

QUANTITATIVE MEASUREMENT OF CYANIDE SPECIES IN SIMULATED HANFORD WASTE

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ABSTRACT

Analytical methods were examined for the quantitation of cyanide species in Hanford simulated high-level radioactive waste. Methods studied included infrared spectroscopy (solid state and solution), Raman spectroscopy, Mössbauer spectroscopy, x-ray diffraction, scanning electron microscopy-energy dispersive spectroscopy, and ion chromatography. Of these techniques, infrared, Raman, x-ray diffraction, and ion chromatography showed promise for the cyanide concentration range of interest. For these latter four techniques, quantitation limits were demonstrated to be about 0.1 wt% (as cyanide) using simulated Hanford wastes.

INTRODUCTION

Radioactive waste from defense operations has accumulated in underground waste tanks at the Hanford Site since the early 1940s. During the 1950s, additional tank space was required to support the defense mission. To obtain this additional storage volume quickly and without constructing additional storage tanks, Hanford Site scientists developed a process to scavenge radiocesium from tank waste liquids by precipitating cesium nickel ferrocyanide. This process caused the addition of about 140 metric tons of ferrocyanide to 24 single shell tanks (SSTs).

Ferrocyanide is a stable complex of ferrous ion and cyanide that is considered nontoxic because it does not easily 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. 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.

The threshold concentration of total cyanide within the tank waste matrix that is expected to be a safety concern is estimated to be about 1 to 3 wt%. To bound the safety concern, methods to detect and identify cyanide species in actual waste are needed to definitively quantitate to a lower limit of at least 0.1 wt% the amount of ferrocyanides present within the waste tanks.

This paper summarizes the results of studies conducted at Pacific Northwest Laboratory (PNL) under contract to Westinghouse Hanford Company (WHC) to develop methods to identify and quantitate cyanide species in ferrocyanide tank waste. These methods can be divided into two major categories for convenience: 1) direct analytical methods that can be performed on the tank waste solids with little or no waste pretreatment or preparation, and 2) indirect analytical methods that can be used only after substantial modification of the original sample matrix, such as sample dissolution before analysis.

Direct analytical methods to quantitate cyanide species include:

- Fourier transform infrared spectroscopy (FTIR)

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

Indirect analytical methods to quantitate cyanide species include:

- solution FTIR spectroscopy
- ion chromatography (IC).

DIRECT ANALYTICAL METHODS DEVELOPMENT

Direct analytical methods require little or no sample pretreatment or preparation to quantitate cyano species in tank waste solids. Solid samples for direct methods analysis were prepared using standard matrix materials consisting of salts listed in U-Plant and In-Plant flowsheets, (1) which were the protocols used in the 1950 cesium scavenging campaigns. Salts used in the simulated waste matrix included Na₂SO₄, Na₃PO₄, NaNO₃, NaNO₂, and Sr(NO₃)₂ in various mole ratios. The concentration of Na₂NiFe(CN)₆ in these simulated wastes was added as a pure solid or was formed *in situ* by adding NiSO₄ and Na₄Fe(CN)₆ as called for in the flowsheet.

FTIR Spectroscopy

FTIR spectroscopy has been identified as an attractive method to quantitatively determine cyanide species within ferrocyanide tank waste. (2) Absorbance FTIR spectra can be obtained with little or no sample preparation by using attenuated total reflectance (ATR) sample cells. Solid sample spectra discussed in this section were taken using an FTIR spectrometer equipped with a zinc selenide ATR cell.

