PNL--8399

DE93 007231

Ferrocyanide Safety Project--Task 3.5 Cyanide Species Analytical Methods Development FY1992 Annual Report

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January 1993

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

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Summary

This report summarizes the results of studies conducted in FY 1992 to develop methods for the identification and quantification of cyanide species in ferrocyanide tank waste. Currently there are 24 high-level waste storage tanks at the Hanford Site that have been placed on a Ferrocyanide Tank Watchlist because they contain an estimated 1,000 g-moles or greater amount 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. The threshold concentration of total cyanide within the tank waste matrix that is expected to be a safety concern is estimated at approximately 1 to 3 wt%. Methods for detection and speciation of ferrocyanide complexes in actual waste 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% in order to bound the safety concern.

Initial work for this study involved gathering and reviewing current literature on methods of measuring various cyano species. (The literature review is presented in the appendix of this report.) Based on the literature review, along with analytical resources at Pacific Northwest Laboratory, and work described in this report, several direct analytical methods were identified for the quantification of cyanide species on solid samples. These methods include infrared spectroscopy, Raman spectroscopy, and Mössbauer spectroscopy. X-ray diffraction and scanning electron microscopy-electron dispersive spectroscopy were also demonstrated on ferrocyanide tank waste "simulants." Of these, infrared, Raman, and x-ray diffraction techniques show promise for the concentration range of interest. Quantitation limits for these three techniques were demonstrated on ferrocyanide waste simulants to be approximately 0.1 wt% ferrocyanide.

In addition to the direct analytical methods, two wet chemical methods for indirect analysis of dissolved waste are recommended for further development. These methods are based on ion chromatography and Fourier transform infrared techniques. Both methods are capable of differentiating between free cyanide (CN^-), ferrocyanide [$Fe(CN)_6^{-4}$], and ferricyanide [$Fe(CN)_6^{-3}$] species in solution. A lower level of the quantitation limit for both techniques is estimated at 0.1 wt% based on the ferrocyanide in the original undiluted sample. Dissolution of the insoluble cyano complex salts is required before analysis by these wet methods, therefore, a dissolution method was developed to allow for the solution determination of ferrocyanide without altering the cyano complex ion.

Acronyms

ATR	-	attenuated total reflectance
CCD	-	charged coupled device
DOE	-	U.S. Department of Energy
EDTA	-	ethylenediaminetetraacetate
EPA	-	U.S. Environmental Protection Agency
FEIS	-	Final Environment Impact Statement
FTIR	-	Fourier transform infrared spectroscopy
FTIR-ATR	-	Fourier transform infrared spectroscopy-attenuated total reflectance
HLW	-	high-level waste
IC	-	ion chromatography
ICP-AES	-	inductively coupled plasma-atomic emission spectroscopy
IR	-	infrared
MSA	-	method of standard additions
PNL	-	Pacific Northwest Laboratory
SEM-EDS	-	scanning electron microscopy-energy dispersive spectroscopy
SST	-	single-shell tank
USQ	-	Unreviewed Safety Question
WHC	-	Westinghouse Hanford Company
XRD	-	x-ray diffraction

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1.0 Introduction

Radioactive waste from defense operations has accumulated at the Hanford Site in underground waste tanks since the early 1940s. During the 1950s additional storage volume was required to support 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 an 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 known 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, 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 that could cause a ferrocyanide explosion in the Hanford Site SSTs (Burger 1984; Burger and Scheele 1988). These efforts resulted in a final environmental impact statement (FEIS), (DOE 1987) issued in 1987. The FEIS projected that the bounding "worst case" accident in a ferrocyanide tank would be an explosion resulting in a short-term 200-mrem radiation dose to the public. 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 FEIS (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.

Using process knowledge, transfer records, and an ongoing evaluation process, the Task Team identified 24 SSTs that potentially contain 1,000 g-mole (465 lb) or more of $Fe(CN)_6^{-4}$ species ferrocyanide. In October 1990, the U.S. Department of Energy (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 (WHC 1986). Work in and around any of the ferrocyanide tanks requires detailed planning with the preparation of supporting safety and environmental

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documentation and approval by DOE top management. These restrictions are required for safety, but greatly increase the time needed to accomplish tasks, such as monitoring and maintenance, to or to install equipment in the tanks.

There are essentially four components within the Ferrocyanide Safety Program dealing with the resolution of the USQ. 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 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 will focus on the third component of the Ferrocyanide Safety Program, characterization of ferrocyanide waste. This work specifically involves development of methods for the quantitative measurement of cyanide species within ferrocyanide tank waste. An important goal of this study is to select, develop, and deploy analytical methods specific for cyanide species within the ferrocyanide waste.

2.0 Results of Literature Review

Initial work within this subtask involved reviewing the literature for current and past methods of detecting and quantitatively measuring cyanide-containing complexes. The ultimate objective of the literature review was to identify potential methods for measuring various cyano species that may be present in stored Hanford high-level waste (HLW). Two analytical strategies offer the most promise: direct analysis of solids and indirect analysis of dissolved waste using wet chemical methods.

The various direct analytical methods available to identify and measure specific cyano complexes and compounds include infrared (IR) spectroscopy, Raman spectroscopy, Mössbauer spectroscopy, and ^{13}C nuclear magnetic resonance spectroscopy. Infrared and Raman appear to be the most promising of these methods. Infrared has been used for analysis of ferro- and ferricyanides, and Mössbauer has been used to elucidate the bonding structure of various cyanoferrate salts.

Numerous wet methods applicable to aqueous solutions may be useful, including a large variety of chromatographic methods for separating various specific cyano complexes from each other and from impurity ions. The most limiting aspect of these wet methods may be the required dissolution of the insoluble cyano complex salts, which are expected to be present in the Hanford waste, without altering the species. However, potential dissolution methods, such as dissolution in an ethylenediaminetetraacetate (EDTA) solution, may be applicable.

The literature review, which is presented in the Appendix, briefly describes the cesium scavenging processes used at Hanford, the likely cyano products, potential aging products, a description of both indirect wet chemical methods and direct physical methods, and tabulations of Chemical Abstract Numbers of reports that may provide supplemental information or identify another potential method.

3.0 Choice of Methods Investigated

Based on the results of the literature review and on experience gained at PNL, several techniques were chosen for development efforts to produce methods for the analytical detection of cyanide species within ferrocyanide tank waste. The cyanide species are thought to be concentrated in the solid phase, mainly in the form of nickel-ferrocyanide salts, but it is possible for solution species of free or complexed cyanides to exist. These techniques may be divided into two major categories for convenience: 1) direct analysis of the tank waste solids with little or no waste pretreatment or preparation, and 2) indirect analysis only after substantial modification of the original sample matrix. Modifications for use by the indirect methods would include, for example, dissolution of the sample matrix prior to analysis.

Direct analytical techniques for determination of cyanide species include:

- IR spectroscopy
- Raman Spectroscopy
- x-ray diffraction (XRD)
- scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS)
- Mössbauer spectroscopy

Indirect analytical methods for quantitative determination of cyanide species include:

- ion chromatography (IC)
- solution IR spectroscopy

Included with the indirect methods is the development of a dissolution method to dissolve pure ferrocyanide complexes and waste "simulants" containing ferrocyanide complexes representative of those present in ferrocyanide tank waste.

4.0 Direct Methods Development

Direct analytical methods may be used to identify cyano species present in tank waste solids. These direct methods require little or no waste pretreatment or preparation. Direct analytical techniques discussed in this section include, Fourier transform IR spectroscopy (FTIR), Raman spectroscopy, XRD, SEM-EDS, and Mössbauer spectroscopy.

4.1 Preparation of Ferrocyanide Waste Simulants

Ferrocyanide waste simulants have been produced in other Tasks within Westinghouse Hanford Company's (WHC) Ferrocyanide Safety Technology Program and in PNL's Ferrocyanide Safety Project. In many cases, these simulants have been subjected to various analytical procedures to identify their composition with respect to elemental and molecular components. When possible, these simulants have been used as secondary standards for testing analytical methods.

Samples used in standard addition determinations were prepared using the PNL flowsheet simulant materials FeCN-19 or FeCN-36. These two materials have been determined to contain 64.1 and 70 wt% $Na_2NiFe(CN)_6$ by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and IC. Details of the analyses of FeCN-19 and FeCN-36 can be found in Hallen et al. (1992).

Solid samples for analysis were prepared using a standard matrix material consisting of salts listed in the U-Plant flowsheet (Scheele et al. 1991), a protocol used in the 1950 cesium scavenging campaigns. Salts mixed in the matrix included Na_2SO_4, Na_3PO_4, $NaNO_3$, $NaNO_2$, and $Sr(NO_3)_2$ in various mole ratios. Concentrations of constituents in the standard matrix are listed in Table 4.1.

Table 4.1. Composition of Standard Matrix for Preparation of Standard Addition Samples

Components	Dry Weight (g)	Waste Matrix (wt%)
Na_2SO_4	28.4	50.3
Na_3PO_4	24.6	43.5
$Sr(NO_3)_2$	0.9	1.5
$NaNO_3$	1.8	3.1
$NaNO_2$	0.9	1.6
Total	56.5	100

4.2 Infrared Spectroscopy

Infrared spectroscopy has been identified from the literature and earlier work as an attractive method for the quantitative determination of cyanide species within ferrocyanide tank waste. Absorbance IR spectra can be obtained with little or no sample preparation by using attenuated total reflectance (ATR) sample cells. Solid sample spectra reported within this section were taken using an FTIR spectrometer equipped with a zinc selenide internal reflectance cell.

Spectra of the commercially supplied reagent grade $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ solids, as well as waste simulants prepared using the U-Plant (WHC-1) and In-Farm (FeCN-19) flowsheets, are presented in Figure 4.1. This figure shows the IR absorbance bands for $K_3Fe(CN)_6$ found at 2116, 2119 cm^{-1}; bands for $K_4Fe(CN)_6$ are observed at 2023, 2041, 2061, 2071, and 2092 cm^{-1}. Bands for both compounds are consistent with literature values for cyanide ligands bound to single Fe(III) and Fe(II) centers, respectively.

The IR spectra of the flowsheet materials in Figure 4.1 reveal a single band at ca. 2088 cm^{-1} (WHC-1 has a shoulder at ca. 2070 cm^{-1}). This observed band is consistent with the stretching mode expected for cyanide bridging between Fe(II) and Ni atoms (C bonded to iron). It has been noted (Nakamoto 1978) that if the M-C≡N group forms a M-C≡N-M' type bridge, υ(C≡N) shifts to a higher frequency. Since the υ(C≡N) band (2088 cm^{-1}) for the flowsheet simulants was found to be higher than υ(C≡N) for Fe(II)-C≡N in $K_4Fe(CN)_6$ and lower than υ(C≡N) for Fe(III)-C≡N in $K_3Fe(CN)_6$, results suggest the flowsheet simulants retained the Fe in the +2 oxidation state (e.g., Fe(II)-C≡N-Ni).

Similarities noted in band positions for CN stretching regions of the flowsheet simulants indicate the mode of cyanide bonding in each of the flow-sheet preparations is similar. This is not surprising because the major difference expected between preparations is principally a function of the alkali metal counter ions used (e.g., Na and K) or the coprecipitated solids (e.g., $Fe(OH)_2$) in the samples; neither factor will affect the metal-cyanide stretch markedly.

A large shift in the absorbance spectrum is expected if the central Fe^{+2} metal is oxidized from the ferrocyanide to ferricyanide (Fe^{+3}). Evidence for these oxidized compounds was observed in the aging studies of U-plant simulated wastes (Lilga et al. 1992).

Using the ATR internal reflectance IR cell, the possibility was demonstrated of using the characteristic absorbance band intensity for υ(C≡N) in the ferrocyanide sample as an indicator of the ferrocyanide concentration. In Figure 4.2, the characteristic band for υ(C≡N) at 2088 cm^{-1} in an In-Farm flowsheet simulant is very intense and well isolated from other absorbance bands in the spectrum. Bands of this nature are excellent candidates for use in quantitative spectrophotometric analysis.

To demonstrate that the υ(C≡N) band follows Beer's Law, and therefore can be applied for quantitative analysis, simulants representing ferrocyanide tank wastes were prepared according to

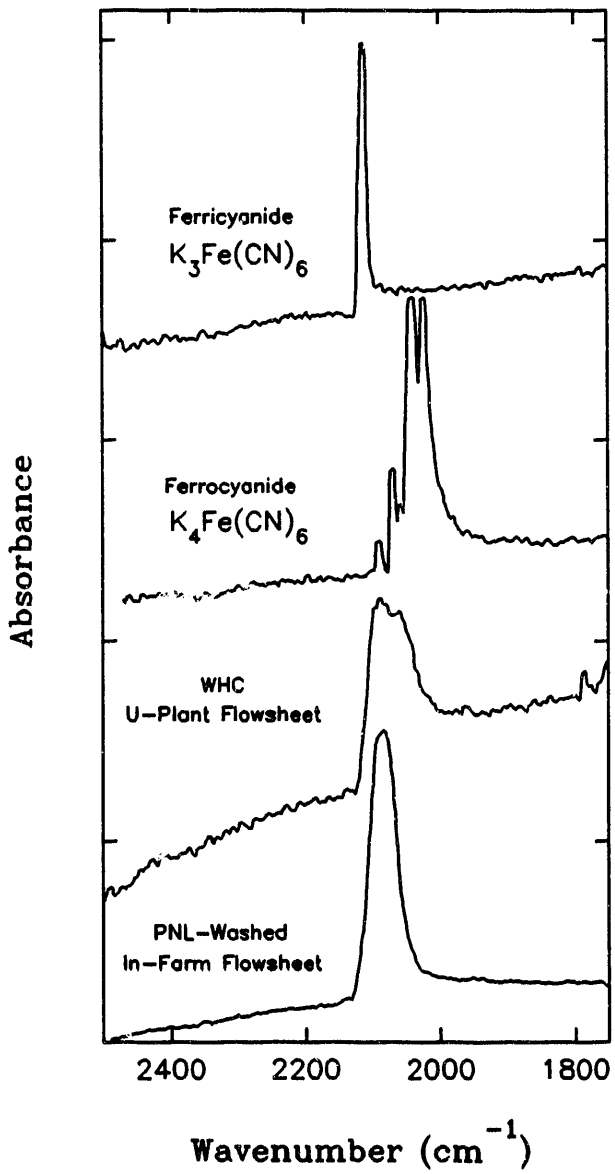

Figure 4.1. IR Bands in the $\upsilon(C\equiv N)$ Region Show that "Free" Ferri- and Ferrocyanides Can Be Differentiated from Ferrocyanide Flowsheet Simulant

Table 4.1 and analyzed using FTIR. The amount of pure source $Na_2NiFe(CN)_6$ was varied in each preparation. The FTIR analytical results are plotted in Figure 4.3. In this analysis, absorbance was a function of wt% ferrocyanide added to each sample. The linearity of the absorbance at 2088 cm^{-1} ($\upsilon C\equiv N$) vs concentration of $Na_2NiFe(CN)_6$ in the samples demonstrates that this technique should be effective for quantitative ferrocyanide analysis of solid waste samples.

