

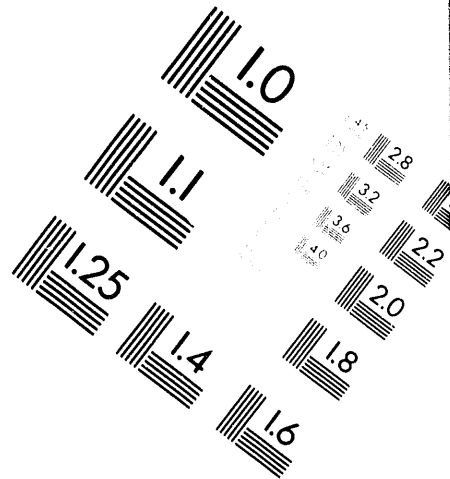
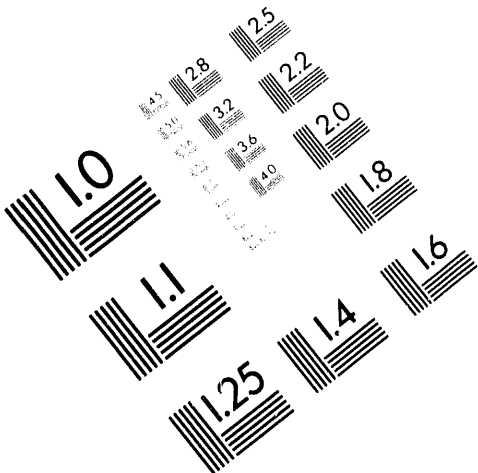


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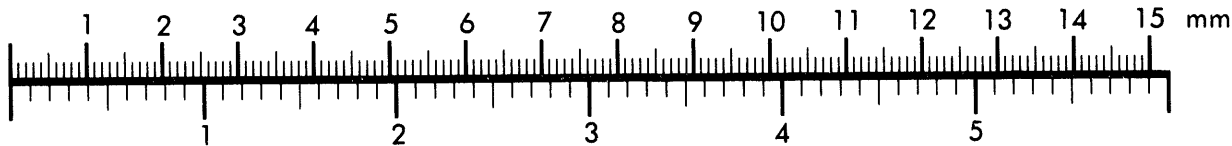
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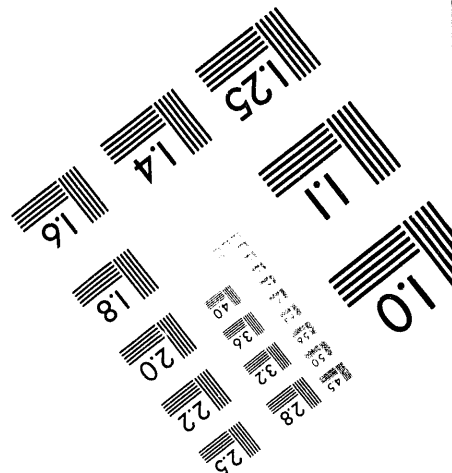
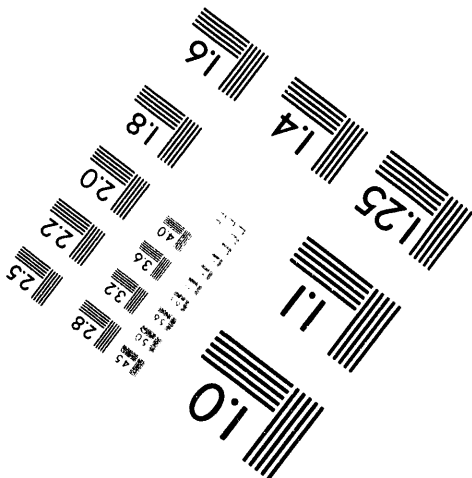
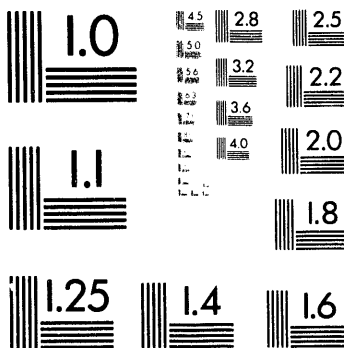
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# Determination of Total Cyanide in Hanford Site High-Level Wastes

