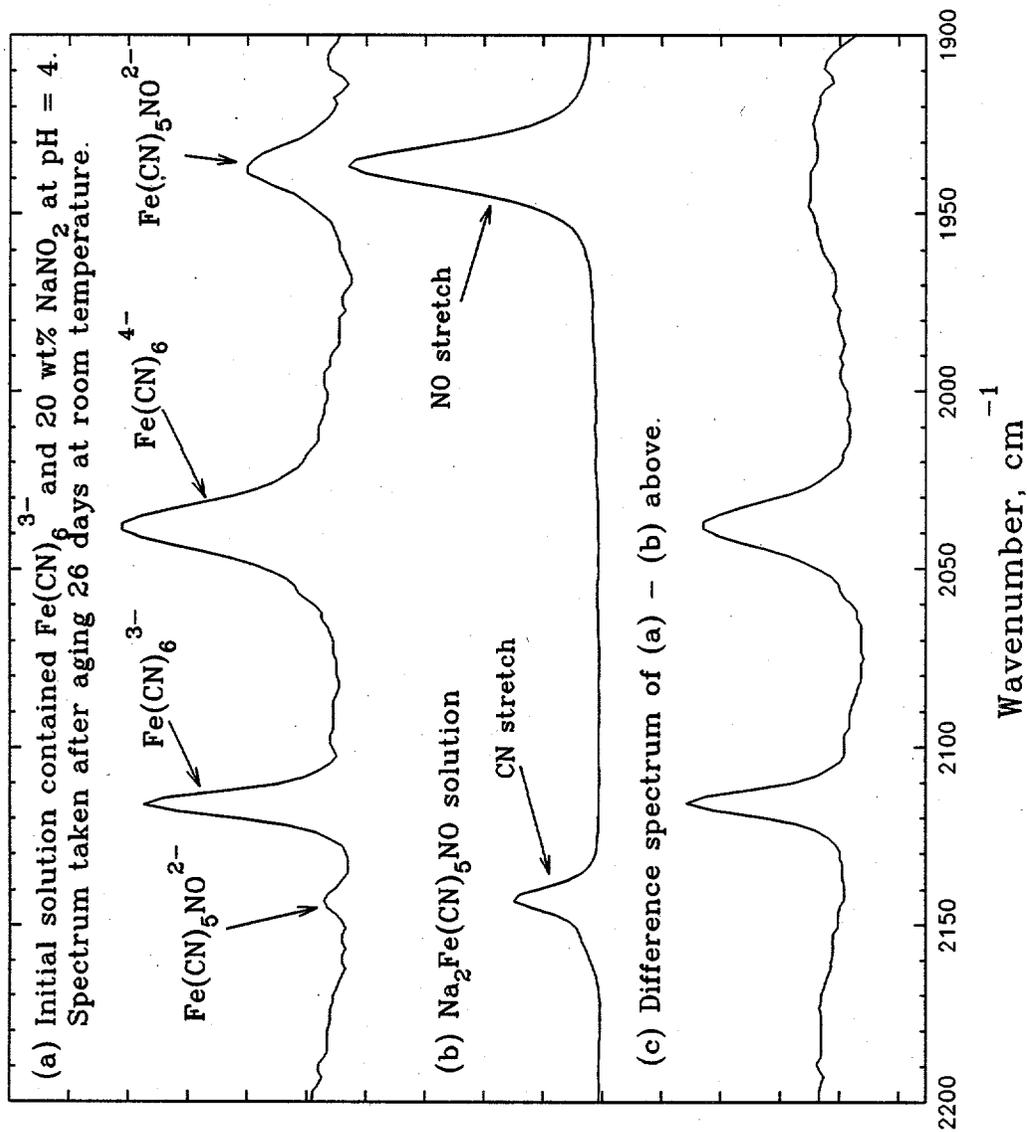


Figure 4.2. Infrared Spectra of (a) Solution Initially Containing 20 wt% NaNO_2 and $\text{Fe}(\text{CN})_6^{3-}$ at pH 4, (b) Reference Solution of $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO}$, and (c) a Difference Spectrum of (a)-(b).