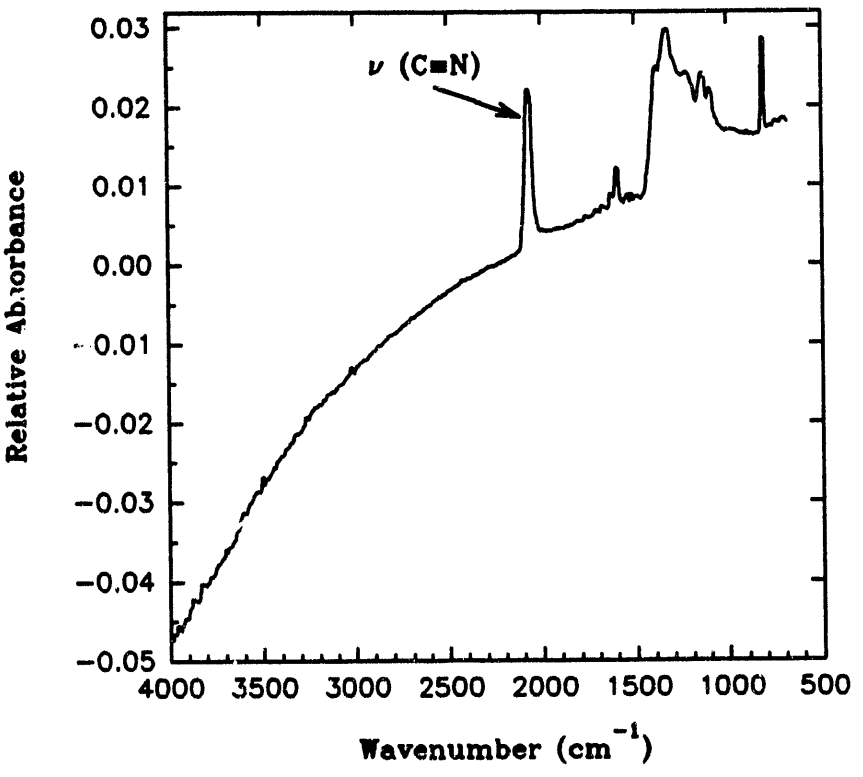

Figure 4.2. Full-Scale FTIR Spectrum of Ferrocyanide In-Farm Flowsheet Simulant

We have shown above that concentrations of $Na_2NiFe(CN)_6$ between 1 and 10 wt% in a waste simulant matrix can be determined in the solid state using Fourier transform infrared-attenuated total reflectance (FTIR-ATR) detection methods. The upper level of ferrocyanide concentration in waste not considered a safety concern is in the range of approximately 1 to 3 wt%. To demonstrate that this detection method is applicable at ferrocyanide concentration levels well below the accepted level for safety concern, a series of experiments was performed using concentrations of $Na_2NiFe(CN)_6$ below 1 wt%. The amount of pure source $Na_2NiFe(CN)_6$ was varied in each preparation from 0.1 to 1 wt% analyte in the waste matrix. Figure 4.4 shows the absorbance vs concentration for these samples. It is evident from this figure that Beer's Law is followed at these concentrations.

Standard addition samples were prepared following U.S. Environmental Protection Agency (EPA) procedures for the quantitative determination of $Na_2NiFe(CN)_6$ in a ferrocyanide U-plant flowsheet simulant, FeCN-33 (Hallen et al. 1992). The standard addition reagent used in this experiment was a pure $Na_2NiFe(CN)_6$ material (FeCN-36) prepared and analyzed at PNL (Hallen et al. 1992); the analysis indicated a high level of purity with no other salts observed by XRD. The results of the standard addition determination are presented in Figure 4.5. The method of standard additions (MSA) used

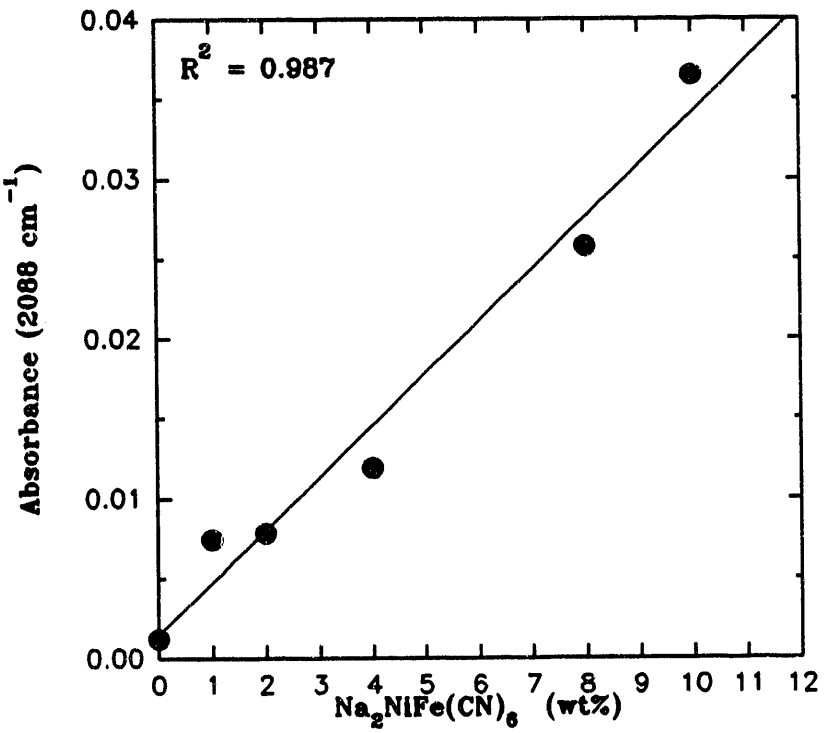

Figure 4.3. FTIR Data Taken on Solid Samples Using Internal Reflectance Cell

to determine ferrocyanide species by FTIR was patterned after the EPA method SW846 (1988) of standard additions in Atomic Absorption Spectroscopy. The experimental method is outlined in the following four steps:

1. Prepare four samples for use in the MSA determination. Each sample will consist of a given amount of the unknown sample plus varying ratios of the spiking material and diluent. The amount of spiking material to be added should be enough to give absorbance readings of 50%, 100% and 150% of the value expected from the unknown sample. A fifth sample will consist of only the diluent.

   For example, the unknown sample gives an IR absorbance reading of 0.100 at 2100 cm^{-1}, and the standard sample gives an IR absorbance reading of 0.500 at 2100 cm^{-1}. The first MSA sample would be prepared by adding 0.3 g of diluent to 1 g of the unknown sample and then homogenizing the mixture. The second MSA sample would be prepared by adding 0.1 g of the standard sample and 0.2 g of the diluent to 1 g of unknown sample and homogenizing the mixture. For the third MSA sample, 0.2 g of the standard sample and 0.1 g of the diluent would be added to 1 g of the unknown sample, and this mixture would

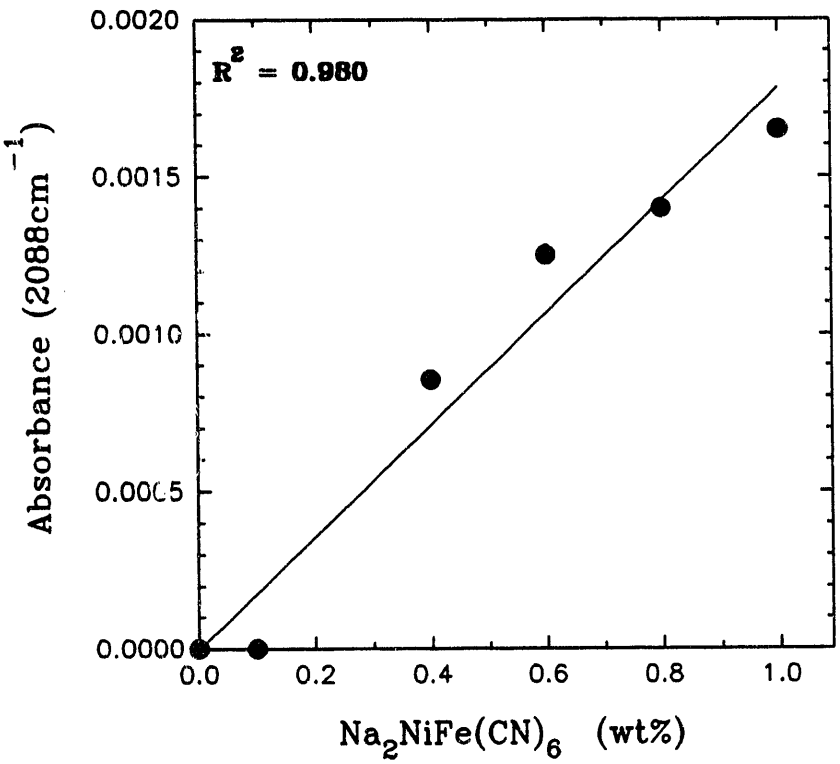

Figure 4.4 Plot of FTIR Absorbance Values of $Na_2NiFe(CN)_6$ at 2088 cm^{-1} as a Function of Concentration Within a Waste Simulant Matrix

be homogenized. The fourth MSA sample would be prepared by adding 0.3 g of the standard sample to 1 g of the unknown sample, followed by homogenization. The final sample would be 1.3 g of the diluent. The diluent used in these experiments was 150-mesh alumina, and the standard was a previously characterized ferrocyanide waste simulant, FeCN-36.

2. Analyze each of the five samples by FTIR and determine the absorbance of each at the characteristic wavelength.

3. Plot the five results in absorbance vs concentration of the standard in the samples (i.e., the unknown will be at a concentration of zero), and perform a linear regression analysis on the plot. The EPA criteria for a linear relationship is a linear correlation coefficient of ≥ 0.995.

4. If the plot is linear (according to Beer's Law), then the absolute value of the x-intercept will be the concentration of the species in the unknown.

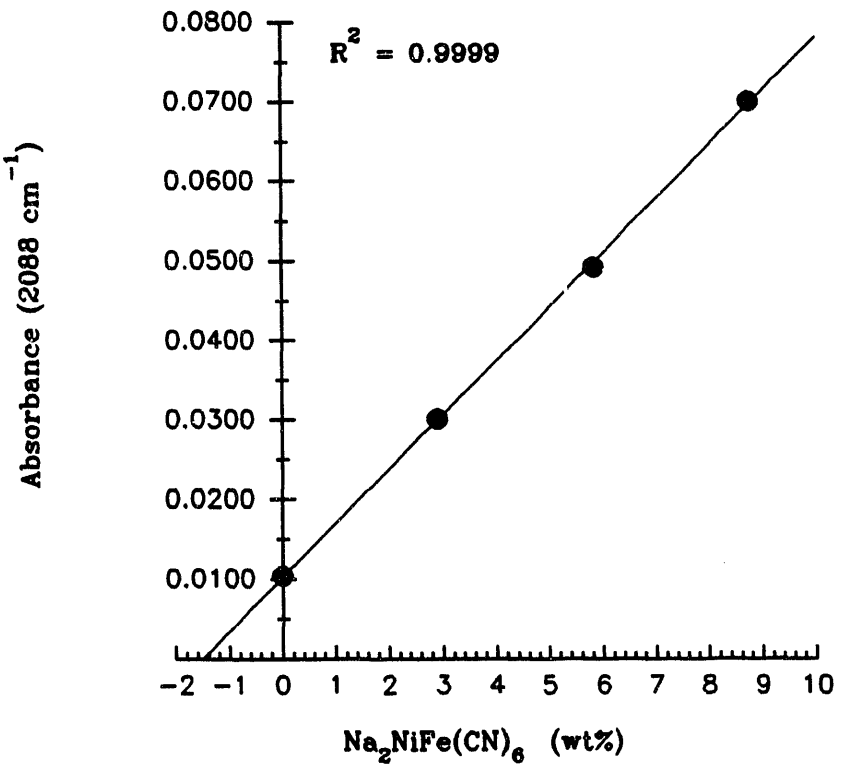

Figure 4.5. Standard Addition Determination of $Na_2NiFe(CN)_6$ Using Solid FTIR with an ATR Cell

To determine the ferrocyanide content of FeCN-33, five MSA samples were prepared as shown in Table 4.2.

Table 4.2. Composition of Five MSA Samples

Sample	FeCN-33 Added (g)	FeCN-36 Added (g)	Al_2O_3 Added (g)
1	0.500	0.0	0.101
2	0.500	0.075	0.025
3	0.500	0.050	0.050
4	0.500	0.025	0.075
5	0.0	0.0	0.600

These samples were then analyzed by FTIR with an ATR solid sample cell. The absorbance peak heights for the samples were measured and displayed in Figure 4.5. From this MSA, the concentration of $Na_2NiFe(CN)_6$ in the unknown sample (FeCN-33) was determined to be 1.81 wt% (when corrected for the dilution factor). This translates to 1.21 wt% $Fe(CN)_6^{-4}$ or 0.89 wt% total cyanide (as CN^-) within the sample.

Solid-state IR spectroscopy has been demonstrated here as an analytical tool for the determination of cyanide species within simulated ferrocyanide tank waste. It is recommended that this technique be developed as an analytical method for quantitative determination of ferrocyanides in tank waste.

4.3 Raman Spectroscopy

Raman spectra of powdered ferrocyanide samples were taken by using 800 nm excitation radiation from a 150 to 200 mW laser source. In a typical experiment, approximately 20 mg of solid analyte was placed on a glass coverslip in the sample compartment. The scattered laser light was collected in a 90° backscattering geometry. The collected light was passed through a triple spectrophotometer and dispersed on a liquid nitrogen-cooled charged coupled device (CCD) detector. The wavelength scale of the CCD detector was calibrated using known emission lines from a neon lamp. For each sample the Raman signal was collected in two segments: one centered at 876.5 nm resulting in a Raman spectral window from about 900 cm^{-1} to 1350 cm^{-1} and the other centered at 960.5 nm resulting in a Raman spectral window from about 1940 cm^{-1} to 2300 cm^{-1}. The use of two "windows" was required because of the large dispersion of scattered light from the choice of gratings and the long wavelength of the laser excitation used. The entrance and exit slits were set at 0.5 mm and 200 μm, respectively, for all samples. The exposure time for the low frequency region was 100 s; for the high frequency region 600 s was required to obtain an acceptable signal-to-noise ratio for each spectral window.