W. I. Winters  
Westinghouse Hanford Company

K. H. Pool  
Pacific Northwest Laboratory

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**Westinghouse  
Hanford Company**

P.O. Box 1970  
Richland, Washington 99352

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DETERMINATION OF TOTAL CYANIDE IN HANFORD SITE  
HIGH-LEVEL WASTES

William I. Winters  
Westinghouse Hanford Company  
P.O. Box 1970  
Richland, Washington 99352  
(509) 373-1951

Karl H. Pool  
Pacific Northwest Laboratory  
P.O. Box 999  
Richland, Washington 99352  
(509) 376-1753

ABSTRACT

Nickel ferrocyanide compounds ( $\text{Na}_{2-x}\text{Cs}_x\text{NiFe}(\text{CN})_6$ ) were produced in a scavenging process to remove  $^{137}\text{Cs}$  from Hanford Site single-shell tank waste supernates. Methods for determining total cyanide in Hanford Site high-level wastes are needed for the evaluation of potential exothermic reactions between cyanide and oxidizers such as nitrate and for safe storage, processing, and management of the wastes in compliance with regulatory requirements. Hanford Site laboratory experience in determining cyanide in high-level wastes is summarized. Modifications were made to standard cyanide methods to permit improved handling of high-level waste samples and to eliminate interferences found in Hanford Site waste matrices. Interferences and associated procedure modifications caused by high nitrates/nitrite concentrations, insoluble nickel ferrocyanides, and organic complexants are described.

INTRODUCTION

Most Hanford Site high-level wastes were generated from the following chemical operations for processing spent nuclear fuel and for waste treatment:

- Bismuth phosphate fuel reprocessing
- Metal (uranium) recovery
- Reduction oxidation fuel reprocessing (REDOX)
- Plutonium-Uranium Reduction Extraction fuel reprocessing (PUREX)

- Fission product recovery.

The diversity and composition of wastes from these processes have created several problems in developing reliable cyanide methods.

During metal recovery processing in the 1950s, additional tank space was needed to support defense production activities. A nickel ferrocyanide carrier precipitation process was used to remove  $^{137}\text{Cs}$  from the supernate. This process resulted in the addition of an estimated 140 metric tons of ferrocyanides to the tanks. The potential for exothermic reactions between cyanide and nitrates in the wastes has made the determination of cyanide important to safety evaluations. Cyanide's toxicity and regulatory significance makes the determination of cyanide important to waste treatment and other waste management programs. Methods capable of measuring cyanide in trace and macroquantities in complex high-level wastes are needed to meet these requirements.

STANDARD METHODS FOR TOTAL  
CYANIDE ANALYSIS

Standard methods for determining total cyanide require the distillation of hydrogen cyanide (HCN) from a high acid ( $\text{H}_2\text{SO}_4$ ) matrix using glass distillation equipment (Figure 1). A catalyst ( $\text{MgCl}_2$ ) is used to assist the disassociation of metal cyanide complexes. The distilled hydrogen cyanide is trapped in dilute sodium hydroxide (NaOH). The concentration of cyanide in the trap solution may be measured using several techniques.

Glass distillation equipment has several disadvantages when applied to highly radioactive waste samples:

- Adaptability to hot cell/hood operations
- Decontamination/safety of glassware
- Sample throughput
- Large liquid waste volumes
- Cross contamination/blank control.

