RLAB Method

No. 3135.2I

CYANIDE, TOTAL AND AMENABLE IN AQUEOUS AND SOIL SAMPLES AUTOMATED COLORIMETRIC WITH MANUAL DIGESTION

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by

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A. SCOPE AND APPLICATION

1. This method is applicable to the determination of cyanide in drinking, ground, and surface waters, domestic and industrial waste waters, sediments and solid waste. This method detects inorganic cyanides that are present as either simple soluble salts or complex radicals. It is used to determine values for both total cyanide and cyanide amenable to chlorination. It is not intended to determine if a waste is hazardous by the characteristic of reactivity.

2. The applicable range is 0.003 to 0.500 mg/L CN in the distillate. This range can be expanded by sample dilution, either by using less sample for distillation or diluting the distillate.

3. This procedure is based on Test Methods for Evaluating Solid Waste (SW-846, 3rd edition) 9012B and 9010C, EMSLC 335.4, and Lachat QuickChem Method 10-204-00-1-A.

B. SUMMARY OF METHOD

1. The cyanide is released by refluxing the sample with strong acid. The HCN is distilled and collected in an absorber-scrubber containing sodium hydroxide (NaOH) solution. The cyanide ion in the absorbing solution is then determined by automated colorimetry.

2. In the colorimetric measurement, the cyanide is converted to cyanogen chloride (CNCl) by reaction with Chloramine-t at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-barbituric acid reagent. The red colored complex is measured at 570 nm. The concentration of NaOH must be the same in the standards, the scrubber solutions, and any dilutions of the original scrubber solution to obtain colors of comparable intensity.

3. Cyanide amenable to chlorination is determined by calculating the difference between total cyanide and cyanide remaining after chlorination.

C. DEFINITIONS

1. **Laboratory Control Samples (LCS)** – A control matrix (blank) which has been spiked with the method analyte obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials. For soils, this can be blank sand in reagent water with externally prepared test material added.

2. **Matrix Spike (MS) and Matrix Spike Duplicate (MSD)** – An aliquot of an environmental sample to which known quantities of the method analyte is added in the laboratory. The MS and MSD are analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentration of the analyte in the sample matrix must be determined in a separate aliquot and the measured values in the MS and MSD corrected for background concentrations.

3. **Method Blank (MB)** – An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, and reagents that are used with other samples. The MB is used to determine if the method analyte is present in the laboratory environment, the reagents, or the apparatus. For soils, this can be blank sand in reagent water.

4. **Method Detection Limit (MDL)** – The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

5. **Reporting Limit Check (RLC) Sample** – A sample prepared at 1-2 times the reporting limit (RL) with results falling within the established acceptance limits for RLC samples. Analysis of this sample verifies the validity of the RL.

D. INTERFERENCES

1. Interferences are eliminated or reduced by procedures described in Sections K.2.b, K.2.c, and K.2.d.

2. Sulfides adversely affect the colorimetric procedures. Test samples with lead acetate paper. A darkening of the paper signifies the presence of sulfide which can be removed by the addition of cadmium carbonate powder followed immediately by filtration. (see Ref. 3, Page 4)

3. False positives may be produced by samples that contain nitrate and/or nitrite greater than 10 PPM. During the distillation, nitrate and nitrite form nitrous acid which reacts with some organic compounds to form oximes. These compounds decompose under test conditions to generate HCN. The possible interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid just before distillation (Section K.2.c).

4. Oxidizing agents such as chlorine, oxygen, and ozone decompose most cyanides. Chlorine interference is eliminated by pre-treatment with ascorbic acid (Section K.2.d).

E. SAFETY

Hydrogen cyanide is highly toxic if inhaled. All preparations, chlorinations, and neutralizations should be conducted in a laboratory exhaust hood so that any HCN gas that may escape is safely vented.

F. EQUIPMENT AND SUPPLIES

1. Midi Distillation Apparatus: As shown in Fig. 2
2. MicroDist Distillation Device: As shown in Fig. 3
    a. Collector Tubes
    b. Collector Tube Caps
    c. Collector Tube Membranes
3. Potassium Iodide-Starch Test Paper or chlorine test kit.
4. Nitrate-Nitrite Test Paper
5. Lead-Acetate Test Paper
6. Lachat QuickChem 8500 system consisting of the following components:
    a. Sampler
    b. Multichannel Proportioning Pump
    c. Reaction Unit or Manifold
    d. Colorimetric Detector with Flowcell and 570 nm Filter.
    e. Computer with Windows and Omnion software.
    f. LaserJet Printer
7. Sample Cups: 10 mL
8. Charcoal Boiling Chips

9. Magnetic Stirring Device

10. Recirculating Chiller or recirculating chilled water

11. pH Test Strips

12. Filter Paper, rapid flow.

13. 1 Liter vacuum flask.