Raman peaks observed in the low frequency region correspond to the internal vibrational modes of the nitrate, phosphate, and sulfate ions that compose the bulk of the matrix for the samples. No vibrational modes corresponding to the nitrite ion exist in this spectral window (Adams and Tan 1981). Peaks in the high frequency region correspond to the vibrational modes assigned to the cyanide stretching motion and are shown in Figure 4.6.

The intensity ratio of the vibrational mode of the cyanide complex at 2135 cm^{-1} to an internal stretching mode of the PO_4^{-3} ion at 992 cm^{-1} was chosen to determine the concentration of sodium nickel ferrocyanide in the powdered samples. Use of an intensity ratio to determine relative concentration is preferred to the direct comparison of Raman intensity because absolute Raman intensity measurements are dependent on a variety of variables as well as concentration. The 992 cm^{-1} and 2135 cm^{-1} peaks were chosen because the phosphate concentration in each sample matrix was constant, and these peaks are relatively isolated from other peaks in the spectra, which minimizes the uncertainty in determining their intensity. The intensity ratio 2135 cm^{-1}/992 cm^{-1} as a function of weight percent ferrocyanide is shown in the plot in Figure 4.7. With minor exception, a linear relationship is observed.

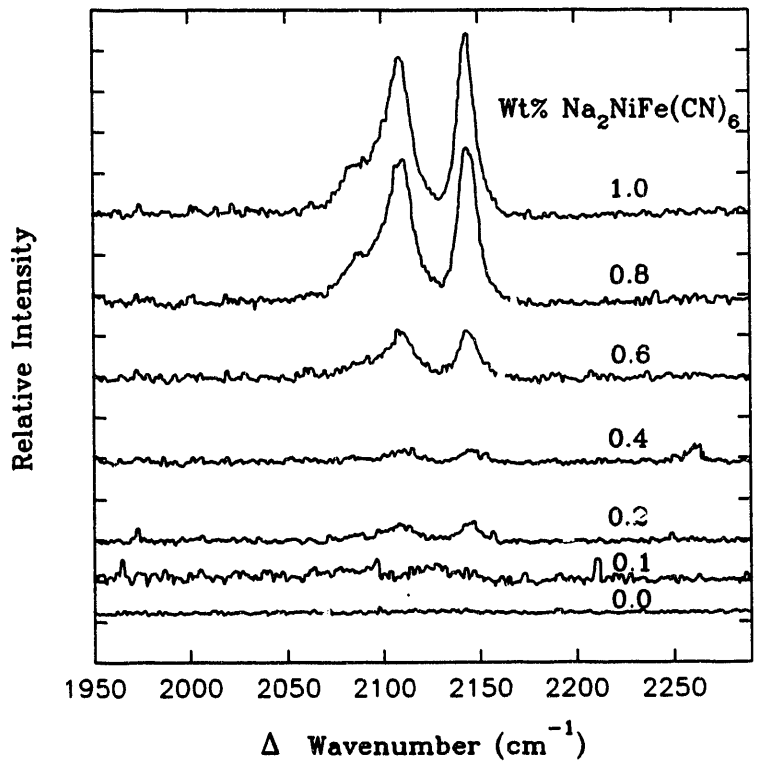

Figure 4.6. Raman Spectra of $Na_2NiFe(CN)_6$ at Various Concentrations in Flowsheet Waste Simulant

The scatter in the data observed in Figure 4.7 is thought to arise from the heterogeneity of the sample matrix. Although great care was taken to grind each pure component to a fine powder ($\leq$200 mesh) before blending to form the final waste matrix, it is believed that nonideal mixing of the sample occurred. Raman spectroscopy is particularly sensitive to nonhomogeneity since the laser excitation beam focuses on a relatively small surface area of the sample.

Solid-state Raman spectroscopy shows promise as an analytical tool for the determination of cyanide species within ferrocyanide tank waste. Based on this work, it is recommended this technique be developed further to provide a method for the quantitative measurement of cyanide species in ferrocyanide tank waste.

4.4 X-Ray Diffraction

In earlier reports, XRD methods have been shown to be suitable for the identification of $Na_2NiFe(CN)_6$ within solid waste simulants (Hallen et al. 1992; Lilga et al. 1992). To determine whether XRD is suitable for the ferrocyanide safety program, this technique must first be used to quantitatively measure the ferrocyanide salts within the waste matrix.

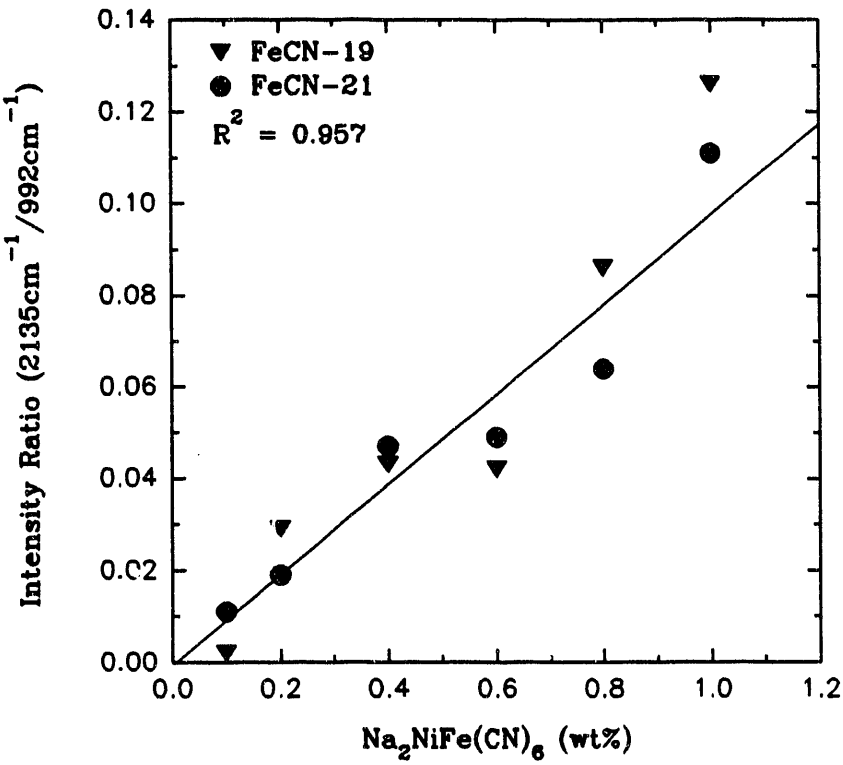

Figure 4.7. Raman Response is Linear with Respect to $Na_2NiFe(CN)_6$ Concentration in Ferrocyanide Waste Simulant

To demonstrate that this method of detection is applicable at ferrocyanide concentration levels well below the accepted level for safety concern, a series of experiments was performed using $Na_2NiFe(CN)_6$ concentration levels at and below 1 wt%. The amount of a pure source of $Na_2NiFe(CN)_6$ was varied in each preparation from 0.1 to 1 wt% analyte in the waste matrix. The waste simulants that were used are given in Table 4.1 and their preparation is discussed in Section 4.1.

Figure 4.8 shows the XRD response vs concentration for these samples. According to Figure 4.8, this technique gives a linear response over the concentration range of interest (0.1 to 1 wt% $Na_2NiFe(CN)_6$). By using the standard addition method, this technique could be considered for use on more complicated flowsheet materials.

These XRD diffractograms were obtained from equipment routinely used to characterize radioactive samples from actual high-level radioactive waste. For this reason, it is estimated that an XRD method for the determination of solid ferrocyanide materials could be established with very little modification to current procedures.

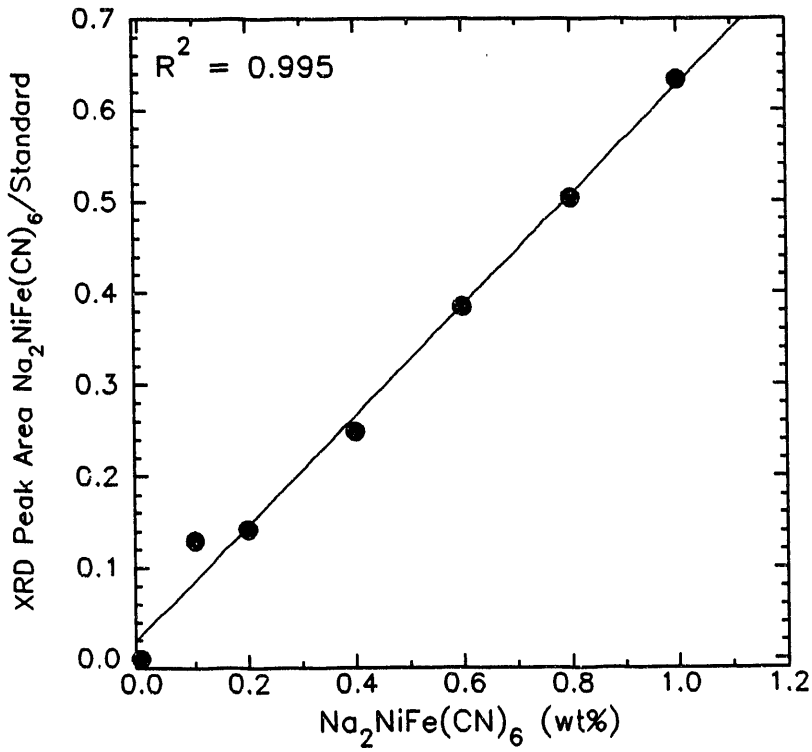

Figure 4.8. XRD Analysis of $Na_2NiFe(CN)_6$ in Ferrocyanide Waste Simulant. Plot of XRD Response vs wt% $Na_2NiFe(CN)_6$.

This technique is limited because the solid sample must be in a crystalline form to exhibit a diffraction pattern for detection. This is a significant problem, since these solids are known to form colloidal suspensions and may not precipitate into well characterized crystalline structures. For this reason, XRD is not recommended for further development.

4.5 Scanning Electron Microscopy-Energy Dispersive Analysis

Scanning electron microscopy-energy dispersive spectroscopy analysis has been used in past work to analyze sodium nickel ferrocyanide material (Hallen et al. 1992). This technique was shown to be useful for identifying contaminants within supposedly pure ferrocyanide compounds prepared off-site. Although this technique is semi-quantitative for elements with an atomic mass greater than that for boron, this technique was not a useful tool to identify specific ferrocyanide compounds. Therefore, SEM-EDS is not recommended for further development as a method for the quantitative measurement of ferrocyanides tank waste.

4.6 Mössbauer Spectroscopy

Mössbauer spectroscopy has been suggested for use in defining the Fe(II)/Fe(III) ratio in solid samples of ferro- and ferricyanides (Hallen et al. 1992). Further studies indicate that this technique can be used to estimate the lower limit for the total number of different molecular species containing iron (Lilga et al. 1992). Based on work by Lilga et al. (1992), this technique could not, however, be considered a means to definitively identify specific cyanide-containing iron complexes. For this reason, Mössbauer spectroscopy is not recommended for further development as a quantitative method to determine ferrocyanide complexes in Hanford tank waste.

5.0 Indirect Methods Development

The indirect analytical methods investigated in this section include IC and solution IR spectroscopy. Use of these indirect analytical methods to quantitatively determine cyanide species requires dissolution of the sample matrix before analysis. Implementation of these indirect methods requires the development of a technique to dissolve pure ferrocyanide-bearing wastes. This section describes the development of a dissolution method for pure alkali nickel ferrocyanides and simulated ferrocyanide-bearing wastes followed by descriptions of the development of IC and IR methods.

5.1 Solids Dissolution Techniques

A dissolution technique has been developed for $Na_2NiFe(CN)_6$ and for flowsheet simulants that contain this compound. The technique uses a solvent of 5 wt% ethylenediamine (en) and 5 wt% ethylenediaminetetraacetic acid (H_4Y) in water. This solvent is a true solution that can be used directly for IC analysis or for IR analysis. $Na_2NiFe(CN)_6$ and flowsheet simulants can be dissolved to form 10 wt% (perhaps higher) true solutions using this en/H_4Y reagent.

Once dissolved, samples can be analyzed for ferrocyanide ion, ferricyanide ion, and free CN^- by any number of instrumental and/or wet chemical methods. The two analytical methods that have received the most attention to date, IR, and reverse phase IC, are discussed below.

5.2 Solution Infrared Spectroscopy

Earlier, it was shown that concentrations of $Na_2NiFe(CN)_6$ between 0.1 and 10 wt% in a solid waste simulant matrix can be determined in the solid state using FTIR-ATR detection methods. The upper level of ferrocyanide in waste that is not considered a safety concern is approximately 1 wt%. Even though ferrocyanide can be measured well below the threshold for the safety concern using pure mixtures of salts, there is some uncertainty in the measured absorbance when analyzing solids. This is largely due to the heterogeneity of the matrix.

Detection of the cyanide complexes in aqueous solution is possible by IR using the ATR cell. With solution IR techniques, the uncertainty of the absorbance measurements is reduced because the solutions are homogeneous. Figure 5.1 shows IR spectra of standard solutions containing ferricyanide, ferrocyanide, and free cyanide. This figure also contains solution spectra of dissolved WHC In-Farm 1, In-Farm 2, and U-Plant 2 flowsheet simulants. According to Figure 5.1, the only cyanide species in the flowsheet simulants is the ferrocyanide complex, as would be expected based on makeup.

Figure 5.2 is a spectrum of a solution containing free cyanide, ferrocyanide, and ferricyanide. This spectrum demonstrates that the cyanide complexes of interest can be detected and differentiated even when they are present in the same solution.

