MU012R[(a)]

Total Cyanide by Remote Microdistillation and Argentometric Titration

1.0 Scope and Application

This procedure provides a method for determining total cyanide in radioactive waste tank matrices where the concentration of total cyanide is *greater than approximately 0.1% by weight* (concentrations greater than 1 g CN^-/kg). The method as written has general utility for moderately high levels of cyanide, but was specifically developed for samples that must be handled in a hot cell.

2.0 Summary of Method

Sample pretreatment with ethylenediamine and acid-form ethylenediaminetetraacetic acid is performed to ensure complete dissolution of acid-insoluble alkali nickel ferrocyanide compounds. Cyanide is then released from most of its complexes and converted to hydrogen cyanide by treatment with acid in the presence of magnesium ions. Hydrogen cyanide (HCN) is distilled from acidified samples and captured with sodium hydroxide. Standard silver nitrate is used to titrate the cyanide using rhodamine indicator. The detection limit for this procedure is approximately 20 μg cyanide per sample.

3.0 Interferences and Limitations

No significant interferences were encountered with samples containing complexed ferrocyanides in the range indicated. The following interferences are known to occur in cyanide determinations, especially with cyanide in the mg/kg range.

3.1 Cobalticyanide complexes are known to be incompletely converted to HCN by distillation from acid.

3.2 Nitrate/nitrite may interact with certain organic materials, creating species that will decompose to HCN when distilled. If matrices contain nitrate and/or nitrite and significant ketone or organic acid content, then pretreatment with sulfamic acid will eliminate this interference.

3.3 Aldehydes will convert cyanide to cyanohydrin, which will form a nitrile during distillation.

(a) This method was supplied K. H. Pool (Pacific Northwest Laboratory, Richland, Washington).

4.0 Safety

Radiochemical safety protocol and requisite training in the use of associated equipment (e.g., hot cell procedures) are assumed for highly radioactive samples.

5.0 Apparatus and Materials

- Micro-distillation tubes (Lachat® part no. 1700-001 or equivalent; see Figure 1)
- Temperature controlled heating block designed to accommodate at least five micro-distillation tubes simultaneously
- Micro-distillation tube assembler/disassembler (MDTA/D; see Figure 2)
- Pipets (adjustable or fixed volume)
- Disposable pipet tips
- Repipetor, 500 mL
- Analytical four-place balance
- Buret, 10 mL, readable to nearest 0.02 mL
- Magnetic stirrer
- Vials, glass, 15 mL
- Stir bars, glass
- Ice cream cartons (sample transfer containers)
- Cardboard cartons (secondary containment vessels)
- Tissue or Kleenex® (secondary containment vessel packing)
- Silicone grease