Microdistillation systems (Figure 1) minimize many of these problems. The Lachat® microdistillation system uses a two-piece plastic tube separated by a hydrophobic, porous membrane. The sample, catalyst and acid are added to the lower tube and quickly sealed to the upper tube which contains the NaOH trapping solution. The sample is digested in a heating block for 30 minutes which results in the HCN passing through the membrane into the upper tube containing the trapping solution. These systems have been adapted for use in hotcells and significantly improve the quality and productivity of the analysis. Even though microdistillation is the preferred method for analyzing radioactive samples, the method does have several disadvantages:

- Limited sample size (<5 mL)
- Containment (bubbling) of sample on acidification
- Flexibility for reagent addition/ distillation volume.

A comparison of several methods for measuring cyanide is provided in Table 1. Ion chromatography and spectrophotometric methods are the most sensitive techniques and applicable to many environmental applications. The argentimetric titration is the least sensitive but the most accurate. It is suitable for determining high concentrations of cyanide found in the Hanford Site ferrocyanide wastes. Selective ion electrodes are easy to use, have a large dynamic range

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but are generally not as reproducible as the other methods. Fourier transform infrared spectrometry (FTIR) provides cyanide speciation information and is applicable to higher cyanide concentrations. Over the last 6 years different combinations and variations of these methods have been used by the Hanford Site laboratories to determine total cyanide in Hanford Site high-level wastes.

#### CYANIDE MEASUREMENTS IN HIGH CONCENTRATIONS OF NITRATES AND NITRITES

Initial cyanide method development was for the support of the Hanford Site grout program. The composition of a typical grout feed and other tank wastes are summarized in Table 2. Cyanide was measured in several different matrices using the high acid distillation and the HACH® version of the pyrazolone colorimetric cyanide method. The results of these tests shown in Table 3, indicate that high concentrations of nitrate or nitrite would cause large negative interferences in determining cyanide. These data also indicated that high levels of aluminum could cause low results.

Initially, it was believed that the loss of cyanide was caused by the oxidation of cyanide by nitrate or nitrite in the high acid distillation matrix. This led to investigating a low acid distillation procedure. This method based on the work of Csikai and Barnard<sup>1</sup>, uses an acetate buffer to control the pH at 4.0 and ethylenediaminetetraacetic acid (EDTA) to disassociate metal complexes.

Sulfamic acid was added to eliminate interference from nitrite. Results of this method on a synthetic double-shell tank waste are summarized in Table 4. This method was effective in eliminating problems associated with nitrate, nitrite, and aluminum. Test results for ferrocyanide were all biased consistently high because of the hygroscopic ferrocyanide chemicals used to make the spikes.

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After developing this low acid distillation procedure, Pacific Northwest Laboratory (PNL) investigators discovered that the cause of the nitrate interference was a reaction between nitrate and chloride from the magnesium chloride catalyst. This reaction produces free chlorine which oxidizes cyanide to cyanogen chloride. Cyanogen chloride undergoes rapid hydrolysis in the NaOH trapping solution to produce cyanate which is not measured in the spectrophotometric method. The nitrate problem was eliminated by using magnesium sulfate in place of magnesium chloride.

#### CYANIDE MEASUREMENTS IN WASTE CONTAINING NICKEL FERROCYANIDES

The ferrocyanide scavenging process resulted in the precipitation of alkali nickel ferrocyanide salts,  $\text{Na}_2\text{xCs}_\text{x}\text{NiFe}(\text{CN})_6$ . Some typical compositions for these waste are provided in Table 2. These salts are not soluble in sulfuric acid; therefore, the standard high acid distillation methods were not quantitative for these type of wastes. Studies at PNL on synthetic nickel ferrocyanide salts indicated that the standard distillation procedure may not be complete even after 2 hours. Recent solubility studies at PNL have shown that the salts are soluble in sodium hydroxide (>0.1 M) and in EDTA solutions. This would indicate that the low acid procedure with EDTA should provide better results for nickel ferrocyanide wastes.