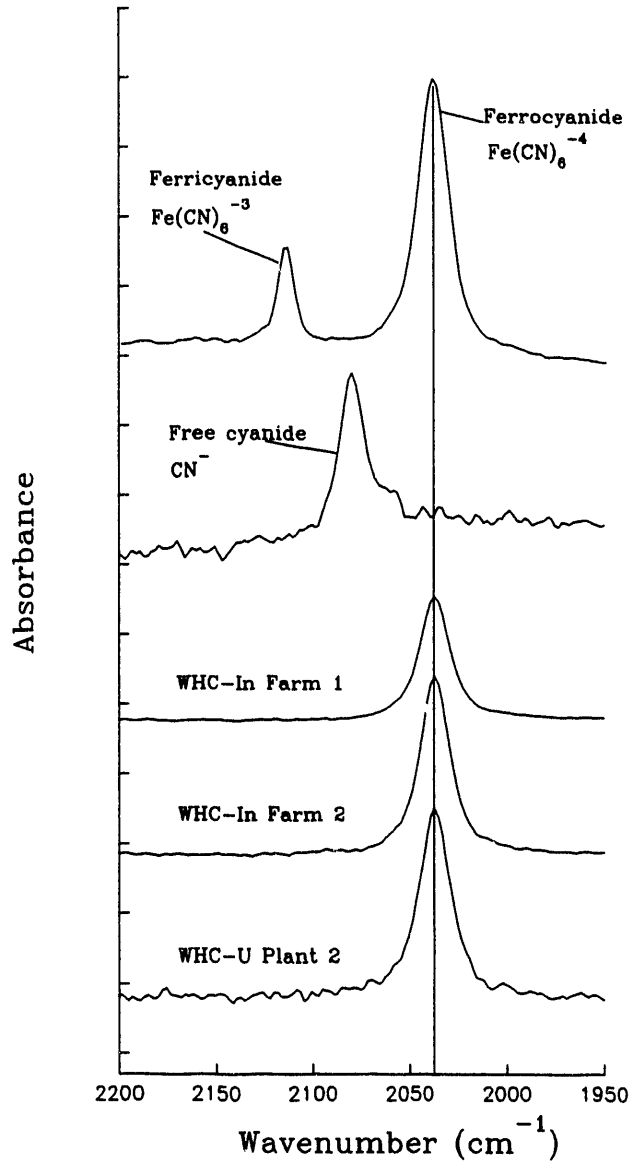

Figure 5.1. Solution FTIR Spectra of Cyanide Standards and Various Flowsheet Materials

The standard curves for ferrocyanide showing the absorbance at the peak maximum versus the concentration in solution are shown in Figures 5.3 and 5.4. These figures show that the IR technique gives a linear response over the concentration range 0.01 to 10 wt% $Fe(CN)_6^{-4}$ in aqueous solution. This technique is also stable over time. The different symbols on each standard curve indicate measurements taken on the same standard solution one week apart. Quantitation of free $Fe(CN)_6^{-4}$ in solution to approximately 0.01 wt%, enables the quantitative detection of ferrocyanide to approximately 0.1 wt% in the original undiluted solid sample. This trend needs to be verified for free CN^- and ferricyanide. Future study includes this work.

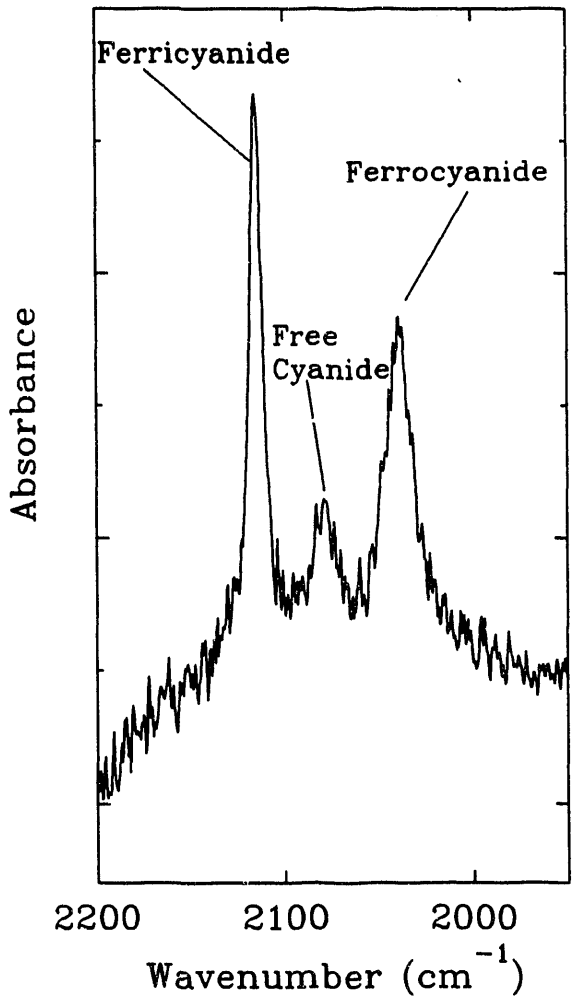

Figure 5.2. Infrared Spectrum of a Solution Containing Free Cyanide, Ferricyanide, and Ferrocyanide

Six ferrocyanide flowsheet simulants prepared by John Wong of WHC were analyzed by IR for the detection of cyanide species. The six simulants are the top and bottom layers of each of three flow sheet preparations, In-Farm 1, In-Farm 2, and U-Plant 2. Each of these samples was dissolved using the dissolution technique described earlier and analyzed using FTIR-ATR.

The results of these IR analyses are listed in Table 5.1. In all cases, only the $Fe(CN)_6^{-4}$ (ferrocyanide) complex was observed in these samples. The concentrations presented in Table 5.1 are calculated as wt% $Fe(CN)_6^{-4}$ and as wt% total CN^- in the original sample. By inspection, it can be seen that the analyses by IR methods are in agreement with the analyses by IC (Section 5.3).

Based on this work, it is recommended that a method based on the solution IR detection of cyanide species within ferrocyanide waste be developed further.

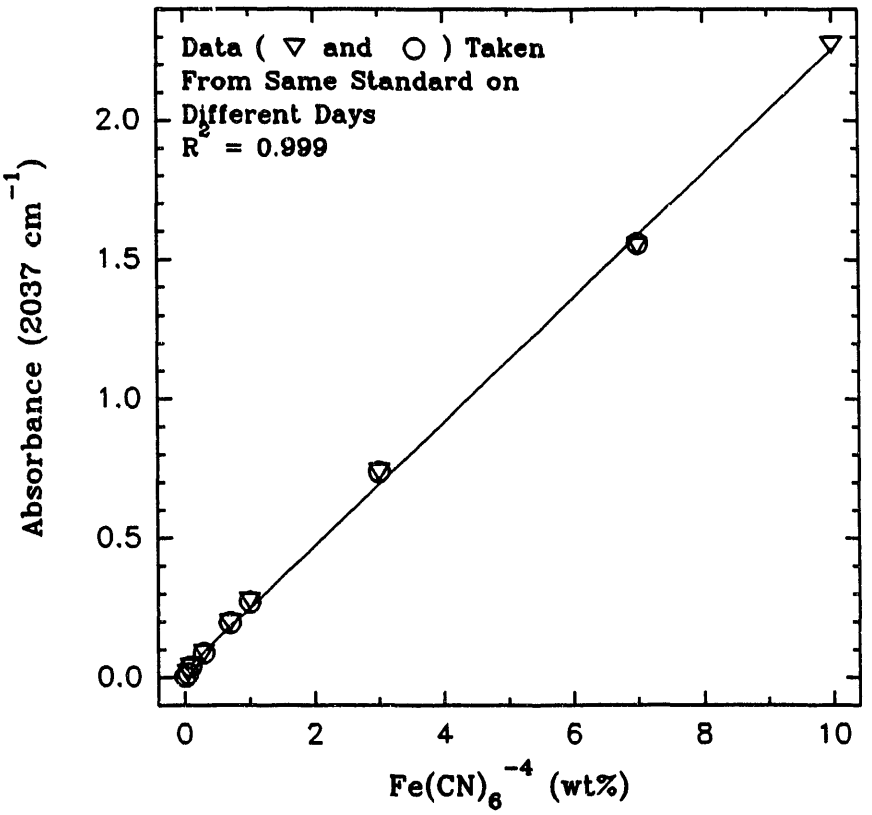

Figure 5.3. Standard Curve for the $Fe(CN)_6^{-4}$ Complex in Solution Showing 0.01 to 10 wt%

5.3 Ion Chromatography

Ion chromatography methods have been shown to separate the ferrocyanide complex from the ferricyanide complex in aqueous solution by using reversed phase suppressed conductivity detection. Reversed phase IC analyses of $Na_2NiFe(CN)_6$-containing samples and related materials dissolved in the en/H_4Y reagent were performed using the following equipment and operational details.

Hardware: Dionex® 4000i system consisting of a gradient pump, NG1/NS1 columns, MPIC membrane suppressor, conductivity detector, and a strip chart recorder

Eluent: mixture containing 660 mL CH_3CN (acetonitrile), 675 mL deionized water (DIW), 405 mL 10 mM tetra n-butylammonium hydroxide in DIW, 300 mL 1 mM Na_2CO_3 in DIW

Flow Rate: 1.0 mL/min

Sample Loop: ~100 μL

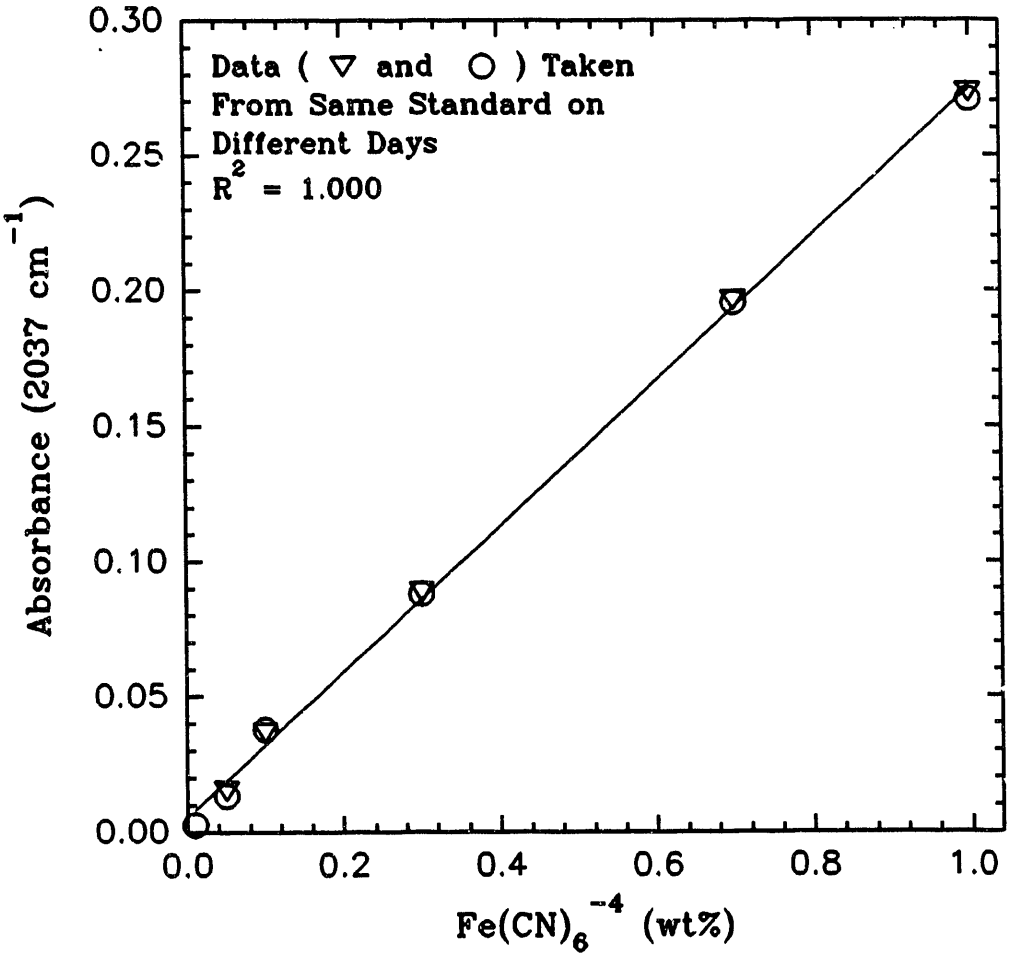

Figure 5.4. Standard Curve for the $Fe(CN)_6^{-4}$ Complex in Solution Showing the Concentration Range from 0.01 to 1 wt% Analyte

Table 5.1. Cyanide Species Analysis. Comparison of FTIR and IC methods on six ferrocyanide flowsheet simulants.

	Method			
	FTIR (wt%)		IC (wt%)	
Material	$Fe(CN)_6^{-4}$	Total CN^-	$Fe(CN)_6^{-4}$	Total CN^-
In-Farm 1 (Top)	6.3	4.7	5.3	3.9
In-Farm 1 (Bottom)	8.9	6.5	8.4	6.2
In-Farm 2 (Top)	5.5	4.1	5.5	4
In-Farm 2 (Bottom)	7.5	5.5	7.6	5.6
U-Plant 2 (Top)	1.4	1	1.3	0.97
U-Plant 2 (Bottom)	2	1.5	2	1.5

Detector Setting: 30 μ siemens-full scale

Retention Times: using the operation conditions specified; $Fe(CN)_6^{-3}$ (ferricyanide) ~7 min; $Fe(CN)_6^{-4}$ (ferrocyanide) ~14 min

The general procedure for running a typical IC experiment was as follows. Samples dissolved in en/H_4Y reagent (Section 5.1) were diluted with DIW (100 to 250 times) to achieve analyte concentrations compatible with column loading considerations and instrumental parameters. Approximately 0.2 g solid Ca_2CO_3 was added to 100 mL of diluted sample solution, and the solution was well agitated. The resulting slurry was loaded into the sample loop by injection through a 0.45 μm syringe filter.

Calibration standards of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ were prepared in the same dissolution reagent matrix and injected into the instrument sample loop using identical Ca_2CO_3 treatment and syringe filtering. Sample analyses were completed by directly comparing observed chromatographic peak heights to those obtained from matrix-matched, similarly treated standards.

Note here that the procedural and instrumental details described above have not been truly optimized. It is highly probable that lower detection limits and better resolution at shorter analysis times can be achieved by fine tuning the many chemical variables involved with the overall procedure.

Figure 5.5 is an example of actual chromatograms run on three consecutive samples: ferrocyanide, ferricyanide, and an In-Farm 1 flowsheet simulant, respectively. This series of chromatograms shows that ferro- and ferricyanide can be differentiated by their retention times and peak shapes. The In-Farm 1 sample shows the presence of the $Fe(CN)_6^{-4}$ (ferrocyanide) complex only. The In-Farm 1 solution sample used here was prepared by the dissolution technique described earlier. Similar results were obtained for the other In-Farm and U-Plant flowsheet simulants.