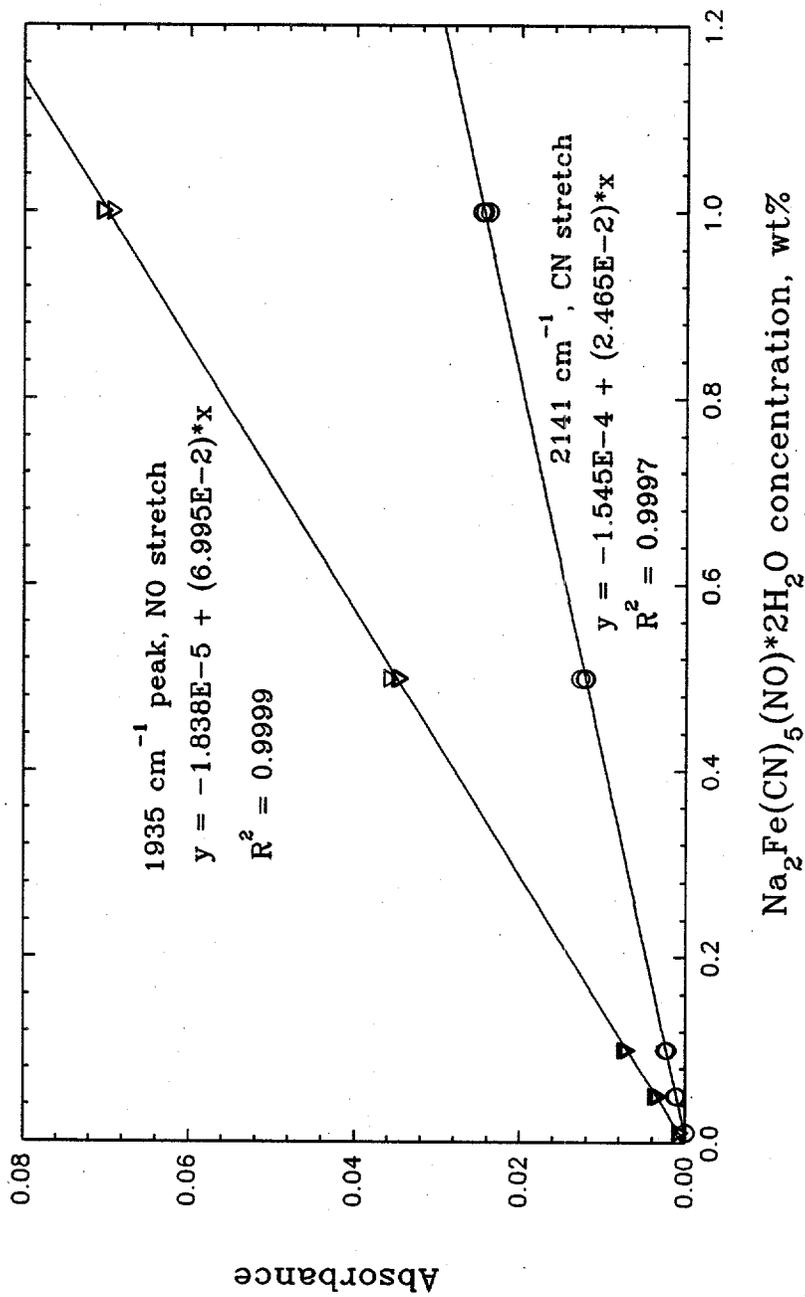


Figure 4.3. Infrared Absorbance vs. Concentration for Two Spectral Bands from $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO}$.

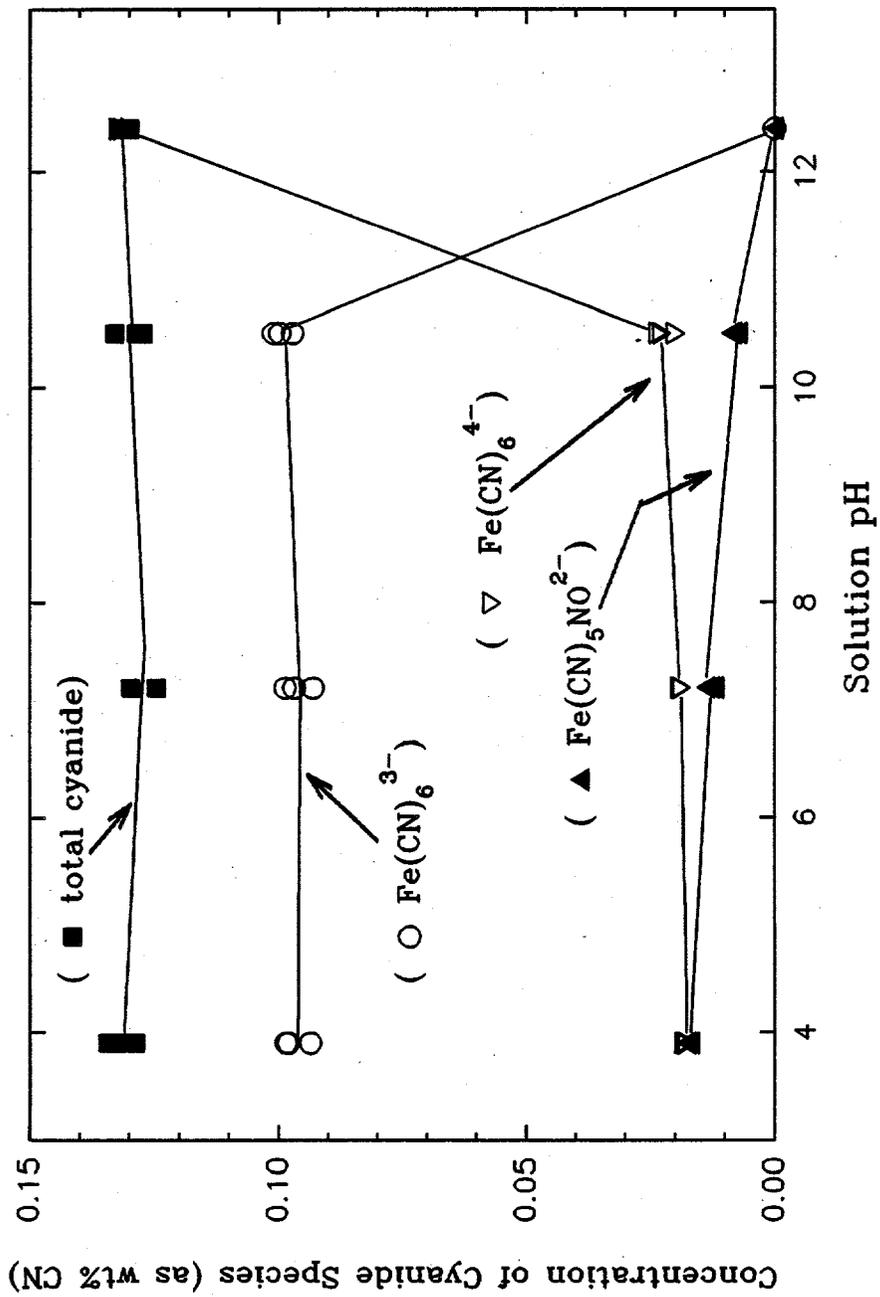


Figure 4.4. Ferricyanide ○, Ferrocyanide ▽, $\text{Fe}(\text{CN})_5\text{NO}^{2-}$ ▲, and Total Cyanide ■ of Various Solutions 23 Days After Preparation. These solutions initially contained 20 wt% nitrite and 0.12 wt% ferricyanide.