Ferrocyanide tank samples stored from the 1980s were used to evaluate the high acid, low acid and microdistillation (high acid) procedures. The results of these tests are summarized in Table 5. Reproducibility of the results was affected by the heterogeneity of the sample. However, the low acid method results with EDTA are higher than the high acid method results. The microdistillation tests were performed almost a year later. The higher results for microdistillation are partly from the sample drying out over that time. Because of the high concentrations of cyanide, small (0.01 to 0.05 g) aliquots of the waste were used in the microdistillation. These data and the results on a synthetic salt indicate that the high acid microdistillation system may be more effective for disassociating these compounds than the larger glass distillation systems. Other studies indicated that the distillation efficiency

may also be a function of the actual composition, structure and process history of these complex salts.

A method to solubilize nickel ferrocyanide wastes was needed to (1) eliminate the potential for low bias in results and (2) improve the representativeness of subsampling by using larger samples. Karl H. Pool (1994), from PNL, developed a method for dissolving these compounds using a mixture of acid form EDTA and ethylenediamine (EN). The EN acts as a buffer keeping the pH near 10 and the EDTA disassociates the nickel ferrocyanide complex. An aliquot of the dissolved sample is carried through the microdistillation method and the cyanide in the trap solution is determined by argentimetric titration. This dissolution method was tested on synthetic ferrocyanide wastes and on an actual cyanide waste (C-109 and C-112). Dissolved spikes of synthetic nickel ferrocyanides were added to C-109 and C-112 samples for procedure evaluation. The results of these tests are summarized in Table 6. WHC-2 and FeCN-36 are synthetic nickel ferrocyanides prepared from different process flowsheets. The completeness of dissolution was confirmed by x-ray diffraction as well as iron and nickel analyses<sup>2</sup>. This dissolution method can be used for both high-or low-level concentrations of cyanide waste to ensure complete dissolution of ferrocyanide containing solids.

#### CYANIDE MEASUREMENTS IN WASTE CONTAINING ORGANICS

Waste generated during the fission product recovery process contained large quantities of complexants such as EDTA, HEDTA, hydroxyacetic acid and citrates. These complexants have undergone hydrolysis and radiolysis to create a complex mixture of compounds. During the analysis of one of these types of wastes from tank SY-101, a potential interference to the cyanide method due to organics was discovered.

Because the cyanide results on samples from this tank were higher than expected, several tests on synthetic tank SY-101 waste with different organics but no cyanide were analyzed by the laboratory. These results, Table 7, show that several organics give false positive results. The higher values reported for the initial high acid spectrophotometric tests are the results

of using smaller sample sizes (0.05 g versus 0.5g). Synthetics with sugar added were exceptionally high. All tests used microdistillation before measuring the cyanide with either the pyridine-barbituric acid spectrophotometric (Spec.) method or by ion chromatography (IC). Tests were run in both the high acid and the EDTA/EN distillation medium.

Organics can cause either positive or negative results in the cyanide methods. Sugars and aldehydes will react with free cyanide to form cyanohydrins which decompose to nitriles. This reaction is relatively rapid at pH of 11 to 12. This negative effect can be eliminated by the addition of ethylenediamine which reduces the cyanohydrin back to form free cyanide. When nitrites and organics are present in the acid distillation system, nitration of the organics can occur which leads to the formation of free cyanide. One proposed mechanism for this reaction is that the organics are nitrated to form oximes which then decompose to give off hydrogen cyanide. Some of the organics reported<sup>3</sup> to undergo this type of reaction are shown in Table 8.

These organic-nitrite reactions can be eliminated by the addition of sulfamic acid which reduces nitrite to nitrogen gas. Samples of SY-101 were analyzed with and without the additions of sulfamic acid. The sample results with sulfamic acid (457  $\mu\text{g/g}$ ) were only 4% lower than samples analyzed without sulfamic acid (475  $\mu\text{g/g}$ ). Based on the results from Table 7, the magnitude of the organic interference could account for at most 20 to 25% of the cyanide observed in SY-101. This indicates that the cyanide found in the SY-101 waste was not caused by an organic interference.

