Total Cyanide Analysis of Tank
Core Samples: Analytical Results
and Supporting Investigations

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Summary

The potential for a ferrocyanide explosion in Hanford site single-shelled waste storage tanks (SSTs) poses a serious safety concern. This potential danger developed in the 1950s when ^{137}Cs was scavenged during the reprocessing of uranium recovery process waste by co-precipitating it along with sodium in nickel ferrocyanide salt. Sodium or potassium ferrocyanide and nickel sulfate were added to the liquid waste stored in SSTs. After the insoluble alkali nickel ferrocyanide compounds settled, the remaining supernate, virtually free of radioactivity, was removed from the tank and pumped to a crib. The tank storage space resulting from the scavenging process was subsequently used to store other waste types. Ferrocyanide salts in combinations with oxidizing agents, such as nitrate and nitrite, are known to explode when key parameters (temperature, water content, oxidant concentration, and fuel [cyanide]) are in place. Therefore, reliable total cyanide analysis data for actual SST materials are required to address the safety issue. Accepted cyanide analysis procedures do not yield reliable results for samples containing nickel ferrocyanide materials because the compounds are insoluble in acidic media. Analytical chemists at Pacific Northwest Laboratory (PNL) have developed a modified microdistillation procedure (see below) for analyzing total cyanide in waste tank matrices containing nickel ferrocyanide materials.

Pacific Northwest Laboratory analyzed samples from Hanford Waste Tank 241-C-112 cores 34, 35, and 36 for total cyanide content using technical procedure PNL-ALO-285 "Total Cyanide by Remote Microdistillation and Argentometric Titration," Rev. 0. This report summarizes the results of these analyses along with supporting quality control data, and, in addition, summarizes the results of the test to check the efficacy of sodium nickel ferrocyanide solubilization from an actual core sample by aqueous EDTA/en to verify that nickel ferrocyanide compounds were quantitatively solubilized before actual distillation.

Using x-ray fluorescence, if all the soluble iron is assumed to have originally been in the form of hexacyanoferrate and no other sources of cyanide are in the core 34 sample, the cyanide content of the original sample is calculated to be 0.933%. Using x-ray diffraction, the concentration of sodium nickel ferrocyanide in the untreated core 34 composite material is estimated to be on the order of 1%. This indicates that sodium nickel ferrocyanide is effectively leached and dissolved from actual "ferrocyanide tank" sample matrices by EDTA/en treatment.

The PNL procedure used appears to provide reliable and consistent total cyanide analyses for typical ferrocyanide waste tank samples and can be confidently used as part of the characterization of similar tank core samples in the future.

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Background

In the 1950s, ^{137}Cs was scavenged during the reprocessing of uranium recovery process waste by co-precipitating it along with sodium in nickel ferrocyanide salt, $\text{Na}_{2-x}\text{Cs}_x\text{NiFe}(\text{CN})_6$. The scavenging process added sodium or potassium ferrocyanide and nickel sulfate to the liquid waste stored in single-shelled tanks (SSTs). After the insoluble alkali nickel ferrocyanide compounds settled, the remaining supernate, virtually free of radioactivity, was removed from the tank and pumped to a crib. The tank storage space resulting from the scavenging process was subsequently used to store other waste types.

Ferrocyanide salts in combinations with oxidizing agents, such as omnipresent nitrate and nitrite, when heated to sufficiently high temperature ($>220^\circ\text{C}$), are known to react exothermally and uncontrollably. The potential of a ferrocyanide explosion in Hanford site SSTs constitutes a serious safety concern, and considerable effort in recent years has been spent attempting to define boundary conditions for such explosions. The key parameters have been identified to be temperature, water content, oxidant ($\text{NO}_3^- + \text{NO}_2^-$) concentration, and fuel (cyanide) concentration. Therefore, reliable total cyanide analysis data for actual SST materials are required to address the safety issue.

Accepted routine cyanide-analysis procedures, such as EPA method 9010, do not yield reliable results for samples containing nickel ferrocyanide materials due to the insolubility of such compounds in acidic media.. Analytical chemists at Pacific Northwest Laboratory (PNL)^(a) have developed a modified microdistillation procedure for the analysis of total cyanide in waste tank matrices containing nickel ferrocyanide materials. Data supporting method validation can be found in "Assay Development Status Report for Total Cyanide" WHC-EP-0635, February 1993.