5.0 Implementation of FTIR Equipment into Radiologically Controlled Zone

In order to perform analyses on actual ferrocyanide tank waste, it was necessary to relocate the FTIR equipment, including FTIR bench and remote detector, into a radiologically controlled laboratory. Figure 5.1 is a photograph of the FTIR with the remote detector compartment attached via an optical light guide. This photograph was taken prior to relocation into the controlled laboratory. The remote detector compartment is the smaller attachment on the right side of the laboratory bench. The main FTIR bench and computer system are pictured to the left in Figure 5.1. The light guide has been placed between the remote compartment and the main compartment so that the remote compartment can rest within a radiologically controlled hood for use with radioactive samples. A hole is placed in the side of the radiologically controlled hood for the light guide to connect between the IR compartments.

5.1 Method Detection Limit (MDL) for Ferrocyanide Analysis Using Remote FTIR Compartment

The method detection limit (MDL)^(a) for detecting ferrocyanide in solution was measured by FTIR techniques using the auxiliary detector compartment, which was separated from the main FTIR bench compartment by the light guide (remote attachment). The detection limit also was measured with the auxiliary compartment attached directly to the main bench. Table 5.1 presents the method detection limits for both the direct attachment and remote attachment modes.

The detection limit for the direct connection of the sample compartment to the main IR bench is slightly lower than the detection limit for the remote location of the sample compartment. However, this data shows that location of the detector compartment in a remote fashion does not affect the detection limit to any appreciable degree. This data also indicates that the MDL is approximately 10 ppm.

(a) Definition and Procedure for the Determination of the Method Detection Limit-Revision 1.11. Federal Register, Vol. 49, No. 209, October 26, 1984, pp 198-199.

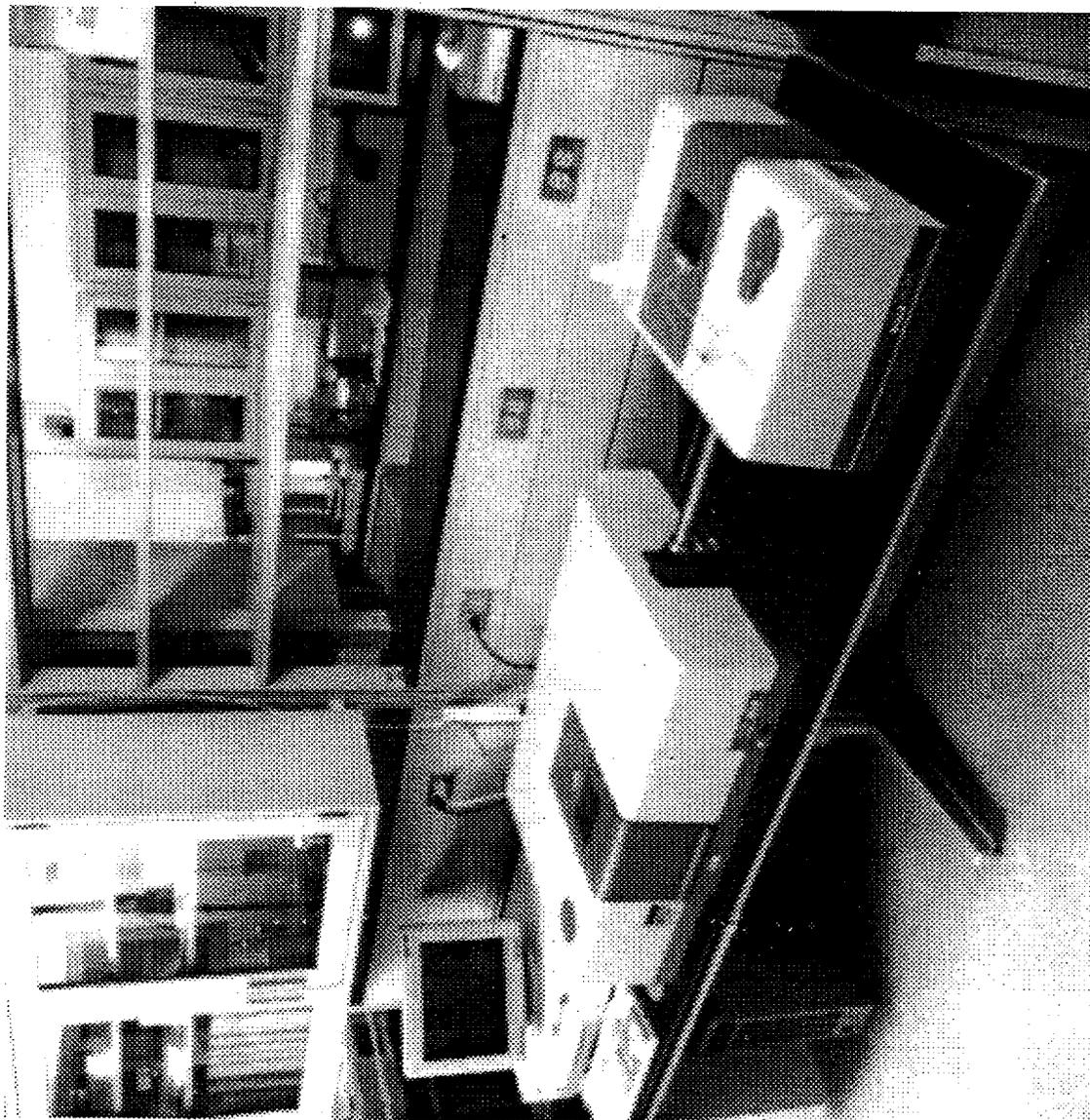


Figure 5.1. Photograph of FTIR with the Remote Detector Compartment Attached via an Optical Light Guide. The remote detector compartment is pictured on the right.

Table 5.1. Method Detection Limit for Ferrocyanide Using the Auxiliary Detection Compartment in Remote and Direct Connection with the FTIR Bench.