Spectra of the reagent grade K₃Fe(CN)₆ and K₄Fe(CN)₆ solids, as well as simulated wastes prepared using U-Plant and In-Farm flowsheets, are presented in Fig. 1. This figure shows the FTIR absorbance bands for K₃Fe(CN)₆ found at 2116, and 2119 cm⁻¹; bands for K₄Fe(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 FTIR spectra of the flowsheet materials in Fig. 1 reveal a single band at about 2088 cm⁻¹ (the In-Plant material

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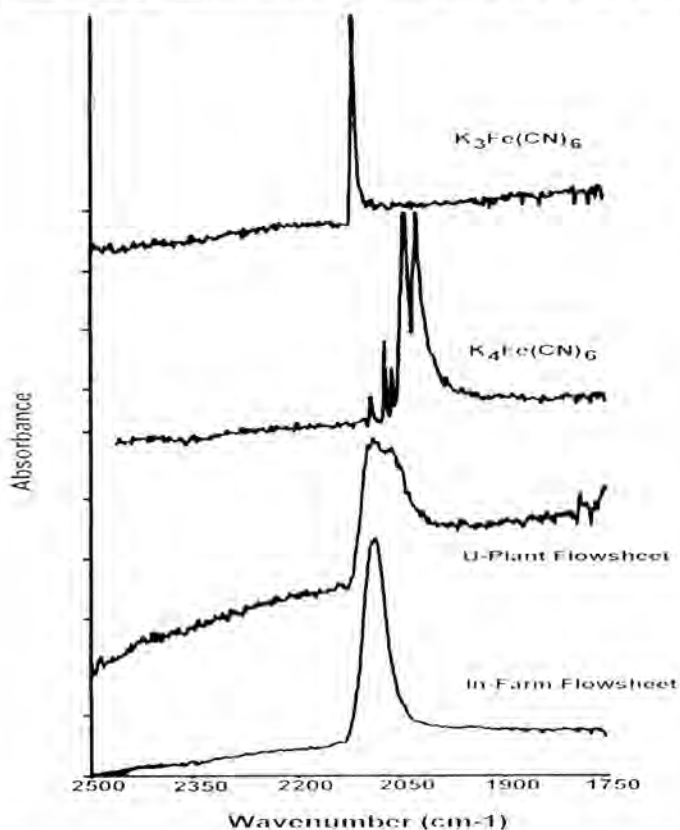


Fig. 1. IR Bands in the $\nu(\text{C}\equiv\text{N})$ region show that "free" ferri- and ferrocyanides can be differentiated from ferrocyanide flowsheet simulated wastes.

has a shoulder at about 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 (3) that if the M-C \equiv N group forms a M-C \equiv N-M' type bridge, $\nu(\text{C}\equiv\text{N})$ shifts to a higher frequency. Since the $\nu(\text{C}\equiv\text{N})$ band (2088 cm^{-1}) for the flowsheet simulated wastes was found to be higher than $\nu(\text{C}\equiv\text{N})$ for Fe(II)-C \equiv N in $\text{K}_4\text{Fe}(\text{C}\equiv\text{N})_6$ and lower than $\nu(\text{C}\equiv\text{N})$ for Fe(III)-C \equiv N in $\text{K}_3\text{Fe}(\text{C}\equiv\text{N})_6$, results suggest the flowsheet simulated wastes retained the Fe in the +2 oxidation state [e.g., Fe(II)-C \equiv N-Ni].

Band positions for CN stretching regions of the flowsheet simulated wastes indicate the mode of cyanide bonding is similar in each of the flow-sheet preparations. This similarity 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., $\text{Fe}(\text{OH})_2$] in the samples; neither factor will markedly affect the metal-cyanide stretch.

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. (4)

To demonstrate that the $\nu(\text{C}\equiv\text{N})$ band follows Beer's Law, and therefore can be applied for quantitative analysis, a U-Plant flowsheet simulated waste, prepared by Hallen et al. (5) was analyzed by standard addition procedures.