(a) Pacific Northwest Laboratory is operated for the U. S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

Introduction

Pacific Northwest Laboratory analyzed samples from Hanford Waste Tank 241-C-112 cores 34, 35, and 36 for total cyanide content. According to the technical procedure used (PNL-ALO-285, "Total Cyanide by Remote Microdistillation and Argentometric Titration," REV. 0), samples were slurried in an aqueous ethylenediamine (en) + ethylenediamine-tetra-acetic-acid (EDTA) solution that quantitatively dissolved ferrocyanide compounds including alkali nickel ferrocyanides. Aliquots of sample slurries were acidified with sulfuric acid and subjected to distillation. The HCN evolved was trapped in a NaOH solution that was subsequently analyzed for cyanide content by titration with standard AgNO_3 .

This report summarizes the results of these analyses along with supporting quality control data.

In addition, the efficacy of sodium nickel ferrocyanide solubilization from an actual core sample by aqueous EDTA/en was examined to verify that nickel ferrocyanide compounds were quantitatively solubilized before actual distillation. The results of this test are presented in the next section.

Results

Total Cyanide Content of Tank 241-C-112 Samples

The results obtained from application of procedure PNL-ALO-285 (Appendix A) to dried aliquots of available Tank 241-C-112 samples are given in Tables 1 and 2. Also presented are results from two unfiltered drainable liquid composites (Cores 34 and 35). Quality Control data pertaining to these analyses are given in Table 3.

Table 1
Total Cyanide Analyses Results
Core 34 Tank 241-C-112

Sample Identification		Percent Cyanide found (dry weight basis)	Precision^(a)	Analysis Date
WHC - ID	ALO - ID			
Quarter Segment 1D	92-06733	Average = 0.522 0.509, 0.539, 0.518	1.7	2/11/93
Quarter Segment 2B	92-06734	Average = 0.428 0.430, 0.426	0.94	2/11/93
Quarter Segment 2C	92-06735	Average = 0.831 0.868, 0.793	7.9	2/18/93, 2/22/93
Quarter Segment 2D	92-06736	Average = 0.747 0.770, 0.743, 0.729	1.6	2/12/93
Segment 2 composite	92-06740	Average = 0.965 0.953, 0.965, 0.976	0.07	2/10/93
Drainable liquid composite	92-06747	Average = 0.461 0.453, 0.468 (wet basis)	3.3	2/22/93, 2/23/93

(a) Precision expressed as relative percent difference when n=2; for n>2, precision is given as percent relative standard deviation of the mean.

Table 2
Total Cyanide Analyses Results
Core 36 Sludges and
Core 35 Drainable Liquid Composite,
Tank 241-C-112

<u>Sample Identification</u>		<u>Percent Cyanide found</u>	<u>Precision</u>	<u>Analysis Date</u>
<u>WHC - ID</u>	<u>ALO - ID</u>	(dry weight basis)	(Relative percent difference)	
Quarter Segment 1D	92-06762	Average = 0.717 0.729, 0.705	3.3	2/22/93
Quarter Segment 2A	92-06763	Average = 0.923 0.906, 0.940	3.7	2/22/93
Quarter Segment 2B	92-06764	Average = 0.745 0.749, 0.742	0.9	2/22/93
Quarter Segment 2C	92-06765	Average = 0.402 0.410, 0.394	4.0	2/23/93
Quarter Segment 2D	92-06766	Average = 0.561 0.574, 0.548	4.6	2/23/93
Segment 2 composite	92-06767	Average = 0.706 0.704, 0.709	0.7	2/23/93
Drainable liquid composite Core 35	92-06774	Average = 0.286 0.295, 0.277 (wet basis)	6.3	2/23/93

Table 3
Quality Control Data

A. Control Standard, a.k.a. Blank Spike, Recovery Data

<u>Analytical Session - Date</u>	<u>Percent Recovery</u>
2/10/93	97
2/11/93	98
2/12/93	99
2/18/93	96
2/22/93	88
2/23/93	94

A solution of simulant "In Farm 2 Rev. 21" dissolved in aqueous 5% EDTA/en, which had been well characterized for cyanide content, was used as the control standard. Total cyanide content of the control standard was approximately 1 mg.