Method Detection Limit for Ferrocyanide (wt% as CN)	
<u>Direct Detector Attachment</u>	<u>Remote Detector Attachment</u>
0.00059% (5.9 ppm)	0.00074% (7.4 ppm)

6.0 Solids Analysis by FTIR

Methods for reproducibly measuring solid samples for analytes of interest without or with very little sample preparation has utility in many aspects of the Ferrocyanide Tank Safety Program. Due to the inability to measure radioactive samples, because of the 325 Building closure, we used this opportunity to revisit the issue of measuring solid samples.

In previous publications, it has been reported that the absorbance in the infrared region for cyanide showed a linear response as a function of sodium nickel ferrocyanide in solid samples. In other words, Beer's Law was followed for sodium nickel ferrocyanide over the concentration range of interest for solid simulated waste preparations. This is one condition that must be met if this analytical method is to be used as a standard addition method for measuring an unknown quantity of nickel ferrocyanide in a sample using a known added standard.

A second condition that must be met for a standard addition method to be successful is to adequately match a standard to the analyte material that is to be quantitatively analyzed. This is a much more difficult condition than the first, because it requires not only that the analyte and standard both obey Beer's Law, but that they also both have the same extinction coefficient in the IR region responsible for the C≡N vibrational mode. Put another way, it means that two different samples containing the same concentration of nickel ferrocyanide will yield the same absorbance in the C≡N stretching region of the IR.

We have shown previously that the first condition stated above applies to ferrocyanide simulated waste; that is, each ferrocyanide waste simulant obeys Beer's Law. However, the second condition, that nickel ferrocyanide simulants produced from various preparations have the same extinction coefficient, has not been demonstrated.

The following sections detail two potential FTIR methods for quantitating nickel ferrocyanide in the solid state. The first technique, ATR is a quick sampling method that utilizes IR reflected off the surface of the sample with virtually no sample preparation. The second, transmittance IR requires minor preparation of the sample prior to measuring the infrared light transmitted through the bulk of the sample. The advantage of the ATR technique is the lack of sample preparation. The advantage of the transmittance technique is that the IR measurement is taken for the bulk of the sample, not just a surface layer, as in the ATR technique.

6.1 FTIR-ATR Technique

In order for the standard addition method to yield correct analytical results, the extinction coefficient (ϵ) defined from Beer's Law (Equation 6.1) of the standard and the analyte in the sample matrix must be the same value. Beer's Law is defined as

$$A = \epsilon \cdot b \cdot c$$

Equation 6.1

where A = absorbance, ϵ = extinction coefficient, b = sample path length, and c = concentration of analyte.

Measurements of a wide variety of ferrocyanide waste simulants and relatively pure sodium nickel ferrocyanide complexes have been made using the FTIR-ATR solid method. The absorbance at the C≡N vibrational mode maximum (2090 cm⁻¹) for these samples is summarized in Table 6.1. Comparisons of the extinction coefficients (ϵ) of these samples is important, but the extinction coefficient cannot be calculated directly from Equation 1, because the path length for ATR experiments is difficult to measure. However, because the path length for the ATR cell, b , is a constant, the value $\epsilon \cdot b$ is also constant between experimental samples. Rearrangement of Equation 1 yields $\epsilon \cdot b = A/c$. The value A/c is conveniently measured from the measured absorbance, A , and knowledge of the concentration, c , of the analyte.

Table 6.1 contains the ferrocyanide concentration for each sample measured independently using solution techniques (Bryan et al. 1993b) as well as the calculated value A/c ($= \epsilon \cdot b$). The value A/c (labeled Normalized Absorbance) is displayed in Figure 6.1. This figure shows that for the different nickel ferrocyanide simulants, the value A/c (and therefore $\epsilon \cdot b$) has great variability depending on the source of sample. The wide variability in the extinction coefficient between samples leads to the conclusion that a solid sample method based on using ATR will not yield accurate results; the standard and the sample could have widely different response factors proportional to the differences in their extinction coefficients (see, for example, the differences in values of A/c for WHC-3 and IF1-21A in Figure 6.1).

Table 6.1. Measured Normalized Absorbance Values for Various Ferrocyanide Simulated Wastes. Normalized absorbance (A/c) is equal to the extinction coefficient multiplied by path length ($\epsilon \cdot b$).

Sample	ATR Absorb. (error)	wt% CN*	$A/c = \epsilon \cdot b$ (error)
FECN-36	2.42E-02 (5.00E-03)	32.12	7.54E-04 (1.56E-04)
FECN-33	1.57E-03 (5.00E-04)	0.98	1.59E-03 (5.08E-04)
IF2-26B	5.27E-03 (5.00E-03)	11.55	4.56E-04 (4.33E-04)
IF2-25B	6.75E-03 (4.00E-03)	10.37	6.51E-04 (3.38E-04)
IF1-24	4.37E-03 (1.00E-04)	13.75	3.18E-04 (7.27E-06)
IF1-21A	1.14E-01 (5.00E-02)	11.45	9.93E-03 (4.37E-03)
WHC-3	2.58E-02 (2.50E-02)	35.75	7.21E-04 (6.99E-04)
UP2-15B	3.21E-02 (5.00E-02)	3.11	1.03E-02 (1.61E-02)
WHC-2	1.96E-02 (1.00E-02)	29.48	6.66E-04 (3.39E-04)

* Measured by alternate method (Bryan et al. 1993b).

