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Ferrocyanide Safety Program Cyanide Speciation Studies FY 1993 Annual Report

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September 1993

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

Pacific Northwest Laboratory
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Summary

This report summarizes Pacific Northwest Laboratory's (PNL) FY 1993 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 (DOE) 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 the amount of ferrocyanides present within actual waste tanks to a lower limit of at least 0.1 wt% up to approximately 15 wt%. The target analyte concentration for cyanide in waste is approximately 0.1 to 15 wt% (as CN) 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 CN).

In FY 1992, 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 during FY 1993. 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^-, $Fe(CN)_6^{4-}$, and $Fe(CN)_6^{3-}$] 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 (over 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. For the ferricyanide analyte, nitrite was the only inorganic additive observed to interfere with the detection of that species by the quantitative conversion of the ferricyanide complex to ferrocyanide. Several organic additive 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^-, $Fe(CN)_6^{4-}$, and $Fe(CN)_6^{3-}$] expected in samples from the Hanford ferrocyanide waste tanks. We have selected these analytes since 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 CN) 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.

Glossary

ATR	attenuated total reflectance
DI	deionized
DOE	U.S. Department of Energy
EDTA	ethylenediaminetetraacetic acid
EIS	environmental impact statement
en	enthylenediamine
FTIR	Fourier transform infrared
FY	fiscal year
HEDTA	hydroxyethyl-ethylenediaminetriacetic acid
HWL	high-level waste
IC	ion chromatography
IDA	iminodiacetic acid
IR	infrared
MCT	mercury cadmium telluride
NPH	normal paraffin hydrocarbon
NTA	nitrilotriacetic acid
PNL	Pacific Northwest Laboratory
SST	single-shell tank
TBP	tributylphosphate
USQ	unreviewed safety question

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1.0 Introduction

Radioactive waste from defense operations has accumulated in underground waste tanks at the U.S. Department of Energy's (DOE) Hanford Site since the early 1940s. During the 1950s, additional storage volume was required to continue supporting the defense mission. To meet this need quickly and without constructing additional storage tanks, Hanford Site scientists developed a process to scavenge radiocesium from tank waste liquids by precipitating alkali nickel ferrocyanide. This process rendered the defense waste suitable for storage in underground tanks, and approximately 140 metric tons of ferrocyanide was added to 24 underground single-shell tanks (SSTs).

Ferrocyanide is a stable complex of ferrous ion and cyanide that is considered nontoxic because it does not dissociate in aqueous solutions. However, in the presence of oxidizing materials such as nitrates and nitrites, ferrocyanide can explode when heated to high temperatures (above 285°C) or when exposed to an electrical spark of sufficient energy. While the explosive nature of ferrocyanide in the presence of an oxidizer has been understood for decades, the conditions under which the compound can undergo an uncontrolled exothermic reaction have not been thoroughly studied. Because the radiocesium scavenging process initiated in the 1950s involved precipitating ferrocyanide from solutions containing nitrate and nitrite, intimate mixtures of ferrocyanides and nitrates and nitrites may exist in parts of some of the SSTs.

Efforts have been underway at Pacific Northwest Laboratory (PNL)[a] since the mid 1980s to develop an understanding of conditions necessary for a ferricyanide explosion in the Hanford Site SSTs (Burger 1984; Burger and Scheele 1988). Based partly on this research, a final environmental impact statement (EIS) (DOE 1987) was issued in 1987. The EIS projected that the bounding "worst case" accident in a ferrocyanide tank would be an explosion resulting in a subsequent short-term radiation dose to the public of 200 mrem. However, a General Accounting Office study (Peach 1990) postulated a greater worst case accident with independently calculated doses one to two orders of magnitude greater than the 1987 EIS (DOE 1987). A special Hanford Site Ferrocyanide Task Team was commissioned in September 1990 to address all issues involving the ferrocyanide tanks, including the consequences of a potential accident. Shortly after, DOE declared the ferrocyanide issue an Unreviewed Safety Question (USQ) because the safety envelope for these tanks may no longer be bounded by the existing safety analysis report.

To work toward resolving the USQ, the Task Team implemented the four-component Ferrocyanide Safety Program. The first component is tank monitoring. This activity involves the maintenance, development, and deployment of instrumentation for continuous monitoring of the tank contents. The second program component is the modeling and analysis of existing tank data. This effort allows for 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

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space, surface samples, and core samples from the ferrocyanide tanks. The fourth program component is research and development. This activity has the objective 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 discusses a comparison of various methods for dissolving ferrocyanide materials. Section 3.0 discusses the influences of inorganic and organic chemical additives on cyanide species. Section 4.0 is a test procedure for determining cyanide species in ferrocyanide flowsheet materials. Section 5.0 presents the results of analyses of flowsheet materials achieved using Fourier transform infrared, ion chromatography, and microdistillation methods. Section 6.0 contains a reference list.

2.0 Comparison of Various Methods for Dissolving Ferrocyanide Materials

In Bryan et al. (1993), we discussed the merits of several methods for dissolving ferrocyanide materials. Of those methods, two were considered at the top of the list: 1) aqueous ethylenediaminetetraacetic acid (EDTA) and ethylenediamine (en) solution, and 2) aqueous sodium hydroxide solution.

We chose the EDTA/en solution method over the NaOH method for four reasons. First, a true solution was achieved with each simulated ferrocyanide waste that was examined. Second, the use of hydroxide to free the ferrocyanide resulted in the formation of $Ni(OH)_2$ precipitate as a necessary product of the reaction, which must be filtered before analysis. The following equilibria illustrate these first two points:

NaOH treatment leads to:

$$Na_2NiFe(CN)_{6(s)} + 2OH^- \rightarrow 2Na^+ + Fe(CN)_6^{4-} + Ni(OH)_{2(s)}$$

EDTA/en treatment leads to:

$$Na_2NiFe(CN)_{6(s)} + EDTA^{4-} \rightarrow 2Na^+ + Fe(CN)_6^{4-} + Ni(EDTA)^{2-}$$

Third, the EDTA/en mixture is an excellent buffer material that resists pH changes with dilution of the sample, which is important because of the decreased solubility of the nickel ferrocyanide complex at lower pH values. Buffer capacity is demonstrated by the experimental results listed in Table 2.1. As the solution was diluted by as much as 10,000 times the original concentration, the pH changed by approximately 1 unit.

Table 2.1. Samples Containing 1% "Washed Vendor Material" and 5% EDTA/en Solution Diluted with Deionized Water at Various Dilution Factors and Resulting pH

Sample	pH
undiluted	9.97
10x	9.84
100x	9.76
1000x	9.64
10,000x	8.87

A fourth point in favor of using EDTA/en as the solvent is that it dissolves both cesium nickel ferrocyanide and sodium nickel ferrocyanide compounds. Although sodium hydroxide effectively dissolves most of the sodium nickel ferrocyanide, it is not effective at dissolving any of the cesium nickel ferrocyanide.

The dissolution capacities of EDTA/en, NaOH and deionized (DI) water when used with simulated ferrocyanide wastes were tested, and the results appear in Table 2.2. The quantity of ferrocyanide dissolved was measured using an FTIR solution method (Bryan et al. 1993). The three solvents, 5% EDTA/en solution, 1 M NaOH solution, and DI water, were tested with solid samples of $Na_2NiFe(CN)_6$ and $Cs_2NiFe(CN)_6$. These solids were chosen because both (or a mixed Na/Cs form) are believed to be present in actual ferrocyanide tank waste.

As seen in Table 2.2, the EDTA/en solvent dissolved approximately 4% more of the $Na_2NiFe(CN)_6$ than the NaOH, and over 90% more than DI water. In the $Cs_2NiFe(CN)_6$ dissolution experiment, the EDTA/en solvent dissolved all the solids (no solids were observed in the dissolution flask); however, by using the NaOH solvent, no detectable cyanide species were observed in solution. This simple test clearly shows the advantage of the EDTA/en solvent over the NaOH.

Table 2.2. Results of Dissolution of $Na_2NiFe(CN)_6$ and $Cs_2NiFe(CN)_6$ Using 5% EDTA/en, 1 M NaOH, and DI Water

	Percent Dissolved[(a)]	
Solvent Tested	$Na_2NiFe(CN)_6$	$Cs_2NiFe(CN)_6$
5% EDTA/en solution	100	100
1 M NaOH	96	~0
DI water	~8	NA[(b)]

(a) Relative to 5% EDTA/en solution.

(b) NA = not analyzed.

3.0 Influence of Chemical Additives on Cyanide Species Analysis

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 interferant 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).

3.1 Influence of Inorganic Chemical Additives on Cyanide Species Analysis

3.1.1 Inorganic Influence on Ferrocyanide [$Fe(CN)_6^{4-}$] Analysis

Each solution listed in Table 3.2 was routinely analyzed in triplicate using IR techniques. Absorbance measurements of the $Fe(CN)_6^{4-}$ ion were taken at the characteristic frequency for $Fe(CN)_6^{4-}$(2037 cm^{-1}). In each case, the matrix-matched sample was used as the reference solution for each of the ferrocyanide-containing solutions in Table 3.2. For example, solution 0A was used as the reference solution for sample 2B.

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	Tributylphosphode (TBP) (saturated)
$NaNO_3$	Glycerin
$NaAlO_2$	Ethylenediaminetetraacetic acid (EDTA)
	Sodium glycolate
	Iminodiacetic acid (IDA)
	Glycine
	Nitrilotriacetic acid (NTA)
	N-butanol
	Ethylenediamine (en)

Table 3.2. Compositions of Solutions Containing Various Potential Interferants and Ferrocyanide

Sample	Solution Components
0A	0.01 M NaOH
0B	0.01 M NaOH + $Fe(CN)_6^{4-}$ 0.011 wt% (as CN)
1A	0.5% Na_2SO_4 + 0.01 M NaOH
1B	0.5% Na_2SO_4 + 0.01 M NaOH + $Fe(CN)_6^{4-}$ 0.011 wt% (as CN)
2A	2.5% Na_2CO_3 + 0.01 M NaOH
2B	2.5% Na_2CO_3 + 0.01 M NaOH + $Fe(CN)_6^{4-}$ 0.011 wt% (as CN)
3A	2.7% Na_3PO_4 + 0.01 M NaOH
3B	2.7% Na_3PO_4 + 0.01 M NaOH + $Fe(CN)_6^{4-}$ 0.011 wt% (as CN)
4A	5.0% NaCl + 0.01 M NaOH
4B	5.0% NaCl + 0.01 M NaOH + $Fe(CN)_6^{4-}$ 0.011 wt% (as CN)
5A	20.0% $NaNO_2$ + 0.01 M NaOH
5B	20.0% $NaNO_2$ + 0.01 M NaOH + $Fe(CN)_6^{4-}$ 0.011 wt% (as CN)
6A	1.5% Na_2CrO_4 + 0.01 M NaOH
6B	1.5% Na_2CrO_4 + 0.01 M NaOH + $Fe(CN)_6^{4-}$ 0.011 wt% (as CN)
7A	0.5% NaF + 0.01 M NaOH
7B	0.5% NaF + 0.01 M NaOH + $Fe(CN)_6^{4-}$ 0.011 wt% (as CN)
8A	15.0% $NaNO_3$ + 0.01 M NaOH
8B	15.0% $NaNO_3$ + 0.01 M NaOH + $Fe(CN)_6^{4-}$ 0.011 wt% (as CN)
9A	2.5% $NaAlO_2$ + 0.01 M NaOH
9B	2.5% $NaAlO_2$ + 0.01 M NaOH + $Fe(CN)_6^{4-}$ 0.011 wt% (as CN)

The results of these absorbance measurements are shown in Figure 3.1. The $Fe(CN)_6^{4-}$concentration data are displayed as the ratio of the measured concentration of that species in each solution to the concentration measured in the standard sample (e.g., sample 0B, Table 3.2). According to these results, the presence of the potential interfering species does not change the measured concentration of ferrocyanide to any appreciable degree. The measured ferrocyanide concentrations in each solution were within 5% of the standard solution, except for the solution containing $NaAlO_2$, which was approximately 6% above the standard value. These results are very encouraging because 1) the $Fe(CN)_6^{4-}$ concentration was on the low concentration extreme expected to be encountered (0.0106%

