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Assay Development Status Report for Total Cyanide

B. C. Simpson
Westinghouse Hanford Company

T. E. Jones
K. H. Pool
Pacific Northwest Laboratory

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**Westinghouse
Hanford Company**

P.O. Box 1970
Richland, Washington 99352

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ACRONYMS

DSC	differential scanning calorimetry
EDTA	ethylenediaminetetraacetic acid
EPA	U.S. Environmental Protection Agency
FTIR	fourier transform infrared
HDW-EIS	Hanford Defense Waste-Environmental Impact Statement
IC	ion chromatography
PNL	Pacific Northwest Laboratory
SST	single-shell tank
TGA	thermogravimetric analysis
WHC	Westinghouse Hanford Company

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ASSAY DEVELOPMENT STATUS REPORT FOR TOTAL CYANIDE

1.0 INTRODUCTION

A validated cyanide assay that is applicable to a variety of tank waste matrices is necessary to resolve certain waste tank safety issues and for purposes of overall waste characterization. The target for this effort is an assay with an applicable range of greater than 1,000 ppm (0.10 wt%) total cyanide and a confidence level greater than 80%. Figure 1 illustrates the operating regime of the proposed cyanide assay method.

The *Assay Development Status Report for Total Cyanide* will summarize the past experience with cyanide analyses on tank waste matrices and will rate the status of the analytical methods used to assay total cyanide (CN^- ion) in the tank waste matrices as acceptable or unacceptable. This paper will also briefly describe the current efforts for improving analytical resolution of the assays and the attempts at speciation.

2.0 BACKGROUND

2.1 SUMMARY

In the 1950's, ^{137}Cs was scavenged during the reprocessing of single-shell tank (SST) waste by co-precipitating it along with sodium in nickel ferrocyanide salt, $\text{Na}_{2-x}\text{Cs}_x\text{NiFe}(\text{CN})_6$. Heated ferrocyanide salts in combination with oxidizing agents, such as nitrate and nitrite, are known to be thermodynamically unstable, and their potential presence in the SST wastes has been identified as a safety issue. Preliminary identification of tanks of concern was made on the basis of 1,000 g-moles of $\text{Fe}(\text{CN})_6^{4-}$ ion received, based on historical data (Postma 1992; Grigsby et al. 1992). Reliable total cyanide analysis data for SST materials are required to address the safety issue. However, it has not been possible to obtain reliable total cyanide analysis data for samples containing the nickel ferrocyanide materials using accepted, routine procedures because of the insolubility of the nickel ferrocyanide materials in acidic media. The situation was further exacerbated by the limited amount of ferrocyanide SST materials available and the need to have data on samples from small intervals along the length of the cores recovered from the waste tanks. A decision was made to delay total cyanide analyses of tank C-112 core samples until a more reliable method could be developed.

2.2 UNREVIEWED SAFETY QUESTION DECLARATION

Efforts have been under way since the mid 1980's to evaluate the potential of a ferrocyanide explosion in Hanford Site SSTs (Burger and Scheele 1991; Burger 1984). In 1988, the *Final Environmental Impact Statement*

Figure 1. Total CN Assay Range.

for the Disposal of Hanford Defense High Level, Transuranic, and Tank Wastes, hereinafter referred to as the final Hanford Defense Waste-Environmental Impact Statement (HDW-EIS) (DOE 1988) was issued. In the HDW-EIS it was projected that the bounding "worst-case" accident in a ferrocyanide tank would be an explosion resulting in a subsequent short-term radiation dose to the public of 200 mrem.

A recently completed General Accounting Office study (Peach 1990) postulates a greater "worst-case" accident with independently calculated doses one to two orders of magnitude greater than the HDW-EIS (DOE 1988). The potential for an exothermic reaction of this magnitude in the cesium-nickel ferrocyanide/sodium nitrate waste matrix is outside the bounds of the current safety analyses in those waste tanks suspected of containing 1,000 g-moles or more of ferrocyanide precipitates. A special Hanford Ferrocyanide Task Team was commissioned in September 1990 to address all issues involving the ferrocyanide tanks, including the consequences of a potential accident. On October 9, 1990, Secretary of Energy James D. Watkins announced that a supplemental environmental impact statement would be prepared that would contain an updated analysis of safety questions for the Hanford Site SSTs, including a hypothetical ferrocyanide explosion.

Using a computer model output (Jungfleisch 1984), process knowledge, and transfer records, 24 tanks were initially identified at the Hanford Site as containing 1,000 g-mol (465 lb) or more of ferrocyanide (as $\text{Fe}(\text{CN})_6^{4-}$ ion). Because the consequences of this safety condition were very much greater than those considered in the HDW-EIS (DOE 1988), the ferrocyanide issue was declared an unreviewed safety question in October 1990.

2.3 APPROACH

Scientists at Battelle-Pacific Northwest Laboratory (PNL) and Westinghouse Hanford Company (WHC) have been exploring various modifications and improvements to the U.S. Environmental Protection Agency (EPA)-accepted total cyanide analysis methods to make them more applicable to high-level radioactive samples. The present SW-846 (EPA 1984) method involves releasing the cyanide from the waste matrices as HCN by means of a reflux-distillation procedure. The cyanide is absorbed in a NaOH scrubber and the dissolved cyanide is determined colorimetrically. The following are three difficulties associated with this procedure.

- The EPA procedure calls for using nearly a liter of solution in the assay. When analyzing high-level waste materials, this generates a large amount of waste that must be disposed. Laboratory personnel have adapted the procedure to a microdistillation to reduce the amount of sample and solution necessary to perform the assay.
- There is the potential for a high bias interference from a combination of organics and high nitrate concentration in the sample matrices. The investigators are attempting to correct for this interference by controlling the pH in the distillation vessel. A pH level of about 4 in the distillation vessel greatly diminishes the co-distillation of potentially interfering species (e.g., NO_x).

- The sample matrix itself is highly resistant to dissolution.

Thus, a number of new sample dissolution methods were tested on several ferrocyanide simulants. A sample dissolution method using an ethylenediamine/ethylenediaminetetraacetic acid (EDTA) mixture was promising. A test plan was developed to evaluate the candidate methodology with excess sample material from SST C-112.

The primary approach used was to test the new dissolution methodology with reasonably well characterized ferrocyanide simulant materials, tank C-112 materials and C-112 materials spiked with the "known" ferrocyanide materials. The known ferrocyanide materials are listed in Table 1. A second approach was to analyze the same suite of samples with a furnace-type carbon analyzer. Results from previous tests have suggested that it might be possible to quantify selected groups of carbon compounds by operating the furnace at selected temperatures. Organic carbon can be converted to carbon dioxide at relatively low temperatures (400-500 °C), while ferrocyanide carbon would be converted to carbon dioxide at a higher temperature (700 °C). At very high temperatures (1,000 °C), all carbon is expelled as carbon dioxide. However, in the presence of nitrates and nitrites, the synthetic ferrocyanide sludges have been observed to react at about 250 °C (Fauske 1992). The exact temperature for each of these processes appears to be a function of the sample matrix. In spite of the uncertainties, it was felt that the carbon measurements would provide an estimate of the upper limit of the amount of carbon (and thus total cyanide) in the SST C-112 materials. The differential scanning calorimetry (DSC) measurements routinely made on SST core materials also provide an energy-based estimate of the upper concentration limit of ferrocyanide in the SST materials. In addition to the wet chemical assays; investigation of simulant materials and tank waste matrices using nondestructive technologies, such as fourier transform infrared (FTIR) and Raman spectroscopy, for characterization will continue.