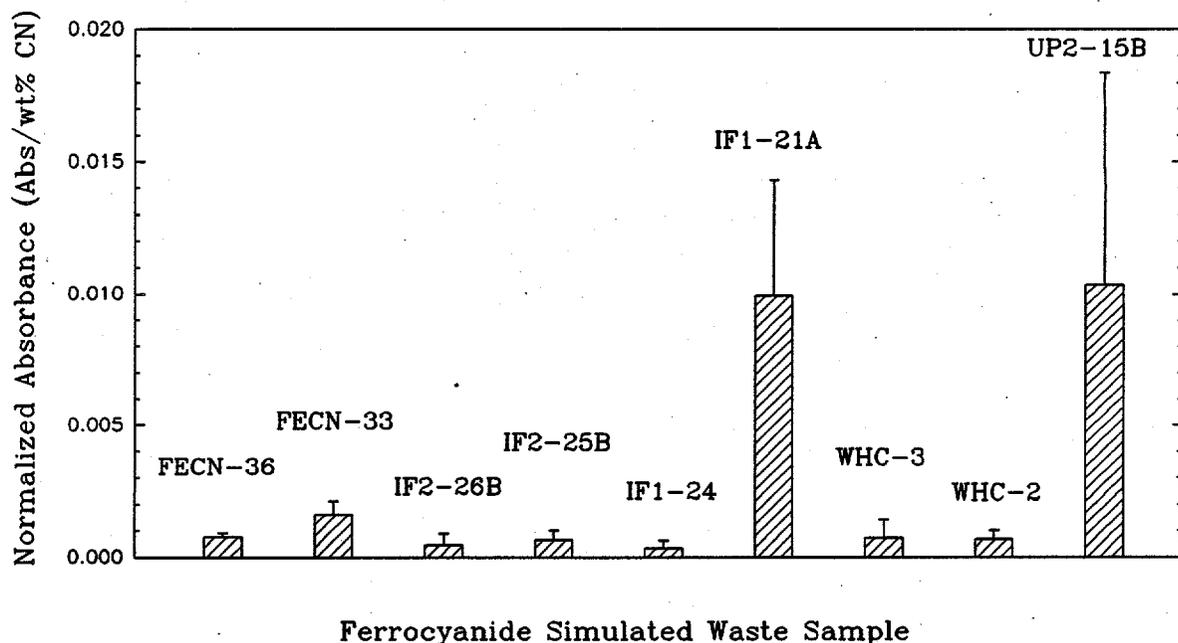


Figure 6.1. Measured Normalized Absorbance Values for Various Ferrocyanide Simulated Wastes. Normalized absorbance (A/c) is equal to the extinction coefficient multiplied by path length ($\epsilon \cdot b$).

6.2 Transmission FTIR Technique

Transmission FTIR sampling techniques on solid samples is possible by mounting a dilute sample within an IR-transparent film. This enables the direct bulk property IR measurement of the entire solid sample. This technique has advantages over the ATR method (detailed in Section 6.0) if for some reason the concentration of the analyte at the surface is different from the average bulk concentration. Differences between surface and bulk concentration of analytes may happen for small or colloidal particles that co-precipitate with ionic species coating the surfaces of the solids.

The most common solid sampling technique for transmission measurements involves grinding the sample with potassium bromide (KBr) (0.01 to 0.5 wt% mixture) followed by pressing the mixture (at 20,000 psi), forming a KBr glass matrix containing a finely mixed dispersed sample. Infrared absorbance measurements can be made directly by placing the KBr sample pellet in the infrared sample compartment.

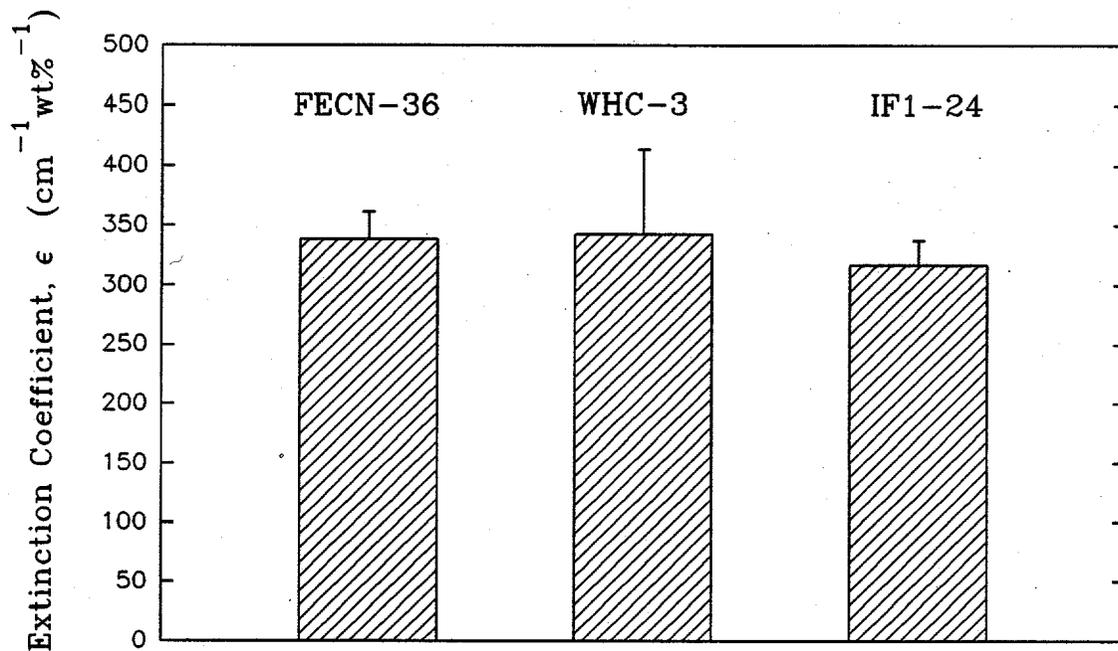
Absorbance measurements were performed on KBr sample pellets prepared using various nickel ferrocyanide samples. The extinction coefficients for KBr pellets can readily be measured using Equation 6.1 with knowledge of the concentration and absorbance, because the path length of the KBr pellet can be directly measured. The extinction coefficients measured for these samples are included in Table 6.2 for comparison.

Table 6.2. Extinction Coefficients for Various Ferrocyanide Simulated Waste from Transmission FTIR Measurements.