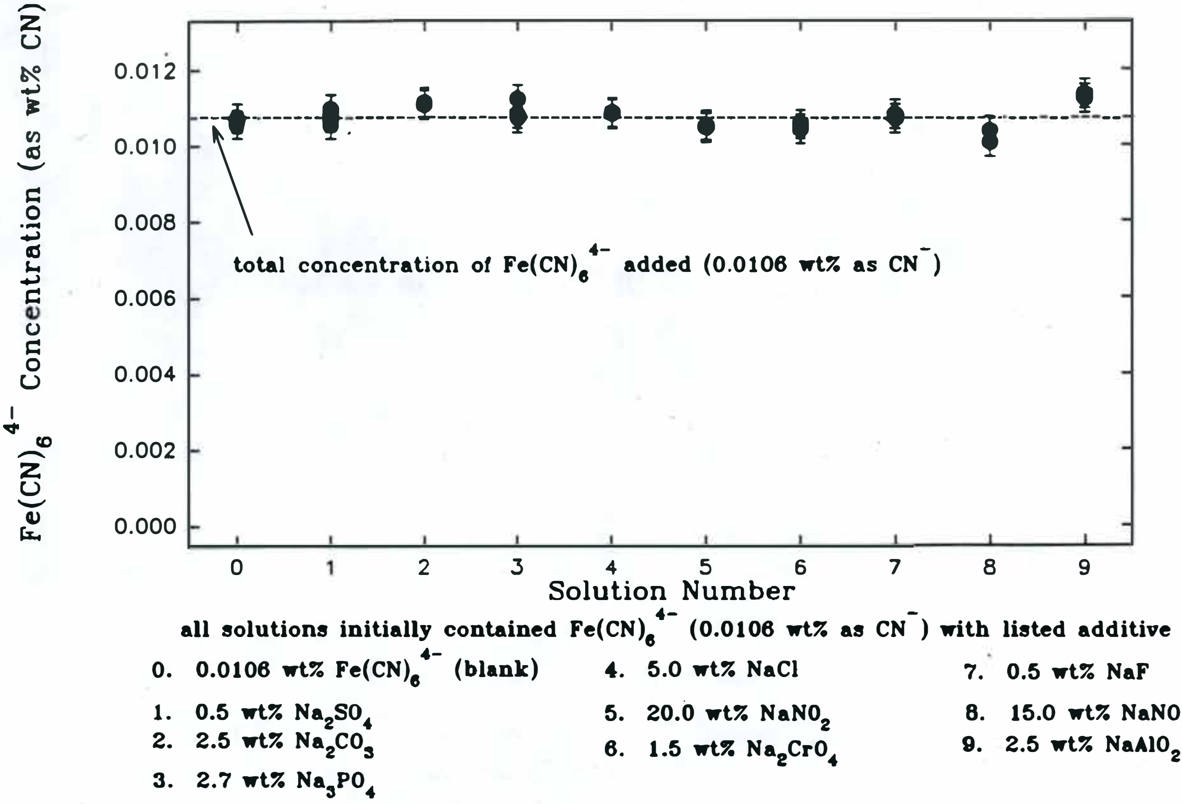


Figure 3.1. Concentration of Ferrocyanide in Solutions Containing Potential Interferants

as CN in each solution), and the potential interfering species was at the highest value expected in the analyzed samples. 2) There was no indication that the ferrocyanide (Fe^{2+}) complex oxidized to form ferricyanide (Fe^{3+}). Neither the Fe^{3+} product nor any other cyano complex was observed by IR measurements, as was confirmed by the excellent agreement in mass balance measurements indicated in Figure 3.1. 3) The potential interferants did not react with the solution cell or ATR element used in the experiment. It is critical that the solution cell and the ATR element be inert toward the solutions and species expected to be present within ferrocyanide waste samples.

3.1.2 Inorganic Influence on Ferrocyanide Analysis After 11 Weeks of Aging

The testing that was described in Subsection 3.1.1 was repeated after an aging period of 11 weeks. The results shown in Figure 3.2 indicate the presence of the potential interfering species did not change the measured concentration of ferrocyanide to any appreciable degree during the

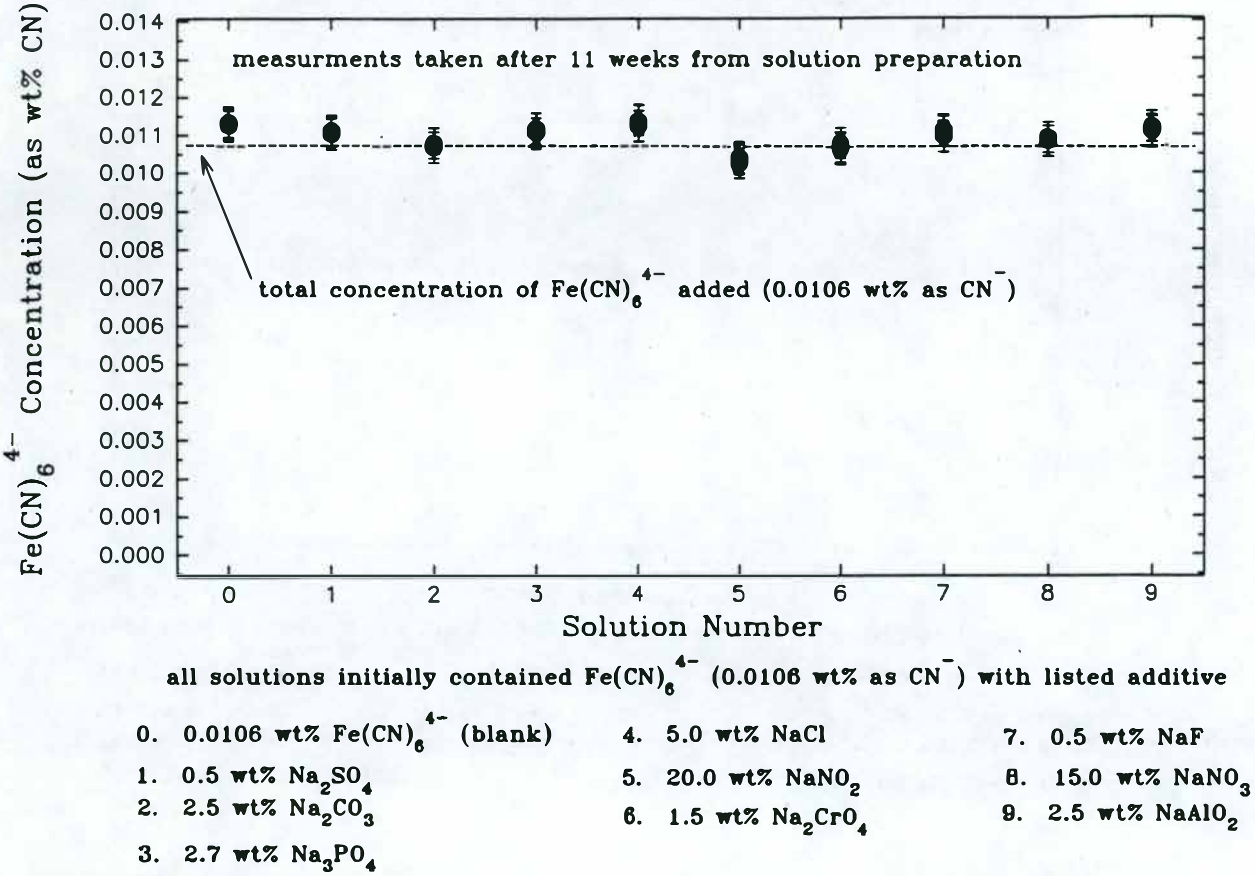


Figure 3.2. Concentration of Ferrocyanide in Solutions Containing Potential Interferants. These solutions were aged for 11 weeks before analysis.

11-week period. The measured concentration of the ferrocyanide in each solution containing a potential interferant was within 5% of the standard solution, except for the solution containing $NaNO_2$, which was approximately 8% below the standard value. These results are encouraging considering that the concentration of the $Fe(CN)_6^{4-}$ was on the low concentration extreme expected to be encountered (0.0106% as CN in each solution), and the potential interfering species was at the highest value expected in any of the analyzed samples. Further, there was no indication that the ferrocyanide (Fe^{2+}) complex oxidized to form ferricyanide (Fe^{3+}). Neither the Fe^{3+} product (nor any other cyano complex was observed by IR measurements.

3.1.3 Inorganic Influence on Ferricyanide [$Fe(CN)_6^{3-}$] Analysis

Solutions containing $Fe(CN)_6^{3-}$ (0.050 wt% as CN^-) with additive species were prepared as for the cyanide tests described in Subsection 3.1.1. Although dilute solutions of the ferricyanide species were shown to obey Beers Law, we observed a reaction of the ferricyanide complex (Fe^{3+}) in the presence of the additive species. Ferricyanide was converted stoichiometrically to the ferrocyanide complex (Fe^{2+}) when the analyte solution remained in the IR solution cell for more than several seconds.

Figure 3.3 shows the dynamic interconversion of the ferricyanide complex (band decreasing at 2118 cm^{-}) to the ferrocyanide complex (band growing at 2038 cm^{-}). The elapsed time for this interconversion was approximately 10 min. The reaction was not sensitive to the type of interfering species present, but occurred noticeably faster in the presence of a high ionic strength solution compared to the Beers Law analysis performed earlier with very low ionic strength solutions in which no redox interconversion was observed.

The reaction is described in Equation (1) in which the source of the reductant is most likely the stainless steel cell body of the IR solution cell. We can eliminate reduction from other sources since this reaction was independent of the interfering species, and the IR sensing element (constructed of cubic zirconia and not capable of acting as a reductant) had no measurable change in performance. The analyte solution did not contact any other material.

$$Fe^{III}(CN)_6^{3-} + e^- \rightarrow Fe^{II}(CN)_6^{4-} \qquad (1)$$

To demonstrate that this ferricyanide-to-ferrocyanide interconversion was quantitative, we followed the reaction of 0.025 wt% ferricyanide in 0.5 wt% Na_2SO_4 to completion using the IR method. The reactants were introduced directly into the stainless steel ATR IR cell. The absorbance data for ferricyanide and ferrocyanide species were converted to concentration units using standard Beers Law analysis techniques and are presented in Figure 3.4. According to Figure 3.4, the ferricyanide reduction is directly offset by the gain of ferrocyanide in solution, and the conversion is quantitative.

If the reduction of the ferricyanide complex to the ferrocyanide complex over time is dictated by a 1:1 stoichiometry according to Equation (1), then the disappearance rate of the Fe^{III}-cyanide complex should equal the appearance rate of the Fe^{II}-cyanide complex. Equation (2) models the concentration of the iron-cyanide complex as a function of time for a first order reaction. The concentration of the iron-cyanide complex follows pseudo first order reaction kinetics.

$$[\text{concentration of } Fe(CN)_6^{-3}] = a * e^{(-k*t)} + b \qquad (2)$$

where k is the first order rate constant, t is time, and a and b are constants.