B. Spike Recovery Data

<u>Analytical Session - Date</u>	<u>Percent Recovery</u>	<u>Sample Spiked</u>
2/10/93	89, 104	92-06740
2/11/93	90, 95	92-06733
2/12/93	103, 98	92-06736
2/18/93	79	92-06735
2/22/93	96	92-06762
2/23/93	88	92-06765

The spiking solution used was composed of FeCN-36 ($\text{Na}_2\text{NiFe}(\text{CN})_6$) dissolved in aqueous 5% EDTA/en. Weighed aliquots of this solution (approximately 1 mg CN^-/g solution) were added to samples.

Analyses of Dissolution Residues

The slurry remaining from treatment of Core 34 Segment 2 composite sample (92-06740) with 5% aqueous EDTA/en was vacuum filtered (0.45 μm). The filtrate was analyzed by x-ray fluorescence (XRF) to determine the identity and quantity of elements actually dissolved by EDTA/en treatment.

In addition, the washed and dried solids from filtration along with a dried portion of untreated sample (92-06740) were analyzed by x-ray diffraction (XRD) to verify that sodium nickel ferrocyanide had been effectively leached and dissolved by the EDTA/en dissolution procedure.

XRF Results

The concentrations ($\mu\text{g/mL}$) of elements in the filtrate as determined by XRF were

Fe	197 $\pm$ 11
Ni	162 $\pm$ 9
Pb	133 $\pm$ 8
Ca	448 $\pm$ 32
U	109 $\pm$ 8

Using the XRF determined value for iron concentration of the filtrate and dilution factors involved in treatment of sample 92-06740 with EDTA/en solution, the soluble iron content of the original (dry) sample is calculated to be 0.334%. If all the soluble iron is assumed to have originally been in the form of hexacyanoferrate and no other sources of cyanide are in the sample, the cyanide content of the original sample is calculated to be 0.933%. This value compares very well with the micro-distillation value for total cyanide (0.966%).

XRD Results

Comparison of the XRD spectrum of untreated core 34 composite material with the XRD spectrum of residue from EDTA/en treated material indicates that sodium nickel ferrocyanide was present in the original sample, but undetectable in the EDTA/en treated residue.

Although several uncertainties are involved, the concentration of sodium nickel ferrocyanide in the untreated core composite material is estimated to be on the order of 1% (1% of $\text{Na}_2\text{NiFe}(\text{CN})_6 \approx 0.5\% \text{CN}^-$).

The complete report of XRD examination of sample 92-06740 (Core 34 composite) is attached as Appendix B.

Discussions - Conclusion

The evidence presented here suggests that sodium nickel ferrocyanide is effectively leached and dissolved from actual "ferrocyanide tank" sample matrices by EDTA/en treatment.

Total cyanide analyses of actual waste tank core samples by the microdistillation-argentometric titration procedure are consistent and reliable in terms of currently accepted QC criteria. Replicate analyses of the same sample are in reasonably close agreement, control standard recoveries are well within acceptable limits, and spike recoveries are all within acceptable limits except for one value (79%), which is just barely below the procedure defined lower limit of 80%. The procedure appears to provide reliable and consistent total cyanide analyses for typical ferrocyanide waste tank samples and can be confidently used as part of the characterization of similar tank core samples in the future.

Personnel contributing to this work:

F. Vaughn Hoopes - hot-cell work including preparation of samples and performing the total cyanide microdistillations

Evan D. Jensen - x-ray diffraction analyses and interpretation

Ron W. Sanders - x-ray fluorescence analyses

Nancy J. Stajduhar - typing and formatting this report

Karl H. Pool - direction and supervision of the overall effort

APPENDIX A

PNL-ALO-285

**Total Cyanide by Remote Microdistillation
and Argentometric Titration**

This procedure includes revisions per ICN-PNL-ALO-285.1 R0, dated March 5, 1993.

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-285, Total Cyanide by Remote Microdistillation and Argentometric Titration

APPLICABILITY

This procedure provides a method for determining total cyanide in waste tank matrices where the concentration of total cyanide is greater than approximately 0.1 weight percent. The detection limit for this procedure is approximately 20 µg cyanide.

DEFINITIONS

Batch - A group of samples of similar matrix treated and distilled at the same time. A batch can not exceed (N-4) samples, where N is the number of available spaces in the heating block used. For analyses performed in support of Single Shell Tank (SST) characterization, all samples are to be analyzed in duplicate. Therefore, the maximum number of samples that would constitute a batch when working with SST samples will be (N-3)/2. Where N is the number of available spaces in the heating block used.