<u>Sample</u>	<u>Extinction Coefficient, ϵ, $\text{cm}^{-1}\text{wt}\%^{-1}$ (std dev)</u>
FECN-36	338.3 (23.3)
WHC-3	342.6 (71.0)
IF1-24	317.3 (19.8)

The agreement between values for the extinction coefficient for the three samples in Table 6.2 is excellent. These data are displayed in Figure 6.2. The agreement of the extinction coefficients between samples enables any of these different samples to be used as a standard for the quantification of the other samples using the KBr pellet method of solid sampling. WHC-3 and FECN-36 were prepared to be relatively pure ferrocyanide samples, and have been analyzed repeatedly in earlier work (Bryan et al. 1993b); therefore, they can be used as standards for the In-Farm-1 sample, IF1-24.

Two sets of standard addition samples were prepared using IF1-24 as the unknown in each, with WHC-3 and FECN-36 as the known standard in the first and second set, respectively. KBr pellets were prepared for these samples and analyzed using standard transmission FTIR techniques. The standard addition plot of the results is displayed in Figure 6.3. Analysis of this figure directly yields the concentration of the cyanide content within the KBr pellet; by correcting for the dilution with KBr, the concentration of the original IF1-24 sample is calculated as 14.42 (± 0.77) wt% (as cyanide). This result agrees well with the accepted value of 13.75 wt% for this sample (Bryan et al. 1993b).



Ferrocyanide Simulated Waste Sample

Figure 6.2. Extinction Coefficients for Various Ferrocyanide Simulated Waste from Transmission FTIR Measurements.

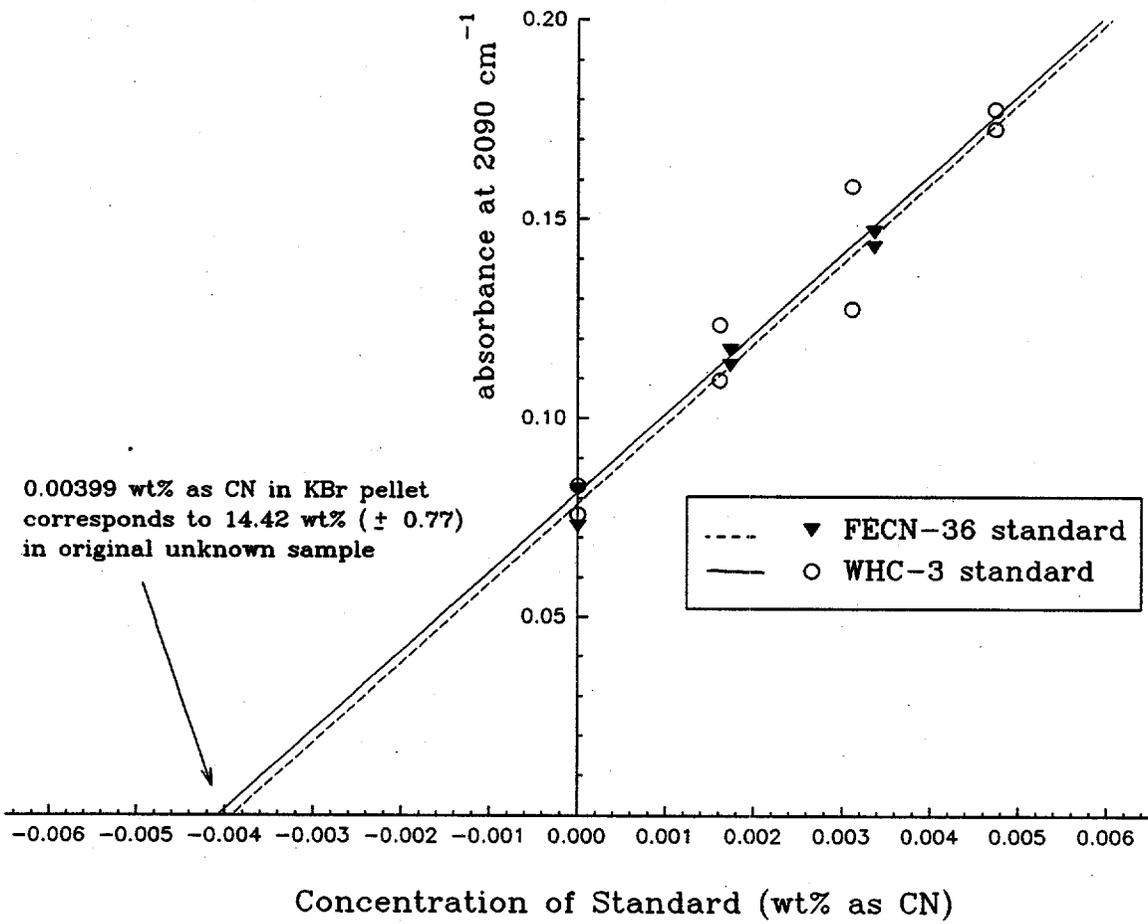


Figure 6.3. Standard Addition Method for Solid Ferrocyanide Simulated Waste Samples Using Transmission FTIR Technique.

7.0 Status of Cyanide Speciation Studies

This section summarizes the status of work performed during FY 1994 within the Cyanide Speciation Task of the Ferrocyanide Safety Program. In FY 1994, we continued the investigation of measuring the influence of chemical additives on the IC and FTIR analytical methods as well as adapted the FTIR analytical hardware into a radiation zone for handling radioactive samples. The status of these activities are described below:

1. *Influence of Chemical Additives on Cyanide Species Analysis.* We found that for IC there is qualitative measurement of the ferricyanide and ferrocyanide with added organic interferents. Quantitative measurements for these cyanide complexes also were found with added inorganic interferents, with the exception of nitrate and nitrite ions. This problem is not associated with the ability of the IC system to separate the nitrate or nitrite ions from the ferricyanide and ferrocyanide species, but is due to the co-absorbance of these interfering ions with the cyanide complexes of interest. This problem is currently being resolved by the use of matrix-matched standards for the ferri- and ferrocyanide complexes.