Table 1. Known Ferrocyanide Materials Available for Testing.

Material	Name and Source	(% Cyanide)	(% Carbon)
$\text{Na}_2\text{NiFe}(\text{CN})_6$	WHC-2 Unwashed	27.7	12.8
$\text{Na}_2\text{NiFe}(\text{CN})_6$	FeCN-36 (J. Tingey prep)	34.5	15.9
$\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$	Vendor	37.0	17.1

3.0 CURRENT ANALYTICAL TECHNIQUES

3.1 ANALYTICAL FINDINGS--WESTINGHOUSE HANFORD COMPANY

The 222-S Laboratory has had experience with total cyanide measurements on five previous occasions. Assays were done on samples with no prior sample preparation, samples that had been prepared by dissolution, and sometimes both. A brief summary of the results from those tests follow.

3.1.1 Beaker Test Report

Total CN^- content was requested on synthetic nickel ferrocyanide sludges and supernates where the total potassium ferrocyanide additions were known in the *Report of Beaker Tests of Ferrocyanide Scavenging Flow Sheets*, WHC-SD-WM-TRP-071 Rev 0, (Bechtold 1991b). The CN^- performance was spotty, but reliable in cases where adequate amounts of CN^- were available. There was some loss of recovery in the very richest mixtures. Tables 5-19 through 5-21 and A-27 through A-39 (excerpted from the report and included as Appendix A in this report) present assay results and mass balance checks. Also, the exothermic response of the synthetic sludge samples increased with increased cyanide values (refer to Figure 6.4, also included in Appendix A).

Conclusion: The CN^- assay method functioned for these samples and was appropriate for semiquantitative measures of cyanide content in ferrocyanide spiked sludges.

3.1.2 Vendor Compound Analysis

The "pure" vendor-prepared sodium nickel ferrocyanide (WHC-2) was analyzed after dissolution in the series of experiments reported in *Analysis of Vendor Prepared Sodium Nickel Ferrocyanide*, Internal Memo 28110-PCL91-086 (Bechtold 1991a). Results gave a molar ratio of 5.6 CN^- : 1 Fe : 1 Ni and also found SO_4^{2-} as a major impurity. Thermal gravimetric analysis of the material indicated approximately 5.4 waters of hydration. Total CN^- assay results were in reasonable agreement with PNL's analysis (Total CN^- --WHC: 26.4 wt%; PNL: 27.7 wt%).

Conclusion: CN^- assay method, with dissolution sample preparation step, is appropriate for use on these samples.

3.1.3 U-Plant Solids Characterization

U-Plant sludge simulant material was analyzed in *Analysis of In-Plant Ferrocyanide Solids*, Internal Memo 12110-PCL92-014 (Bechtold 1992). Total CN^- analyses were done as well as a limited physical and chemical characterization. There were several different sample preparation treatments performed on the specimens. Results of the composite sludge analysis had a

molar ratio of $0.8 \text{ CN}^- : 1 \text{ Fe} : 0.1 \text{ Ni}$. Total cyanide is approximately 0.10 wt%. The material was mostly water (61 wt%, after centrifugation) and had a weak exothermic response when examined using DSC, consistent with the low cyanide content.

Conclusion: CN^- assay method, with dissolution sample preparation step, is appropriate for use on these samples.

3.1.4 Miscellaneous Sludge Analysis

Miscellaneous CN^- analyses were performed on dry tank sludges that had been stored in the laboratory for over 10 years. On examination, none of the samples had more than background values of CN^- . Analyses were performed without sample preparation. Four spike recoveries were done on the samples; the lowest recovery was 94%.

Conclusion: The CN^- assay results suggest the method functioned without the sample preparation step for these samples. The sample matrices may have been more tractable to analysis than the ferrocyanide simulants.

3.1.5 SY-101 Simulant Analysis

Two blind standards made from synthetic glycolate-containing SY-101 slurry spiked with sodium sulfate and potassium ferrocyanide (not sodium nickel ferrocyanide) were made up and submitted for analysis. Total cyanide analysis was performed on the standards.

1st Blind Standard   Calculated CN^- : 45.1 ppm.
                              Found CN^- : 44.2 ppm, 45.1 ppm.

2nd Blind Standard   Calculated CN^- : 72 ppm
                              Found CN^- : 57.8 ppm, 58.1 ppm.

Conclusion: The CN^- assay method somewhat functioned for these samples and was appropriate for semiquantitative measures of cyanide content in non-ferrocyanide sludges.

3.2 ANALYTICAL FINDINGS--PACIFIC NORTHWEST LABORATORY

PNL is under contract to WHC to develop an improved total cyanide assay that is appropriate for use on several different waste matrices. The method that has been developed requires sample dissolution in an EDTA/ethylenediamine preparation and uses a microdistillation separation with an argentometric titration. Scoping results from the initial trials can be found in Appendix A. Further results using the polished procedure are presented here. The assay is presently undergoing validation trials for approval. A brief description of the assay procedure and the validation test plan is attached as Appendix B.

Total cyanide in Core 34 segment 2D material was found to be 0.45 wt% on a wet basis or 0.94 wt% for a dry sample. The reliability of the method can

be inferred from an examination of the data on analyses of the knowns (refer to Table 2). Analyses of the "knowns" gave about 70% to 90% recoveries and best results were obtained when the samples were dissolved prior to analysis (refer to Table 3). Spike recoveries for Core 34 material averaged about 85% (refer to Table 4). Therefore, the total cyanide measurement in the sample could be biased 15 to 20% low. An upper limit for total cyanide could be ~0.6 wt% (wet) or 1.3 wt% (dry).

Table 2. Total Cyanide Analysis Results for Core 34 Segment 2D Using Proposed Method.

Sample/Standards	No. of Assays	% Cyanide
Core 34 Segment 2D	5	0.45 ± 0.06
Blank	2	~0.02*
Core 34 Segment 2D (w/o pretreatment)	1	0.18

*--Blank value estimated based on ~20ug CN⁻ found in blank and a hypothetical 0.1 g sample size.

Table 3. Total Cyanide Analysis Results for Knowns.

Knowns	% CN ⁻	No. of Assays	% Recovery as CN ⁻
WHC-2 Unwashed	27.7	2	95, 89
FeCN-36	34.5	3	69, 64, and 96**

**--The 96% recovery was obtained when the FeCN-36 material was pre-dissolved prior to introduction of the sample into the distillation apparatus.

Aliquots of the Core 34 segment 2D sample were spiked with "known" ferrocyanide materials and total cyanide analyses were completed. The results are presented in Table 4. The purpose of this test was to assess any sample matrix effects on the analytical method. Two nickel ferrocyanide (WHC-2 Unwashed and FeCN-36) and potassium ferrocyanide were used as spiking compounds.