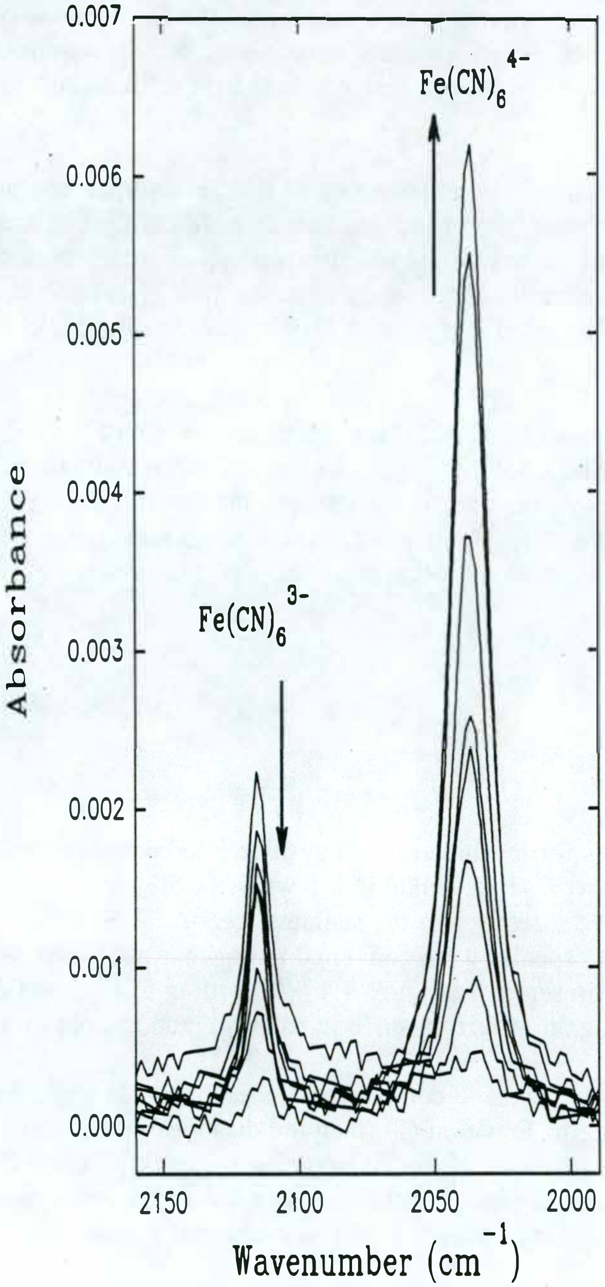


Figure 3.3. Infrared Spectral Changes Showing Ferricyanide Interconversion to Ferrocyanide by Reaction with Stainless Steel IR Solution Cell

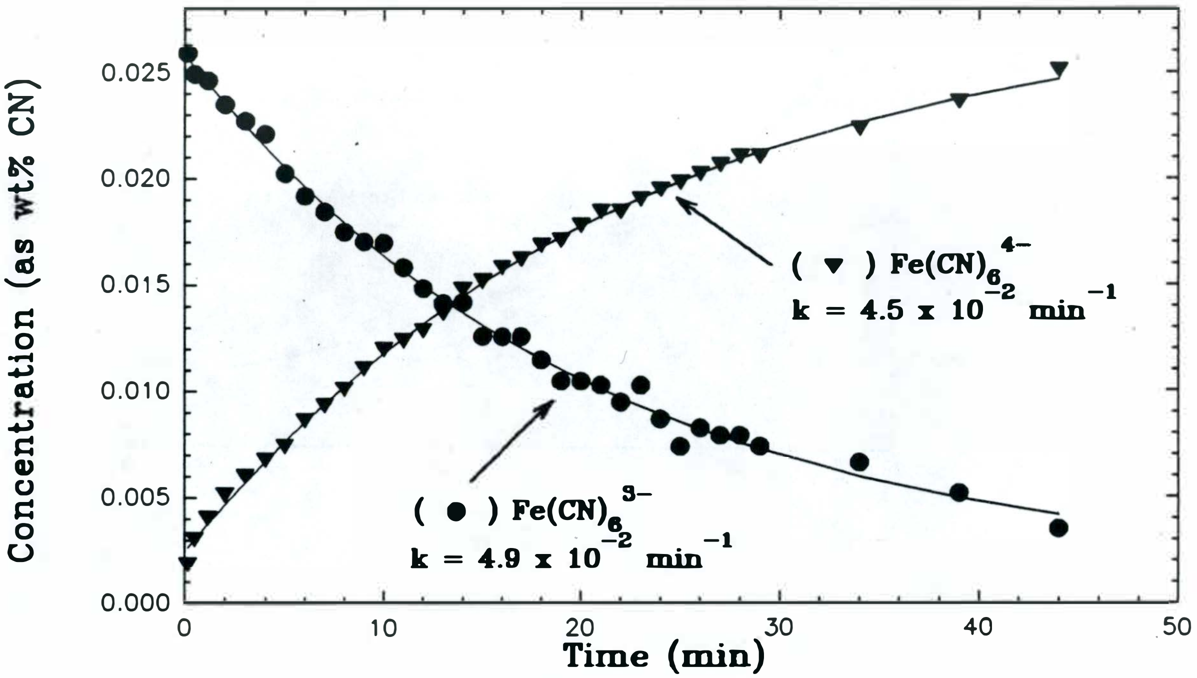


Figure 3.4. Concentration Versus Time Dependence Showing Ferricyanide Interconversion to Ferrocyanide by Reaction with Stainless Steel IR Solution Cell

The curves drawn in Figure 3.4 are fits of the data to Equation (2). The agreement between the calculated rate constants (k) derived independently for the Fe^{III} decrease (4.9×10^{-2} min^{-1}), and the concomitant Fe^{II} increase (4.5×10^{-2} min^{-1}) gives further evidence that the reactions are quantitative, with no measurable intermediate or side products. By demonstrating the quantitative conversion between species, the requirement to identify other species in solution was reduced.

The problem of the stainless steel IR cell acting as a reactant was considered a possibility when this method was designed. This problem can be eliminated by replacing the stainless steel cell with a similarly designed cell that is internally coated with Teflon. To demonstrate, a ferricyanide solution was measured by IR methods using both the stainless steel ATR cell and a Teflon-coated ATR cell. The concentration of the ferricyanide species for both experiments is shown in Figure 3.5.

The reaction of ferricyanide with the stainless steel ATR cell body was essentially eliminated by using the Teflon-coated ATR cell. These data indicate there was only about 5% loss of ferricyanide over a 30-min period using the Teflon-coated cell, but about 80% loss over the same period using the stainless steel cell. The sampling time after each solution was introduced into the ATR cells was approximately 1 min, which essentially eliminated the problem of the ferricyanide reaction with the cell.

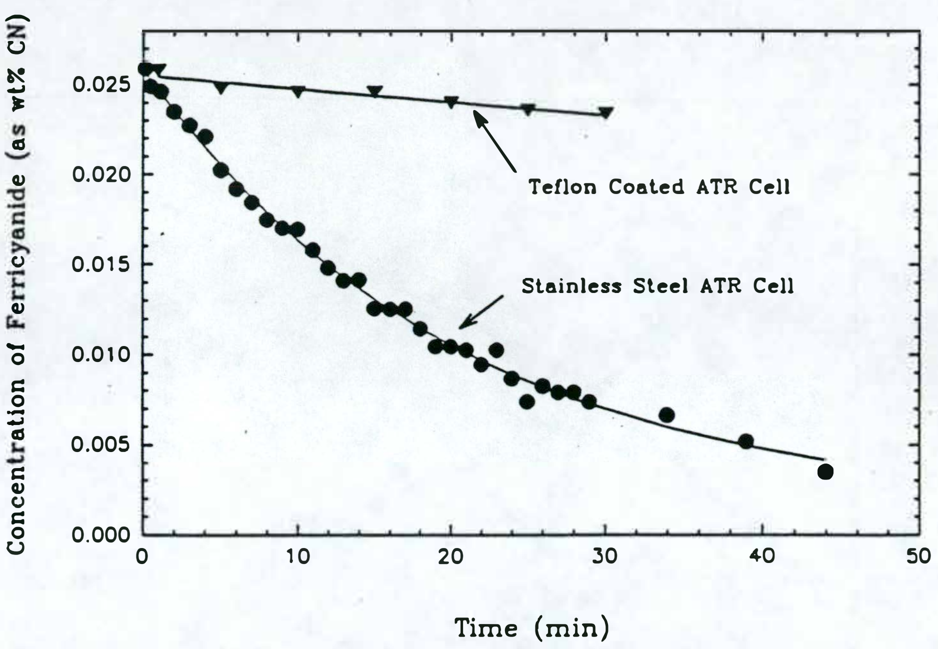


Figure 3.5. Ferricyanide Concentration in Solution Within a Stainless Steel ATR-IR Cell and Teflon Coated ATR-IR Cell

The standard curves for potassium ferricyanide solutions are shown in Figure 3.6. Absorbance data at the characteristic frequency for $Fe(CN)_6^{3-}$ (2114 cm^{-1}) were taken in triplicate at each concentration. Figure 3.6 shows data from standard solutions that were aged 2 months before analysis and solutions measured within 1 day of preparation. There is essentially no difference between the two data sets, indicating a shelf life of at least 2 months for ferricyanide standard solutions. Based on the signal-to-noise ratio of the most dilute standard, and on this equipment configuration, we conservatively estimate the detection limit of $Fe(CN)_6^{3-}$ to be approximately 0.005 wt% (calculated as CN^-).

Table 3.3 lists the solutions that were prepared containing suspected interfering species and the ferricyanide [$Fe(CN)_6^{3-}$] ion. The species concentrations were chosen based on ferrocyanide (U-Plant and In-Farm) and SST simulated waste flowsheets. Each solution was routinely analyzed in triplicate using IR techniques. Absorbance measurements of the cyanide ion were taken at the characteristic frequency for $Fe(CN)_6^{3-}$ (2114 cm^{-1}). In each case, the matrix-matched sample was used as the reference solution for each of the ferricyanide-containing solutions in Table 3.3. For example, solution 0A was used as the reference solution for sample 2B.

The results of these absorbance measurements are shown in Figure 3.7. The cyanide concentration data are displayed as the ratio of the measured concentration of that species in each solution to the concentration measured in the standard sample (e.g., sample 0B, Table 3.3).

Figure 3.7 presents both the ferricyanide concentration (●) and the ferrocyanide concentration (▿), as well as the sum of the ferricyanide and ferrocyanide concentrations (□). These results show that the presence of the potential interfering species does not change the total measured concentration

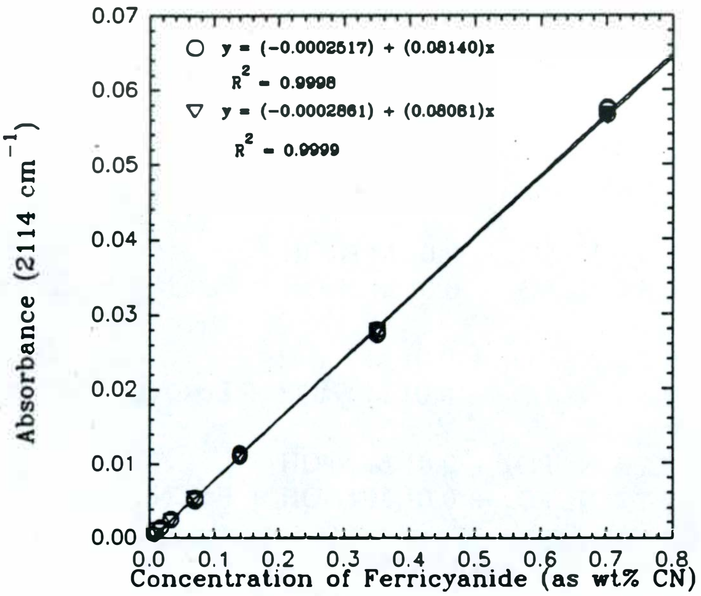


Figure 3.6. Standard Curve for Ferricyanide in Aqueous Solution

of ferricyanide and ferrocyanide (□) to any appreciable degree. For all the solutions except that containing nitrite ion (NO_2^-), the ferrocyanide concentration (▿) was essentially zero, and the ferrocyanide concentration (●) was essentially equal to the sum of ferricyanide and ferrocyanide in solution (□). The measured ferricyanide concentration in each solution containing a potential interferant was within about 5% of the standard solution, except for the solution containing $NaNO_2$; the measured concentration of ferricyanide and ferrocyanide (□) in each solution containing a potential interferant was within about 10% of the standard solution, *including* the solution containing $NaNO_2$.

The solutions containing nitrite and ferricyanide were prepared and measured immediately. The contact time of the solution with the IR solution cell (Teflon coated) was approximately 1 min, the nominal sample time for each solution. The times indicated in Figure 3.7 for the nitrite-containing solutions indicate the time span between solution preparation and sample analysis.