Figure 5.6 is the standard curve for ferrocyanide in solution by IC methods. This curve shows the detection limit in solution for $Fe(CN)_6^{-4}$ is quantitative to the ppm level. This translates to a quantitation limit of approximately 0.1 wt% ferrocyanide in the original undiluted solid sample.

Six ferrocyanide flowsheet simulants received from WHC were analyzed by IC methods for the detection of cyanide species. They are the top and bottom layers of each of three flowsheet preparations, In-Farm 1, In-Farm 2, and U-Plant 2. Each of these samples was dissolved using the dissolution technique described above before analysis by IC methods discussed earlier in this report.

The results of the IC analyses are listed in Table 5.1, along with results from IR analysis. In all cases, for IC analysis only the $Fe(CN)_6^{-4}$ complex was observed in these flowsheet samples. The concentrations presented in Table 5.1 are calculated as wt% $Fe(CN)_6^{-4}$ and as wt% total CN^- in the original sample. Based on an inspection of the results obtained using IR and IC analytical methods, these two methods for quantitation of cyanide species are in agreement. This work supports the recommendation that methods using IC be further developed for quantitative determination of cyanide species within ferrocyanide tank waste.

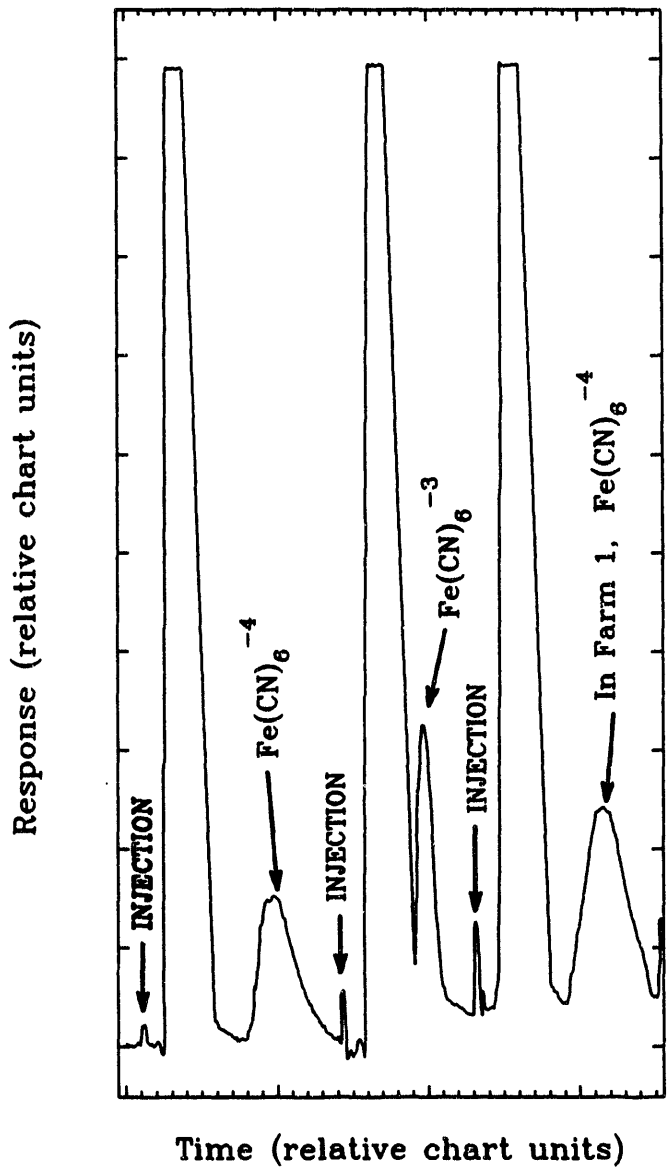

Figure 5.5. Successive Ion Chromatograms of $Fe(CN)_6^{-4}$, FE $(CN)_6^{-3}$, and In-Farm 1 (a flowsheet material containing ferrocyanide)

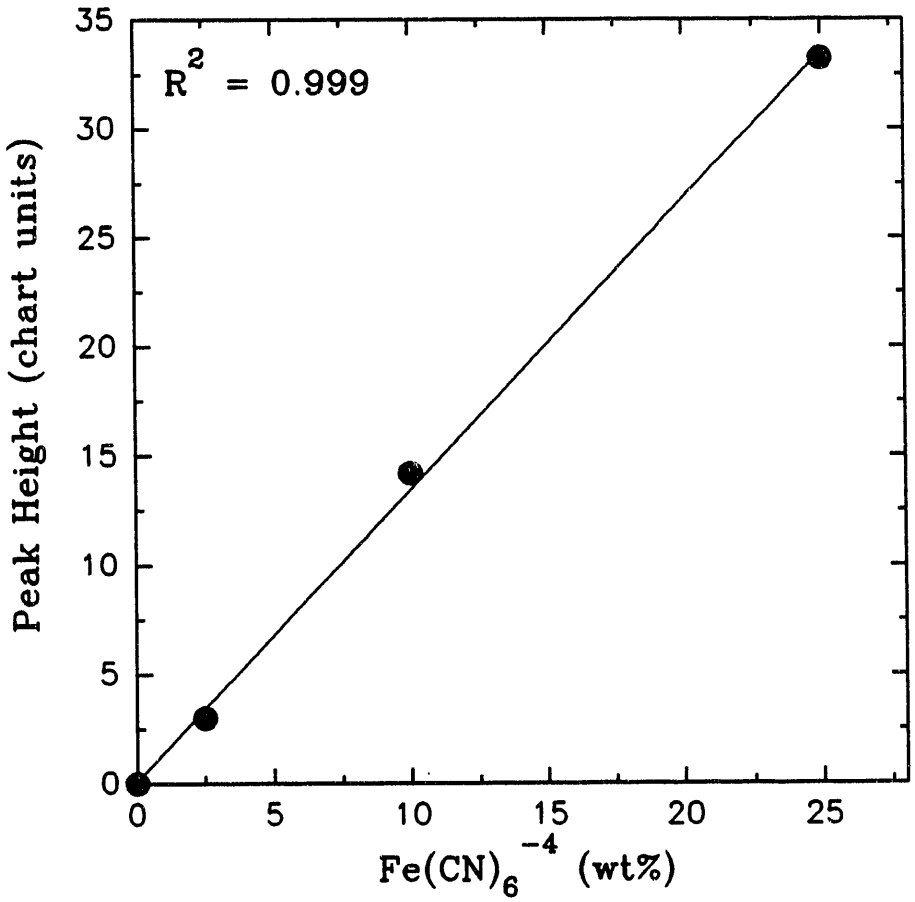

Figure 5.6. IC Standard Curve for $Fe(CN)_6^{-4}$ for the Range 0 to 25 ppm

6.0 References

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Appendix

Literature Search Relating to Developing of Waste Tank Cyano-Complex Speciation

Summary

The objective of this literature review was to identify potential methods for measuring various cyano species that may be present in stored Hanford waste. Two analytical strategies that could be used together in conjunction appear to offer the most promise. These two approaches are indirect analysis of dissolved waste using wet chemical methods and direct analysis of solids.

Numerous wet methods, including a large variety of chromatographic methods for separating various specific cyano complexes from each other and from impurity ions, are available for cyanoferrate complexes and may have application to Hanford waste. Dissolution of the insoluble cyano complex salts, expected to be present in the waste, without alteration of the species may be the most limiting aspect to the applicability of wet methods, but potential dissolution methods such as dissolution in an ethylenediamine tetraacetate (EDTA) solution may be applicable.

Alternatively and in conjunction with the wet chemistry methods, various physical methods are available for identifying and possibly measuring specific cyano complexes and compounds. These include infrared spectroscopy, Raman spectroscopy, Mössbauer spectroscopy, and ^{13}C nuclear magnetic resonance spectroscopy. Infrared and Raman appear to be the most promising of these methods. Infrared has been used for analysis of ferro- and ferricyanides and Mössbauer has been used to elucidate the bonding structure of various cyanoferrate salts.

This report provides brief descriptions of the cesium scavenging processes used at Hanford, the likely cyano products, potential aging products, a brief description of promising methods (both indirect wet chemical methods and direct physical methods), and tabulations of Chemical Abstract Numbers of reports which may provide supplemental information or identify another potential method.

Introduction

During the 1950s at the Hanford site, ferrocyanide was added to high-level waste as part of a carrier precipitation process to remove radioactive cesium from the slightly alkaline waste supernates (Burns and Stedwell 1957). After allowing adequate time for in-tank settling (at least 7 days but typically 20 to 31 days), these Cs-depleted supernates were discharged to cribs (Abrams 1956). The procedures used were to add the ferrocyanide first to either basic tank farm waste (29 tank farm campaigns), to acidic waste from U Plant Uranium Recovery waste (56 campaigns), or to acidic T-Plant Bismuth Phosphate waste (6 campaigns) (Borsheim and Kirch 1991). This was followed by addition of an equimolar amount of nickel sulfate. In the case of the acidic waste, this addition was usually made by continuous addition during neutralization, but part of the time the nickel was added after neutralization. At some times, the neutralized waste was actually thermally concentrated before $NiSO_4$ was added (Abrams 1956). The ferrocyanide was initially added as $K_4Fe(CN)_6XH_2O$ but this was later changed to technical-grade $Na_4Fe(CN)_6XH_2O$. The quantities of ferrocyanide and nickel sulfate were also changed from 0.005 M each to 0.0025 M each during the operation of the process. In addition, cobalt, at about one twentieth of the ferrocyanide concentration, was added during part of the scavenging campaigns to improve ^{60}Co decontamination.

Although the Cs scavenging process has been normally referred to as the precipitation of $Cs_2NiFe(CN)_6XH_2O$, this is far from a complete description. Nickel ferrocyanide in the presence of all alkali metals except Li^+ forms a range of variable stoichiometry compounds with a single fcc structure. Loos-Neskovic et al. (1989) have represented this material as $M^I_{2x}Ni_{2-x}Fe(CN)_6XH_2O$ where $M^I = Na^+, K^+, Cs^+, NH_4^+$, and H^+. Although they do not include Rb^+, it should be apparent that Rb^+ would also act as M^I. They found that Li^+ did not act as M^I. Although they report X to be always in the range 0.0 to 0.8, two of their preparations (their Table 4), have $X > 0.9$ and it appears more reasonable to conclude, as others have done, that X is in the range 0.0 to 1.0.

These highly insoluble ferrocyanides, as well as many other transition metal ferrocyanides that are also insoluble, act as ion exchangers in a manner similar to zeolites with the M^I ions being exchangeable. Most, if not all, of these ferrocyanides show a pronounced preference for Cs over the other alkali metals, and in particular the nickel and cobalt compounds show very high affinities for Cs.

Even though nickel was added to the waste in the same molar quantity as ferrocyanide, it can be assumed that other transition metals present in the waste and capable of producing insoluble ferrocyanides (including Fe, Co, and UO_2^{2+}) would have been adequate to ensure that essentially all of the $Fe(CN)_6^{4-}$ was precipitated. Any that was not precipitated would have been cribbed. The overall result would be a solid containing $M^I_{2X}Ni_{2-x}Fe(CN)_6$ where M^I is a combination of all the Cs and Rb present and possibly (if present) some NH_4^+ with K and Na constituting the rest of M^I. Some of the Ni was probably substituted by other transition metals or, depending on their crystal structures, the other transition metals might have precipitated separate ferrocyanide salts.

The system is further complicated by the possibility of chemical and/or radiolytic oxidation of ferrocyanide to ferricyanide. Insoluble transition metal salts form with ferri- as well as with ferrocyanides. It is known (Loos-Neskovic et al. 1989) that alkali metal nickel ferricyanides can be prepared either by direct precipitation or by oxidation of the ferrocyanide by boiling nitric acid. Whether mixed alkali nickel ferro-ferricyanides can form is uncertain. It is known that mixed iron oxidation state compounds form where the nickel is replaced by iron (Prussian blue, Berlin green, etc.) (Sharpe 1976, pp. 121-126).

Mixtures of solid ferro- or ferricyanides with solid $NaNO_3$ and/or $NaNO_2$ can act as explosives (Burger 1984, Burger and Scheele 1988, Burger and Scheele 1991). This fact and the fact that some of the tank waste has been evaporated to crystallization of $NaNO_3$ and $NaNO_2$ have raised considerable interest in the nature and fate of these aged ferrocyanide compounds.

The purpose of this report is to present preliminary results of a literature search of analytical methods or of chemistry indicative of potential analytical methods to characterize the cyanide solids present in the waste tanks. The goals of the literature search (in order of priority and likelihood of success) are to identify methods or the chemistry on which to base methods for the determination of:

1. the total ferro- and ferricyanides and related cyano complexes in the waste solids,

2. the amount of ferro- versus ferricyanide and whether other cyano complexes, in which the metal coordinated to the cyanide carbon is not Fe, have or have not formed (coordination of the cyanide carbon to metals other than Fe is considered unlikely),

3. the extent of CN^- substitution in hexacyano ferrates to produce species such as the nitrosopentacyanoferrate(II) (nitroprusside) ion, and

4. the nature and amounts of metals other than Ni and Na bound to the ferro- and ferricyanides, particularly the transition metals.

Because many of the transition metal ferrocyanides are isomorphous with the same fcc structures as $M^I_{2x}Ni_{2-x}Fe(CN)_6$, it may not be possible to determine the value and nature of M^I as well as degree and nature of substitution of Ni by other transition metals (item 4 above) for materials in waste tank sludges.

Results

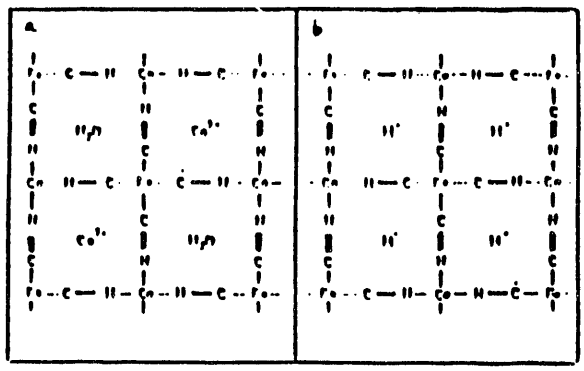
The ferrocyanide ion is a very stable species and is kinetically inert to substitution of the cyanide ion by other ligands such as water and nitrite (Sharpe 1976). Alkali nickel ferrocyanides, and possibly other transition metal ferrocyanides were added to Hanford waste approximately 35 to 40 years ago and presumably have been exposed to an alkaline nitrate-nitrite environment in the presence of β and γ (and some alpha) radiation ever since. Over such periods and conditions, reactions known to be very slow, and even reactions not observed under normal laboratory conditions, may have occurred.