Standard addition samples were prepared following a modified U.S. Environmental Protection Agency (EPA) procedure SW84 (6) for the quantitative determination of $\text{Na}_2\text{NiFe}(\text{CN})_6$ in the ferrocyanide U-plant flowsheet simu-

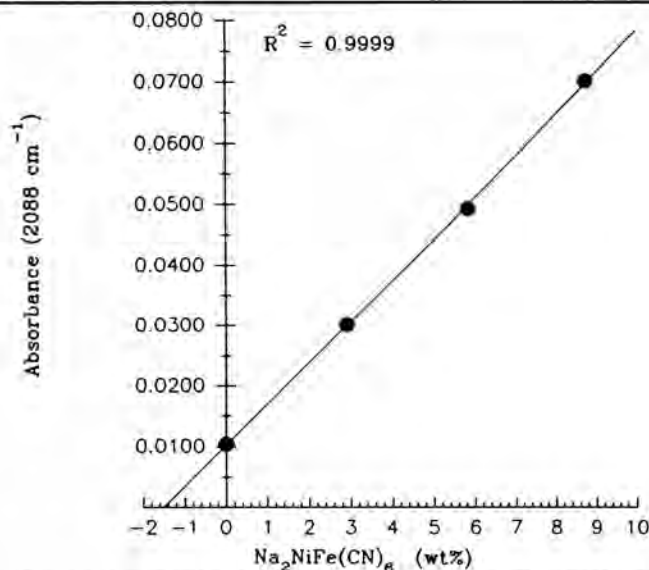


Fig. 2. Standard addition determination of $\text{Na}_2\text{NiFe}(\text{CN})_6$ using solid FTIR with an ATR cell.

lated wastes. The standard addition reagent used in this experiment was a pure $\text{Na}_2\text{NiFe}(\text{CN})_6$ material also prepared and analyzed by Hallen et al. (5)

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 Fig. 2. From this analysis, the concentration of $\text{Na}_2\text{NiFe}(\text{CN})_6$ in the unknown U-Plant flowsheet sample was determined to be 1.81 wt% (when corrected for the dilution factor). This translates to 1.21 wt% $\text{Fe}(\text{CN})_6^{4-}$ or 0.89 wt% total cyanide (as CN^-) within the sample.

The upper level of ferrocyanide concentration not considered a safety concern in tank waste is in the range 1 to 3 wt%. The results of this investigation demonstrate the FTIR method is capable of measuring cyanide complexes below that limit.

Raman Spectroscopy

Raman spectroscopy was identified as a method for the quantitative analysis of cyanide-containing complexes within ferrocyanide tank wastes. (2) Raman spectroscopy can be performed directly on solid samples without special preparations.

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.

For each sample, the Raman signal was collected in two segments: the first centered at 876.5 nm, resulting in a Raman spectral window ranging from about 900 to 1350 cm^{-1} . The second segment centered at 960.5 nm, resulting in a Raman spectral window ranging from about 1940 to 2300 cm^{-1} . 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 were observed in this spectral window, consistent with

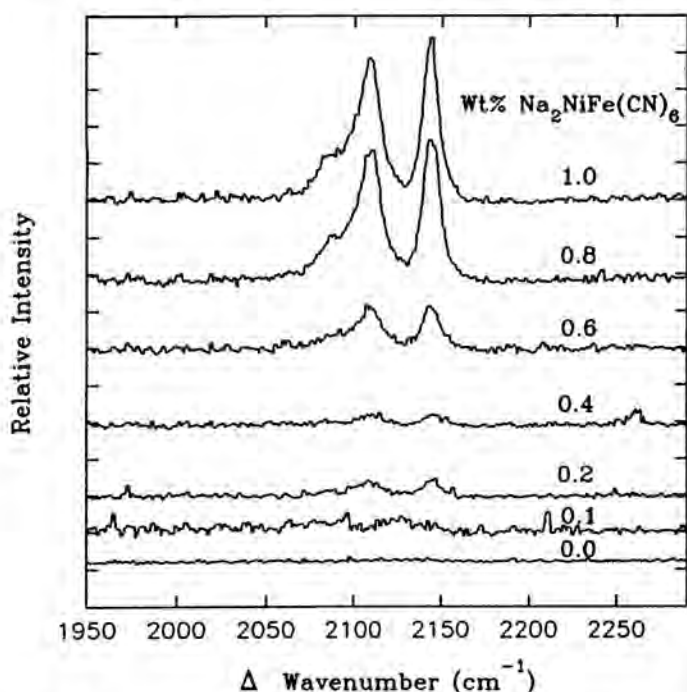


Fig. 3. Raman spectra of $\text{Na}_2\text{NiFe}(\text{CN})_6$ at various concentrations in flowsheet simulated waste.