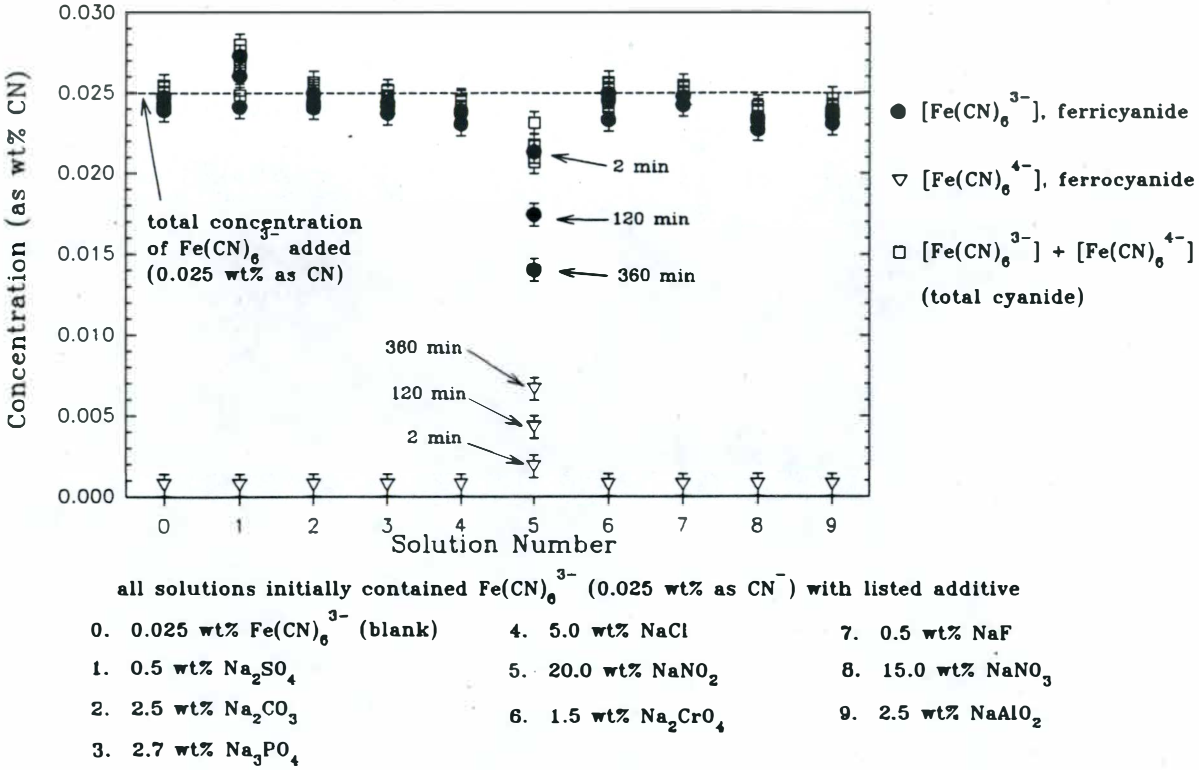
For the solutions containing nitrite (Figure 3.7), the ferricyanide concentration (●) decreased rather quickly over time, with a concurrent increase in the ferrocyanide concentration (▿). These results are very encouraging, especially considering the ferricyanide concentration was on the low concentration extreme expected to be encountered (0.025% as CN in each solution), and the potential interfering species was at the highest value expected in any of the samples to be analyzed.

Table 3.3. Compositions of Solutions Containing Various Potential Interferants and Ferricyanide

Sample	Solution Components
0A	0.01 M NaOH
0B	0.01 M NaOH + $Fe(CN)_6^{3-}$ 0.025 wt% (as CN)
1A	0.5% Na_2SO_4 + 0.01 M NaOH
1B	0.5% Na_2SO_4 + 0.01 M NaOH + $Fe(CN)_6^{3-}$ 0.025 wt% (as CN)
2A	2.5% Na_2CO_3 + 0.01 M NaOH
2B	2.5% Na_2CO_3 + 0.01 M NaOH + $Fe(CN)_6^{3-}$ 0.025 wt% (as CN)
3A	2.7% Na_3PO_4 + 0.01 M NaOH
3B	2.7% Na_3PO_4 + 0.01 M NaOH + $Fe(CN)_6^{3-}$ 0.025 wt% (as CN)
4A	5.0% NaCl + 0.01 M NaOH
4B	5.0% NaCl + 0.01 M NaOH + $Fe(CN)_6^{3-}$ 0.025 wt% (as CN)
5A	20.0% $NaNO_2$ + 0.01 M NaOH
5B	20.0% $NaNO_2$ + 0.01 M NaOH + $Fe(CN)_6^{3-}$ 0.025 wt% (as CN)
6A	1.5% Na_2CrO_4 + 0.01 M NaOH
6B	1.5% Na_2CrO_4 + 0.01 M NaOH + $Fe(CN)_6^{3-}$ 0.025 wt% (as CN)
7A	0.5% NaF + 0.01 M NaOH
7B	0.5% NaF + 0.01 M NaOH + $Fe(CN)_6^{3-}$ 0.025 wt% (as CN)
8A	15.0% $NaNO_3$ + 0.01 M NaOH
8B	15.0% $NaNO_3$ + 0.01 M NaOH + $Fe(CN)_6^{3-}$ 0.025 wt% (as CN)
9A	2.5% $NaAlO_2$ + 0.01 M NaOH
9B	2.5% $NaAlO_2$ + 0.01 M NaOH + $Fe(CN)_6^{3-}$ 0.025 wt% (as CN)

3.1.4 Inorganic Influence on Ferricyanide [$Fe(CN)_6^{3-}$] Analysis After 2 Months of Aging

The preparations of solutions containing suspected interfering species and ferricyanide [$Fe(CN)_6$-3] are included in Table 3.3 above. The species concentrations were chosen based on ferrocyanide (U-Plant and In-Farm) and SST simulated waste flowsheets. These solutions were analyzed immediately after preparation (reported earlier) and then were aged for 2 months before analysis. Next, each solution was routinely analyzed in triplicate using IR techniques. Absorbance measurements of the ferricyanide ion were taken of those solutions containing that species at the characteristic



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

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

Figure 3.7. Concentration of Ferricyanide (●), Ferrocyanide (▽), and Total Cyanide (□) in Solutions Containing Potential Interferants

frequency for $Fe(CN)_6^{3-}$ (2114 cm^{-1}). The results of these absorbance measurements of the ferricyanide complex in each solution containing potential interfering species are shown in Figure 3.8. The cyanide concentration data are displayed as the ratio of the measured concentration of that species in each solution to the concentration measured in the standard sample.

Figure 3.8 includes both the ferricyanide concentration (●) and the ferrocyanide concentration (▽), as well as the sum of the ferricyanide and ferrocyanide concentrations (□). These results show that the presence of the potential interfering species will not change the total measured concentration of ferricyanide and ferrocyanide (□) to any appreciable degree. For all the solutions except for that containing nitrite ion (NO_2^-), the concentration of ferrocyanide (▽) was essentially zero, and the concentration of ferricyanide (●) was essentially equal to the sum of ferricyanide and ferrocyanide in solution (□). The measured concentration of the ferricyanide in each solution containing a potential interferant was within about 5% of the standard solution, except for the solution containing $NaNO_2$; the measured concentration of ferricyanide and ferrocyanide (□) in each solution containing a potential interferant was within about 10% of the standard solution, *including* the solution containing $NaNO_2$.

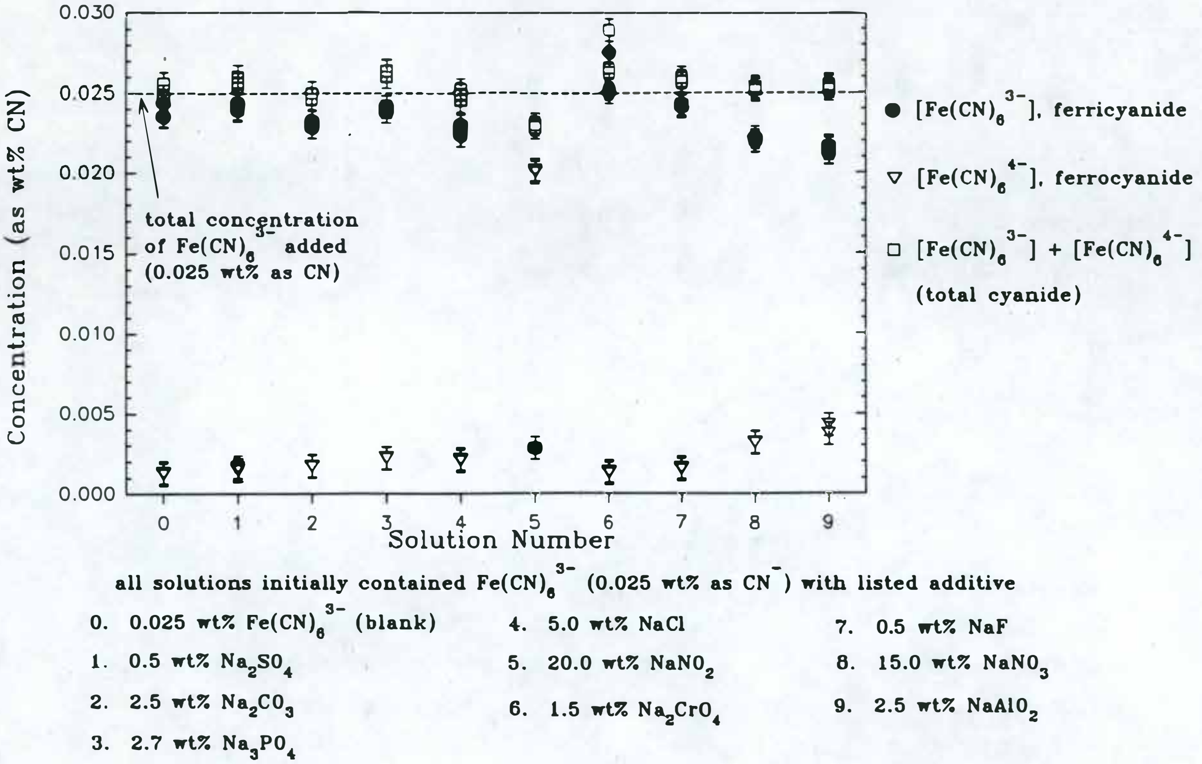


Figure 3.8. Concentration of Ferricyanide (●), Ferrocyanide (▽), and Total Cyanide (□) in Solutions Containing Potential Interferants. These solutions were aged 2 months before analysis.

For the solutions containing nitrite (Figure 3.8), the ferricyanide concentration (●) was approximately 10% of the original concentration; there was a concurrent increase in the ferrocyanide concentration in this solution (▽). The contact time of the solution with the IR solution cell (Teflon coated) was approximately 1 min, the nominal sample time for each solution.

These results are very encouraging considering that the concentration of the ferricyanide was on the low concentration extreme expected to be encountered (0.025% as CN in each solution), and the potential interfering species was at the highest value expected in any of the samples to be analyzed.

3.1.5 Inorganic Influence of pH on Nitrite Reactivity with Ferricyanide

The speciation and quantification of each cyanide complex in solution depend on the relative stability of these complexes during analysis. Therefore, the reactivity of nitrite with ferricyanide to form ferrocyanide under analytical measurement conditions is of interest. We demonstrated earlier (see Subsection 3.1.3) that nitrite will reduce ferricyanide to form ferrocyanide quantitatively. The pH dependence of the ferricyanide reaction with nitrite is important because, depending on conditions, this reaction may occur within the radioactive waste tank or during the required laboratory treatment steps before analysis.

The reaction of ferricyanide with nitrite under various pH conditions is shown in Figures 3.9, 3.10 and 3.11. These reactions correspond to 1 day, 9 days, and 23 days, respectively, of reaction time after preparation. Each solution was prepared with the same ferricyanide concentration (0.12 wt% as CN), 20 wt% $NaNO_2$, with the pH adjusted to the desired level by adding of HNO_3 or NaOH. Aliquots of each solution were analyzed for all cyanide species present. Ferricyanide $[Fe(CN)_6^{3-}]$ and ferrocyanide $[Fe(CN)_6^{4-}]$ complexes were the only cyanide species observed in solution. Figures 3.9 through 3.11 show that the conversion of ferricyanide to ferrocyanide is slow at low pH values and increases with pH and time. These data indicate that although the reaction is not extremely fast, it is fast enough to occur in the time frames of tank waste aging.

Identical solutions were prepared containing ferricyanide at the various pH values, (no nitrite was added). In these solutions, shown in Figures 3.12, 3.13, and 3.14, no conversion of ferricyanide was observed after 1 day of reaction time. At longer reaction times, the solutions containing ferrocyanide at higher pH values (10.5 and 12.4) showed slow conversion of ferricyanide to ferrocyanide.