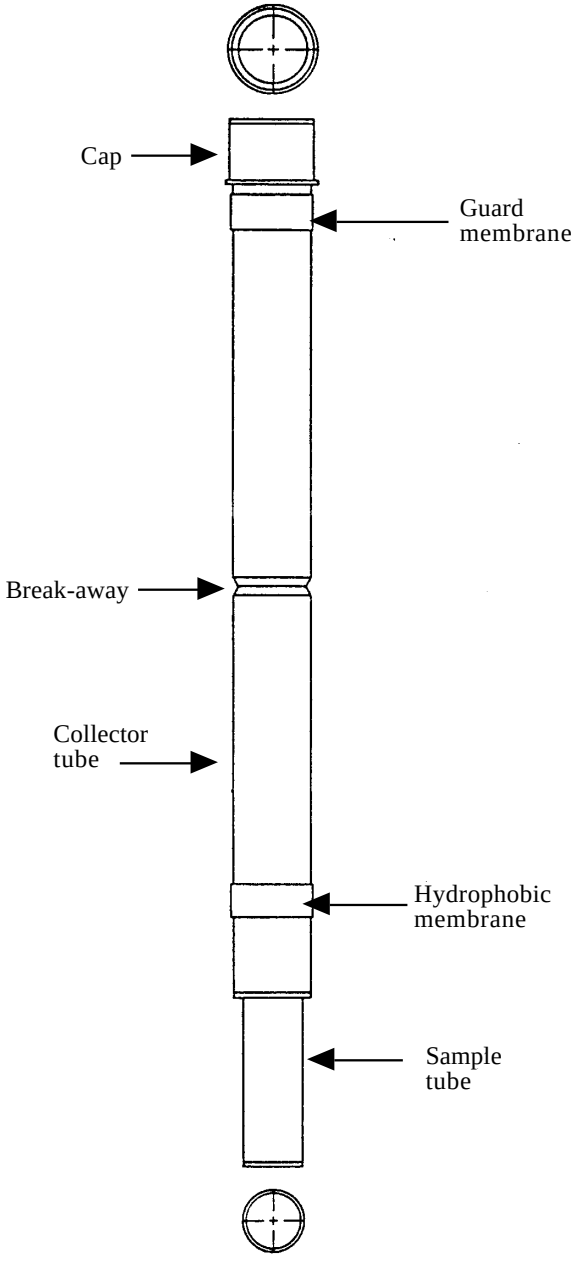

Figure 1. Micro-distillation Tube

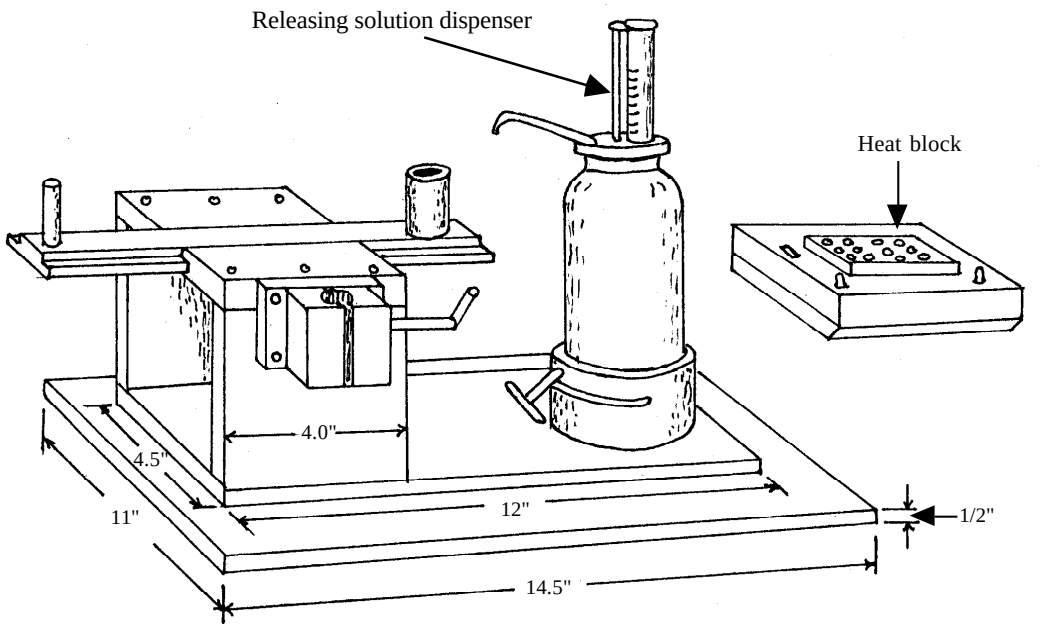

Figure 2. Micro-distillation Tube Assembler/disassembler (MDTA/D)

6.0 Reagents

6.1 A solution of 0.0192 N $AgNO_3$ (titer: 1.00 mg CN^-~/mL): A 3.2647 ± 0.0002-g quantity of crushed primary standard grade (99.9% or better) $AgNO_3$, which has been dried to constant weight at 40°C, should be weighed, dissolved in deionized water (DIW), and diluted to 1000 mL. Alternatively, a certified $AgNO_3$ solution from a commercial source may be used.

6.2 Sample pretreatment solution: Acid form ethylenediaminetetraacetic acid (EDTA) and ethylenediamine. Five grams of acid form EDTA and 5.0 g Ethylenediamine in DIW are dissolved to a total volume of 100 mL.

6.3 Releasing solution: 7.11 M H_2S0_4 + 0.79 M $MgSO_4$: A 47.5-g quantity of $MgS0_4$ (anhydrous) is dissolved in approximately 150 mL of DIW. A 350-g quantity of concentrated H_2SO_4 is added slowly to avoid overheating to the point of boiling. The sample is diluted to 500 mL final total volume. If undissolved solids persist, the sample should be filtered.

6.4 Deionized water, greater than 15 Mohm/cm, as indicated by the deionizer meter readout.

6.5 Rhodanine Indicator Solution: Two grams of p-dimethylamino-benzalrhodanine are dissolved in 100 mL of acetone.

6.6 Stock Standard CN^- spiking solution(s): A solution of $K_4Fe(CN)_6$ and/or $Na_2NiFe(CN)_6$ is dissolved in the sample pretreatment solution. The concentration should correspond to l mg CN-/mL.