RESPONSIBLE STAFF

- Cognizant Scientist
- Analyst/Technician

PROCEDURE

1.0 Equipment and Materials

- 1.1 Micro-Distillation Tubes (Lachat® part no. 1700-001 or equivalent)
- 1.2 Temperature controlled heating block designed to accommodate at least 5 Micro-Distillation tubes simultaneously
- 1.3 Micro-Distillation Tube Assembler/Disassembler (MDTA/D)
- 1.4 Pipets (adjustable or fixed volume)
- 1.5 Disposable pipet tips
- 1.6 Repipetor, 500 mL
- 1.7 Analytical four place balance
- 1.8 Buret, 10 mL, readable to nearest 0.02 mL
- 1.9 Magnetic stirrer
- 1.10 Vials, glass, 15 mL

Author	Date	Project Mgr.	Date	PQ Representative	Date
KH Pool		SG McKinley		TL Ehlert	
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
SA Bryan		AG King		ALL ORIGINAL SIGNATURES ON FILE	
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- 1.11 Stir bars, glass
- 1.12 Ice cream cartons (sample transfer containers)
- 1.13 Drug cartons (secondary containment vessels)
- 1.14 Tissue or Kleenex® (secondary containment vessel packing)
- 1.15 Silicone grease

2.0 Reagents

- 2.1 0.0192 N AgNO₃ solution (Titer: 1.00 mg CN⁻/mL): Weigh 3.2647 ± 0.0002 g crushed primary standard grade (99.9% or better) AgNO₃ which have been dried to constant weight at 40°C, dissolve in deionized water (DIW), and dilute to 1000 mL. Alternatively a certified AgNO₃ solution from a commercial source may be used.
- 2.2 Sample pretreatment solution: Acid form EDTA and Ethylenediamine. Dissolve 5.0 grams acid form EDTA and 5.0 grams Ethylenediamine in Deionized Water (DIW) to a total volume of 100 mL.
- 2.3 Releasing solution: 7.11 M H₂SO₄ + 0.79 M MgSO₄: Dissolve 47.5 g MgSO₄ (anhydrous) in approximately 150 mL of DIW. Add 350 g concentrated H₂SO₄ slowly to avoid overheating to the point of boiling. Dilute to 500 mL final total volume. Filter, if undissolved solids persist.
- 2.4 Deionized water, greater than 15 megohm, as indicated by the deionizer meter readout.
- 2.5 Rhodanine Indicator Solution: Dissolve 0.02 g of p-dimethylaminobenzalrhodanine in 100 mL of acetone.
- 2.6 Stock Standard CN⁻ spiking solution(s): K₄Fe(CN)₆ and/or Na₂NiFe(CN)₆ dissolved in the sample pretreatment solution. Concentration ~1mg CN⁻/mL.
- 2.7 0.25 M NaOH solution: Dissolve 10.0 ± 0.2 gram Reagent grade NaOH pellets in 1.0 liter of DIW.

3.0 Predistillation Preparation

- 3.1 Unpackage the required number of micro-distillation tubes to complete the batch. Verify that the sealed upper portion of each tube contains approximately 1.5 mL of vendor supplied sodium hydroxide trap solution.
- 3.2 Label the upper and lower halves of each micro-distillation tube with the appropriate sample identification information. Every batch will consist of samples, a duplicate sample, spike, a control sample, and a methods blank. For QC requirements, see Section 7.0. Label the required number of 15 mL glass vials

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needed to transfer the distillates out of the hot cell. Place a disposable glass stir bar in each vial. Place the vials in secondary containment to keep them externally free of radioactive contamination.

- 3.3 Lightly grease the joint where the upper and lower portions of each tube join. Use silicon grease.
- 3.4 Turn on the power to the heat block. Allow at least 30 minutes for the unit to warm up. Verify that the temperature of the heating block is 128 ± 3 degrees C, using a calibrated thermometer or thermocouple. Record actual temperature on a bench sheet (see Exhibit 1).
- 3.5 Perform a balance performance check in accordance with PNL-ALO-052.
- 3.6 Check and document the delivery of all pipets that will be used both in-cell and out. Document the checks on the bench sheet.
- 3.7 Pipet or weigh the appropriate amount of spike solutions into the lower parts of the appropriate micro-distillation tubes prior to introducing them into the hot cells. The appropriate amounts will be provided by the Cognizant Scientist. Place the lower tube sections into an ice cream carton to keep them upright while they are being transferred into the cells.
- 3.8 Weigh approximately 0.5 g sample (nearest 0.1 mg) into a tared scintillation vial. Add approximately 5 g pretreatment solution (nearest 0.1 mg) to the vial along with a magnetic stir bar. Record weights of sample and pretreatment solution. Stir the sample + pretreatment solution mixture in the capped vial vigorously for approximately 30 minutes to dissolve the alkali-nickel-ferrocyanide compounds.