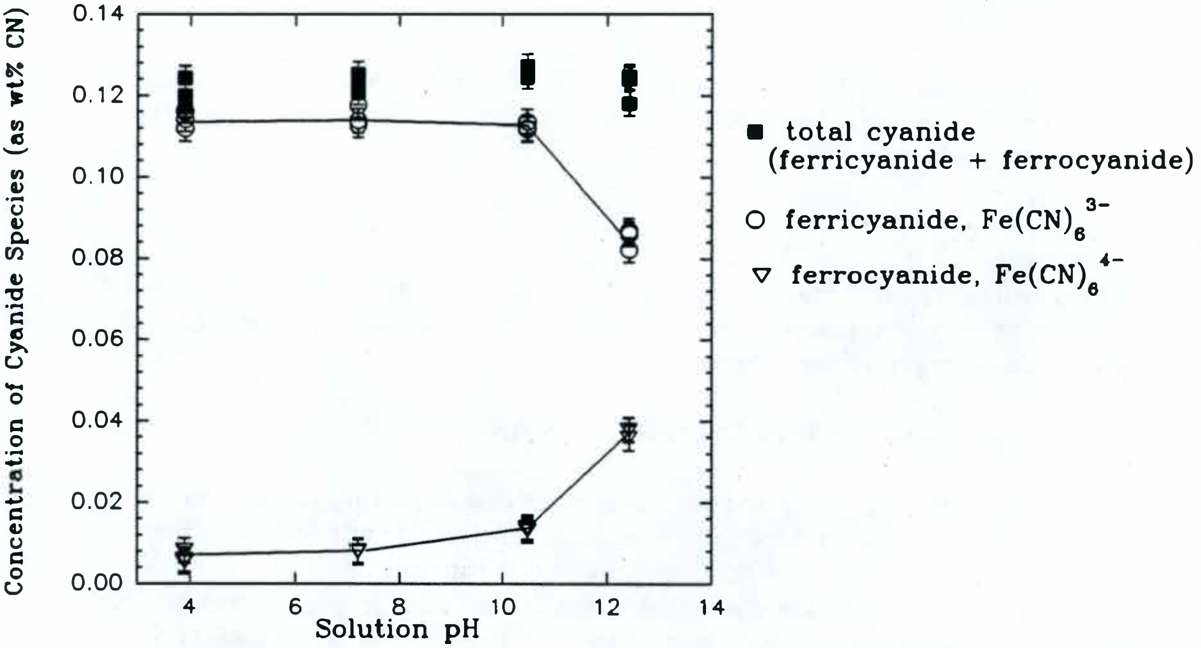


Figure 3.9. Concentration of Ferricyanide (○), Ferrocyanide (▽), and Total Cyanide (■) in Various Solutions 1 Day After Preparation. These solutions initially contained 20 wt% nitrite and 0.12 wt% ferricyanide.

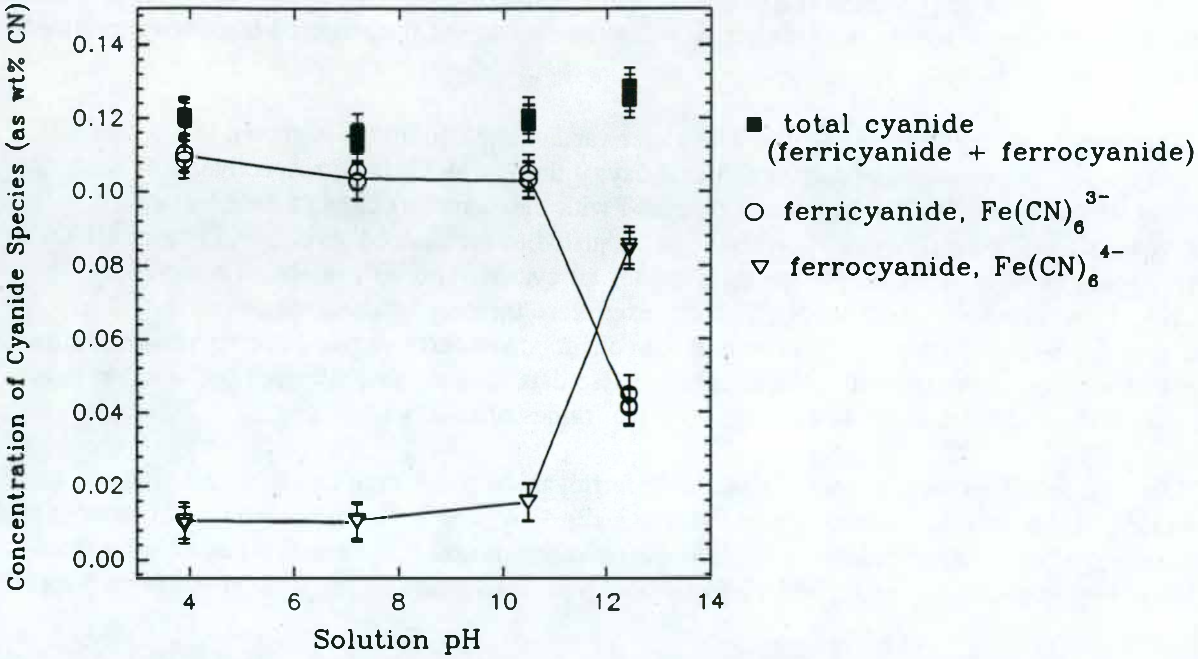


Figure 3.10. Ferricyanide (○), Ferrocyanide (▽), and Total Cyanide (■) of Various Solutions 9 Days After Preparation. These solutions initially contained 20 wt% nitrite and 0.12 wt% ferricyanide.

These reactions demonstrate that the conversion of ferricyanide to ferrocyanide will proceed at any pH with the addition of nitrite; however, the conversion of ferricyanide to ferrocyanide will proceed without nitrite addition at pH 10.5 and higher.

3.1.6 Inorganic Influence on Free Cyanide (CN^-) Analysis

Table 3.4 lists the solutions prepared containing suspected interfering species and free cyanide (CN^-). The species concentrations were chosen based on ferrocyanide and SST simulated waste flowsheets. Each solution in Table 3.4 was routinely analyzed in triplicate using IR techniques. Absorbance measurements of the cyanide ion were taken at the characteristic frequency for CN^- (2080 cm^{-1}). In each case, the matrix-matched sample was used as the reference solution for each of the cyanide-containing solutions in Table 3.4. For example, solution 0A was used as the reference solution for sample 0B.

The results of these absorbance measurements are shown in Figure 3.15. The cyanide concentration data are displayed as the ratio of the measured concentration of that species in each solution to the concentration measured in the standard sample (e.g., sample 0B, Table 3.4).

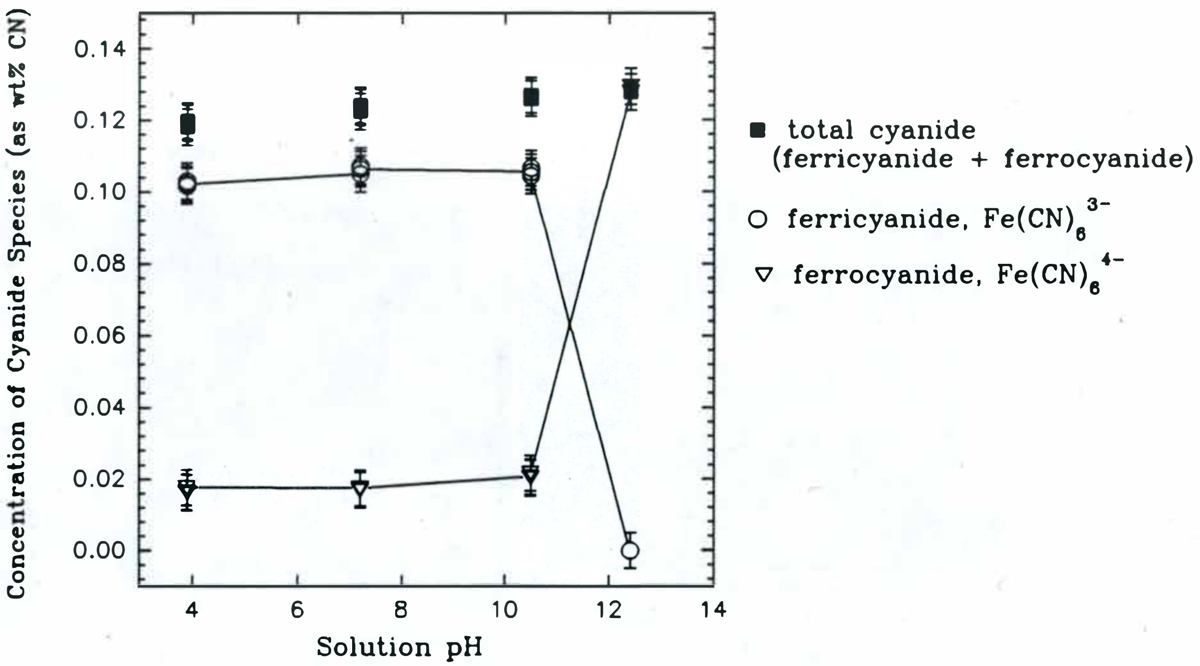


Figure 3.11. Ferricyanide (○), Ferrocyanide (▽), and Total Cyanide (■) of Various Solutions 23 Days After Preparation. These solutions initially contained 20 wt% nitrite and 0.12 wt% ferricyanide.

These results show that the presence of the potential interfering species does not change the measured ferrocyanide concentration to any appreciable degree. The measured ferrocyanide concentration in each solution containing a potential interferant was within 5% of the standard solution, except for those solutions containing NaCl and $NaNO_2$, which showed one reading each outside the 5% interval around the standard value. These results are very encouraging considering that the concentration of the CN^- was on the low concentration extreme expected to be encountered (0.15% as CN in each solution), and the potential interfering species was at the highest value expected in any of the samples to be analyzed. Also, there was no indication that the cyanide ion oxidized. No other cyanide-containing species was observed in these IR measurements, as confirmed by the excellent agreement in mass balance measurements indicated in Figure 3.15. And, there was no evidence that any of the potential interferants reacted with the solution cell or ATR element used in the experiment. It is critical that the solution cell and the ATR element be inert toward the solutions and species expected to be present in ferrocyanide waste samples.

3.1.7 Inorganic Influence on Free Cyanide (CN^-) Analysis After 2 Months of Aging

The tests described in Subsection .1.6 were repeated after an aging period of 2 months. The results of the absorbance measurements that were taken are shown in Figure 3.16. The cyanide concentration data are displayed as the ratio of the measured concentration of that species in each solution

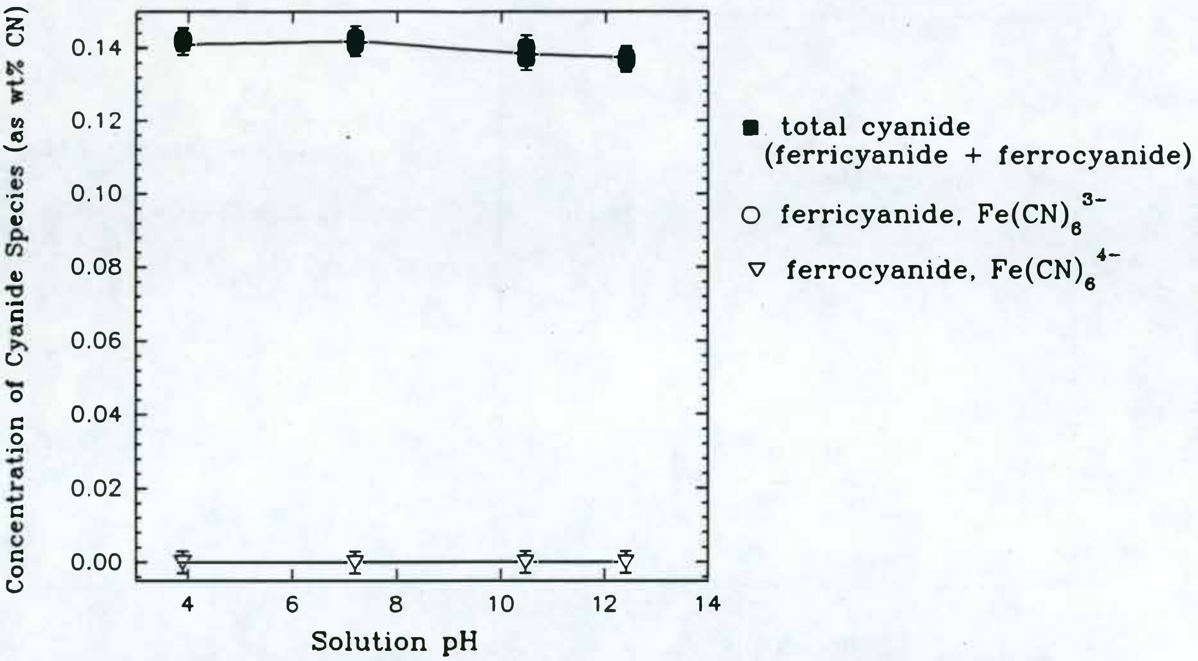


Figure 3.12. Ferricyanide (○), Ferrocyanide (▽), and Total Cyanide (■) of Various Solutions 1 Day After Preparation. These solutions initially contained no nitrite and 0.14 wt% ferricyanide.

to the concentration measured in the standard sample. These results show that the presence of the potential interfering species does not change the measured concentration of ferrocyanide to any appreciable degree. The measured concentration of the ferrocyanide in each solution containing a potential interferant was within 5% of the standard solution, except for the solutions containing Na_3PO_4, which showed readings outside the 5% interval around the standard value.