Table 4. Total Cyanide Analysis Results for Core 34 Segment 2D Samples Plus Spike.

Sample + Spike	No. of Assays	% Spike Recovery as CN ⁻
Core 34 Segment 2D + WHC-2 Unwashed	3	86, 88, and 88
Core 34 seg. 2D + FeCN-36	3	83, 86, and 96 ^{***}
Core 34 seg. 2D + K ₄ Fe(CN) ₆	1	85

^{***}--96% recoveries obtained when FeCN-36 spike were dissolved prior to introduction into the distillation apparatus.

3.3 INDIRECT MEASUREMENT

Although the total cyanide values discussed above are internally consistent, there is the possibility that the analytical method could consistently fail to recover a significant fraction of cyanide in the sample. Two other analytical measurements provide additional insight into this question, total carbon analysis and DSC. Total carbon analysis would include carbon from all sources, even cyanide. The exothermic response from DSC can be used to infer total cyanide or ferrocyanide concentration. The higher the ferrocyanide content in the sample (Tables 5, 6, and 7), the greater the exothermic behavior during the DSC analysis.

Table 5. Total Carbon Analysis Results.

Carbon Analyses by Furnace Technique (1,000 °C furnace temperature)			
Sample	No. of Assays	Results (as % carbon)	% Recovery
Core 34 seg 2D	3	1.12 ± 0.16	--
Na ₄ Fe(CN) ₆ ·10H ₂ O	3	15.5 ± 0.3	104
WHC-2 washed	2	17.7	99
Core 34 seg. 2D + Na ₄ Fe(CN) ₆	1	--	127 [*]
Core 34 seg 2D + WHC-2 Washed	1	--	99 [*]

^{*}--Percent Spike Recovery.

Table 6. Carbon Results at Total Organic Carbon Assay Conditions (700 °C furnace temperature).

Sample	Results (in % carbon)	% Recovery
$\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$ (Theoretical = 14.89)	13.3 % C and 12.5	89.3 and 84.0
WHC-2 washed (Theoretical = 17.9)	17.8 % C	99.4

Table 7. Carbon Results at Total Organic Carbon Assay Conditions (Hot Persulfate Method¹).

Sample	Results (in % carbon)	% Recovery
$\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$ theoretical	1.0 to 1.9%	6.7 to 12.1% of theoretical
WHC-2 washed	10.0 to 10.5%	57 to 59% of theoretical

¹The hot persulfate method dissolves a sample in a sulfuric acid solution (90 °C+) to liberate inorganic carbon (carbonate). $\text{K}_2\text{S}_2\text{O}_8$ is then added and organic carbon is converted to CO_2 , which is measured by conductivity. The poor performance of the hot persulfate method suggests incomplete solubilization of the sample.

The total carbon value of 1.12% in the Core 34 sample would include all forms of carbon that were present in the sample such as carbonate, bicarbonate, organics such as normal paraffin hydrocarbon, as well as cyanide. If all of the carbon found was present as cyanide, then the upper limit for total cyanide would be ~2.5% (dry). Because the total cyanide value range (0.94-1.3%) is less than the value for total carbon, if reported as total cyanide (~2.5%), the results from these assays are relatively consistent.

3.3.1 Differential Scanning Calorimetry and Thermogravimetric Analyses

DSC and thermogravimetric analyses (TGA) were performed as part of physical characterization of the In-Farm simulants and the C-112 core samples. DSC provides thermal decomposition temperatures, heats of reactions, and reaction temperatures, while TGA provides mass changes as a function of temperature. These measurements can be used to estimate concentrations of reactive components in a sample. Previous studies of sodium and cesium nickel ferrocyanides have shown that an exotherm is expected in the region of 300 to 425 °C, which corresponds to the decomposition of ferrocyanide. Such exotherms were observed in the DSC analysis of the C-112 sample with an enthalpies ranging from -3 to -38 cal/g dry sample. The upper limit for

total cyanide in this sample, based on the highest enthalpy value, would be estimated to be 2 wt% cyanide (dry). Thus, DSC results are consistent with the total cyanide value reported above.

4.0 CONTINUING EFFORTS

4.1 TASK OBJECTIVES

One of the goals of the Ferrocyanide Safety Program is to establish qualified analytical procedures for the quantitative measurement of cyanide species within ferrocyanide tank waste through the use of simulated ferrocyanide flowsheet waste. Based on experience gained in this task, a recommended technical procedure has been drafted. This procedure presumably will be used by the laboratory personnel at the 325 Laboratory for the analysis of ferrocyanide tank core samples, with eventual technology transfer to the 222-S Laboratory.

4.2 INSTRUMENTAL METHODS WITH SAMPLE PREPARATION SUBTASK

The goal of this subtask is to establish methods for the detection and speciation of cyanide species in prepared ferrocyanide tank waste simulants by instrumental methods. Instrumental methods analyses for ferrocyanides include using FTIR and ion chromatography (IC) techniques on solutions prepared from dissolved ferrocyanide flowsheet materials. This procedure presumably will be developed and then used by the operators of the "hot" FTIR and IC equipment to be deployed in the 325 Building.

4.2.1 Dissolution Method Optimization

Dissolution techniques will be optimized using existing simulated waste materials. Using the EDTA/ethylenediamine dissolution method developed in fiscal year 1992 as a starting point, optimum solvent solute ratios, temperature, complexants, etc., will be explored. Simulants to be used include U-Plant, In-Farm 1, In-Farm 2, J. M. Tingey prepared $\text{Na}_2\text{NiFe}(\text{CN})_6$, vendor-prepared $\text{Na}_2\text{NiFe}(\text{CN})_6$, and $\text{Cs}_2\text{NiFe}(\text{CN})_6$.

4.2.2 Interferences with Solution Technique

IC and solution infrared techniques will be studied to determine the extent that species such as NO_3^- , NO_2^- , CrO_4^{2-} , BiPO_4 , OH^- , etc. may interfere with the detection or quantitation of cyanide species of interest.

4.2.3 Interconversion of Cyanide Species

The interconversion of oxidation states of Fe^{+2} and Fe^{+3} in the ferro- and ferricyanide complexes can be influenced by many factors relating to the redox properties of the matrix. These factors include the concentration and nature

of reducing species in solution (e.g., organics or oxidizing species such as oxy-anions [NO_2^- , NO_3^- , CrO_4^{2-} , etc.]) and the presence of complexing ligand (e.g., EDTA, nitrilotriacetic acid [NTA], oxalate, chloride, etc.). The influence of typical redox active factors on the stability of $\text{Fe}(\text{CN})_6^{4-}$, $\text{Fe}(\text{CN})_6^{3-}$, and CN^- will be assessed. These effects will be determined by using blanks and spikes during the dissolution of cyanide species in simulated wastes.

4.2.4 Quantification of Cyanide Species

Portions of the available simulants (In-Farm 1, In-Farm 2, and U-Plant 2) and surplus core sample material (if available) will be repeatedly analyzed using Quality Control protocols that include duplicates, spikes (ferrocyanide, ferricyanide, and cyanide), and blanks. The data so obtained will be used to generate sufficient statistical information to verify analytical method efficacy with respect to reproducibility (precision), accuracy (spike recovery and bias), and preliminary control charts for the method.