Attempts to study the effect of organic-nitrite reactions on the cyanide method have been difficult because of poor reproducibility of the experiments. Other factors such as acid concentration, kinetics, temperature, reagent addition and synthetic composition could be important in these evaluations. The addition of sulfamic acid to remove nitrites is more difficult in the microdistillation system than the classical glass systems because of the small distillation volume and the need to seal the distillation tube immediately after

acidifying. Additional work is needed to ensure a reliable method for eliminating the organic-nitrite reactions in microdistillation systems is achieved.

#### ADDITIONAL CYANIDE MEASUREMENT STUDIES

Additional work has been done by the Hanford Site laboratories on the determination of cyanide speciation in Hanford Site wastes. FTIR and raman systems are being developed for these applications and for real-time measurements on extruded waste. This capability will permit a better understanding of how the cyanide is distributed in the waste and allow more knowledgeable selection of samples for further study. Table 9 shows a comparison of FTIR cyanide determinations and results from microdistillation. Methods for automating the final measurement of cyanide by flow injection analysis also are being evaluated.

#### ACKNOWLEDGEMENTS

Many individuals have contributed to the development of cyanide methods at the Hanford Site. We would like to express appreciation to Judy Watts, Ed Colvin, Jim Lachut, and Debbi Hiller of WHC and Sam Bryan, Jim Robbins, Evan Jenson and Vaughn Hoopes of PNL for their support and contributions to this document.

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Table 1. Cyanide Measurement Methods.

Method	Range	Comment
Spectrophotometric	1-20 $\mu\text{g CN}$	EPA method
Pyridine-pyrazolone	(50 mL) <sup>a</sup>	40-min color development
Spectrophotometric	1-20 $\mu\text{g CN}$	EPA method
Pyridine-barbituric acid	(50 mL) <sup>a</sup>	8-min. color development
Selective ion electrode	> 6 $\mu\text{g CN}$	Simple to perform
	(25 mL) <sup>a</sup>	Reproducibility not as good
Argentimetric titration	> 100 $\mu\text{g CN}$	Simple to perform
	(0.0192 N Ag) <sup>b</sup>	Good reproducibility
Ion chromatography	> 2 $\eta\text{g/mL CN}$	Best sensitivity/selectivity
	(50 $\mu\text{L}$ ) <sup>c</sup>	Amperometric detection
Fourier transform	> 10 $\mu\text{g CN/mL}$	Cyanide speciation
Infrared spectroscopy		Expensive instrumentation

<sup>a</sup>Final measurement volume

<sup>b</sup>Titrant normality: 1 mL = 1 mg CN

<sup>c</sup>Injection volume

Table 2. Composition of Typical Hanford Wastes.

	Ferrocyanide Sludge			
	Grout feed ( $\mu\text{g/mL}$ )	TY Farm ( $\mu\text{g/g}$ )	C Farm ( $\mu\text{g/g}$ )	SY-101 ( $\mu\text{g/g}$ )
Na	1.0E5	1.1E5	1.1E5	1.1E5
Al	1.2E4	4.2E3	3.0E4	3.9E4
Fe	1.5E1	2.4E4	2.3E4	1.2E3
Ni		2.5E3	1.8E4	2.7E2
OH/pH	2.7E4	10.9	10.3	1.7E4
NO <sub>3</sub> <sup>-</sup>	7.8E4	1.6E5	8.0E4	1.3E5
NO <sub>2</sub> <sup>-</sup>	3.4E4	8.1E3	6.2E4	8.5E4
TOC	2.3E3	1.5E3	3.0E3	2.0E4



Table 3. Effect of High Nitrate/Nitrite Matrix on Standard Cyanide Method (HACH Reagents).