These results are very encouraging considering that the CN^- concentration was on the low concentration extreme expected to be encountered (0.15% as CN in each solution), and the potential interfering species was at the highest value expected in any of the samples to be analyzed. In addition, there was no indication that the cyanide ion oxidized during the 2-month period in solution. No other cyanide containing species were observed.

3.2 Influence of Organic Chemical Additives on Cyanide Species Analysis

3.2.1 Organic Influence on Ferrocyanide [$Fe(CN)_6^{3-}$] Analysis

Table 3.5 lists the solutions prepared containing organic species that could interfere with the ferrocyanide species analysis if present within the sample matrix. These organic species were chosen

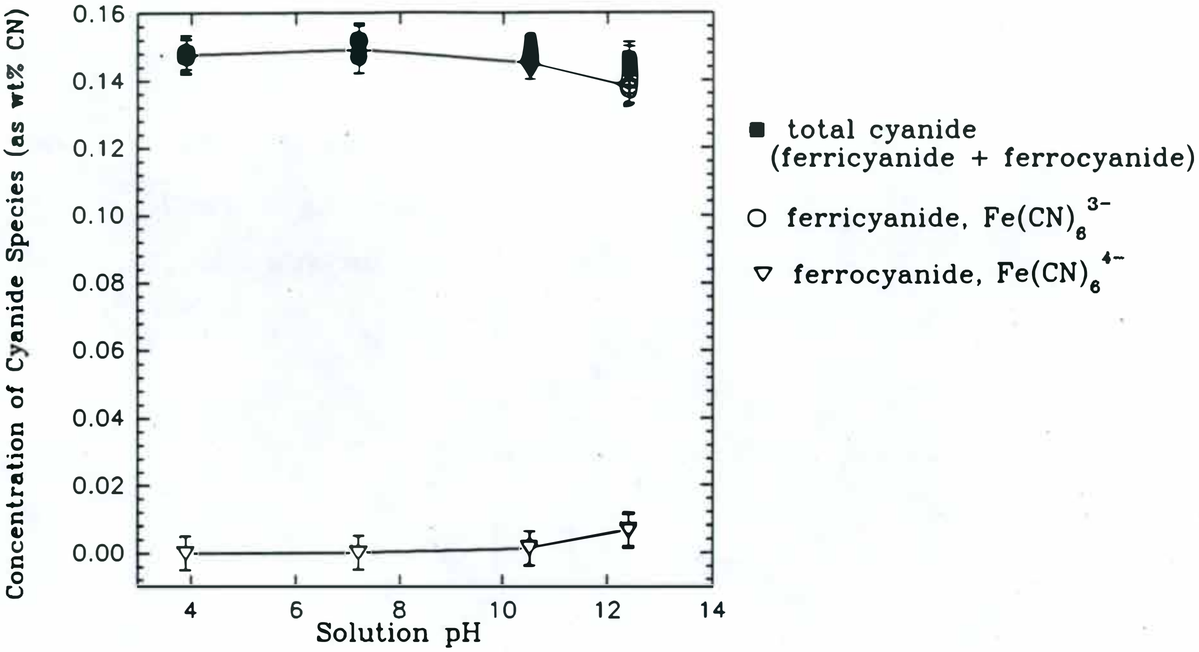


Figure 3.13. Ferricyanide (○), Ferrocyanide (▽), and Total Cyanide (■) of Various Solutions 23 Days After Preparation. These solutions initially contained no nitrite and 0.14 wt% ferricyanide.

based on organics known to be present in high-level waste (HLW) tanks used within waste flowsheets. Each solution in Table 3.5 was routinely analyzed in triplicate using IR techniques. Absorbance measurements of the $Fe(CN)_6^{4-}$ ion were taken at the characteristic frequency for $Fe(CN)_6^{4-}$ (2037 cm^{-1}). In each case, the matrix-matched sample was used as the reference solution for each of the ferrocyanide-containing solutions in Table 3.5. For example, solution 0A was used as the reference solution for sample 0B.

The results of these absorbance measurements are shown in Figure 3.17. The analyzed $Fe(CN)_6^{4-}$concentration data are displayed as wt% CN. These results show that the presence of the potential organic interferant species does not change the measured concentration of ferrocyanide to any appreciable degree. In each solution containing a potential organic interferant, the measured ferrocyanide concentration was within the analytical error of the experiment [equal to the added concentration of $Fe(CN)_6^{4-}$]. These results are encouraging because the concentration of the $Fe(CN)_6^{4-}$ was on the low concentration extreme expected to be encountered (0.025% as CN in each solution), and the potential interfering species was at the high value extreme expected in the samples to be analyzed.

Also, there was no indication that the ferrocyanide (Fe^{2+}) complex oxidized to form ferricyanide (Fe^{3+}). The Fe^{3+} product (or any other cyano complex) was not observed by IR measurements, as confirmed by the excellent agreement in mass balance measurements (Figure 3.17). Furthermore, the

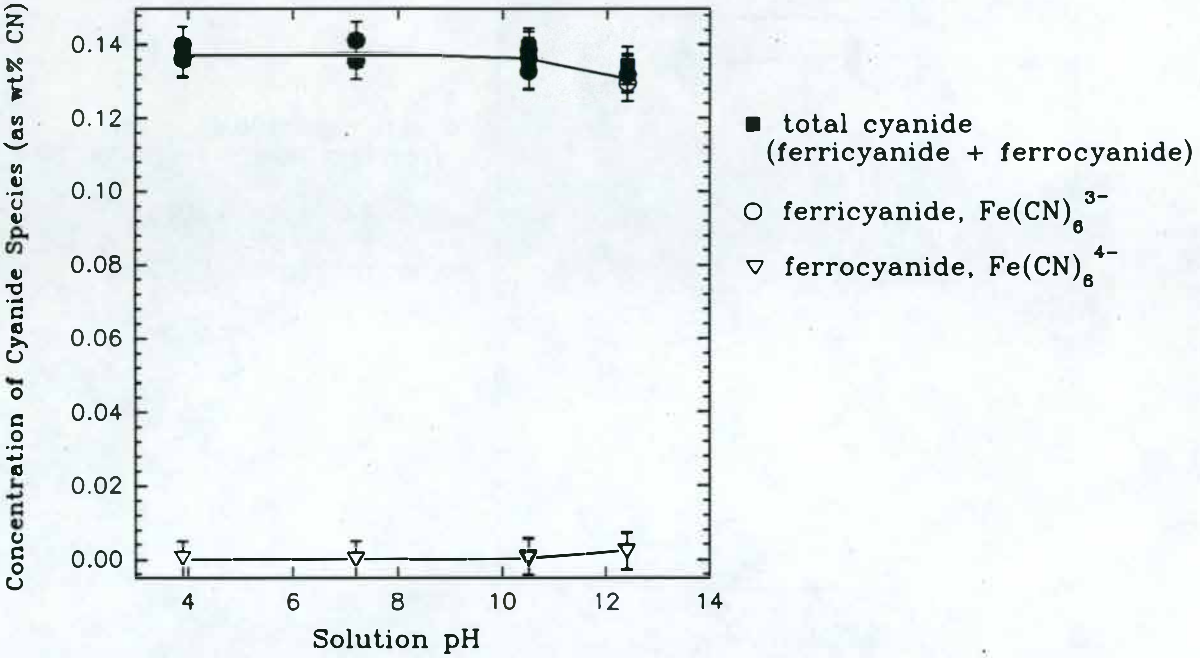


Figure 3.14. Ferricyanide (○), Ferrocyanide (▽), and Total Cyanide (■) of Various Solutions 9 Days After Preparation. These solutions initially contained no nitrite and 0.14 wt% ferricyanide.

potential interferants did not react with the solution cell or ATR element used in the experiment. It is critical that the solution cell and the ATR element be inert toward the solutions and species expected to be present in ferrocyanide waste samples.

3.2.2 Organic Influence on Ferricyanide [$Fe(CN)_6^{3-}$] Analysis

Table 3.6 lists the solutions prepared containing organic species that could interfere with the ferricyanide species analysis if present within the sample matrix. These organic species were chosen based on organics known to be present in HLW tanks and on those used within waste flowsheets.

Each solution in Table 3.6 was routinely analyzed in triplicate using IR techniques. Absorbance measurements of the ferricyanide ion were taken at the characteristic frequency for $Fe(CN)_6^{3-}$ (2114 cm^{-1}). For solutions in which the $Fe(CN)_6^{4-}$ion was observed, the absorbance at the characteristic frequency for $Fe(CN)_6^{4-}$(2037 cm^{-1}) was used to quantitate that species. In each case, the matrix-matched sample was used as the reference solution for each of the ferricyanide-containing solutions in Table 3.6. For example, solution 0A was used as the reference solution for sample 0B.

Table 3.4. Compositions of Solutions Containing Various Potential Interferants and Free Cyanide

Sample	Solution Components
0A	0.01 M NaOH
0B	0.01 M NaOH + 0.15 wt% CN^-
1A	0.5% Na_2SO_4 + 0.01 M NaOH
1B	0.5% Na_2SO_4 + 0.01 M NaOH + 0.15 wt% CN^-
2A	2.5% Na_2CO_3 + 0.01 M NaOH
2B	2.5% Na_2CO_3 + 0.01 M NaOH + 0.15 wt% CN^-
3A	2.7% Na_3PO_4 + 0.01 M NaOH
3B	2.7% Na_3PO_4 + 0.01 M NaOH + 0.15 wt% CN^-
4A	5.0% NaCl + 0.01 M NaOH
4B	5.0% NaCl + 0.01 M NaOH + 0.15 wt% CN^-
5A	20.0% $NaNO_2$ + 0.01 M NaOH
5B	20.0% $NaNO_2$ + 0.01 M NaOH + 0.15 wt% CN^-
6A	1.5% Na_2CrO_4 + 0.01 M NaOH
6B	1.5% Na_2CrO_4 + 0.01 M NaOH + 0.15 wt% CN^-
7A	0.5% NaF + 0.01 M NaOH
7B	0.5% NaF + 0.01 M NaOH + 0.15 wt% CN^-
8A	15.0% $NaNO_3$ + 0.01 M NaOH
8B	15.0% $NaNO_3$ + 0.01 M NaOH + 0.15 wt% CN^-
9A	2.5% $NaAlO_2$ + 0.01 M NaOH
9B	2.5% $NaAlO_2$ + 0.01 M NaOH + 0.15 wt% CN^-

The results are shown in Figure 3.18. The ferricyanide and ferrocyanide concentration data are displayed as the measured concentration in wt% CN. The total cyanide concentration (sum of ferricyanide and ferrocyanide) is also presented.

Figure 3.18 presents both the ferricyanide concentration (●) and the ferrocyanide concentration (▿), as well as the sum of the ferricyanide and ferrocyanide concentrations (□). The results of this experiment show that the presence of the potential interfering species does not change the total measured concentration of ferricyanide and ferrocyanide (□) to any appreciable degree.