4.3 DIRECT METHODS SUBTASK

Development of methods for "real-time" determination of cyanide species is needed. At present, there are no methods available for in situ or in-hot cell use for the characterization of cyanide species contained in ferrocyanide tank waste. The goal of this subtask is to establish methods for the detection and speciation of cyanide species in ferrocyanide tank wastes by direct methods. Direct methods include FTIR and Raman techniques on solid samples with little or no preparation. This task will focus on the chemistry side of the problem to identify the proper conditions for these methods to provide defensible analytical results.

Infrared and Raman techniques will be studied to determine the extent that species (e.g., NaNO_3 , NaNO_2 , Na_2CrO_4 , BiPO_4 , NaOH , etc.) may interfere with the detection or quantitation of cyanide species of interest. The solids will be selected based on their probability for interfering with the analyses and for their relative abundance in actual tank waste.

5.0 CONCLUSIONS AND RECOMMENDATIONS

Nickel and ferrocyanide compounds were added to certain process streams during the reprocessing of materials that had been stored in SSTs at the Hanford Site. These compounds were added to the process to separate ^{137}Cs as the insoluble sodium cesium nickel ferrocyanide salt. Insoluble nickel ferrocyanide salts have proven to be intractable to the application of "EPA-accepted" total cyanide analysis procedures. Poor analytical recoveries were observed because of the difficulty of re-solubilizing the ferrocyanide salts. A new sample dissolution methodology has been developed which routinely provides a recovery of approximately 90% for total cyanide for a number of nickel ferrocyanide materials.

Total cyanide analytical results using the new methodology with SST C-112 core materials are consistent with upper limits of total cyanide estimated from independent calorimetry and total carbon measurements. All available data suggest the ethylenediamine/EDTA dissolution methodology provides a reasonable approach for semi-quantitative analysis of total cyanide. It appears likely that recoveries could be improved and could approach quantitative recovery by refining the in-cell dissolution steps. Based on these results it is recommended that analyses of the complete suite of samples from tank C-112 be completed under the direct guidance of Dr. Karl H. Pool using the new methodology. Further investigation of direct sample analysis using spectroscopic methods will also be pursued.

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APPENDIX A

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Table 5-19. Summary Composition of In-Farm Supernate					
Analyte	Value mg/L or other	Weight %	Mole/Gram	Mole Ratio	Charge Equiv./Gram
Fe	1.71e+1	1.26e-2	2.26e-7	1.	4.52e-7
K	8.04e+2	5.91e-2	1.51e-5	6.70e+1	1.51e-5
Na	1.69e+5	1.24e+1	5.41e-3	2.39e+4	5.41e-3
Ni	2.24	1.65e-4	2.81e-8	1.24e-1	5.62e-8
CN ⁻	4.32e+1	3.18e-3	1.22e-6	5.41	-1.22e-6
Cl ⁻	1.26e+3	9.26e-2	2.61e-5	1.16e+2	-2.61e-5
NO ₃ ⁻	3.93e+5	2.89e+1	4.66e-3	2.06e+4	-4.66e-3
PO ₄ ³⁻	2.20e+4	1.62	1.71e-4	7.56e+2	-5.12e-4
SO ₄ ²⁻	3.50e+4	2.58	2.68e-4	1.19e+3	-5.37e-4
H ₂ O	55.53%	5.55e+1			
SpG	1.36				
pH	9.44				
mass balance %		101.16	minus:plus charge ratio		1.06

Table 5-20. Summary Composition of In-Farm as Settled Sludge					
Analyte	Value mg/g or other	Weight %	Mole/Gram	Mole Ratio	Charge Equiv./Gram
Fe	5.99	5.99e-1	1.07e-4	1.	2.15e-4
K	--	--	--	--	--
Na	1.26e+2	1.26e+1	5.49e-3	5.11e+1	5.49e-3
Ni	5.53	5.53e-1	9.43e-5	8.81e-1	1.89e-4
CN ⁻	1.36e+1	1.36	5.22e-4	4.86	-5.22e-4
Cl ⁻	2.98	2.98e-1	8.41e-5	7.86e-1	-8.41e-5
NO ₃ ⁻	2.71e+2	2.71e+1	4.38e-3	4.08e+1	-4.38e-3
PO ₄ ³⁻	1.88e+1	1.88	1.98e-4	1.84	-5.93e-4
SO ₄ ²⁻	2.44e+1	2.44	2.53e-4	2.36	-5.07e-4
%H ₂ O	53.65%	5.37e+1			
mass balance %		101.53	minus:plus charge ratio		1.03

Table 5-21. Summary Composition of In-Farm Compacted Sludge					
Analyte	Value mg/g or other	Weight %	Mole/Gram	Mole Ratio	Charge Equiv./Gram
Fe	3.00e+1	3.00	5.37e-4	1.	1.07e-5
K	1.28	1.28e-1	3.29e-5	6.13e-2	3.29e-5
Na	1.19e+2	1.19e+1	5.16e-3	9.59	5.16e-3
Ni	3.11e+1	3.11	5.29e-4	9.85e-1	1.06e-3
CN ⁻	7.98e+1	7.98	3.07e-3	5.71	-3.07e-3
Cl ⁻	4.65	4.65e-1	1.31e-4	2.44e-1	-1.31e-4
NO ₃ ⁻	2.40e+2	2.40e+1	3.87e-3	7.19	-3.87e-3
PO ₄ ³⁻	1.84e+1	1.84	1.94e-4	3.61e-1	-5.81e-4
SO ₄ ²⁻	1.73e+1	1.73	1.80e-4	3.35e-1	-3.60e-4
% H ₂ O	43.635%	4.36e+1			
mass balance %		97.75	minus:plus charge ratio		1.28

Table 5-22. Compare Total Dissolved Solids in Compacted Sludges Derived from Chemical and Thermal Analyses		
Compacted Sludge	Total Dissolved Solids	
	from Chemical	from Thermal
In-Plant 1st Run	24.35%	24.03%
In-Plant 2nd Run	197.58%	20.56%
Early In-Plant 1st Run	24.74%	24.27%
Early In-Plant 2nd Run	26.95%	25.64%
In-Farm 1st Run	53.58%	35.46%
In-Farm 2nd Run	41.38%	34.73%

Table A-26. Early In-Plant, 2nd Run Supernate-Sludge Mass Balance Check							
Analyte	Total Moles	As Settled Sludge			Compacted Sludge		
		Supernate %	Sludge %	Total %	Supernate %	Sludge %	Total %
Fe	0.01996	0.222	88.3 ⁱ	88.5 ⁱ	0.261	89.5 ⁱ	89.8 ⁱ
K	0.02	90.8	15.4 ⁱ	106. ⁱ	107.	<0.25 ⁱ 3.33 ⁱ	107. ⁱ 110. ⁱ
Na	3.919	85.8	14.6 ⁱ	100. ⁱ	101.	3.57 ⁱ	104. ⁱ
Ni	0.005	1.31	85.5 ⁱ	86.8 ⁱ	1.54	87.8 ⁱ	89.3 ⁱ
CN	0.03	0.0963	105. ^d	105. ^d	0.113		
NH ₃	0.05984	31.8			37.4	1.92 ⁱ	39.3 ⁱ
NO ₃	3.2736	87.1			102.	3.49 ⁱ	105. ⁱ
PO ₄	0.132	28.6			27.4	5.70 ⁱ 3.13 ⁱ	33.1 ⁱ 30.5 ⁱ
SO ₄	0.06484	58.3			68.4	10.0 ⁱ	78.4 ⁱ

ⁱ Based on ignition results.