literature. (7) Peaks in the high frequency region correspond to the vibrational modes assigned to the cyanide stretching motion and are shown in Fig. 3.

Using an intensity ratio of Raman bands 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 intensity ratio of the cyanide complex vibrational mode (2135 cm^{-1}) to the internal stretching mode of the PO_4^{3-} ion (992 cm^{-1}) was used to determine the concentration of $\text{Na}_2\text{NiFe}(\text{CN})_6$ in the powdered samples. The phosphate peak and the $\text{Na}_2\text{NiFe}(\text{CN})_6$ peak were chosen because the phosphate concentration in each sample matrix was constant, and both these peaks are relatively isolated from other peaks in the spectra, which minimizes the uncertainty in determining their intensity. The intensity ratio $2135\text{ cm}^{-1}/992\text{ cm}^{-1}$ as a function of weight percent ferrocyanide is shown in Fig. 4.

The data scatter observed in Fig. 4 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 (≤ 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 non-homogeneity since the laser excitation beam focuses on a relatively small surface area of the sample.

It is evident from the data in Fig. 4 that Raman spectroscopy may be used to quantitatively measure concentrations of $\text{Na}_2\text{NiFe}(\text{CN})_6$ at and below 1 wt%.

X-Ray Diffraction

Methods using XRD have been shown suitable for the identification of $\text{Na}_2\text{NiFe}(\text{CN})_6$ within solid simulated waste. (5,4) To demonstrate that XRD is suitable for the analytical determination of ferrocyanide complexes, this technique was

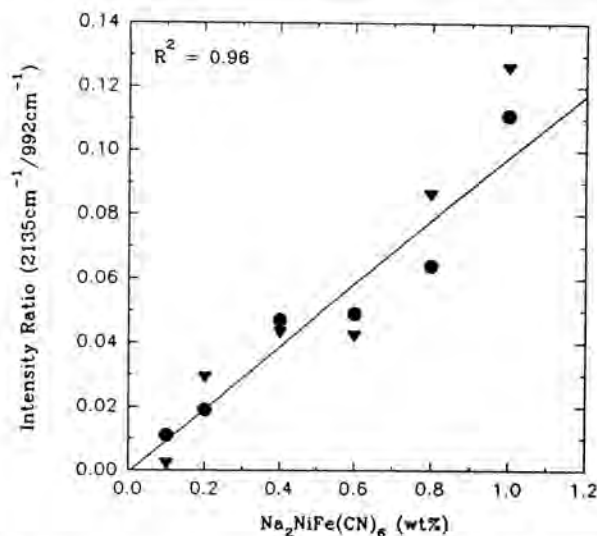


Fig. 4. Linear Raman response with respect to $\text{Na}_2\text{NiFe}(\text{CN})_6$ concentration in ferrocyanide simulated waste.

used to quantitatively measure ferrocyanide salts within a simulated waste matrix.

The XRD method of detection was tested for applicability at ferrocyanide concentration levels well below the accepted level for safety concern. A series of experiments was performed using $\text{Na}_2\text{NiFe}(\text{CN})_6$ concentration levels at and below 1 wt%. The amount of a pure source of $\text{Na}_2\text{NiFe}(\text{CN})_6$ was varied from 0.1 to 1 wt%.