Unlike the ligand substitution reactions, electron-transfer reactions are very fast, and ferrocyanide can be rapidly oxidized to ferricyanide and ferricyanide can be rapidly reduced back to ferrocyanide. Although the standard potential of the ferro-ferricyanide couple is 0.36 volts (close to that of Cu^0-Cu^{2+}), the potential changes appreciably with the solution composition. Ferrocyanide undergoes ion-pair formation with alkali metal ions in solution increasing this potential (making ferrocyanide a weaker reductant). The precipitation of ferrocyanide as the very insoluble alkali nickel ferrocyanide will further stabilize the ferrocyanide against oxidation to ferricyanide. However, it is known that nickel ferricyanide is also insoluble, and the solid ferrocyanide can be oxidized to an insoluble ferri-salt by either hot nitric acid (Loos-Neskovic et al. 1989) or by Ag^{2+}.

On the above basis, it is possible that cyanide compounds present in the Hanford waste tanks exist as either Fe(II) or Fe(III) cyanides and that substitution reactions may have occurred. Anions that might be expected to possibly form from soluble ferrocyanide in the environment of Hanford waste tanks include $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, $[Fe(CN)_5H_2O]^{3-}$, $[Fe(CN)_5H_2O]^{2-}$, $[Fe_2(CN)_{10}]^{6-}$, $[Fe_2(CN)_{10}]^{5-}$, $[Fe_2(CN)_{10}]^{4-}$, $[Fe_2(CN)_{11}]^{5-}$, $[Fe(CN)_5NO]^{2-}$, and $[Fe(CN)_5NO_2]^{4-}$. Some of these species, such as the nitroso and nitrite pentacyanoferrates, are well known species in solutions and salts (Sharpe 1976).

Although the above ions might certainly form under solution-phase conditions, it is far less likely that they would form in nickel (or other transition metal) salts, at least unless new phases form. The structures of $Co_2Fe(CN)_6$ and $M_2CoFe(CN)_6$ are shown in Figure A.1 (Ćeranić 1978), and the Ni compounds are isomorphous with the Co compounds. It can be seen that cyanide provides linear bridging between the iron, bonded to carbon, and Ni (or Co or other transition metals) bonded to nitrogen. The $Fe(CN)_6^{4-}$ ion does not exist as a discrete free entity in such a completely polymeric structure, neither would ions such as $[Fe_2(CN)_{10}]^{6-}$. Likewise, the nitrosyl ion, NO^+, and water do not bridge in this linear manner and it is not clear that they could replace CN^- in such a lattice in the same manner as they do in $[Fe(CN)_5H_2O]^{3-}$ and $[Fe(CN)_5NO]^{2-}$. It is known that in cyano compounds of similar structure such as Prussian blue there can be vacant lattice sites. Thus it may not be impossible that substitution of cyano groups can occur without them acting as a bridge, and it is, of course, also possible that separate phases can form.

A somewhat brief and limited literature search was made of analytical methods or properties of ferro- and ferricyanide ions and related species in solutions and salts. This literature search was aimed



(a) $CoCoFe(CN)_6$.
(b) $M_2CoFe(CN)_6$, $M^+ = K^+, NH_4^+, Cs^+$, etc.

Figure A.1. Schematic Diagram of the Cross Section of the Crystallite Unit Cell. From Ćeranić (1978).

at providing analytical methods or directions to pursue in developing analytical methods to characterize cyanide-containing solids in the waste tanks. This literature search covered Chemical Abstracts of the 25-yr period 1962 through 1986. This search involved a reasonably thorough review the Chemical Abstracts indices and indices of many abstracts of potential analytical significance were collected. Only a relative few (~70) abstracts were duplicated, and of these only a very few articles were obtained in their entirety.

There are two potential approaches to the determination of cyanide complex species in the waste. The first of these involves the more classical wet chemistry of dissolution, separation of the various species resulting from dissolution, and determination of the various separated cyano complexes, and the other involves direct physical measurements on undissolved and unseparated waste tank solids. The former will be titled Wet Methods and discussed first below, and the latter will be referred to as Physical Methods.

Wet Methods

Very limited information was found on dissolution methods for transition metal ferrocyanides which would be appropriate for speciation of the dissolved cyano complexes. It is reported (Sharpe 1976) that "Hot dilute sulfuric acid liberates hydrogen cyanide from hexacyanoferrates(II), but sparingly soluble double salts are also formed; the concentrated acid liberates carbon monoxide . . ." No reference to the original work is cited, so it must be assumed that "double salts" refer to insoluble iron

cyanoferrates of some type. If this is the case, it may well be that quantitative recovery of HCN by acid treatment is not possible and would not provide a method for total cyanide in the highly insoluble transition metal salts.

Nickel and other transition metal ferrocyanides are attacked by strong hydroxide solutions forming nickel hydroxide (or other transition metal hydroxides) and ferrocyanide in solution. In the absence of light, ferro- and ferricyanide are stable in such alkaline solutions (Williams 1943). This may be a potential method of dissolving the solid salts and separating ferro- and ferricyanide ions from Ni and other transition metals before determining $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$. It does not appear that it is a feasible method for substituted iron cyanides such as $[Fe(CN)_5H_2O]^{3-}$ and $[Fe(CN)_5H_2O]^{2-}$ because these are converted to hexacyanoferrate(II) and (III) by hot alkali (Williams 1943).

Using chelating agents appears to be the most promising dissolution method for getting highly insoluble ferro- and ferricyanides and their substituted derivatives into solution with minimum likelihood of chemical change of the complex species. Both ferro- and ferricyanides are nonlabile complexes and are kinetically inert (Basolo and Pearson 1967; Sharpe 1976) particularly in alkaline solution, and except for photochemically induced substitution (Sharpe 1976 and references therein; Williams 1943), should be very stable to displacement of cyanide by the chelating agents. The other transition metals (Ni, Co, Cu, etc.) bonded through nitrogen (Figure A.1) are labile and can be complexed with chelating agents such as ethylenediamine tetraacetate (EDTA) thereby dissolving these salts and releasing the cyanoferrate complexes. Insoluble alkali transition metal ferrocyanides have been dissolved by 0.25 M sodium EDTA at pH 9 to 11 to recover ^{137}Cs (Kyrs and Benes 1966). Cheng (1955) used EDTA in an analytical method based on the selective precipitation of manganese and zinc ferrocyanide at pH 1 to 3. At pH 2.3 to 2.5 (acetic acid solution), most transition metal ferrocyanides including Ni, Co, Cu, etc. are not precipitated. (Ag^+, Fe^{2+}, and Zr^{4+} ferrocyanides also precipitate at that pH.) At higher pH values (up to 9.5) the Mn^{2+} and Zn compounds are also soluble, and it is assumed here that the Ag^+, Fe^{2+}, and Zr(IV) salts probably also dissolve at higher pH values. This then opens the possibility of dissolving cyanide complexes in tank waste (no doubt along with certain other transition metal compounds in the waste) with chelating agents such as EDTA or related compounds. One reference (CA vol. 101, Abst. No. 122120p) was found in which the Chemical Abstracts Index indicated that successive complexiметric titration with EDTA was used to determine Cu and Fe in $CsCuFe(CN)_6$, but the abstract itself did not mention cyanoferrates. The full paper was not obtained, because it was not available onsite.

Separation of the cyanoferrate complexes from the complexed transition metals might be accomplished by anion exchange, by amine extraction of the cyanoferrate ions, or by various chromatography methods. Many chromatography processes are reported to be capable of separating the cyanoferrate complexes (including, in some cases, substituted complexes) into individual species. Table A.1 lists

Table A.1. Chemical Abstracts on Ferrocyanide Chromatography

Volume	Abstract Number	Footnotes	Volume	Abstract Number	Footnotes
57	11836i	a, b	86	64930m	a, b
58	6169e	a, b	88	79495p	b
59	10752h	b	88	181811a	a, b
60	12646a	b	89	70085t	b, d
60	12350b		90	92497b	a, b, c
63	7630b	b	90	179494x	a, b
63	17144b	b	92	103669d	b
64	11903c		92	121105w	a, b
65	19290e	a	92	190636g	a, b
67	87395n	a, b	94	10631m	a, b
68	18429k	b	94	202105q	a, b
69	92707m	a, b	95	34727u	a, b
70	43667k	b	95	103417g	e
70	63780v	d	95	107849x	a, b
70	111299u		95	180034g	a, b
71	105628e	a, b	96	45420k	d
77	83153r	b	97	65573m	a, b
78	118811d	a, b	99	32324a	b
78	48338d	b	100	114094x	a, b
80	41548e		100	184902h	a, b
81	114112r	d	101	65052s	a, b
83	21440x	a, b	101	198305y	e
84	98814a	b	103	226559w	b
86	11461c	a, b	104	141201u	b

(a) Abstract obtained.
(b) Ferricyanide studied also.
(c) Separation from $[Fe(CN)_5NO]^{2-}$ also.
(d) Contains $Fe(CN)_6^{4-}$ data but may or may not contain $Fe(CN)_6^{3-}$ data.
(e) Contains $[Fe(CN)_5NO]^{2-}$ or $[Fe(CN)_5NO]^{-}$ data but may or may not contain $Fe(CN)_6^{4-}$ data.
(f) $[Fe(CN)_5H_2O]^{3-}$

Chemical Abstracts references to chromatographic separation of ferro- and ferricyanide and related complexes. Table A.2 lists Chemical Abstracts references to anion exchange and amine extraction of these complexes.

There are numerous colorimetric and other methods for determining the separated cyanoferrate complexes. Many of these can be found in the references cited in the work on chromatographic separation referenced in Table A.1. Other sources cited in Chemical Abstracts under Detection (Table A.3) and Determination (Table A.4) can be expected to give information on this as well as potentiometric, titrimetric, and various other methods--including other separations methods. Some of these references probably also include chromatographic methods as well.

As can be seen in Table A.4, many methods have been used to determine ferrocyanide and related cyanoferrate complexes. Virtually all, if not all, of these methods are aimed at analyzing cyanoferrates in solution. Without examining a significant number of them, it cannot be ascertained whether good methods are available for analyzing even total cyanide in mixtures of the very insoluble transition metal cyanides with other insolubles, organic carbon, etc. (such as tank sludges).

Physical Methods

Several physical methods provide insight into the structure and composition of insoluble transition metal ferrocyanides and related cyanoferrate species. These include infrared, ^{13}C NMR, Mössbauer, x-ray diffraction (XRD), etc. Of these, XRD has often been used to determine species in solids, but these have to be crystalline solids and must have discretely separate crystal structures. A very large number of the transition metal ferrocyanides, including $M_{2x}Ni_{2-x}Fe(CN)_6$ where X is 0 to 1.0 are isomorphous fcc crystals having very similar lattice parameters of about 10.2 Å. It thus appears that the applicability of XRD may be limited to the identification of the presence or absence of this phase in the waste tank sludge.

The infrared spectra of ferrocyanides, including nickel ferrocyanides, have a characteristic absorption band at about 2100 cm^{-1} (Nakagawa and Shimanouchi 1962; Loos-Neskovic et al. 1989). If nickel ferrocyanide is treated with hot nitric acid or if nickel ferricyanide is precipitated instead, a band is observed at 2170 cm^{-1} presumably due to ferricyanide (Loos-Neskovic et al. 1989). This is presumably an asymmetric CN stretching frequency, and its energy varies with the oxidation state of the central metal ion (Shriver et al. 1965). Thus, this transition is at 2047 cm^{-1} for $K_4Fe(CN)_6$ and at 2125 cm^{-1} for $K_3Fe(CN)_6$. Formation of cyanide bridges between iron and other transition metals such as nickel, cobalt, and copper apparently increases this frequency by about 30 cm^{-1} (Shriver et al. 1965). For the bivalent transition metal complexes, the frequencies of this transition fall in roughly the same order as the stabilities.

Table A.5 lists Chemical Abstracts references to papers giving information on the ultraviolet, visible, near infrared, infrared, and Raman spectra of cyanoferrates. Other references can be found in

Table A.2. Ion Exchange and Solvent Extraction of Cyanoferrates

Volume	Abstract Number	Comment	Footnotes
58	13191g	Ion exchange	a
64	8342c	Amine extraction	a
66	32248r	Ion exchange	
67	87395n	Ion exchange	a
68	60160r	Ion exchange	b
70	20194a	Ion exchange	a, b
70	20195b	Ion exchange	b
71	3978b	Ion exchange	b
74	68126d	Ion exchange	
75	67833r	Ion exchange	b
77	105890h	Ion exchange	a
83	168194d	Ion exchange	a, b
86	64930m	Ion exchange	a, b
86	96491k	Ion exchange	
88	42099m	Ion exchange	
88	4226a	Ion exchange	a
90	44196f	Amine extraction	a, b
90	175436g		
91	27910n	Ion exchange	
91	97218s	Ion exchange	b
91	129450e	Ion exchange	
91	163535w	Ion exchange	b
93	115591e	Amine extraction	
98	10788a	Anion exchange	
99	182402g	Amine extraction	
104	25016p	Amine extraction	

(a) Abstract obtained.
(b) Ferrocyanide studied also.

Table A.3. Detection of Cyanoferrate Ions

Volume	Abstract Number	Comment	Footnotes
56	6287b		
57	13169i		b
57	11840g	Ir spectroscopic	
58	1898b	Ir spectroscopic	a, b
59	10a		b
59	12154e		
59	14577g		b
59	6965d		e
60	3488g		
61	2482e		b
62	4592c		b
63	15528h		b
64	7342c		b
64	5729d		b
64	4243d	Ag_2CrO_4 impregnated paper	a, b
68	56176h		
70	64027s		b
70	25388r		
70	33959t		b
70	102693r		
73	56003c		
74	18953a		
78	37493z		b
78	11881k	With dyes	b
78	168105x		
80	90699p	With fluorescent materials	b
82	67693q	Spot test	
84	11750e		
85	28149j	Spot test	
86	18201b		
90	96930k		
94	26927y		
98	100540t		
105	90361g	Colorimetric	

(a) Abstract obtained.
(b) Ferrocyanide studied also.