^l Based on water leachate results.

^d Based on direct analysis results.

Table A-27. In-Farm 1st Run Supernate CJ-78-I #R-9902						
#R-9902 Analysis		Converted to Supernate				
analyte	value mg/L or other	mg/g	weight %	moles/ gram	mole ratio	charge equiv./ gram
Fe	8.2	6.03e-3	6.03e-4	1.08e-7	1.	2.16e-7
K	734	5.40e-1	5.40e-2	1.38e-5	1.28e+2	1.38e-5
Na	152000	1.12e+2	1.12e+1	4.86e-3	4.50e+4	4.86e-3
Ni	0.244	1.79e-4	1.79e-5	3.06e-9	2.83e-2	6.11e-9
CN ⁻	24.2	1.78e-2	1.78e-3	6.84e-7	6.33	-6.84e-7
Cl ⁻	<20	<0.0140	<0.001	--	--	--
NO ₃ ⁻	369000	2.71e+2	2.71e+1	4.38e-3	4.05e+4	-4.38e-3
PO ₄ ³⁻	23000	1.69e+1	1.69	1.78e-4	1.65e+3	-5.34e-4
SO ₄ ²⁻	39400	2.90e+1	2.90	3.02e-4	2.79e+3	-6.03e-4
%H ₂ O	55.4%		55.4			
SpG	1.36					
pH	9.18					
mass balance %			98.35 %	minus:plus charge ratio		1.13

Table A-28. In-Farm 1st Run As Settled Sludge Direct CN ⁻ CJ-83-A #R-9975			
analyte	value	mg/g	weight %
CN ⁻	1.50e+4 μ g/g	15	1.50

Table A-29. In-Farm 1st Run As Settled Sludge Chelate Dissolution CJ-79-F #R-9988						
#R-9988 Analysis		Converted to As Settled Sludge				
analyte	value mg/L or other	mg/g	weight %	mole/ gram	mole ratio	charge equiv./ gram
Fe	6.23e+01	6.00	6.00e-1	1.07e-4	1.	2.15e-4
K	<1.02e+01					
Na	2.230e+03	1.26e+2*	1.26e+1	5.49e-3	5.11e+1	5.49e-3
Ni	5.75e+01	5.53	5.53e-1	9.43e-5	8.78e-1	1.89e-4
CN ⁻	1.46e+02	1.41e+1	1.41	5.40e-4	5.03	-5.40e-4
Cl ⁻	3.096e+01	2.98	2.98e-1	8.40e-5	7.83e-1	-8.40e-5
NO ₃ ⁻	2.820e+03	2.71e+2	2.71e+1	4.38e-3	4.08e+1	-4.38e-3
PO ₄ ³⁻	1.95e+02	1.88e+1	1.88	1.98e-4	1.84	-5.93e-4
SO ₄ ²⁻	2.53e+02	2.44e+1	2.44	2.54e-4	2.36	-5.07e-4
%H ₂ O	99.5%		53.7 (fr. TGA)			
SpG	0.989					
pH	10.3					
mass balance %			100.57	minus:plus charge ratio		1.04

*919.6 mg/L Na contributed by EDTA subtracted out.

Table A-30. In-Farm 1st Run Compacted Sludge Chelate Dissolution CJ-91-A #R-15						
#R-15 Analytical Data		Converted to Compacted Sludge				
analyte	value	mg/g	weight %	mole/gram	mole ratio	charge equiv./gram
Fe	7.932e-03 M	2.91e+1	2.91	5.21e-4	1.	1.04e-3
K	3.260e-04 M	8.38e-1	8.38e-2	2.14e-5	4.11e-2	2.14e-5
Na	4.730e-01 M	4.73e+2 ¹	4.73e+1	2.06e-2	3.95e+1	2.06e-2
Ni	7.440e-03 M	2.87e+1	2.87	4.89e-4	9.38e-1	9.78e-4
CN ⁻	1.198e+03 mg/L	7.87e+1	7.87	3.03e-3	5.81	-3.03e-3
Cl ⁻	7.940e+01 mg/L	5.22	5.22e-1	1.47e-4	2.82e-1	-1.47e-4
NO ₃ ⁻	masked ²	~200	~20	3.23e-3	6.19	-3.23e-3
PO ₄ ³⁻	2.800e+02 mg/L	1.84e+1	1.84	1.94e-4	3.72e-1	-5.82e-4
SO ₄ ²⁻	2.680e+02 mg/L	1.76e+1	1.76	1.83e-4	3.52e-1	-3.67e-4
%H ₂ O	98.33%		4.24e+1 (fr. TGA)			
SpG	0.998					
pH	10.68					
mass balance %			127.53	minus:plus charge ratio		3.25e-1

¹The Na contributed by EDTA subtracted out.

²The nitrate value was masked by the large EDTA peak. The value given is estimated from the water leach of compacted sludge.

Table A-31. In-Farm 1st Run Water Leachate of Compacted Sludge CJ-91-B #R-16				
#R-16 Analytical Data			Converted to Compacted Sludge	
analyte	value	weight % sample	mg/g	% of compacted sludge
Fe	5.64e-5 M	3.18e-4	1.00e-1	1.00e-2
K	2.64e-4 M	1.04e-3	3.28e-1	3.28e-2
Na	3.86e-1 M	8.95e-1	2.81e+2	2.81e+1
Ni	1.64e-5 M	9.72e-5	3.06e-2	3.06e-3
CN ⁻	7.59 mg/L	7.66e-4	2.41e-1	2.41e-2
Cl ⁻	1.03e+2 mg/L	1.04e-2	3.27	3.27e-1
NO ₃ ⁻	6.35e+3 mg/L	6.41e-1	2.02e+2	2.02e+1
PO ₄ ³⁻	4.89e+2 mg/L	4.93e-2	1.55e+1	1.55
SO ₄ ²⁻	1.05e+3 mg/L	1.06e-1	3.33e+1	3.33
%H ₂ O	99.48%	9.95e+1		
SpG	0.991			
pH	10.15			
mass balance %		101.18	total soluble %	53.58

Table A-32. In-Farm 1st Run X-ray Diffraction & X-ray Florescence CJ-103-A #R-595	
Technique	Findings
XRD	unable to identify any specific compound
XRF	major - Fe, Ni minor to trace - Zn, Ca, K, P