14. Vortex mixer.

15. Disposable pipets – varying volumes.

G. REAGENTS AND STANDARDS

Reagent grade chemicals must be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

1. DI water: Deionized Water. Can be degassed on a vacuum.

2. 0.25 N NaOH Absorber Solution: Dissolve 10 g of Sodium Hydroxide in approximately 800 mL DI water and dilute to 1 liter with DI water. This is also the Sampler Wash solution.

3. 0.333 N NaOH MicroDist Trapping Solution: Dissolve 10 g of Sodium Hydroxide in approximately 500 mL DI water and dilute to 750 mL with DI water. This solution is good for 1 year.

4. 0.025 N NaOH: Dilute 100 mL of 0.25 N NaOH (Section G.4) to 1 liter with DI water.

5. Stock Phosphate buffer: Dissolve 97 g of potassium phosphate monobasic anhydrous (KH_2PO_4) in 800 mL of DI water and dilute to 1 liter. Refrigerate when not in use. This solution is good for 6 months.

6. Chloramine-t: Dissolve 0.4 g of Chloramine-t in 100 mL of degassed DI water. Prepare fresh weekly.

7. Pyridine Barbituric Acid Reagent: Place 7.5 g of barbituric acid in a 500-mL dark bottle. Wash the sides of the bottle with about 100 mL of degassed DI water. While stirring, add 37.5 mL of pyridine. Add 15 mL of 1:1 HCl and mix. Dilute

to 500 mL with degassed DI water. Store at 4°C. This reagent is stable for 6 months.

CAUTION: **Prepare this solution in a hood. Barbituric acid is an acute irritant and is toxic!**

8. Stock Cyanide: 1000 PPM standard purchased from Standards supplier. Store in the refrigerator. Replace when expiration date is exceeded.

9. Intermediate Standard and Matrix Spiking Solution: 10 PPM. Pipet 1 mL of stock cyanide (Section G.8.) into 100 mL volumetric flask and dilute to mark with 0.25 N NaOH (Section G.2). Use to make working standards and as a spiking solution. Store in the refrigerator. This standard is good for three months.

10. Working CN Standards: Make a series of working standards covering the entire range. Make all working standards in 0.25 N NaOH (Section G.2) and store in the refrigerator. Standards are good for 3 months.

Concentration	Standard Solution (mL/100 mL 0.25 N NaOH)
0.500 mg/L	5 mL of intermediate (Section G.10)
0.200 mg/L	2 mL of intermediate (Section G.10)
0.100 mg/L	1 mL of intermediate (Section G.10)
0.050 mg/L	0.5 mL of intermediate (Section G.10)
0.010 mg/L	10 mL of 0.10 mg/L standard
0.003 mg/L	3 mL of 0.10 mg/L standard

11. Ascorbic Acid Crystals

12. Powdered Cadmium Carbonate: $CdCO_3$

13. Sulfamic Acid Solution: Dissolve 20 g of sulfamic acid in DI water. Dilute to 500 mL. Refrigerate. This solution is good for 1 year.

14. Sulfuric Acid, 1:1: Slowly add 500 mL of concentrated H_2SO_4 to 500 mL of DI water.

CAUTION: This is an exothermic reaction. **SOLUTION IS HOT!**

15. 7.11 M Sulfuric Acid/0.79 M Magnesium Chloride MicroDist Releasing Agent: Dissolve 32.2 g $MgCL_2 \cdot 6H_2O$ in 100 mL DI water. Slowly add 139 g concentrated sulfuric acid. Dilute to 200 mL with DI water. This solution is good for at least 1 year. Do not refrigerate.

CAUTION: This is an exothermic reaction. **SOLUTION IS HOT!**

16. Magnesium Chloride Solution: Weigh 510 g of $MgCL_2 \cdot 6H_2O$ into a 1000 mL flask, dissolve, and dilute to 1 L with DI water. This solution is good for at least 1 year. Do not refrigerate.

17. Calcium Hypochlorite Solution: Reagent grade 5% hypochlorite.

H. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

1. Collect aqueous samples in plastic or glass bottles of 1-L size. Collect soil samples in wide mouth glass jars.

2. Oxidizing agents such as chlorine decompose most cyanides. To determine whether oxidizing agents are present, test a drop of the aqueous sample with acidified potassium iodide (KI)-starch test paper at the time the sample is collected; a blue color indicates the need for treatment. Add ascorbic acid a few crystals at a time until a drop of sample produces no color on the indicator. Then add an additional 0.6 gm of ascorbic acid for each liter of water prior to preserving with sodium hydroxide.