4.0 Distillation

- 4.1 Transfer the still separated micro-distillation tube sections into the hot cell.
- 4.2 Place the upper tube sections in the large holding block in a logical sequential order.
- 4.3 Place the bottom tube sections in the small holding block in logical order.
- 4.4 Weigh approximately 1 g of sample/pretreatment solution mixture (Section 3.8) into the appropriate lower tube section and record

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the weight on the bench sheet. The weight of mixture taken should be measured to the nearest milligram or better.

- 4.5 Fill the lower tube section to the flange with sample pretreatment solution.
- 4.6 Using the MDTA/D, add 0.6 mL of the $\text{H}_2\text{SO}_4/\text{MgSO}_4$ releasing solution to the lower tube section. Seal the upper and lower tube sections together. **NOTE:** This sealing operation must be done as quickly as possible to minimize the potential loss of HCN. Place the sealed tubes in the heating block.
- 4.7 Allow the heating/distillation process to proceed for at least 30 minutes but no longer than 40 minutes.
- 4.8 Using the MDTA/D, disconnect the lower portions of the tubes from the upper and discard the lower section. The elapsed time between the removal of a tube from the heat block and parting the upper and lower sections should be minimized to prevent the potential "suck-back" of distillate into the lower tube sections. Failure to minimize the time interval may result in low recoveries.
- 4.9 With each upper tube section, hold horizontally and rotate slowly to rinse the walls with the distillate. Tap the tube section on a firm hard surface (e.g., the hot cell floor) to ensure that all of the trap solution is in the lower portion just above the semi-permeable membrane. Break the upper tube section in the location pre-scored by the manufacturer. Transfer the distillate into a prelabeled 15 mL glass vial. Rinse each half of the upper tube section with approximately 5 mLs of 0.25 M NaOH (squeeze bottle) and add the rinses to the glass vial.
- 4.10 Transfer the glass vials containing the distillates and rinses out of the hot cell and to the fume hood where the titrations are to be done.

5.0 Titrations

For each sample:

- 1) Fill a clean 10 mL buret with 0.0192 N AgNO_3 .
- 2) While stirring the sample by means of magnetic stirrer and stirbar, add 3 drops of Rhodanine indicator to the vial.
- 3) Continue stirring sample and titrate to the first permanent appearance of a "salmon" color. Record the volume of AgNO_3 used on the bench sheet.

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6.0 Calculations

6.1 Since the titer of 0.0192 N AgNO₃ is 1.00 mg CN⁻/mL, the volume of the titrant used (in mL) is numerically equal to the mg CN⁻ in the distillate. Therefore,

$$\text{mg CN}^- \text{ found} = \frac{(\text{mL AgNO}_3 \text{ used to titrate distillate})}{(\text{mL AgNO}_3 \text{ used to titrate distillation blank})}$$

6.2 Let:

W_1 = weight (g) sample taken (Section 3.8)

and

W_2 = weight (g) pretreatment solution taken (Section 3.8)

$$\text{Then, the weight fraction of sample in mixture} = \frac{W_1}{W_1 + W_2} \equiv X$$

For samples and blank spikes:

$$\% \text{ CN}^- = \frac{\text{mg CN}^- \text{ found}}{(W_s)(X) \times 10^3} \times 100$$

where: W_s = weight (g) mixture (Section 4.4) taken.

6.3 Spiked Samples

$$\text{Spike recovery (\%)} = \frac{[V_{SP} - V_B - \frac{(W_s)(X)}{1000} \times \frac{A}{100}]}{W_{SP}} \times 100$$

where: V_{SP} $\equiv$ mL AgNO₃ used to titrate spiked sample distillate

V_B $\equiv$ mL AgNO₃ used to titrate blank distillate

W_{SP} $\equiv$ weight (mg) of CN⁻ in added spike

W_s $\equiv$ weight (g) mixture (Section 4.4) taken

A $\equiv$ % CN⁻ found for unspiked sample.