Test	Cyanide form <sup>a</sup>	Matrix	Result (% recovery)
1	NaCN	NaOH - 1.0 M	81
2	NaCN	NaOH - 1.0 M	55
	K <sub>3</sub> Fe(CN) <sub>6</sub>	NaAlO <sub>2</sub> - 0.5 M	58
3	NaCN	NaOH - 1.0 M NaNO <sub>3</sub> - 1.0 M	0
4	NaCN	NaOH - 1.0 M NaNO <sub>2</sub> - 0.5 M	0
5	NaCN	Al(NO <sub>3</sub> ) <sub>3</sub> - 0.5 M	0
6	K <sub>4</sub> Fe(CN) <sub>6</sub>	NaOH - 1.0 M	0
		NaNO <sub>3</sub> - 1.0 M	
7	K <sub>3</sub> Fe(CN) <sub>6</sub>	NaOH - 1.0 M	116

<sup>a</sup>All tests performed at the 10 µg CN level.

Table 4. Performance of Low Acid Cyanide Distillation Procedure (HACH Reagents).

Test	Cyanide form <sup>a</sup>	Matrix	Result (% recovery)
1	NaCN	NaOH - 0.25 M	104
2	NaCN	NaOH - 0.25 M	105
		NaNO <sub>3</sub> - 0.5 M	
3	NaCN	NaOH - 0.25 M	99
		NaNO <sub>3</sub> - 0.5 M	
		Al(NO <sub>3</sub> ) <sub>3</sub> - 0.1 M	
4	NaCN	NaOH - 1.0 M	97
		NaAlO <sub>2</sub> - 0.5 M	
		NaNO <sub>3</sub> - 5.0 M	
		NaNO <sub>2</sub> - 0.5 M	
5	K <sub>3</sub> Fe(CN) <sub>6</sub>	Same as Test 4	116

<sup>a</sup>All tests performed at the 10 µg CN level.

Table 5. Comparison of Distillation Methods for Nickel Ferrocyanide Salts (Pyridine-Barbituric Acid).

Sample	Low acid (µg/g)	High acid (µg/g)	Microdistillation (µg/g)
TY-101	3580 (± 7%)	2173	4284 (± 11%)
TY-103	2508-3034	1275 (± 5%)	5185
Cs <sub>2</sub> NiFe(CN) <sub>6</sub>			88 ± 19% <sup>a</sup>

<sup>a</sup>Percent recovery of stoichiometric cyanide in synthetic Cs<sub>2</sub>NiFe(CN)<sub>6</sub>.

WHC-SA-2433-FP

Table 6. Cyanide Results from Distillation of EDTA/EN Dissolved Nickel Ferrocyanides (Argentimetric Titration).

Sample	EDTA/EN (wt %)	No dissolution (wt %)	Spike recovery (%)
C-112	0.45 ( $\pm 0.06$ )	0.18	87.4 $\pm$ 4.2
WHC-2	95 and 89*		
FeCN-36	96*	69 and 64*	

\*Percent recovery of stoichiometric cyanide in synthetic nickel ferrocyanide wastes.

Table 7. Effect of Organics on Cyanide Measurements in Synthetic Tank SY-101 Wastes.

Organic	High acid spec. ( $\mu\text{g/g}$ )	High acid spec. ( $\mu\text{g/g}$ )	EDTA/EN spec. ( $\mu\text{g/g}$ )	High acid IC ( $\mu\text{g/g}$ )	EDTA/EN IC ( $\mu\text{g/g}$ )
Oxalate	16	3.5	7.2	11.5	11
IDA	22	3.5	8.5	12.4	4.9
EDTA	25	10.9		24	
Sucrose	102	13.9	7.6	25	12
None		3.2	5.7	9.9	12.5