3. Preserve aqueous samples with sodium hydroxide pellets to sample pH $\geq$12 at the time of collection.

4. Refrigerate samples at 4°C and analyze as soon as possible after collection. The maximum holding time is 14 days for aqueous samples.

I. QUALITY CONTROL

1. A Laboratory Control Sample (LCS) is run daily and for every 20 unknown samples. The LCS is prepared from a source independent of the standards. It is carried through the same distillation procedure as the unknowns. The LCS is reported in the laboratory data system. If the LCS falls outside the reporting range (Attachment 2 or acceptance limits supplied with the control sample), the LCS must be remade and redistilled along with the samples and reanalyzed.

2. A Matrix Spike (MS) is run daily for each series of 20 samples or less. For distillation by Midi, to 50 mL of sample (soil sample in 50 mL of 0.025N NaOH), add 500 µL of 10 PPM cyanide spiking solution (Section G.9) to achieve a spike of 0.100 PPM CN. For a MicroDist distillation, add 60 µL of 10 PPM cyanide spiking solution (Section G.9) to achieve a spike of 0.100 PPM CN. Adjust the amount of spiking solution to achieve the desired amount of spike. A Matrix Spike Duplicate (MSD) is prepared in the same way. Carry spiked samples through the same distillation procedure as the samples. If the MS or MSD fall outside the reporting range, redistill the samples and spikes and reanalyze, if time

is available. If the recovery is still outside the range, see SOP 2410.10 for data qualification.

3. Analyze a method blank with each series of 20 samples or less. The method blank is 0.025 N NAOH (Section G.5). Carry the blank through the same distillation procedure as the samples. If blanks are not less then the MDL (Attachment 2), contamination should be suspected and all samples and blanks should be redistilled and reanalyzed, if time is available. If the recovery is still above the MDL, see SOP2410.10 for data qualification.

4. The MDL is established according to 40 CFR Pt. 136 App. B by analyzing 7-8 replicates of a low standard, computing the standard deviation, and multiplying the standard deviation by 3.14267 (the *t* value for 7 replicates) or by 2.99795 (the *t* value for 8 replicates).

5. The MDL must be initially verified by qualitative identification in a QC sample at a concentration of 2-3 times the MDL. If the concentration of the initial MDL verification check samples is detected at any level above the concentration of the concurrently run blank, then the MDL is to be considered valid.

J. CALIBRATION AND STANDARDIZATION

1. A series of five (or six when using the 0.5 PPM) standards are run at the beginning of the analysis to establish a standard curve. The Omnion software uses a first order equation for the standard curve. A second order curve can also be used to obtain the best fit. A correlation coefficient of 0.995 or greater is acceptable.

2. A mid-range standard (i.e., 0.100 or 0.200) is designated CCV for Continuing Calibration Verification. The CCV should be run after the standard curve is established, after every 20 samples, and again at the end of analysis. It should fall within 90% to 110% recovery. If not, remake all standards and rerun analysis.

K. PROCEDURE

1. Pretreatment for Cyanides Amenable to Chlorination

   a. Two sample aliquots are required to determine cyanides amenable to chlorination.

      For aqueous samples: to one 50-mL aliquot, or to a volume diluted to 50 mL, add calcium hypochlorite solution (Section G.15) dropwise while

agitating and maintaining the pH between 11 and 12 with sodium hydroxide (Section G.2).

For soil samples: for each aliquot, accurately weigh to two decimal places 1 to 3 grams of sample. Place one aliquot in a digestion tube, add 0.025N NaOH to the 50 mL line and mix on a vortex mixer. Place the second aliquot in a 250 mL beaker, add 50 mL of 0.025N NaOH and stir on a magnetic stirrer in the hood, add calcium hypochlorite solution (G.15) dropwise while agitating and maintaining the pH between 11 and 12 with sodium hydroxide (Section G.2).

CAUTION: The initial reaction product of alkaline chlorination is the very toxic gas cyanogen chloride; this reaction must be performed in a hood. For convenience, the sample may be agitated in a 250-mL beaker by means of a magnetic stirring device.

b. Test for residual chlorine with KI-starch paper (Section F.2) and maintain this excess for one hour while continuing agitation. A distinct blue color on the test paper indicates a sufficient chlorine level. If necessary, add additional hypochlorite solution.

c. After one hour, add 0.1 gm portions of ascorbic acid until KI-starch paper shows no residual chlorine. Add an additional 0.1 gm of ascorbic acid to ensure the presence of excess reducing agent.

d. Transfer quantitatively to digestion tube. Distill and test for total cyanide in both the chlorinated and unchlorinated aliquots. The difference of total cyanide in the unchlorinated and chlorinated aliquots is the cyanide amenable to chlorination.