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PNL TECHNICAL PROCEDURE

7.0 Quality Assessment

Each analytical session (distillation + titration) shall include as a minimum: one blank, one spiked sample, one sample duplicate, and one spiked blank a.k.a. control sample. For SST samples, all samples will be analyzed in duplicate.

The preparation/method blank and control sample represent known performance indicators for this procedure and may render the analytical session suspect. Evidence of contamination in the blank and/or control sample recovery falling outside 80-120% warrant immediate corrective action. Notify the Cognizant Scientist immediately when one or both of these situations occur.

Sample spike recoveries should fall within 80-120%. When this recovery limit is exceeded contact the Cognizant Scientist.

The relative percent difference (RPD) for duplicate samples shall not exceed 15%, if the cyanide content of the is ≥ 10 times the method detection limit.

The Cognizant Scientist is responsible for investigating all incidents of QC failure and directing appropriate corrective action.

8.0 Records

Records will be maintained and controlled so as to conform to requirements of the Analytical Chemistry Laboratory Quality Assurance Plan, MCS-033.

9.0 Tolerances

Tolerances for all measurements made during an analysis shall be specified in the following manner: 1) a tolerance limit can be stated with a measurement value given in a method, or 2) if a tolerance limit is not stated with a measurement value, then the following system of tolerances shall be in effect:

- a) Unless otherwise specified, all values for measurements stated in the methods (volume, weight, time, etc.) are approximate values. The actual measurements used, however, shall be within $\pm 10\%$ of the stated value.
- b) When one or more significant figures are given to the right of the decimal point, the tolerance limit is ± 5 in the next digit located beyond the last one stated.

10.0 References

Winters, W.I., 'Analytical Methods for Determining Cyanide in Hanford Nuclear Waste,' RHO-SD-WM-TI-315, Rockwell Hanford Operations, Richland, WA, September, 1987.

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'Micro-Dist Distillation System Reference and Methods Manual,' Lachat Instruments, 6645 West Mill Road, Milwaukee, WI 53218, December 28, 1989.

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APPENDIX B

X-Ray Diffraction Examination of Core 34 composite Sample (92-06740)

Date April 13, 1993
To K. H. Pool
From E. D. Jenson
Subject XRD Examination of Sample 92-6740

Author

Reviewer

E. Jenson 4/13/93
J. Robbins 4-15-93

SUMMARY

Sample 92-6740, radioactive tank waste used for development of an analytical technique for determination of sodium nickel ferrocyanide, has been examined using X-ray diffraction. Comparison of the XRD spectra from the residue of washed and unwashed samples indicates that sodium nickel ferrocyanide could have been present. The difference in concentration of sodium nickel ferrocyanide in the two samples would be on the order of 1%.

RESULTS AND DATA

The determination that sodium nickel ferrocyanide could have been present is based on the comparison of the diffractograms of the unwashed sample and a washed sample. The washed sample should have had the ferrocyanide removed, while it should still be present in the unwashed sample. Subtracting the diffraction data of the washed sample from that of the unwashed sample resulted in a difference spectrum which showed a possible peak at 2-theta 17.24 degrees. The major peak of sodium nickel ferrocyanide, from J. Tingey samples examined earlier, has been found at 17.25 to 17.37, with the best sample showing 17.25 degrees 2-theta. Search for the next most intense peak was unsuccessful due to interference from an adjacent peak, and the lack of data from a washed sample for subtraction of data from phases in common.

The estimate of on the order of 1% as the concentration difference in the washed and unwashed samples was determined as follows:

- count rate on difference spectrum peak, about 3 counts/second, thin sample
- count rate on pure standard, about 900 counts/second, bulk sample

Since the difference spectrum was determined from samples of a thin film, and Tingey's sample was examined as a bulk sample, the difference in X-ray penetration between the 2 samples will have a large effect on the data. Due to the thickness of the sample in the standard (bulk sample), no X-rays would have penetrated the sample. Since these samples were thin films, a large amount of

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the X-rays could have penetrated the sample. Not knowing the thickness of the sample layers, we can only give an educated guess as to the appropriate factor for count rate reduction due to sample thickness. (The sample layers were relatively thick as thin layers go). A reduction to $1/3$ of peak height seen in a bulk sample is assumed. On this basis the concentration should be about 1% as sodium nickel ferrocyanide. Greater intensity reduction and therefore higher concentration is favored by more penetration of the X-rays through the thin samples. These conditions are given by thinner samples and lower average atomic number. Likewise, less intensity reduction and therefore lower concentration would result from less penetration. Thicker samples and higher atomic number favor this effect.