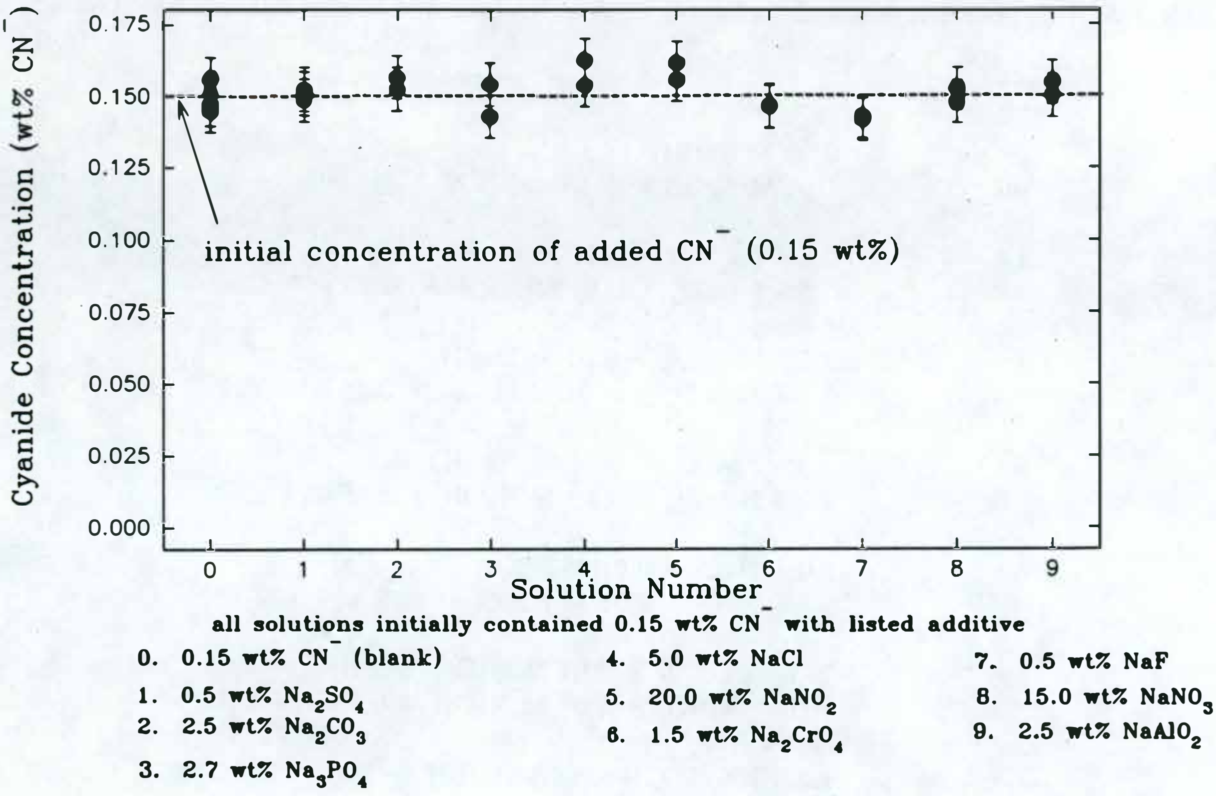


Figure 3.15. Concentration of Free Cyanide in Solutions Containing Potential Interferants

For the solutions containing HEDTA, EDTA, NTA, IDA, glycine, and ethylenediamine (en), the conversion of ferricyanide to ferrocyanide (▽) was quantitative or ≥20% of the original ferricyanide added to the solution after 1 day. The organic compounds that showed ferricyanide to ferrocyanide conversion contained organic amine functionalities within the molecular structure.

Several of the nonamine complexes showed some ferricyanide to ferrocyanide conversion; these complexes were sodium oxalate, sodium glycolate, and n-butanol. Even though these conversion rates are relatively slow compared to the amine-based conversion, the conversion rates are fast compared to the length of time the waste has been stored in the HLW tanks. These compounds (sodium oxalate, sodium glycolate, and n-butanol) are present in the HLW tanks. Most of the remaining compounds in Table 3.6 showed little conversion effect. The measured concentration of ferricyanide and ferrocyanide (□) in each solution containing a potential interferant was within the error of measurement of the initial total added cyanide from ferricyanide.

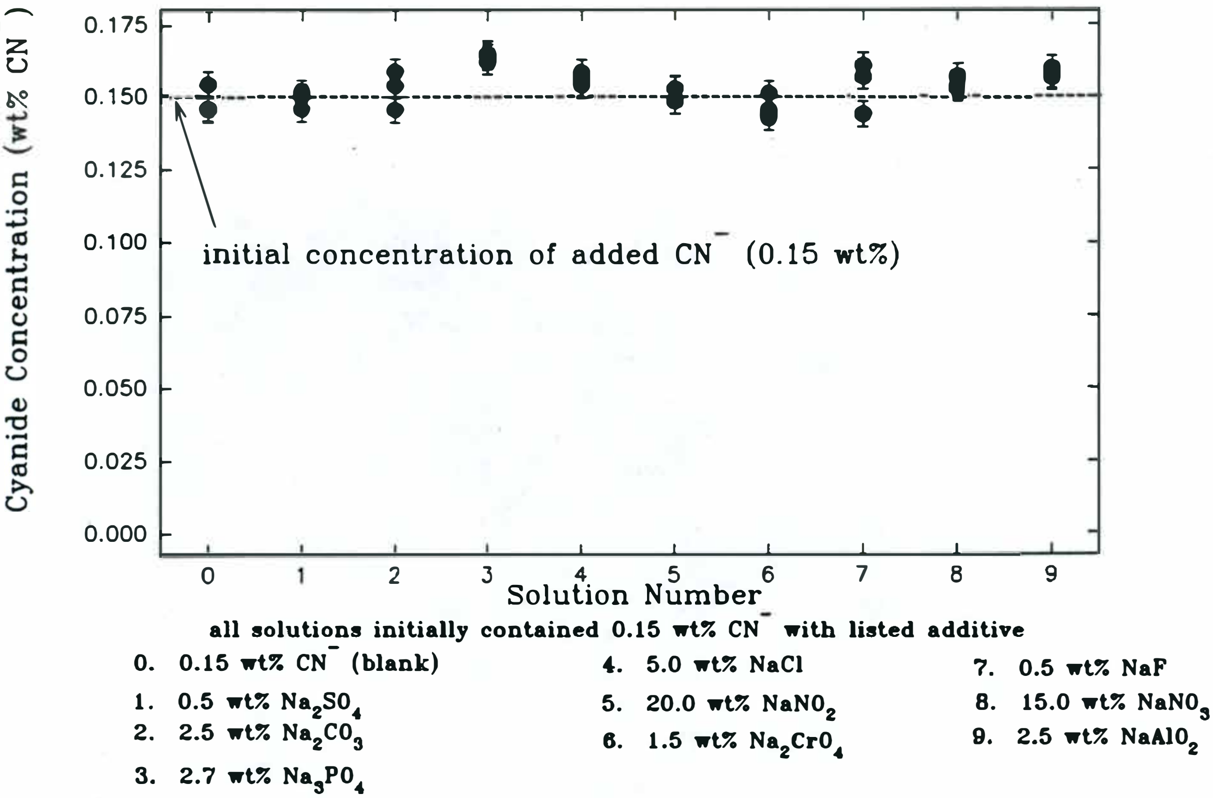


Figure 3.16. Concentration of Free Cyanide in Solutions Containing Potential Interferants. These solutions were aged 2 months before analysis.

To demonstrate the reactivity of ferricyanide with EDTA, we prepared a solution of $Fe(CN)_6^{3-}$ (0.085 wt% as CN) and EDTA (5 wt%) and followed the ferricyanide to ferrocyanide conversion reaction to completion. Figure 3.19 shows the time dependent conversion of ferricyanide (●) to form ferrocyanide (▿). The solutions containing EDTA and ferricyanide were prepared and measured immediately. The contact time of the solution with the IR solution cell (Teflon coated) was approximately 1 min, the nominal sample time for each solution. The times indicated in Figure 3.19 for the EDTA-ferricyanide—containing solutions indicate the time span between sample preparation and sample analysis.

The curves drawn in Figure 3.19 are first order fits of the data according to Equation (3). The first order rate constants (k) listed in the figure describing the $Fe(CN)_6^{3-}$ loss and $Fe(CN)_6^{4-}$ increase are in close agreement, indicating the rate of ferricyanide loss is essentially equal to the rate of ferrocyanide gain within this reaction. The terminal concentration of ferrocyanide corresponds to the initial concentration of ferricyanide within the reaction, which indicates quantitative ferricyanide to ferrocyanide conversion.

Table 3.5. Compositions of Ferrocyanide Solutions Containing Various Potential Organic Interferants. All organic concentrations are 2.5 wt%, unless otherwise stated, each ferrocyanide concentration is 0.025 wt% as CN.

Sample	Sample Composition
0A	0.01 M NaOH
0B	0.01 M NaOH + $Fe(CN)_6^{4-}$
1A	Sodium citrate
1B	Sodium citrate + $Fe(CN)_6^{4-}$
2A	Sodium acetate
2B	Sodium acetate + $Fe(CN)_6^{4-}$
3A	Sodium formate
3B	Sodium formate + $Fe(CN)_6^{4-}$
4A	NPH (saturated)
4B	NPH (saturated) + $Fe(CN)_6^{4-}$
5A	Sodium oxalate
5B	Sodium oxalate + $Fe(CN)_6^{4-}$
6A	HEDTA
6B	HEDTA + $Fe(CN)_6^{4-}$
7A	TBP (saturated)
7B	TBP (saturated) + $Fe(CN)_6^{4-}$
8A	Glycerin
8B	Glycerin + $Fe(CN)_6^{4-}$
9A	EDTA
9B	EDTA + $Fe(CN)_6^{4-}$
10A	Sodium glycolate
10B	Sodium glycolate + $Fe(CN)_6^{4-}$
11A	IDA
11B	IDA + $Fe(CN)_6^{4-}$
12A	Glycine
12B	Glycine + $Fe(CN)_6^{4-}$
13A	NTA
13B	NTA + $Fe(CN)_6^{4-}$
14A	N-butanol
14B	N-butanol + $Fe(CN)_6^{4-}$
15A	Ethylenediamine (en)
15B	Ethylenediamine (en) + $Fe(CN)_6^{4-}$