Table A-33. In Farm 1st Run Supernate-Sludge Mass Balance Check							
Analyte	Total Moles	As Settled Sludge			Compacted Sludge		
		Supernate %	Sludge %	Total %	Supernate %	Sludge %	Total %
Fe	0.00498	2.82	122. ^c	125 ^c	2.92	95.0 ^c	97.9 ^c
K	0.01992	90.1			93.4	0.98 ^c 0.34 ^l	94.4 ^c 93.7 ^l
Na	7.40025	85.4	4.21 ^c	89.6 ^c	88.5	2.52 ^c 1.50 ^l	91.0 ^c 90.0 ^l
Ni	0.005	0.0796	107. ^c	107. ^c	0.0825	88.8 ^c	88.9 ^c
CN	0.02988	2.98	102. ^c 109. ^d	105. ^c 112. ^d	3.09	92.1 ^c	95.2 ^c
Cl	0.019734	<2.6	24.1 ^c	<26.7 ^c	<2.70	6.76 ^c 4.25 ^l	<9.46 ^c <6.95 ^l
NO ₃	6.166875	92.3	4.03 ^c	96.3 ^c	95.7	0.48 ^l	96.2 ^l
PO ₄	0.246675	93.8	4.55 ^c	98.4 ^c	97.3	0.71 ^c 0.60 ^l	98.0 ^c 97.9 ^l
SO ₄	0.350345	112.	4.11 ^c	116. ^c	116.	0.47 ^c 0.90 ^l	11.6 ^c 117. ^l

^l Based on water leachate results.

^d Based on direct analysis results.

^c Based on chelate dissolution results.

Table A-34. In-Farm 2nd Run Supernate CJ-93-A #R-601						
#R-601 Analysis		Converted to Supernate				
analyte	value mg/L or other	mg/g	weight %	moles/ gram	mole ratio	charge equiv./ gram
Fe	26.1	1.92e-2	1.92e-3	3.44e-7	1.	6.88e-7
K	874	6.43e-1	6.43e-2	1.64e-5	4.78e+1	1.64e-5
Na	1.86e+5	1.37e+2	1.37e+1	5.95e-3	1.73e+4	5.95e-3
Ni	4.24	3.12e-3	3.12e-4	5.31e-8	1.55e-1	1.06e-7
CN ⁻	62.2	4.57e-2	4.57e-3	1.76e-6	5.12	-1.76e-6
Cl ⁻	1260	9.26e-1	9.26e-2	2.61e-5	7.60e+1	-2.61e-5
NO ₃ ⁻	4.17e+5	3.07e+2	3.07e+1	4.95e-3	1.44e+4	-4.95e-3
PO ₄ ³⁻	2.11e+4	1.55e+1	1.55	1.63e-4	4.75e+2	-4.90e-4
SO ₄ ²⁻	3.07e+4	2.26e+1	2.26	2.35e-4	6.84e+2	-4.70e-4
%H ₂ O	55.65%		5.57e+1			
SpG	1.36					
pH	9.69					
mass balance %			104.07	minus:plus charge ratio		0.994

Table A-35. In-Farm 2nd Run As Settled Sludge Direct CN ⁻ CJ-93-B #R-612			
analyte	value	mg/g	weight %
CN ⁻	7460 µg/g	7.46	0.75

Table A-36. In-Farm 2nd Run Compacted Sludge Chelate Dissolution CJ-94-B #R-602						
#R-602 Analysis		Converted to compacted sludge				
analyte	value mg/L or other	mg/g	weight %	moles/ gram	mole ratio	charge equiv./ gram
Fe	459	3.09e+1	3.09	5.53e-4	1.	1.11e-3
K	25.7	1.73	1.73e-1	4.43e-5	8.00e-2	4.43e-5
Na	3140	1.19e+2 ¹	1.19e+1	5.16e-3	9.32	5.16e-3
Ni	496	3.34e+1	3.34	5.69e-4	1.03	1.14e-3
CN ⁻	1200	8.08e+1	8.08	3.11e-3	5.61	-3.11e-3
Cl ⁻	60.6	4.08	4.08e-1	1.15e-4	2.08e-1	-1.15e-4
NO ₃ ⁻	3560	2.40e+2	2.40e+1	3.87e-3	6.99	-3.87e-3
PO ₄ ³⁻	273	1.84e+1	1.84	1.94e-4	3.50e-1	-5.81e-4
SO ₄ ²⁻	252	1.70e+1	1.70	1.77e-4	3.19e-1	-3.53e-4
%H ₂ O	99.22%		4.49e+1 (fr. TGA)			
SpG	0.889					
pH	10.5					
mass balance %			99.43	minus:plus charge ratio		1.07

¹The 1379.4 mg/L Na contributed from EDTA subtracted out.

Table A-37. In-Farm 2nd Run Water Leachate of Compacted Sludge CJ-94-C #R-603				
#R-603 Analytical Data			Converted to Compacted Sludge	
analyte	value mg/L or other	weight % sample	mg/gram soluble	% of compacted sludge
Fe	6.15	6.21e-4	1.90e-1	1.90e-2
K	20	2.02e-3	6.19e-1	6.19e-2
Na	3280	3.31e-1	1.02e+2	1.02e+1
Ni	1.35	1.36e-4	4.18e-2	4.18e-3
CN ⁻	15.4	1.56e-3	4.77e-1	4.77e-2
Cl ⁻	30.3	3.06e-3	9.38e-1	9.38e-2
NO ₃ ⁻	8920	9.01e-1	2.76e-2	2.76e+1
PO ₄ ³⁻	485	4.90e-2	1.50e+1	1.50
SO ₄ ²⁻	596	6.02e-2	1.85e+1	1.85
%H ₂ O	99.59%	9.96e+1		
SpG	0.99			
pH	10.5			
mass balance %		100.95	total % soluble	41.38

Table A-38. In-Farm 2nd Run X-ray Diffraction & X-ray Florescence CJ-105-A #R-596	
Technique	Findings
XRD	unable to identify any specific compound
XRF	major - Fe, Ni minor to trace - Zn, Ca, K, P

Table A-39. In-Farm, 2nd Run Supernate-Sludge Mass Balance Check							
Analyte	Total Moles	As Settled Sludge			Compacted Sludge		
		Supernate %	Sludge %	Total %	Supernate %	Sludge %	Total %
Fe	0.00498	9.19			9.45	99.5 ^c	109. ^c
K	0.01992	110.			113.	1.99 ^c 0.712 ^l	115. ^c 114. ^l
Na	7.40025	107.			110.	0.63 ^c 0.54 ^l	111. ^c 111. ^l
Ni	0.005	0.0888			1.45	102. ^c	103. ^c
CN	0.02988	7.84	44.2 ^d	52.0 ^d	8.05	93.3 ^c	101. ^c
Cl	0.019734	176.			181.	5.22 ^c 1.20 ^l	186. ^c 182. ^l
NO ₃	6.166875	107.			110.	0.56 ^c 6.e-5 ^l	111. ^c 110. ^l
PO ₄	0.246675	87.9			90.4	0.71 ^c 0.57 ^l	91.1 ^c 91.0 ^l
SO ₄	0.350345	89.2			91.7	0.45 ^c 0.49 ^l	92.2 ^c 92.2 ^l

^l Based on water leachate results.