The raw data showed a possible very low intensity peak for the unwashed sample at the known position of the sodium nickel ferrocyanide. In the washed sample, this very low intensity peak appears absent. A plot of this data superimposed on one figure are shown in figure 1.

Statistical treatment of the data was used to enhance the peak visibility. Data for step size of 0.01 degrees was generated by interpolating from 0.02 degree (unwashed) and 0.03 degree (washed) steps. These data were then used to generate a spectrum for a window of 0.1 degrees (approximately equivalent to opening the final slits by a factor of 10 for increased count rate). The data for the washed sample was then subtracted from the data for the unwashed sample creating a difference spectrum. The difference spectrum shows the peak at the expected position very plainly. The data for the difference spectrum is shown in figure 2.

The data from the first attempt, (very rough surface) was used to try and determine the phases present. The attempt was unsuccessful, presumably due to large peak shifts due to not satisfying the geometry requirements.

The position of the first few diffraction peaks in the series sodium nickel ferrocyanide, potassium nickel ferrocyanide and cesium nickel ferrocyanide are shown in figure 3. The data for sodium is from earlier work for J. Tingey, while that for potassium and cesium is from the International Centre for Diffraction Data, ICDD, data base. The data is shown in "stick figure" form, ie a vertical line is shown at the position of the line, and its height represents its intensity relative to the most intense line in its spectrum. Labels are attached indicating the 2θ position of each line. The absence of the 17 degree peak in the cesium compound is probably due to the

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inability of the instrumentation employed to reach that angular position.

The abbreviations on the accompanying plot in figure 1 are as follows:

FN = File name.
ID = Sample identification or comments.
Date = Date the run was started.
Time = Time the run was started.
PT = Point count time. Counting time in seconds at each step.
Step = Angular step size, degrees 2-theta.
WL = Wavelength of the X-rays used.

The horizontal axis is 2-theta and the vertical axis is count rate (counts/seconds).

EXPERIMENTAL

Samples were prepared as thin samples on quartz slides in the hot cells in 325 building. The "finely pulverized" samples were mixed with 20% collodion in amyl acetate binder and spread somewhat uniformly over the area the X-ray beam would intercept. Sample amounts were a few cubic millimeters on the end of a spatula. On inserting the samples into the diffractometer stage, it was observed that the first sample was very clumpy, thus violating the requirement of a flat sample. The spectrum was obtained, with the notation that peak positions are likely in error. The data was useful in showing what to expect in the way of peak intensities and background noise. Additional sample preparations were made with much more attention to pulverizing and working the sample into a smooth, thin film. These samples were used for analysis. They were still not as smooth as desirable, but probably as good as could be obtained under the circumstances of preparation in a hot cell.

Sample data was accumulated on the unwashed sample over the range 16.0 to 18.3 and 33.7 to 36.3 degrees 2-theta using a step size of 0.02 degrees and count time of 99 seconds per data position. Data for the washed sample was accumulated over the range 15.5 to 18.5 with step size of 0.03 degrees and count time of 99 seconds per data position. The large count time was necessary to get good counting statistics for the detection of a peak expected to be very low intensity.

The instrument used was the Scintag Pad V X-ray diffractometer located in room 409 of the 325 building, property tag number W24321. X-ray tube conditions were 45 Kv and 40 ma. The tube

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anode was copper, with the $K\alpha$ line utilized. The instrument was operated in the $\theta/2$ - θ mode.

QA STATEMENT

Work was performed to procedure HTA-3-3, Rev 4, Solids Analysis: X-ray Diffraction. Calibration data are in LRB BNW 52334. Daily calibration checks showed the instrument to be within calibration limits at all times. Training records of the operator, E. D. Jenson, are on file in the Analytical Chemistry Laboratory office.

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FIGURE 1

Plot of raw data from sample 92-6740, unwashed and washed samples

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FIGURE 2

Difference spectrum of unwashed and washed samples. Data interpolated for uniform step size and statistical moving window applied.

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FIGURE 3

Representation of positions and relative intensities of first few diffraction lines for sodium-, potassium- and cesium nickel ferrocyanides.

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