6.7 A 0.25 M NaOH solution: A 10.0 ± 0.2-g quantity of reagent grade NaOH pellets is dissolved in 1.0 L of DIW.

7.0 Sample Collection, Preservation, and Handling

In general, radioactive waste tank samples need no preservation. Once samples have been treated with pretreatment solution, however, the distillation should be performed as soon as possible (i.e., within a few days). Distillates should be analyzed within two week of their generation.

8.0 Procedure

8.1 A batch consists of 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, to allow for a blank, spiked sample, sample duplicate, and control sample (see section 10.0) The maximum number of samples that would constitute a batch when working with duplicated samples will be (N-3)/2, where N is the number of available spaces in the heating block.

8.2 Predistillation Preparation

8.2 .1 Enough micro-distillation tubes are unpackaged to complete the batch. It should be verified that the sealed upper portion of each tube contains approximately 1.5 mL of vendor-supplied sodium-hydroxide trap solution.

8.2.2 The upper and lower halves of each micro-distillation tube should be labeled with the appropriate sample identification information. Every batch will consist of samples, a duplicate sample, spike, a control sample, and a method blank. For QC requirements, see Section 10. The required number of 15-mL glass vials used to transfer the distillates out of the hot cell should be labeled. A disposable-glass stir bar should be placed in each vial. The vials are labeled and placed in secondary containment to keep them externally free of radioactive contamination.

8.2.3 The joint where the upper and lower portions of each tube join should be smeared lightly with silicone grease.

8.2.4 The power to the heat block is turned on. At least 30 min should be allowed for the unit to warm up. It should be verified that the temperature of the heating block is 128 ± 3°C, using a calibrated thermometer or thermocouple. The actual temperature should be recorded on a bench sheet.

8.2.5 A balance performance check should be performed.

8.2.6 The delivery of all pipets that will be used both in-cell and out should be checked and documented. The checks on the bench sheet should be documented.

8.2.7 The appropriate amount of spike solutions is pipeted or weighed into the lower parts of the appropriate micro-distillation tubes before introducing them into the hot cells. The appropriate amounts should contain an amount of cyanide approximately equal to that expected in the samples. The lower tube sections should be placed into an ice cream carton to keep them upright while they are being transferred into the cells.

8.2.8 An approximately 0.5-g sample (nearest 0.01 g) is weighed into a tared scintillation vial. Approximately 5 g pretreatment solution (nearest 0.1 mg) are added to the vial along with a magnetic stir bar. Weights of sample and pretreatment solution should be recorded. The sample and pretreatment solution mixture are stirred in the capped vial vigorously for at least 30 min to dissolve the alkali-nickel-ferrocyanide compounds present in the tank material and in the spiked samples.

8.3 Distillation

8.3.1 The still separated micro-distillation tube sections are transferred into the hot cell.

8.3.2 The upper tube sections should be placed in the large holding block in a logical sequential order.

8.3.3 The bottom tube sections should be placed in the small holding block in logical order.

8.3.4 Approximately 1 g of sample pretreatment solution mixture (section 8.2.8) is weighed into the appropriate lower tube section and the weight recorded on the bench sheet. The weight of mixture taken should be measured to the nearest mg or better.

8.3.5 The lower tube section should be filled to the flange with sample pretreatment solution.

8.3.6 Using the MDTA/D, 0.6 mL of the $H_2SO_4/MgSO_4$ releasing solution is added to the lower tube section. The upper and lower tube sections should be sealed together. **Note**: This sealing operation must be done as quickly as possible to minimize the potential loss of HCN. The sealed tubes are placed in the heating block.

8.3.7 The heating/distillation process is allowed to proceed for at least 25 min, but no longer than 35 min.

8.3.8 Using the MDTA/D, the lower portions of the tubes are disconnected from the upper section, and the lower section is discarded. The elapsed time between removing a tube from the heat block and parting the upper and lower sections should be minimized to prevent the potential backflow of distillate into the lower tube sections. Failure to minimize the time interval may result in low recoveries.

8.3.9 Each upper tube section should be held horizontally and rotated slowly to rinse the walls with the distillate. The tube section should be tapped 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 semipermeable membrane. The upper tube section is broken in the location pre-scored by the manufacturer. The distillate is transferred into a prelabeled 15-mL glass vial. Each half of the upper tube section should be rinsed with approximately 5 mL of 0.25 M NaOH (squeeze bottle), and the rinses are added to the glass vial.