The simulant testing using FTIR methods have been completed. Tests on actual tank waste samples will be performed into FY 1995. Test dates on actual waste samples will depend significantly on the timing of the re-opening of the 325 Building for performing routine radioactive sample handling.

2. *Location of FTIR Analytical System into Radiation Zone.* FTIR equipment was transferred and installed within a radiologically controlled laboratory. The detector and analytical cell used for the analysis of solution samples was mounted remotely from the main optical bench in order to allow placement of the detector into a radio-controlled fume hood.

Tests on actual tank waste samples are planned to be performed in FY 1995. Test dates on actual waste samples will depend significantly on the timing of the re-opening of the 325 Building for performing routine radioactive sample handling.

3. *Reduction of ^{137}Cs Content in Actual Waste Samples to Address ALARA Concerns.* Due to the ^{137}Cs content in actual ferrocyanide tank samples, a need was identified to reduce the personnel exposure to as low a reasonably achievable (ALARA). To address this goal, we plan in FY 1995 to adapt existing methods for cesium ion removal currently performed on flammable gas tank wastes (Campbell et al. 1994) to the ferrocyanide tank wastes. This method has been successfully demonstrated for the removal of significant levels of radioactivity from tank samples to allow the samples to be removed from the hot cell environment for bench-top handling. This will benefit the program in terms of reduced personnel exposure as well as time savings during actual sample manipulation and measurement.

8.0 References

- Bryan, S. A., K. H. Pool, L. L. Burger, C. D. Carlson, N. J. Hess, J. D. Matheson, J. L. Ryan, R. D. Scheele, and J. M. Tingey. 1993a. *Ferrocyanide Safety Project, Task 3.5 Cyanide Species Analytical Methods Development, FY 1992 Annual Report*. PNL-8399, Pacific Northwest Laboratory, Richland, Washington.
- Bryan, S. A., K. H. Pool, S. L. Bryan, R. L. Sell, and L. M. P. Thomas. 1993b. *Ferrocyanide Safety Program Cyanide Speciation Studies FY 1993 Report*. PNL-8887, Pacific Northwest Laboratory, Richland, Washington.
- Burger, L. L. 1984. *Complexant Stability Investigations. Task 1. Ferrocyanide Solids*. PNL-5441, Pacific Northwest Laboratory, Richland, Washington.
- Burger, L. L., and R. D. Scheele. 1988. *Interim Report on Cyanide Safety Studies*. PNL-7175, Pacific Northwest Laboratory, Richland, Washington.
- Burger, L. L., and R. D. Scheele. 1990. *The Reactivity of Cesium Nickel Ferrocyanide Towards Nitrate and Nitrite Salts*. PNL-7550, Pacific Northwest Laboratory, Richland, Washington.
- Burger, L. L., D. A. Reynolds, W. W. Schulz, and D. M. Strachan. 1991. *A Summary of Available Information on Ferrocyanide Tank Wastes*. PNL-7822, Pacific Northwest Laboratory, Richland, Washington.
- Campbell, J. A., S. Clauss, K. Grant, V. Hoopes, B. Lerner, R. Lucke, G. Mong, J. Rau, R. Steele. 1994. *Flammable Gas Safety Program Analytical Methods Development: FY 1993 Progress Report*. PNL-9062, Pacific Northwest Laboratory, Richland, Washington.
- Hallen, R. T., L. L. Burger, R. L. Hockey, M. A. Lilga, R. D. Scheele, and J. M. Tingey. 1991. *Ferrocyanide Safety Project FY 1991 Annual Report*. PNL-8165, Pacific Northwest Laboratory, Richland, Washington.
- Hanlon, B. M. April 1991. *Tank Farm Surveillance and Waste Status Report for December 1990*. WHC-EP-0182-33, Westinghouse Hanford Company, Richland, Washington.
- Hepworth, J. L., E. D. McClanahan, and R. L. Moore. 1957. *Cesium Packaging Studies - Conversion of Zinc Ferrocyanide to a Cesium Chloride Product*. HW-48832, Hanford Atomic Products Operation, Richland, Washington.
- Peach, J. D. October 1990. Letter B-241479 to M. Synar, "Consequences of Explosion of Hanford's Single-Shell Tanks are Understated," GAO/RCED-91-34, General Accounting Office, Washington, D.C.

U.S. Department of Energy (DOE). 1987. *Final Environmental Impact Statement, Disposal of Hanford Defense High-Level, Transuranic, and Tank Wastes*. DOE-EIS-0113, U.S. Department of Energy, Washington, D.C.

Scheele R. D., and H. H. Cady. 1989. *Preliminary Safe-Handling Experiments on a Mixture of Cesium Nickel Ferrocyanide and Equimolar Sodium Nitrate/Nitrite*. PNL-7928, Pacific Northwest Laboratory, Richland, Washington.

Scheele, R. D., L. L. Burger, J. M. Tingey, S. A. Bryan, G. L. Borsheim, B. C. Simpson, R. J. Cash, and H. H. Cady. 1991. "Ferrocyanide Containing Waste Tanks: Ferrocyanide Chemistry and Reactivity." In the *Proceedings of Environmental Restoration '91*, University of Arizona, Tucson, Arizona.

Scheele, R. D., L. L. Burger, J. M. Tingey, R. T. Hallen, and M. A. Lilga. 1992. "Chemical Reactivity of Potential Ferrocyanide Precipitates in Hanford Tanks with Nitrates and Nitrites." In the *Proceedings of Waste Management '92*, Tucson, Arizona.