^d Based on direct analysis results.

^c Based on chelate dissolution results.

Figure 6.4. Correlation of Exotherms with Cyanide

CYANIDE ANALYSIS STATUS

presented to

High-Level Waste Tank Advisory Panel

by

K. H. (Karl) Pool
Pacific Northwest Laboratory
September 1-3, 1992

CYANIDE ANALYSES REQUIRED TO RESOLVE USO

- Resolution of USO requires characterization of ferrocyanide tank waste to determine quantity and form of cyanide present in waste
- Information from cyanide analyses will be correlated with chemical reaction and energetics studies to determine hazard potential of ferrocyanide tank wastes
- Determination of cyanide species present will also be useful in evaluating treatment/mitigation options

TABLE 1**CYANIDE ANALYTICAL METHODS UNDER DEVELOPMENT**

Sample Matrix	Sample Preparation Options	Analytical Method Options	Comments
Supernate	no preparation	(1) Distillation (2) IC (3) Spectroscopy solution	(1) DL < 100 ppb (2) DL < 10 ppb (3) DL < 100 ppm
Solid	Complexant Dissolution	(1) Distillation (2) IC (3) Spectroscopy solution	(1) DL < 10 ppm (2) DL < 1 ppm (3) DL < 100 ppm
Solid	no preparation	(1) Distillation (2) Spectroscopy solid	(1) DL < 10 ppm (2) DL ~ 1000 ppm

TABLE 2
Cyanide Species Analyses on Ferrocyanide Materials

<u>Materials Analyzed</u>	<u>Sample Prep</u>	<u>Assay Method</u>	<u>Analyte</u>	<u>Notes</u>
<u>Surrogates (commercial)</u>				
K ₄ Fe(CN) ₆	H ₂ O Dissolution	IC, FTIR	Fe(CN) ₆ ⁻⁴	FTIR DL ¹ < 100 ppm
K ₃ Fe(CN) ₆	H ₂ O Dissolution	IC	Fe(CN) ₆ ⁻³	IC DL ¹ < 1 ppm
KCN	H ₂ O Dissolution	IC	CN ⁻	QL ² < 0.1wt%
K ₄ Fe(CN) ₆	H ₂ O Dissolution	Distillation	CN ⁻	
K ₃ Fe(CN) ₆	H ₂ O Dissolution	Distillation	CN ⁻	
KCN	H ₂ O Dissolution	Distillation	CN ⁻	
<u>Synthetic (Flowsheet)</u>				
Flowsheet Simulant	Complexant Diss.	IC, FTIR	Fe(CN) ₆ ⁻⁴	QL ² ~ 0.1wt%
Flowsheet Simulant	Complexant Diss.	Distillation	CN ⁻	QL ² < 0.1wt%
Na ₂ NiFe(CN) ₆ , Vendor	Complexant Diss.	Distillation	CN ⁻	QL ² < 0.1wt%
Na ₂ NiFe(CN) ₆ , Vendor	Solid, No Prep.	Distillation	CN ⁻	~ 45% recovery
<u>Spiked Synthetic</u>				
Flowsheet Simulant	Complexant Diss.	Distillation	CN ⁻	QL ² < 0.1wt%
K ₄ Fe(CN) ₆ spike	Complexant Diss.	Distillation	CN ⁻	QL ² < 0.1wt%
Na ₂ NiFe(CN) ₆ spike				

(1) DL = detection limit
(2) QL = quantitation limit based on undiluted sludge samples

**Solution FTIR Spectra of Cyanide Standards
and Various Flowsheet Materials**

Typical IC Chromatograms Flowsheet Material Contains $\text{Fe}(\text{CN})_6^{-4}$

Response, Relative Chart Units

Time, Relative Chart Units

PROBLEM

The Microdistillation Method For Total Cyanide Has Yielded Questionable Results On Some Occasions

Current Focus on Microdistillation Method Development

- **Apparent high total cyanide on 101-SY samples**
- **Apparent high total cyanide on organic spiked simulants**
- ***Distilled organics may interfere with colorimetric finish***
- ***Exploring alternate analytic finish***

TABLE 3

**Total Cyanide Analyses on Simulants and Actual Tank 101-SY Samples
by Microdistillation**

<u>Materials Analyzed</u>	<u>Sample Prep</u>	<u>Assay Method</u>	<u>Analyte</u>	<u>Notes</u>
101-SY Simulant K ₄ Fe(CN) ₆ spike	Complexant Diss.	Distillation	CN ⁻	73-115% Recovery
No spike; EDTA 2% TOC	Sludge, No Prep.	Distillation	CN ⁻	28 ppm CN ⁻
No spike; Sucrose 2% TOC	Sludge, No Prep.	Distillation	CN ⁻	102 ppm CN ⁻
No spike; Oxalate 0.34% TOC	Sludge, No Prep.	Distillation	CN ⁻	16 ppm CN ⁻
No spike; IDA 2% TOC	Sludge, No Prep.	Distillation	CN ⁻	23 ppm CN ⁻
<u>Actual Waste</u>				
<u>Tank 101-SY Core Composites</u>				
(1) segments 4-8	Sludge, No Prep.	Distillation	CN ⁻	
(2) segments 9-14(top)	Sludge, No Prep.	Distillation	CN ⁻	
(3) segments 14(bottom)-18	Sludge, No Prep.	Distillation	CN ⁻	
(4) segments 19-22	Sludge, No Prep.	Distillation	CN ⁻	
<u>Tank C-112</u> — segment 20	Complexant Diss.	Distillation	CN ⁻	
			<u>Supernate</u>	<u>Bulk</u>
			90 ppm	152 ppm
			91 ppm	117 ppm
			90 ppm	389 ppm
			394 ppm	409 ppm
				4500 ppm

101-SY Data From WHC, 222-S Laboratory (Window C Report)

Investigation of Apparent False Positive Cyanide Results for Organic Spiked 101-SY Simulants

A-24

- 101-SY Simulant (organic free) spiked with known amounts of $K_4Fe(CN)_6$ and/or selected organics
- Micro-distillation Followed by Colorimetric Analysis and IC with Amperometric Detection
- PNL and WHC Labs Participating

CYANIDE RESULTS FOR MICRODISTILLATION TESTS WITH TANK 101-SY SIMULANTS								
Sample I.D. (run-#)(a,b)	Weight of 101SY simulant added (g)	Weight of CN spike added (ug)(c)	Weight of organic carbon added (mg)	Source of organic carbon	Amount of CN recovered (ug), IC Analysis	ug of CN/g of simulant, IC Analysis	Amount of CN recovered (ug), Colorimetric Analysis	ug of CN/g of simulant, Colorimetric Analysis
1-11	0.3967	0	0	-	4.97	12.5	1.28	3.23
2-5	0.1885	0	0	-	1.86	9.9	1.08	5.73
2-6	0.1878	5	0	-	5.74	30.6	3.64	19.4
1-12	0.4208	10	0	-	8.6	20.4	4.92	11.7
1-3	0	0	7.4	Sucrose	0	-	0	-
1-4	0	10	7.4	Sucrose	9.32	-	8.26	-
1-15	0.4369	0	7.4	Sucrose	11	25.2	6.07	13.9
1-21	0.4364	0	7.4	Sucrose	10.3	23.6	5.78	13.2
2-7	0.1876	0	4	Sucrose	2.26	12	1.43	7.62
1-16	0.3975	10	7.4	Sucrose	12.45	31.3	9.71	24.4
2-8	0.1737	5	4	Sucrose	5.85	33.7	4.05	23.3

(a) Run# labeled 1-(x) employed standard Lachat® Instruments, Inc. recommended conditions; 0.75 mL of releasing agent (7.11 M H₂SO₄ + 0.79 M MgSO₄).
 (b) Run# labeled 2-(x) employed modified conditions; 1 mL of 25% ethylenediaminetetraacetic acid (EDTA)/25% ethylenediamine/50% H₂O plus 0.5 mL releasing agent.
 (c) CN⁻ spikes were in the form of K₄Fe(CN)₆ in both runs.