Figure 5 shows the XRD response vs concentration for these samples. According to Fig. 5, this technique yields a linear response over the concentration range of interest [0.1 to 1 wt% $\text{Na}_2\text{NiFe}(\text{CN})_6$]. These XRD diffractograms were obtained from equipment routinely used to characterize radioactive samples from actual high-level radioactive waste.

In spite of the test results depicted in Fig. 5, XRD is limited for use with an amorphous sample because the solid sample must be in a crystalline form to exhibit a diffraction pattern. This limitation is significant, since these solids are

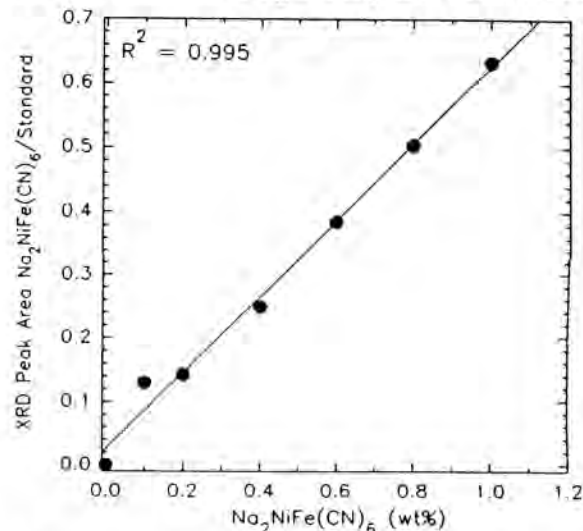


Fig. 5. XRD analysis of $\text{Na}_2\text{NiFe}(\text{CN})_6$ in ferrocyanide simulated waste. Plot of XRD response vs wt% $\text{Na}_2\text{NiFe}(\text{CN})_6$.

known to form colloidal suspensions and may not precipitate into well characterized crystalline structures in actual waste.

Scanning Electron Microscopy-Energy Dispersive Spectroscopy

SEM-EDS has been used in past work to analyze $\text{Na}_2\text{NiFe}(\text{CN})_6$ material. (5) This technique was judged useful for identifying contaminants within supposedly pure ferrocyanide compounds that had been prepared commercially. Although SEM-EDS was shown to be semiquantitative for elements with an atomic mass greater than that for boron, (5) this technique was not considered a useful tool to identify specific ferrocyanide compounds. Therefore, SEM-EDS was not examined further as an analytical tool for cyanide-containing complexes.

Mössbauer Spectroscopy

Mössbauer spectroscopy has been suggested for use in defining the Fe(II)/Fe(III) ratio in solid ferro- and ferricyanide samples. (5) Subsequent studies have indicated this technique may be used to estimate the lower limit for the total number of different molecular species containing iron. (4) Based on work by Lilga et al., (4) this technique could not, however, be considered a means to definitively identify specific cyanide-containing iron complexes. For this reason, Mössbauer spectroscopy was not examined further for the quantitative analysis of cyanide-containing complexes.

INDIRECT METHODS DEVELOPMENT

The indirect analytical methods that were investigated include solution FTIR and IC spectroscopy. Simulated wastes used for indirect methods analysis are based on the U-Plant and In-Farm flowsheets mentioned earlier. Use of these indirect analytical methods to quantitatively determine cyanide species requires dissolution of the sample matrix before analysis.

Solution FTIR Spectroscopy

As discussed in the direct methods section, $\text{Na}_2\text{NiFe}(\text{CN})_6$ concentrations between 0.1 and 10 wt% (Fig. 2) in a solid simulated waste matrix can be determined in the solid state using FTIR-ATR detection methods. Even though ferrocyanide can be measured well below the threshold for safety concern by using pure mixtures of salts, there is some uncertainty in the measured absorbance when analyzing solids. This uncertainty is largely because of the matrix heterogeneity.