8.3.10 The glass vials containing the distillates and rinses should be transferred out of the hot cell to the fume hood where the titrations are to be done.

8.4 Titrations

For each sample:

8.4.1 A clean 10-mL buret is filled with 0.0192 N $AgNO_3$.

8.4.2 While stirring the sample by means of magnetic stirrer and stirbar, three drops of Rhodanine indicator are added to the vial.

8.4.3 The sample is stirred and titrated to the first permanent appearance of a “salmon” color. The volume of $AgNO_3$ used should be recorded on the bench sheet.

9.0 Calculations

9.1 Since the titer of 0.0192 N $AgNO_3$ 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,

mg CN^- found = mL $AgNO_3$ used to titrate distillate - mL $AgNO_3$ used to titrate distillation blank

9.2 Let

W_1 = weight (g) sample taken (section 8.2.8)

W_2 = weight (g) pretreatment solution taken (section 8.2.8)

The weight fraction of the sample in the mixture $= W_1 / (W_1 + W_2) = X$

For samples and blank spikes,

$$\% \, CN^- = \frac{\text{mg } CN^- \text{ found} \bullet 100}{(W_s)(X) \bullet 1000}$$

W_s = weight (g) mixture taken (section 8.3.4)

9.3 Spiked Samples

$$\text{Spike recovery (\%)} = \frac{\left[V_{SP} - V_B - \frac{(W_S)(X)}{1000} \bullet \frac{A}{100} \right]}{W_{SP}} \bullet 100$$

where

V_{SP}	=	mL $AgNO_3$ used to titrate spiked sample distillates
V_B	=	mL $AgNO_3$ used to titrate blank distillate
W_{SP}	=	weight (mg) of CN^- in added spike
W_S	=	weight (g) mixture (Section 8.3.4) taken
A	=	% CN^- found for unspiked sample

10.0 Quality Control

10.1 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. Duplicates of all samples may be required by analytical protocol for single-shell tank wastes.

10.2 The preparation/method blank and control sample represent known performance indicators for this procedure and are used to evaluate the analytical session. Evidence of contamination in the blank and/or control sample recovery falling outside 80 to 120% warrants immediate corrective action.

10.3 Sample spike recoveries should fall within 80 to 120%.

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

10.5 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:

10.5.1 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 ±10% of the stated value.

10.5.2 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.

11.0 Method Performance

Method performance was established with a well characterized standard reference of sodium nickel ferrocyanide {$Na_2NiFe(CN)_6$} prepared by the laboratory. Extensive work with ion chromatography, Fourier transform infrared (FTIR), CHN analysis, and independent total cyanide analysis established this material as containing 34.5% CN^-. A secondary standard material, denoted as a "ferrocyanide waste simulant IF2R21," was also characterized by the method and used in the hot cell as a control sample.

11.1 Sodium nickel ferrocyanide determined by the method on three samples yielded 34.4% ± 0.2% (1 σ) found (34.5% expected) as cyanide.

11.2 Simulant IF2R21 yielded the following data (expressed as % CN^-) in six separate test runs: 6.12%, 6.17%, 6.05%, 6.12%, 6.07%, 6.05%. The average of the results was 6.10%, and the standard deviation was 0.05%.

11.3 Spike recovery using $Na_2NiFe(CN)_6$ as the spiking material and IF2R21 as the sample afforded an average recovery of 96% on four samples; the range was 93 to 99% of the expected value. The samples were spiked with an amount of cyanide equivalent to that

expected from the IF2R21 simulant so that the spiked samples contained approximately twice that found in the normal samples.

11.4 For hot-cell performance evaluation, IF2R21 was used as the control sample, and $Na_2NiFe(CN)_6$ was used as spike material. For the ferrocyanide tank core waste analyzed, the cyanide content was found to range from 0.3 to 1.0% CN^- by weight. Relative percent differences of duplicated runs were between 0.9% and 8.0% of the value obtained for the first run. Spike recovery from the blank matrix (pretreatment solution) yielded values of 89 to 103% of the expected value. Control samples were found to contain 88 to 99% of the expected added CN^-.

12.0 Further Reading

Lachat Instruments. 1989. *Micro-Dist Distillation System Reference and Methods Manual*. 6645 West Mill Road, Milwaukee, Wisconsin 53218.

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