Table A.4. Determination of Cyanoferrate Complexes

Volume	Abstract Number	Comment	Footnotes
56	10901i	Titrimetric, spectrophotometric	a
56	1982f	Amperometric	a
57	5301e		
57	9211e		
58	2846g		
58	8406g	Photometric	
58	11956a		b
58	11958a		
59	8a		
59	12178d		b
59	24g	Titrimetric, pptn.	a, b
59	3304e	In gas main deposits	
60	6214a		
60	8637h		
60	9890d		
6[illegible]	9892f		b
[illegible]8	8406g	Photometric	f
59	3d		d
59	7h		d
59	8119d		d
56	13545f	Colorimetric	d
57	5283e	Amperometric	d
59	9331f	Rivinal in	d
63	14047d	Voltametric	d
65	1381h	Turbidimeric using photochem.	d
59	10763c		e
64	5758e		e
67	39908k	Coulometry	b
67	96485u	Using Pb(IV)	
67	104899z	Coulometric	
68	26552k	Titration with Mn(III)	
68	68939h	Titrimetric	a
68	8947p	Titrimetric with indicator	
68	119088d	Using ascorbic acid	
69	8011z	Titrimetric with indicator	

Table A.4. (contd)

Volume	Abstract Number	Comment	Footnotes
69	8233y		b, e
69	8200k	Titrimetric with indicator	e
69	102826r	Stoichiometric amplification method	
69	92717q	Ascorbic acid titrimetric	b
70	93804y		
71	98056m	Titrimetric	a
71	98057n	Titrimetric	a
72	117433w	Ag oxidation	
72	18206t	Thermometric end-point det'n.	
72	18165d	KIO_3 in amperometric	
72	8848q	Iodimetric	
73	51881c	Iron phenanthroline complexes in	
73	69609e	In coke plant wastewater	a
74	150688x	Indicators for titrimetric	a
74	71189g	Amperometric	
68	74813t	Ceriometric	
68	74820t	Voltametric	
71	59581j	In presence of EDTA	
67	28942r	Titration with Ti	d
68	119088d	Ascorbic acid in	d
68	119146w	Hexacyanomanganate (5-) in	d
69	40930i	Indicators in titration of	d
70	102679r	Triphenylmethane dyes in	d
73	41477m	Peroxide titration	d
74	94099s	Amperometric titration	d
74	119807m	Hydroxylamine titration	d
74	60491y	$Hg(ClO_4)_2$ titration	d
75	157928e	Bis(hydroxypropyl)phenylenediamine in	d
67	113480h	Amperometric	
67	50125y	Vanadium(II) in	
68	74820t	Voltametric	
68	35523d	CuCl titration	
72	18230w	Hydrogen peroxide-amperommetric	
76	135313u	Coulometric	a, b
77	13671j	Photometric	

Table A.4. (contd)

Volume	Abstract Number	Comment	Footnotes
77	134810n	Coulometric	b
78	66498k	Dichromate titration, ferroin indicator	
78	52143d	Ag_2CrO_4 paper in	a
78	140022u	In wastewater	a, b
79	73215q	Potentiometric	
79	142508b	Potentiometric	b
79	100138a	Amperometric, chelatometric	
80	43730g	Infrared	a, b
80	10043g	Det'n. of free HCN in	b
81	44962s	Spectrophotometric	a
81	57804e	Brilliant Cresyl Blue indicator in ceriometric	
81	44949t	Ag_2CrO_4 paper	a, b
81	180641p	Pb-selective electrode for	
81	145076m	Dichromate, ferroin indicator	
83	107721b	Permanganate titration	
83	187800q	Dichromate, oxazine dye indicator	
83	201506g	Catalytic-ring-oven method	
84	189011c	Potentiometric with dibromamine-T	
84	115437z	Dichromate, photometric	
85	28154g	Spectrophotometric	
85	116138k	Ceriometric	b
85	28243k	Potentiometric-titrimetric	
77	82658x	In $K_4Fe(CN)_6$ by β-particle backscattering	b
76	80602e	Cu(III) as oxidant for	
82	P164474b	Ceriometric	
84	11887e	Potentiometric with $Hg(NO_3)_2$	
85	171144j	Coulophoretic	
77	69656a	Potentiometric	d
77	69766m	Spectrophotometric	d
78	52060z	Coulometric	d
78	37627w	Coulometric	d
78	52183s	Titrimetric	d
78	52254r	Electrochemical-titrimetric	d
80	90735x	Coulometric	d
80	43730g	Ir spectrometric	b

Table A.4. (contd)

Volume	Abstract Number	Comment	Footnotes
81	57889y	Rate of ferroin oxidation by chromium	d
82	10775p	Spectrophotometric	d
83	21563q	Coulometric	d
83	37112c	Coulometric with Tin-EDTA complex	d
83	187967z	Redox	d
85	56106m	Titrimetric	d
85	171209j	Iodometric	d
85	28154g	Spectrophotometric	d
85	40371h	Triphenylpropylphosphonium extn.-spctrophotometric	
77	134691z	Coulometric	d
77	134695d	Titanium trichloride titrant	d
78	79319c	Hydrazine sulfate titrimetric	d
81	145249v	Voltammetry	d
83	37059r	Titrimetric	d
76	135309x	Ferroin in det'n.	e
77	28507j	Potentometric	e
81	45039h		e
82	67758q	Ferrion extraction - spectrophotometric	e
84	155768	Spectrophotometric	e
86	164799u	Complexometric	
88	98638d	Spot test	
89	36071a	Iodometric	
86	126770v	Oscillopolarographic	a
89	190339a	Zn sulfate with indicators	
89	35960c	Inverse voltammetry	
89	135045b	In photog. process effluents	b
87	72822p	In photog. process effluents	
87	145249u	Iodometric	
89	172975a	Potentiometric with $AgNO_3$	
89	70394t	With bromossiecinimide	
90	197025z	With dichromate and redox indicator	
95	108014h	By voltammetry	
90	92497b	$Fe(CN)_6^{4-}$ in nitroprusside	a, b, e
90	161612z	Titrimetric	

Table A.4. (contd)

Volume	Abstract Number	Comment	Footnotes
90	97030d	Redox titration	
90	214562s	Voltammetry	
91	150699c	Iodometric	
91	150074a	Potentiometric	
91	167797f	Thiazine dyes as indicators in	
91	150597t	Azine dyes in dichromate titration	
92	157188q	Cetyltrimethyl ammonium bromide as titrant	b
92	144890n	Det'n. in citrate fermentation broth	
92	157172e	Dichloramine B in Potentiometric	
92	33240f	Redox titration with indicators	
93	230215y	By quenching of eosin triplet state	
93	234286v	Polarographic	
93	230132u	Ceriometric with redox indicator	
93	128165v	By rotated porous flow-through electrode	
94	40792g	a.c. oscillog. polarog. titration	
94	184899v	Ceriometric with redox indicators	
94	131543t	Phenothiazine dyes as redox indicators	
94	24426k	Potentiometric titrn.	
95	125433m	Amperometric complexometric titration	
94	26927y	With capillary packed bed electrodes	
86	83149e	Coulometric with generated Cu(III)	
91	167841r	Amonium vanadate in potentiometric titrn.	
90	188570	In Prussian blue	
95	63769q	In Prussian blue	a
87	110877v	Antipyrenepropylmethane in	
86	126770v	Oscillopolarog. in electroplating	a, d
86	182466n	Potentiometric with Fe(II)	d
86	100342g	Titrimetric	a, d
88	114677y	Iron-cyclohexanediaminetetraacetate complex in	d
89	70206h	Redox	d
90	110033d	Using vitreous carbon electrodes	d
90	80262h	Chemiluminescent	d
90	214645w	Coulometric	d
90	47794k	Indicators in redox titration	d
91	167859c	Methylene blue as photoredox indicator	d

Table A.4. (contd)

Volume	Abstract Number	Comment	Footnotes
91	150699c	Iodometric	d
91	2042t	Using vitreous carbon electrode	d
92	152729g	In wastewater, automated system	d
92	51289h	Coulometric	d
93	101257q	In wastewater	d
93	230134w	Indicators for redox titration	d
93	18516c	Potentiometric with quaternary ammonium halides	d
94	24450p	In mixtures with fluorides, potentiometric	d
95	17578d	Semidifferential voltommetry	d
91	167841r	Iodometric	d
92	226018y	In Ag electraplating baths, redox titration	d
96	210148n	Stopped flow voltommetry	
96	115044s	Spectrophotometric with Co complexes	b
97	65558k	Amperometric with EDTA and Redox indicator	a
97	119641c	Flow-injection	
98	154410u	With dichromate, oxazine dye indictor	
98	10788a	Spectrophotometric after IX conc.	b
98	46123u	Polentiometric with permanganate	
98	P190967q	Photometric	b
98	136679j	Redox titration	
98	10895h	Voltammetry	b
98	64739d	Chlorobromamine-B in oxidimetric	
98	27081n	Bromomine-B in redox titration	
99	168731g	Voltammetric	
99	186751t	Diffractive spectroelectrochemical	
99	151404e	Differential pulse voltammetry	
100	131569y	Potentiometric	
100	56586w	Argentometric and photometry	
100	16830q	Potentiometric	
101	97758t	Bromamine-T in titration	
101	16356k	Bipotentiometric with Mn solns.	
101	221480n	Potentiometric redox titration	
101	203513w	Potentiometric redox titration	
101	221830b	Potentiometric redox titration	

Table A.4. (contd)

Volume	Abstract Number	Comment	Footnotes
102	197122v	Spectrophotometric	b
102	71863u	Dichromate titration with phenothiazine indicator	
102	55274x	I_2 oxidation in potentiometric	
102	16788y	Chloramine-T in biamperometric	
102	178280d	Potentiometric titration with Zn salts	
103	81018g	Spectrophotometric with indicators	b
103	115278j	Bromohydantoin as oxidant in	
104	158012f	Selective electrode in	b
104	135987p	In nitroprusside	e
104	27992c	Chlorothalimide as oxidant in titration	
105	182964j	Thymophtalin in spectrophotometric	b
105	202266p	Absorption indicator in pptn. titrimetric	
105	145168g	Carbon paste electrodes in voltammetric	b
97	48755e	Spectrophotometric	
98	27005r	In Ag electroplating baths, potentiometric	
99	168651f	In Ag electroplating baths, potentiometric	
98	27080m	Iodosobenzoate in redox titrimetric	
99	10518h	Photochem. org. carbon analyzer for	
98	46123u	Potentiometric with MnO_4^- and F^-	
100	16833t	Redox indicator in titrimetric	
100	131583y	Catalytic oxidation and chronoamperometry	
100	131582x	Catalytic oxidation and chronoamperometry	
101	212743y	In Prussian blue by titration	
98	P15464v	Reagent for spectrophotometric	d
99	209084u	Electrochemical detector in	d
99	15637f	Amperometric and potentiometric	d
103	16103s	In Ag plating bath by photometry	d
103	42755a	As photodecomp. product of nitroprusside	d
103	136493r	In blood serum, amperometric	d
104	61153q	Titration with cetylpyridinium chloride	d, e
104	P84897z	Seimiconductor-containing-electrode in	d
104	135987p	In nitroprusside soln's.	d, e

Table A.4. (contd)

Volume	Abstract Number	Comment	Footnotes
96	14680r	Redox titration with tin-sorbital complex	d
99	47087t	Polarographic	d
99	224249v	Cr(II) in flow injection spectrophotometric	d
101	143053j	Extraction and photometry	d
101	203503t	V(II) - EDTA complex in flow-injection spectrophotometric	d
101	182888e	Catalytic chemiluminescence	d
102	89117p	Flow-injection spectrophotometry	d
104	161107w	Pptn. titration, oscillopolarographic end-point	d
103	42752x	At glossy carbon and Hg-drop electrodes	e
101	122120p	Successive compleximetric dtn. of Cu and Fe in $CsCuFe(CN)_6$	a, d

(a) Abstract obtained.
(b) Ferricyanide studied also.
(c) Separation from $[Fe(CN)_5NO]^{2-}$ also.
(d) Contains $Fe(CN)_6^{3-}$ data but may or may not contain $Fe(CN)_6^{4-}$ data.
(e) Contains $[Fe(CN)_5NO]^{2-}$ or $[Fe(CN)_5NO]^{-}$ data but may or may not contain $Fe(CN)_6^{4-}$ data.
(f) $[Fe(CN)_5H_2O]^{3-}$.