Detection of the cyanide complexes in aqueous solution is possible by FTIR using an ATR cell. With solution FTIR techniques, the uncertainty of the absorbance measurements is reduced because the solutions are homogeneous. Figure 6 shows FTIR spectra of standard solutions containing ferricyanide, ferrocyanide, and free cyanide. Figure 6 also contains solution spectra of dissolved flowsheet simulated wastes labeled In-Farm 1, In-Farm 2, and U-Plant 2. According to Figure 6, the only cyanide species in the flowsheet simulated wastes is the ferrocyanide complex, $[\text{Fe}(\text{CN})_6]^{4-}$, as would be expected based on makeup.

The standard curve for ferrocyanide showing the absorbance at the peak maximum for $\text{Fe}(\text{CN})_6^{4-}$ (2037 cm^{-1}) vs the concentration in solution is shown in Figure 7. Fig. 7 shows that the solution FTIR technique gives a linear response over the concentration range 0.01 to 10 wt% $\text{Fe}(\text{CN})_6^{4-}$ in aqueous solution. Based on the data in Fig. 7, this technique is also

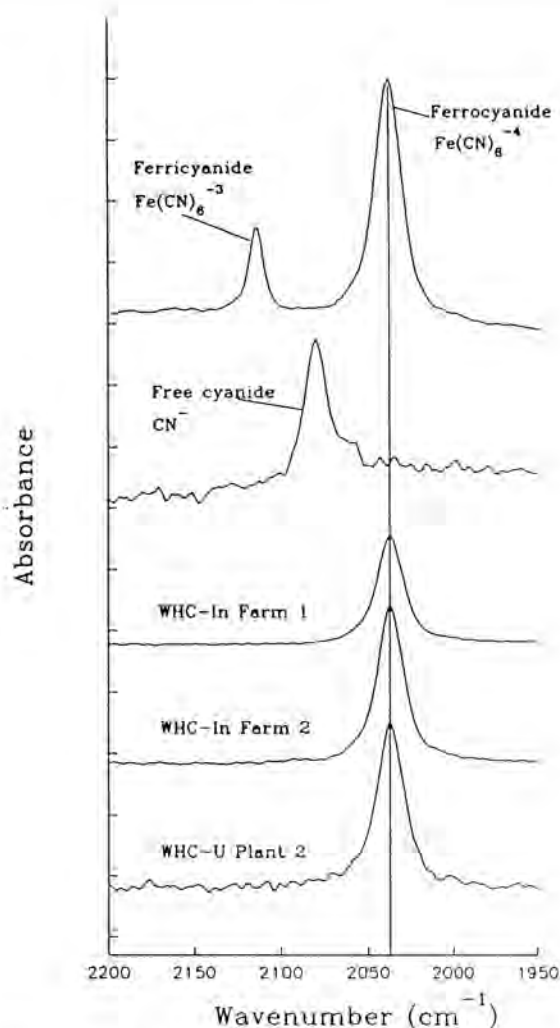


Fig. 6. Solution FTIR spectra of cyanide standards and various flowsheet materials.

stable over time. The different symbols on the standard curve indicate measurements taken on the same standard solution one week apart. Quantitation of free ferrocyanide $[\text{Fe}(\text{CN})_6^{4-}]$ in solution to about 0.01 wt%, enables the quantitative detection of ferrocyanide to about 0.1 wt% in the original undiluted solid sample. This trend has been verified for free cyanide (CN^-) and ferricyanide $[\text{Fe}(\text{CN})_6^{3-}]$.

Ion Chromatography

IC methods have been shown to separate the ferrocyanide complex from the ferricyanide complex in aqueous solution. (2) Calibration standards of $\text{K}_3\text{Fe}(\text{CN})_6$ and $\text{K}_4\text{Fe}(\text{CN})_6$ were matrix matched to the simulated wastes before injection. Sample analyses were completed by directly comparing observed chromatographic peak heights to those obtained from matrix-matched, similarly treated standards.