Distribution

No. of Copies		No. of Copies
	Offsite	
12	DOE/Office of Scientific and Technical Information	Gregory R. Choppin Florida State University Department of Chemistry B-164 Tallahassee, FL 32306
	Charles S. Abrams 1987 Virginia Idaho Falls, ID 83404	Melvin W. First Harvard University 295 Upland Avenue Newton Highlands, MA 02161
	George E. Schmauch Air Products & Chemicals, Inc. 7201 Hamilton Blvd. Allentown, PA 18195-1501	Chester Grelecki Hazards Research Corporation 200 Valley Road, Suite 301 Mt. Arlington, NJ 07856
	James A. Gieseke Battelle Columbus Division 505 King Avenue Columbus, OH 43201-2693	Billy Hudson 202 Northridge Court Lindsborg, KS 67456
	Kamal K. Bandyopadhyay Brookhaven National Laboratory Upton, NY 11973	Thomas S. Kress P.O. Box 2009 9108, MS-8088 Oak Ridge, TN 37831-8088
	David O. Campbell 102 Windham Road Oak Ridge, TN 37830	3 Los Alamos National Laboratory P.O. Box 1663 Los Alamos, NM 87545 ATTN: Steve F. Agnew Steve Eisenhower Thomas E. Larson
	Fred N. Carlson 6965 North 5th West Idaho Falls, ID 83401	
	Gary Powers Design Science, Inc. 163 Witherow Road Sewickley, PA 15143	Mujid S. Kazimi MIT/Dept of Nuclear Eng. 77 Massachusetts Avenue Room 24-102 Cambridge, MA 02139
	Hans K. Fauske Fauske and Associates, Inc. 16W070 W. 83rd Street Burr Ridge, IL 60521	Louis Kovach Nuclear Consulting Services, Inc. P.O. Box 29151 Columbus, OH 43229-0151

**No. of
Copies**

**No. of
Copies**

2 Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831-6385
ATTN: Emory D. Collins, MS-6385
Charles W. Forsberg, MS-6495

Arlin K. Postma
3640 Ballard Road
Dallis, OR 97338

William R. Prindle
1556 Crestline Drive
Santa Barbara, CA 93105

Rice University
5211 Paisley
Houston, TX 77096
ATTN: Andrew S. Veletsos

2 Sandia National Laboratory
P.O. Box 5800
Albuquerque, NM 87185
ATTN: Scott E. Slezak, MS-0741
Dana Powers, MS-0744

Alfred Schneider
5005 Hidden Branches Drive
Dunwoody, GA 30338

3 Science Applications International
Corporation
20300 Century Blvd., Suite 200-B
Germantown, MD 20874
ATTN: Ray S. Daniels (3)

Michael T. Gordon
State of Washington
Department of Ecology
P. O. Box 47600
Olympia, WA 98504-7600

Alex Stone
1315 W. 4th Avenue,
Kennewick, WA 99336

6 U.S. Department of Energy
EM-36, Trevion II
12800 Middlebrook Road
Germantown, MD 20874
ATTN: James V. Antizzo
Charles O'Dell (5)

Thomas C. Temple
U.S. Department of Energy
Savannah River Operations Office
P.O. Box A
Aiken, SC 29808

University of Washington
Center for Process Analytical
Chemistry
Chemistry Department BG-10
Seattle, WA 98195
ATTN: Bruce R. Kowalski

University of South Carolina
Department of Electrical and
Computer Engineering
Swearingen Engineering Center
Columbia, SC 29208
ATTN: Joseph S. Byrd

Vanderbilt University
P.O. Box 1596, Station B
Nashville, TN 37235
ATTN: Frank L. Parker

Donald T. Oakley
Waste Policy Institute
555 Quince Orchard Road,
Suite 600
Gaithersburg, MD 20878-1437

**No. of
Copies**

**No. of
Copies**

Onsite

**12 U.S. Department of Energy
Richland Operations Office**

R. F. Christensen (4), S7-54
R. E. Gerton (4), S7-54
A. G. Krasopoulos, A4-81
Public Reading Room, H2-53
RL Docket File (2), H5-36

H. Toffer, H0-38
W. T. Watson, H0-38
W. D. Winkelman, L5-55
D. D. Wodrich, S7-84
W. F. Zuroff, S7-12
Central Files, L8-04
Document Processing and
Distribution (2), L8-15
EDMC, H6-08
TFIC, R1-20

37 Westinghouse Hanford Company

H. Babad, S7-30
J. B. Billetdeaux, S7-16
D. C. Board, S1-57
G. L. Borsheim, H5-27
R. J. Cash (5), S7-15
M. D. Crippen, L5-31
D. R. Dickinson, L5-31
G. T. Dukelow, S7-15
J. M. Grigsby, H4-62
M. E. Huda, R3-08
M. N. Islam, R3-08
D. W. Jeppson, L5-31
N. W. Kirch, R2-11
C. A. Kuhlman, B3-30
M. Kummerer, H4-62
J. M. McLaren, H0-34
J. E. Meacham, S7-15
N. J. Milliken, H4-62
S. R. Moreno, B3-06
M. A. Payne, S7-14
F. R. Reich, L5-63
C. P. Schroeder, L7-06
B. C. Simpson, R2-12

47 Pacific Northwest Laboratory

R. M. Bean, P8-08
J. W. Brothers, K5-22
S. A. Bryan (20), P7-25
S. L. Bryan, P7-25
L. L. Eyler, K7-15
L. L. Fassbender, K8-18
A. R. Felmy, K6-82
S. C. Goheen, P8-08
B. M. Johnson, K1-78
B. D. Lerner, P8-08
M. A. Lilga, P8-38
B. P. McGrail, K2-38
K. H. Pool, P8-44
A. W. Prichard, K8-34
D. Rai, K6-82
R. D. Scheele, P7-25
G. F. Schiefelbein (2), P8-38
R. L. Sell, P7-25
C. W. Stewart, K7-15
D. M. Strachan, K2-44
L.M.P. Thomas, P8-44
Publishing Coordination
Technical Report Files (5)