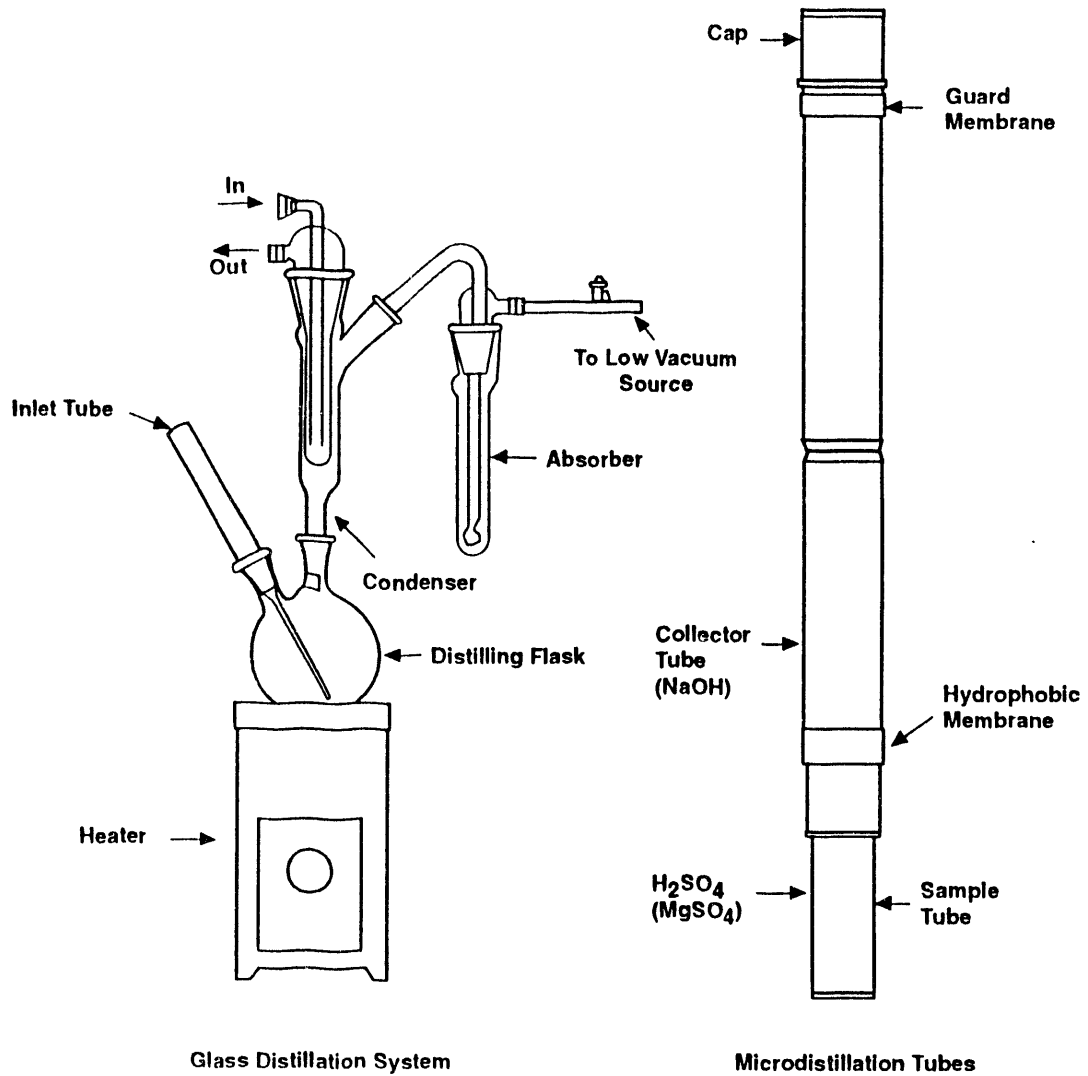
Table 8. Organics Reported to React with Nitrite to Form Cyanide.

Glycine	Ascorbic acid	Aliphatic amines
Aromatic amines	Methyl isobutyl ketone	Phenol
Catechol	Ethyl acetoacetate	Oxalacetic acid
2,4,4-trimethyl pentenes	Aniline	Thiocyanate
	Amino acids	Formaldehyde
	Sugars	

Table 9. Comparison of FTIR and EDTA/EN Microdistillation Cyanide Methods.

Material	FTIR (wt %)	Microdistillation (wt %)
FEEN-36	36.5	36.3
IN Farm	12.05	11.92
U Plant (Rev.8)	4.32	4.28
U Plant (CJ-102-B)	1.16	1.16

Figure 1. Microdistillation Systems.



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