Figure 8 is an example of actual chromatograms for three consecutive samples: ferrocyanide and ferricyanide standards, and an In-Farm 1 flowsheet simulated waste, 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 $\text{Fe}(\text{CN})_6^{4-}$ (ferrocyanide) complex only. Similar results were

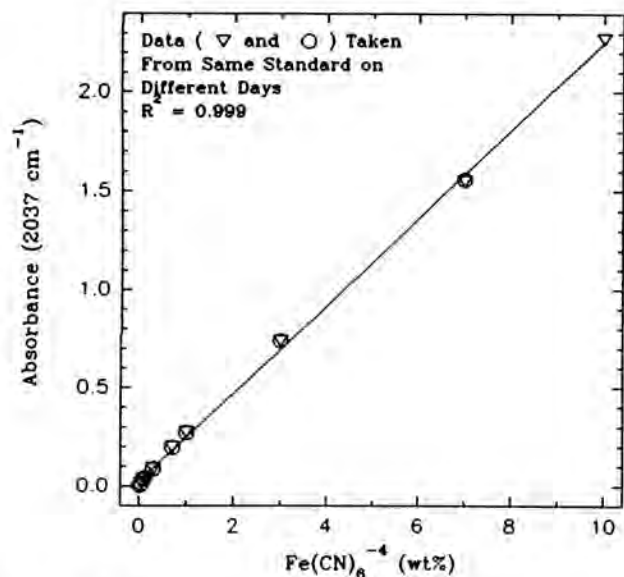


Fig. 7. Solution FTIR standard curve for the $\text{Fe}(\text{CN})_6^{4-}$ complex with concentration ranging from 0.01 to 10 wt%.

obtained for the other In-Farm and U-Plant flowsheet simulated wastes.

Figure 9 is the IC standard curve for ferrocyanide ion [$\text{Fe}(\text{CN})_6^{4-}$] in solution. The IC curve shows that the detection limit in solution for $\text{Fe}(\text{CN})_6^{4-}$ is quantitative to the ppm level. This translates to a quantitation limit of about 0.1 wt% ferrocyanide in the original undiluted solid sample.

Analysis of Flowsheet Simulated Wastes Using Solution FTIR and IC Methods

Six ferrocyanide flowsheet simulated wastes were analyzed for the detection of cyanide species by the solution FTIR and IC methods described above. The six wastes were the top and bottom layers retrieved from three flowsheet preparations, In-Farm 1, In-Farm 2, and U-Plant 2. Each of these samples was dissolved before analysis.

The results of the FTIR and IC analyses are listed in Table I. In all cases, the $\text{Fe}(\text{CN})_6^{4-}$ (ferrocyanide) complex was the only cyanide-containing solution species observed in these samples. The concentrations in Table I are presented as wt% $\text{Fe}(\text{CN})_6^{4-}$ in the original sample. These results obtained using FTIR and IC analytical methods to quantitative cyanide species are in close agreement.

CONCLUSION

Direct and indirect analytical methods were examined for use in quantifying the cyanide species in simulated Hanford high-level radioactive waste. The examined methods included FTIR spectroscopy (solid state and solution), Raman spectroscopy, Mössbauer spectroscopy, XRD, SEM-EDS, and IC. Of these techniques, FTIR, Raman, XRD, and IC showed promise for the ferrocyanide concentration range of interest. Quantitation limits for the four promising techniques were demonstrated to be about 0.1 wt% (as cyanide).