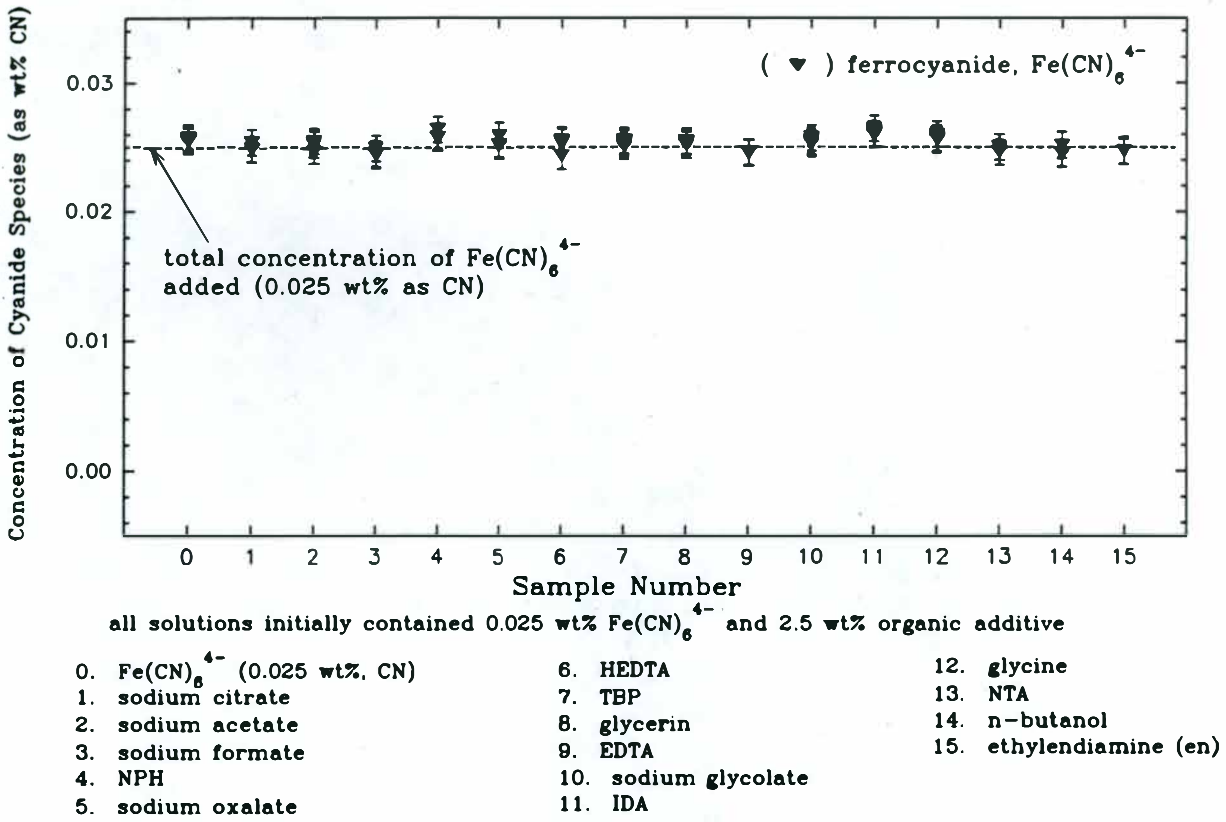


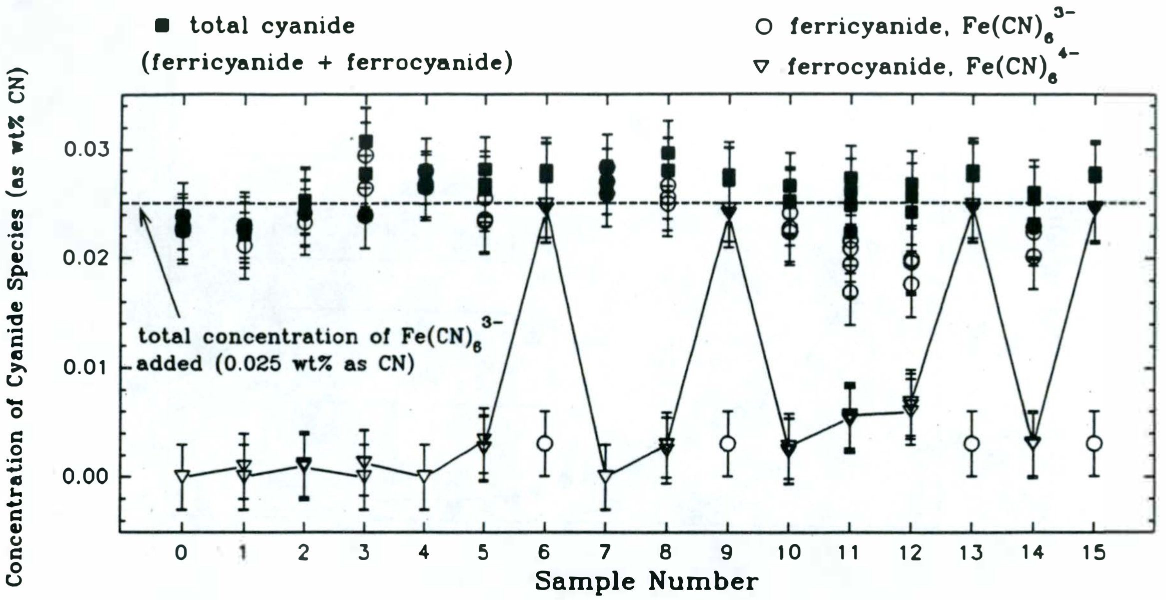
Figure 3.17. Concentration of Ferrocyanide in Solutions Containing Potential Interferants

$$y = a * e^{(-k*t)} + b \tag{3}$$

where y is $Fe(CN)_6^{3-}$ decreasing or $Fe(CN)_b^{4-}$ increasing, a and b are fitted constants, k is the rate constant, and e is the natural log (2.718).

Table 3.6. Compositions of Ferricyanide Solutions Containing Various Potential Organic Interferants. All organic concentrations are 2.5 wt%, unless otherwise stated, each ferricyanide concentration is 0.025 wt% as CN.

Sample	Sample Composition
0A	0.01M NaOH
0B	0.01M NaOH + $Fe(CN)_6^{3-}$
1A	Sodium citrate
1B	Sodium citrate + $Fe(CN)_6^{3-}$
2A	Sodium acetate
2B	Sodium acetate + $Fe(CN)_6^{3-}$
3A	Sodium formate
3B	Sodium formate + $Fe(CN)_6^{3-}$
4A	NPH (saturated)
4B	NPH (saturated) + $Fe(CN)_6^{3-}$
5A	Sodium oxalate
5B	Sodium oxalate + $Fe(CN)_6^{3-}$
6A	HEDTA
6B	HEDTA + $Fe(CN)_6^{3-}$
7A	TBP (saturated)
7B	TBP (saturated) + $Fe(CN)_6^{3-}$
8A	Glycerin
8B	Glycerin + $Fe(CN)_6^{3-}$
9A	EDTA
9B	EDTA + $Fe(CN)_6^{3-}$
10A	Sodium glycolate
10B	Sodium glycolate + $Fe(CN)_6^{3-}$
11A	IDA
11B	IDA + $Fe(CN)_6^{3-}$
12A	Glycine
12B	Glycine + $Fe(CN)_6^{3-}$
13A	NTA
13B	NTA + $Fe(CN)_6^{3-}$
14A	N-butanol
14B	N-butanol + $Fe(CN)_6^{3-}$
15A	Ethylenediamine (en)
15B	Ethylenediamine (en) + $Fe(CN)_6^{3-}$



all solutions initially contained 0.025 wt% $Fe(CN)_6^{3-}$ and 2.5 wt% organic additive

0. $Fe(CN)_6^{3-}$ (0.025 wt%, CN)
1. sodium citrate
2. sodium acetate
3. sodium formate
4. NPH
5. sodium oxalate
6. HEDTA
7. TBP
8. glycerin
9. EDTA
10. sodium glycolate
11. IDA
12. glycine
13. NTA
14. n-butanol
15. ethylendiamine (en)

Figure 3.18. Concentration of Cyanide Species in Solutions Initially Containing Only Ferricyanide and Potential Interferants

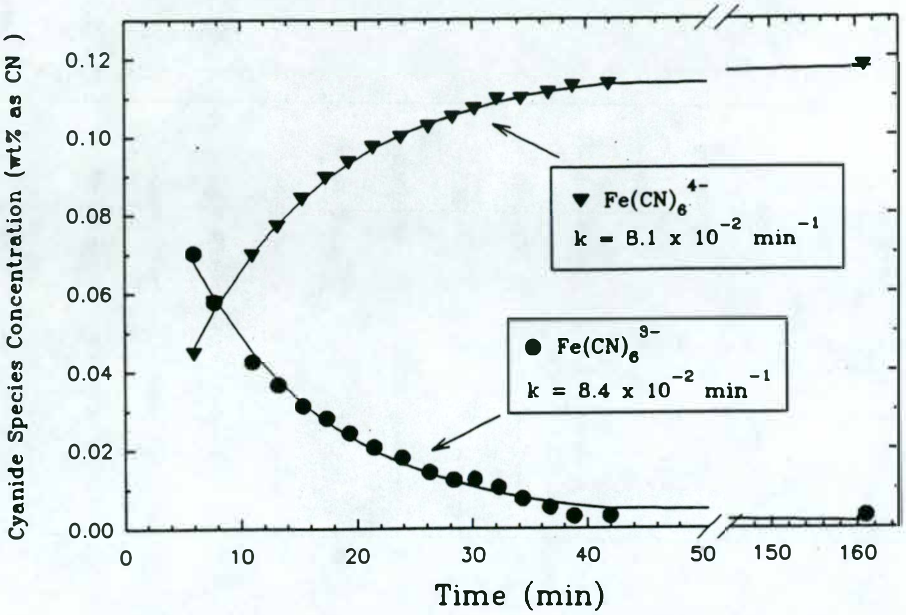


Figure 3.19. Ferricyanide Interconversion to Form Ferrocyanide by Reaction with EDTA

4.0 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^-, $Fe(CN)_6^{4-}$, and $Fe(CN)_6^{3-}$) expected in samples from the Hanford ferrocyanide waste tanks. These analytes were selected since 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 CN) for each method.

Title

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 [$Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, $Fe(CN)_5NO^{2-}$, 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
- Liquid chromatograph system (high-pressure pump, eluent reservoir(s), "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 (±0.01) g NaOH pellets in 1.0 ± 0.05 L of DIW.

Chromatography Eluent: 32.5 vol% acetonitrile, 2 mM tetrabutylammonium hydroxide (TBAOH), 0.6 mM Na_2CO_3.

> Weigh 0.487 ± 0.001 g of 40 wt% TBAOH solution into a 1 L volumetric flask, then adjust the volume with DIW to make a 10 mM TBAOH stock solution. Weigh 0.424 ± 0.001 g of Na_2CO_3 into a 1 L volumetric flask, then adjust the volume with DIW to make a 4 mM Na_2CO_3 stock solution. For 1 L of eluent, mix 325 mL of acetonitrile, 200 mL of the 10 mM TBAOH stock solution, and 150 mL of the 4 mM Na_2CO_3 stock solution in a 1 L volumetric flask and adjust the volume to the mark with DIW.

Stock Standard Solutions:

> KCN, $K_3Fe(CN)_6$, $Na_4Fe(CN)_6 \cdot 10H_2O$ or $K_4Fe(CN)_6$, and $Na_2Fe(CN)_5NO \cdot 2H_2O$ 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 1/2 h to ensure complete dissolution of alkali metal-nickel-cyanoferrate compounds.

Sample Analyses

FTIR

Allow the instrument to stabilize for approximately 1/2 h. If suppressed conductivity detection is used ensure that the suppressor regenerate flow is adequate to reduce background conductivity to less than 10 μS/cm. If UV/Visible photo-diode array detection is used, the background should be less than 0.005 absorbance units prior to analysis. Prepare matrix-matched calibration standards of $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ as described in the immediately preceding subsection. Add solid $CaCO_3$ (~0.05 g/mL) to each calibration standard and sequentially load instrument sample loop (20 to 100 μL) by injection of each standard through 0.45-μm syringe filter.

Inject the standards sequentially into the ATR cell using a plastic syringe (5 or 10 cc) 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

Allow the instrument to stabilize for approximately 1/2 h. If suppressed conductivity detection is used, ensure that the suppressor regenerate flow is adequate to reduce background conductivity to less than 10 μS/cm. If UV/Visible photo-diode array detection is used, the background should be less than 0.005 absorbance units prior to analysis. Prepare matrix-matched calibration standards of $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ as described in the immediately preceding subsection. Add solid $CaCO_3$ (~0.05 g/mL) to each calibration standard and sequentially load instrument sample loop (20 to 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 factor(s), 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 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 $Na_2NiFe(CN)_6$, In-Farm simulated waste, $K_3Fe(CN)_6$, KCN, and/or $Na_2Fe(CN)_5NO \cdot 2H_2O$.

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.

Endnotes

Operations manual published in 1989 by Nicolet Instrument Corporation, P.O. Box 4508, Madison, Wisconsin 53711.

Operations manual published by Dionex Corporation, P.O. Box 3603, Sunnyvale, California 94088.

5.0 Comparison of Flowsheet Materials by Different Analytical Methods

Ferrocyanide flowsheet materials, including various In-Farm and U-Plant simulated wastes and sodium nickel ferrocyanide standard materials such as WHC-3 and FECN-36, were analyzed by different analytical methods. Cyanide analyses were performed by FTIR and IC methods and by total cyanide analysis (distillation method). The analytical results are presented in Table 5.1. In all cases, true solutions were obtained for analysis. Each of the IR samples was analyzed in quadruplicate. Each value listed in the microdistillation method represents an average of at least four replicates. The errors are listed in the table.

Excellent agreement was achieved between each method for all simulated waste and standard materials. According to the results in Table 5.1, there is clearly good agreement between the FTIR solution method and total cyanide by microdistillation method. The fact that the two widely different methods agree so well indicates the validity of these methods.

Table 5.1. Cyanide Species Analyses. Comparison between FTIR, microdistillation, and IC methods.

	Methods (wt% as CN^-)		
Material	FTIR	Microdistillation[(a)]	IC[(a)]
In-Farm 2 (rev 26B)	12.05 (±0.086)[(b)]	11.99, 11.84	NA[(c)]
In-Farm 2 (rev 12)	10.83 (±0.206)	11.04, 10.79	11.0
U-Plant-2 (rev 8)	4.320 (±0.0095)	4.33, 4.23	4.29
U-Plant-2 (rev 7)	3.272 (±0.015)	3.27, 3.20	3.11
U-Plant (CJ-102-B)	1.157 (±0.015)	1.16	NA
U-Plant (CJ-95-B)	1.504 (±0.04)	1.57	NA
In-Farm 2 (CJ-93-B)	8.128 (±0.02)	NA	NA
FeCN-36	36.46 (±0.50)	36.3 (±0.2)	NA
Vendor Material (WHC-3)	34.1 (±2.1)	34.9 (±0.03)	NA

(a) The precision of these measurements is ~ ±1%.
(b) Values represent the standard deviation for each analysis.
(c) NA = not analyzed.

6.0 References

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

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