Conclusions

- **Variety of analytical procedures available for cyanide, both for trace levels and high levels**

Microdistillation

- **Apparent false positive cyanide results confirms results obtained previously**
- **Alternate distillate analysis method (IC with amperometric detection) exhibits unexpected interferences - hydrolyzed NO_x in distillate**

Proposed Future Work

- **Resolve microdistillation interference issues**
- **Focus on more direct analytical procedures**
  - Direct ion chromatography (IC)
  - Direct solution spectroscopic methods
- **Investigate matrix interferences in simulant and actual wastes**
- **Generate qualified analytical procedures**

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APPENDIX B

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Project Number _____

Internal Distribution

File/LB

Date January 13, 1993
To Robert J. Cash, R2-32 / Albert F. Noonan, R2-12
From Karl H. Pool, P8-44 *Karl Pool*
Subject Total Cyanide Analysis Method Validation Test
Plan and Schedule

RECEIVED
JAN 19 1992
A. F. NOONAN

After our meeting early Monday morning (1/11/93), I prepared the attached test plan and schedule as you requested. I hope you will agree that this plan is technically defensible and meets the requirements of your near term agenda.

Please call me on 376-1753 if you have comments and/or concerns.

In my opinion, executing this test plan is above and beyond the originally agreed upon scope of work for Task 307 of the "Methods Development and Technology Transfer Project." Please advise as to the best way of handling this situation from a project management point of view. I am not fully aware of the available options and your preferences.

KHP:cvm

Attachment

**Total Cyanide Analysis of Synthetic FeCN Flow Sheet Materials and Tank C112, Core 34
Segment Samples -- Method Validation Test Plan and Schedule**

INTRODUCTION

The technical procedure to be used is PNL-ALO-285, titled "Total Cyanide by Remote Microdistillation and Argentometric Titration for Samples Containing Greater than Approximately 0.1 Weight % of Total Cyanide". This procedure is currently in PNL's internal review cycle and therefore, is not officially approved for routine use at this time. The procedure needs to be validated as technically sound so that data generated in the future can be accepted as correct within reasonable limits.

The sequential order of tests and approximate dates for completion of each are given below:

Preliminary test to be done before attempting the validation test matrix proper. Several modifications to the originally proposed sample dissolution and actual distillation conditions have shown promising results when applied to synthetic 101SY matrices. In particular, the dissolution solution has been modified to result in a higher pH environment (to preclude potential loss of free cyanide during sample dissolution) and the acidic "releasing solution" has been changed so that the actual distillation is carried out at pH ~4.

The preliminary microdistillation test will apply these newer conditions to $\text{Na}_2\text{NiFe}(\text{CN})_6$ materials. If the results from this test are favorable i.e., agreement of duplicates, >90% spike recovery, and low blanks, these test conditions will be written into the final version of PNL-ALO-285 and used in the actual validation process.

Details of Preliminary Test

Dissolution solution: 1mL of 0.4M Na_4Y (tetrasodium EDTA) + 1.1M
en(ethylenediamine)
Releasing solution: 1 mL of 2M citric acid + 0.9 M $\text{NH}_4^+ \text{H}_2\text{NSO}_3^-$ + 0.1 M
 $\text{H}_2\text{NSO}_3\text{H}$ (sulfamic acid)
Analytical Finish: Argentometric titration

Samples

In Farm 2, duplicates, ~ 100 mg each

FeCN-36, duplicates, ~ 10 mg each

In Farm 2, spiked with WHC-2, duplicates, ~ 50 mg sample + 10 mg spike

Blank (no sample)

$\text{Cs}_2\text{NiFe}(\text{CN})_6 \sim 10 \text{ mg}$

Standard Distillation conditions -- 30 min at 125°C

Measure pH of distillation residue after distillation.

This test will be completed by 1/15/93.

Validation Test Matrix

Test No.	Sample Material	Sample Size (g)	Spiked Samples *	Control Sample	Blank
1	In-Farm 2 (flow sheet material)	0.05, 0.05, 0.10	0.05g sample + 0.01 g WHC-2 in duplicate	0.01 g WHC-2	yes
2	FeCN-36 ($\text{Na}_2\text{NiFe}(\text{CN})_6$, 34.5% CN^-)	0.01, 0.01, 0.02	0.01g sample + 0.01g WHC-2, in duplicate	0.01 g WHC-2	yes
3	Core Composite Segment A, Core 34 Tank C112	0.01, 0.01, 0.02	0.1g sample + 1 mg WHC-2, in duplicate	0.01 g WHC-2	yes
4	Segment B, Core 34 Tank C112	0.01, 0.01, 0.02	0.1g sample + 1 mg WHC-2, in duplicate	0.01 g WHC-2	yes
5	Segment C, Core 34 Tank C112	0.01, 0.01, 0.02	0.1g sample + 1 mg WHC-2, in duplicate	0.01 g WHC-2	yes
6	Segment D, Core 34 Tank C112	0.01, 0.01, 0.02	0.1g sample + 1 mg WHC-2, in duplicate	0.01 g WHC-2	yes

*Use WHC-2 as spiking material; predissolve in EDTA/en solution before adding to sample

This validation test matrix consists of 6 analytical sessions. Each tests consists of:

- one blank
- one control sample
- actual sample in triplicate, and
- duplicate spiked samples.

Tests 1 and 2 utilize non-radioactive materials only. These tests will be carried out in 314 building as "bench top" experiments. Tests 1 and 2 will be completed by January 29, 1993 at the latest.

Tests 3 through 6 will be carried out in the B-hot cells of 325 building. Actual manipulations will be done by one of the hot-cell technicians (preferably Vaughn Hoppes).

Conceivably tests 3 through 6 could be run concurrently with the bench top tests Nos. 1 and 2. This concurrent timing is not recommended, however, due to potential unforeseen difficulties with tests No. 1 and No. 2, as well as the limited quantity of core material available for these tests.

Another consideration is the availability of hot-cell personnel to do the actual work on tests 3 through 6. Scheduling priorities are determined by others (Rick Steele, Gaylord King, et al.).

Even with these caveats, tests involving actual core materials should be finished by the end of February 1993.

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