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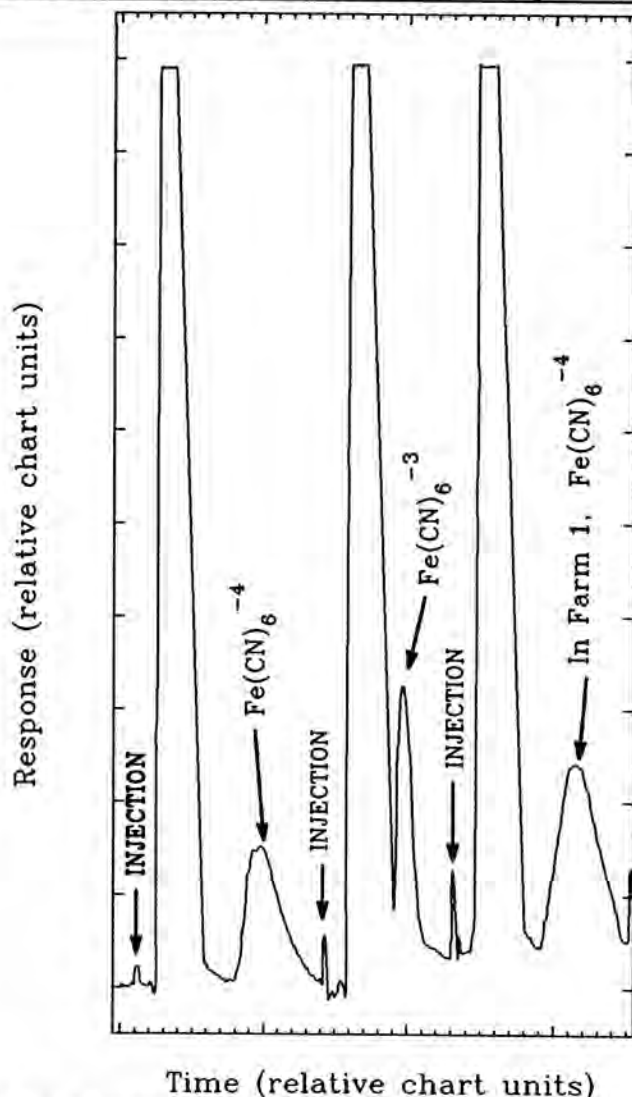


Fig. 8. Successive ion chromatograms of $\text{Fe}(\text{CN})_6^{3-}$, $\text{Fe}(\text{CN})_6^{4-}$, and infarm 1 (a flowsheet material containing ferrocyanide).

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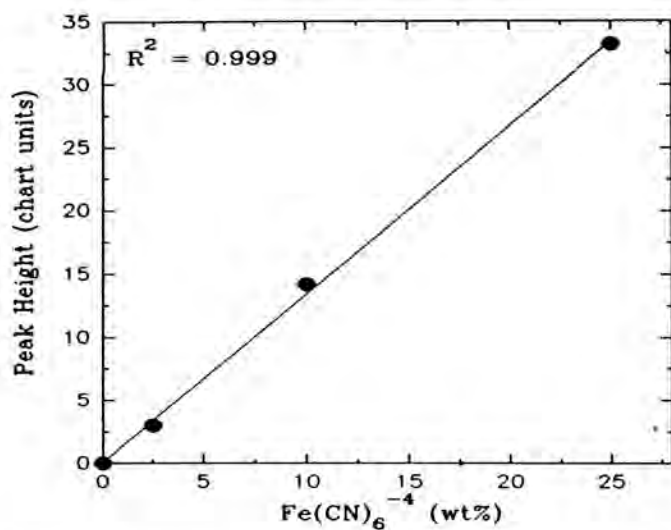


Fig. 9. IC standard curve for $\text{Fe}(\text{CN})_6^{4-}$ for the range 0 to 25 ppm.

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TABLE I
Comparison of FTIR and IC Methods Applied to Six Ferrocyanide Flowsheet Simulated Wastes

Material	Methods	
	FTIR $\text{Fe}(\text{CN})_6^{4-}$ (wt%)	IC $\text{Fe}(\text{CN})_6^{4-}$ (wt%)
In-Farm 1 (top layer)	6.3	5.3
In-Farm 1 (bottom layer)	8.9	8.4
In-Farm 2 (top layer)	5.5	5.5
In-Farm 2 (bottom layer)	7.5	7.6
U-Plant 2 (top layer)	1.4	1.3
U-Plant 2 (bottom layer)	2.0	2.0

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