Table A.5. Spectra of Cyanoferrates

Volume	Abstract Number	Comment	Footnotes
58	1898b	Analytical, infrared	a, b
58	10861f	Spectra and structure	
59	4681d	Spectra and structure	
65	6514h	Spectra and structure	
57	4193e		
57	5479e		b
57	11840g	Analytical, ir	a, b
65	17912h		b
64	13728d	Spectra and solubility of salts, CN^- bridging	
62	44g	Force constants	d
61	1403e		d
62	2369g		d
62	11309d		d
60	7571c		e, f
61	1403e		d, f
60	11499h		e
57	2989i		e
62	4785h		e
63	6507	Mössbauer and spectrum	
57	4198c		
60	1238c		b
60	1241d		b
60	4956d		b
61	15537h		b
62	11309d		
63	155a		
63	14228b		
64	2866d	And vibrational analysis	b
65	8213b	Raman	
58	3006e		d
63	155a		
65	9948g		
68	83099s	Near infrared	a
69	63196p	Infrared	

Table A.5. (contd)

Volume	Abstract Number	Comment	Footnotes
70	72422g	Bonding in relation to	b
70	91934s	Atten. total reflectance	b
72	138015b	Electronic	b
75	69038j	Infrared	
67	48832h	Raman, laser induced	
72	138148	Raman, bonding relation	
71	96535t		
69	63196p	Infrared, bonding relation	
75	69038j		
66	15262y	Laser-induced Raman	d
67	48832h	Laser-induced Raman	d, e
69	111771	Visible-UV	d
70	101345s	UV	d
72	138148x	Bonding in relation to Raman	d
75	156913j	Laser-induced Raman	d
69	63196p	Ir, bonding in relation to	e
71	107315z	Vibrational	e
75	69038j	Ir	e
67	58904x	Ir	e
67	86221r	Ir	e
66	33250x	Ir, vibration analysis	e
70	73683e	Vibrational	e
71	107315z	Vibrational	e
70	110309k	Raman	e
78	77640b	Ir and electronic, in alkali chlorides	b
83	18334k	Laser Raman in chromate mixes	
81	177701c	Ir spectrum, Cu, potassium ferrocyanide, $K_4Ni_4[(FeCN)_6]_3$	
76	119367j	Ir spectrum, Ni_2 $Fe(CN)_6$, $Ni_3[Fe(CN)_6]_2$, $K_3Fe(CN)_6$	
82	147365z	Ir spectrum, $Ni_2Fe(CN)_6$, $Co_2Fe(CN)_6$, $Cd_3[Fe(CN)_6]_2$, $FeFe(CN)_6$, $K_3Fe(CN)_6$, $KFeFe(CN)_6$	
85	93295t	Ir and Mössbauer, $K_4Fe(CN)_6$	
80	101992g	Far-ir, $K_4Fe(CN)_6 \cdot 3H_2O$	

Table A.5. (contd)

Volume	Abstract Number	Comment	Footnotes
79	36670p	Ir, $K_3Fe(CN)_6$, pressure effect	
93	176441u	Raman, $K_4Fe(CN)_6 \cdot 3H_2O$	
90	143789h	Raman, $K_4Fe(CN)_6 \cdot 3H_2O$	
92	101750z	Raman, $K_4Fe(CN)_6 \cdot 3H_2O$	
91	11724u	Ir and Mössbauer, correlation between, $Na_4Fe(CN)_6$	
80	43730g	Analytical, ir	a, b
90	194898a	Absorption and emission spectrum, $K_4Fe(CN)_6$	
93	104127h	Ir, intensities, $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$	a, b
89	112506p	Ir, structure, $CsNiFe(CN)_6$ and many other transition metal relatives	a
93	158525e	Ir, Mössbauer, 1st row trans. metal ferricyanides	a
94	75979a	Ir, XRD	e
86	25404y	Ir, nitroprusside, etc.	a, e
100	111300a	Ir spectroelectrochemistry	b
102	181797h	Ir	b
100	164583b	Ir and Mössbauer, $KLnFe(CN)_6$, various Ln	
101	119589t	Ir and Mössbauer, $KLnFe(CN)_6$, various Ln	
100	129046g	Ir and force constants, $KLnFe(CN)_6$, various Ln	
102	13936j	Spectrum and electroredox, $KFe[Fe(CN)_6]$	
100	586391R	Spectrum of $K_2Ni[Fe(CN)_6]$ on Ni electrode	
98	209188k	Detection in corrosion products by FTIR photoacoustic	
96	152095e	Ir and Mössbauer, $K_4Fe(CN)_6$	
101	140142b	Ir and Mössbauer, $K_4Fe(CN)_6$	b
100	147777a	Ir, $K_4Fe(CN)_6 \cdot 3H_2O$	
100	164585	Ir, $K_4Fe(CN)_6 \cdot 3H_2O$	
100	129051e	Ir, $K_4Fe(CN)_6 \cdot 3H_2O$	
100	93765z	Ir, $K_4Fe(CN)_6 \cdot 3H_2O$	
99	130695k	Raman, $K_4Fe(CN)_6 \cdot 3H_2O$	
96	132487f	Vibrational, $K_4Fe(CN)_6 \cdot 3H_2O$	
97	173861n	Ir, crystal structure, $CsMFe(CN)_6$, M = Co, Zn	
100	150220u	FTIR external reflection and photoacoustic, $Cu_3[Fe(CN)_6]_2$ on electrode	
100	58639q	Ir, $KNiFe(CN)_6$ on Ni electrode and $[Fe(CN)_5NO]^{2-}$	

Table A.5. (contd)

Volume	Abstract Number	Comment	Footnotes
96	152095e	Ir and Mössbauer, $H_3Fe(CN)_6$, $K_3Fe(CN)_6$, $Na_2[Fe(CN)_5NO]$	
96	189889t	Ir and Mössbauer, $K_3Fe(CN)_6$	
104	233211a	Ir of $[Fe(CN)_5NO]^{2-}$ etc. in $K_3Fe(CN)_6$	
104	195974s	Ir, fine structure and NO^+ stretching band in $[Fe(CN)_5NO]^{2-}$	
104	233516d	Ir and Mössbauer in $Ba[Fe(CN)_5NO]$	
101	100478j	Ir, vibrational coupling of NO^+ groups in $Ba[Fe(CN)_5NO]$	
102	35651q	Ir, $Ca[Fe(CN)_5NO]$	
97	63314d	Ir, $Ca[Fe(CN)_5NO]$	
104	98439p	Ir, polarized spectrum	

(a) Abstract obtained.
(b) Ferricyanide studied also.
(c) Separation from $[Fe(CN)_5NO]^{2-}$ also.
(d) Contains $Fe(CN)_6^{3-}$ data but may or may not contain $Fe(CN)_6^{4-}$ data.
(e) Contains $[Fe(CN)_5NO]^{2-}$ or $[Fe(CN)_5NO]^{-}$ data but may or may not contain $Fe(CN)_6^{4-}$ data.
(f) $[Fe(CN)_5H_2O]^{3-}$.

the review by Sharp (1976). The electronic spectra (UV, vis, near-ir) are not discussed here because it is felt that other colored materials in the waste tank sludges would contribute significant interference in this wavelength region, although this might not be true after partial separation of the various species. Most of the references on infrared spectra cited are not on direct use of these spectra for analysis but are more fundamental studies that should be useful in determining what species can be differentiated by infrared. Some analytical use of infrared for differentiating between $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ has been reported both in solution (Drew 1973) and in solids (Al-Kayssi and Magee 1962; Haba and Wilson 1962).

Mössbauer spectroscopy has found a significant amount of use in elucidating the structural relationships and species present in various cyanoferrate compounds as well as in following solid-state reactions involving cyanoferrate complexes, particularly mixed iron oxidation state compounds (Sharpe 1976). Although the Mössbauer shifts are apparently almost identical for $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ (Cotton and Wilkinson 1972), they may be useful for identifying other species present. In addition to references found in Sharpe (1976), Table A.6 cites Chemical Abstracts on Mössbauer studies. It is not known whether any of the references cited in Table A.6 address analytical determination of cyanoferrate complex species in the presence of other material or whether Mössbauer can be useful as a speciation method for cyanoferrate species in waste tank sludges.

Nuclear magnetic resonance (NMR) based on ^{13}C is another method that may have some possible applications to the speciation of cyanoferrate salts. Table A.7 lists Chemical Abstracts references to this subject.

Table A.6. Mössbauer Studies of Cyanoferrates

Volume	Abstract Number	Comment
63	6507	And spectrum
69	22865n	$Fe_4[Fe(CN)_6]_3$, $Co_2Fe(CN)_4$, $FeFe(CN)_6$
73	40292k	$Fe_4[Fe(CN)_6]_3$, $Co_2Fe(CN)_4$, and ir
69	23460p	$Fe_4[Fe(CN)_6]_3$, $Fe_3[Fe(CN)_6]_2$
68	7822g	$Fe_4[Fe(CN)_6]_3$, pressure effect
67	37738t	
72	7751r	$Fe_4[Fe(CN)_6]_3$
75	82178z	$Fe_4[Fe(CN)_6]_3$
67	77714b	$K_4Fe(CN)_6$ containing transition metals
68	7818k	$K_4Fe(CN)_6$, pressure effect on
68	25249e	$K_4Fe(CN)_6$, ^{57}Fe in, also $[Fe(CN)_5NO]^{2-}$
69	6996a	$K_4Fe(CN)_6$, ^{57}Fe in
69	91427h	$K_4Fe(CN)_6$, ^{57}Fe in frozen solutions
72	61149p	$K_4Fe(CN)_6$
73	60996w	$K_4Fe(CN)_6$, theoretical
75	82207h	$K_4Fe(CN)_6$, oxidation-reduction in relation to
69	22865n	$Co_3[Fe(CN)_6]_2$, $Fe_4[Fe(CN)_6]_3$, and structure
69	101591y	$Co_3[Fe(CN)_6]_2$, cation polarizability
66	69113u	$Co_3[Fe(CN)_6]_2$, and structure
72	95036q	$Ni_3[Fe(CN)_6]_2$, $Co_3[Fe(CN)_6]_2$, effect of temp.
72	127072s	$Ni_3[Fe(CN)_6]_2$, $Co_3[Fe(CN)_6]_2$, effect of temp.
73	20211e	$Ni_3[Fe(CN)_6]_2$, $Co_3[Fe(CN)_6]_2$, effect of temp.
73	40292k	$Ni_3[Fe(CN)_6]_2$, $Co_3[Fe(CN)_6]_2$, and ir spectrum
75	27933s	$Ni_3[Fe(CN)_6]_2$, $Co_3[Fe(CN)_6]_2$, temp. effects and theory
75	82178z	$Fe_3[Fe(CN)_6]_2$, isotopic labeling in relation to
67	48726b	$Ni_3[Fe(CN)_6]_2$, effect of ^{57}Fe in
70	72680q	$Ni_3[Fe(CN)_6]_2$
66	69113u	$Ni_3[Fe(CN)_6]_2$, $K_2NiFe(CN)_6$, and others
66	101166b	$[Fe(CN)_5NO]^{2-}$, effect of ^{57}Fe in
70	92008e	$[Fe(CN)_5NO]^{2-}$
71	8301k	$[Fe(CN)_5NO]^{2-}$, in frozen aq. solns.
70	15396c	$Na_2[Fe(CN)_5NO]$
72	26884c	$Na_2[Fe(CN)_5NO]$
73	30503r	$Na_2[Fe(CN)_5NO]$
74	59121w	$Na_2[Fe(CN)_5NO]$

Table A.6. (contd)

Volume	Abstract Number	Comment
75	56412b	$Na_2[Fe(CN)_5NO]$
75	56414d	$Na_2[Fe(CN)_5NO]$
66	108608f	$Fe(CN)_6^{4-}$, on cation resin
67	69126w	$Na_2[Fe(CN)_5NO]\cdot 2H_2O$
68	25255d	$Na_2[Fe(CN)_5NO]\cdot 2H_2O$
70	101491m	$Na_2[Fe(CN)_5NO]\cdot 2H_2O$
70	72433m	$Na_2[Fe(CN)_5NO]\cdot 2H_2O$
71	17174y	$Na_2[Fe(CN)_5NO]\cdot 2H_2O$
72	61149p	$Na_2[Fe(CN)_5NO]\cdot 2H_2O$
77	108064c	$Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, effect of ^{57}Fe in
77	170936s	$Fe(CN)_6^{4-}$, frozen aq. solns., soln. conditions, and $Fe(CN)_6^{3-}$
79	109780m	$Fe(CN)_6^{4-}$, in MO calculations, and $Fe(CN)_6^{3-}$
81	8115j	$Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$
80	32257g	$Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, ^{57}Co decay in cobalt cyano complexes, on
80	21161v	$Fe(CN)_6^{4-}$, in aq. Tween 80
85	133572q	$Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, electron configuration
82	147931f	$K_2CoFe(CN)_6$, effect of Fe valence, also $KCoFe(CN)_6$
82	105038q	$Fe_2Fe(CN)_6$, thermal decomp.
83	88052r	$Fe_2Fe(CN)_6$
85	93295t	$K_4Fe(CN)_6$
78	104206y	$Ni_3[Fe(CN)_6]_2$, $Co_3[Fe(CN)_6]_2$
79	47561e	$Co_3[Fe(CN)_6]_2$, very low temp.
77	54645x	$Ni_3[Fe(CN)_6]_2$, $K_3Fe(CN)_6$, high pressure effects on
76	66036s	$K_3Fe(CN)_6$, proton irradiation
77	27049z	$K_3Fe(CN)_6$
77	132899z	$K_3Fe(CN)_6$
77	170986h	$K_3Fe(CN)_6$, frozen aq. solns.
78	153010p	$K_3Fe(CN)_6$, crystal field splitting in relation to
78	117320f	$K_3Fe(CN)_6$
80	139229b	$K_3Fe(CN)_6$, and photoelectron spectra
83	88074z	$K_3Fe(CN)_6$, of solns.

Table A.6. (contd)

Volume	Abstract Number	Comment
83	35342d	$K_3Fe(CN)_6$, proton irradiation effect on
84	171855w	$K_3Fe(CN)_6$, frozen aq. solns.
85	39053z	$K_3Fe(CN)_6$, in hexocyanocoboltate
87	93186z	$Fe(CN)_6^{4-}$
87	209112d	$Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, in presence of Co^{2+}
88	179785b	$Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, calibration constant for
91	11724u	$Na_4Fe(CN)_6$, correlation with ir.
86	163308w	$K_4Fe(CN)_6$, and photoelectron spectrum
87	60360y	$K_4Fe(CN)_6$, cation exch. resin containing
88	14005j	$K_4Fe(CN)_6$, and photoelectron apectrum
90	78828d	$K_4Fe(CN)_6$
91	131659y	$K_4Fe(CN)_6$
91	136463q	$K_4Fe(CN)_6$
95	159281a	$K_4Fe(CN)_6$, diff. spectrum, quant. anal. of
93	158525e	Various transition metal ferricyanides, ir
97	172764	$Cs_2CuFe(CN)_6$
100	164583b	$KLnFe(CN)_6$, various Ln
101	119589t	$KLnFe(CN)_6$, various Ln
96	152095e	$K_4Fe(CN)_6$, $K_3Fe(CN)_6$, ir, also $H_3Fe(CN)_6$
101	140142b	$K_4Fe(CN)_6$, $K_3Fe(CN)_6$, ir
96	189889t	$K_3Fe(CN)_6$, ir, H-bonding in
104	233516d	$Ba[Fe(CN)_5NO]$, ir

Table A.7. ^{13}C Nuclear Magnetic Resonance of Cyanoferrates

Volume	Abstract Number	Comment
62	8543g	$Fe(CN)_6^{4-}$
66	50612j	$K_3Fe(CN)_6$
66	6870t	$K_3Fe(CN)_6$
73	20253v	$K_3Fe(CN)_6$
79	110086w	$Fe(CN)_6^{4-}$
83	199873d	$Fe(CN)_6^{4-}$
85	54207w	$Fe(CN)_6^{3-}$, ^{14}N-NMR
91	81261q	$Fe(CN)_6^{4-}$, Mössbauer and electronic spectra
86	10426h	$Fe(CN)_6^{4-}$
90	195133j	$Fe(CN)_6^{4-}$
90	159656y	$Fe(CN)_6^{4-}$, Fourier transform
86	130570x	$K_4Fe(CN)_6$
93	195000a	$K_4Fe(CN)_6$, high hydrostatic pressures

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