2. Manual Distillation

There are two distillation units available for manual distillation. The Lachat MicroDist is a micro-distillation device that can be used for the distillation of drinking water, ground and surface water, and domestic and industrial wastewater samples. The Midi-distillation apparatus can be used for the water samples listed above as well as sediments and solid waste samples.

a. Distillation using the MicroDist (Ref. 6)

1) Sample Preparation

a) Use pH test strips to check aqueous samples for proper preservation. The pH should be greater than or equal to 12.

b) Use lead acetate paper to check the sample for the presence of sulfide. A positive test is indicated by a black color on the paper. If positive, treat 25 mL more of the stabilized sample (pH $\geq$ 12) than required for the determination with powdered cadmium carbonate (this can be done in a beaker). Yellow cadmium sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate paper. Filter the solution through a dry filter paper into a dry beaker, and from the filtrate, measure the sample to be used for distillation.

c) Check for the presence of NO_3/NO_2 with test strips. If >10 ppm NO_3/NO_2, add 600 uL of sulfamic acid (G.13) to the 6 mL sample aliquot prior to distillation.

d) Use potassium iodide paper to check the sample for the presence of chlorine. A positive test is indicated by a dark blue color on the paper. Treat positive samples with ascorbic acid (Section H.2).

2) Activate the MicroDist heating block by setting the temperature to 120°C. The block will take about 40 minutes to warm up.

3) Label the open end of each collector tube with the ASR and sample number. Add 4.5 mL of the MicroDist trapping solution (G.3) from the dispenser bottle. Center the membrane on the open end of the tube and press the cap in place. Place in the white collector tube rack with the **M** end up. Repeat for the appropriate number of samples (up to 17 samples per set plus 4 QC samples).

4) Using a disposable or large volume adjustable pipet, pipet 6 mL of sample into the sample tube.

5) Place the sample tube in the base of the press. Add 750 uL of the MicroDist releasing agent (G.15). Place the **D** end of the collector

tube over the sample tube with the top seated in the press cup. Use the press to seal the tubes together until the stop ring on the sample tube hits the **D** end of the collector tube. Place sealed tubes back in the collector tube rack.

6) Repeat Sections K.2.a.4 through K.2.a.5 for each sample to be run, including the quality control samples.

7) Using the heat resistant gloves or a pair of insulated fiber gloves, quickly place each sample into the block, loading the back row first. The tubes may need to be twisted to set them firmly in the heating block. The entire sample tube and the **D** end of the collector tube fit into the block. The collector stop ring must touch the block.

8) Set the timer for 30 minutes.

9) **During sample removal, use heat resistant gloves or a pair of insulated fiber gloves.** Remove the first tube from the block and place the base over the beaker. Wrap your hand over the sample tube with the seam to the collector tube between your index and middle finger (or between your middle and ring finger). Using a downward, twisting motion, immediately pull of the sample tube and drop it quickly into the beaker. Invert the collector tube (with the **D** end up) and place in the collector tube rack. Repeat for each collector tube.

Note: The sample tube must be removed within 4 seconds of removal from the block or suck-back of the sample will occur.

After removal of all tubes, the beaker containing the sample waste and sample tubes may be emptied down the sink drain. Flush with copious amounts of water as waste is acidic.

10) Seal the **D** end of the tube with Parafilm and allow the tubes to cool for at least 10 minutes.

11) For each tube, hold the tube horizontally and rinse its walls with the distillate in order to homogenize. Gather all droplets clinging to the tube walls into the bulk of the distillate.

12) With the **D** end still up, break the collector tube in half. Hold the tube above and below (not over) the seam and break the tube with a back and forth motion. Discard the **D** end.

13) In the remaining **M** end of the collector tube, dilute to the 6.0 mL mark with DI water. This results in the original sample volume, but now in 0.25 N NaOH.

14) Shake the tube with a gentle whipping motion to mix in the diluent water. However, do not invert.

15) Seal the **M** end of the collector tube using Parafilm and store at 4°C until analysis.

b. Distillation using the Midi-distillation Apparatus (Ref. 5)

1) Sample Preparation

a) Use pH test strips to check aqueous samples for proper preservation. The pH should be greater than or equal to 12. For soils, accurately weigh to two decimal places 1 to 3 grams of sample and place in digestion tube. (For sandy soils, use greater amount. For clayish soil or hazardous wastes, use lesser amount.) Add 50 mL 0.025N NaOH. Mix on vortex mixer until soil is uniformly suspended. Use pH test strips to check for proper pH. The pH should be greater than or equal to 12.

b) Use lead acetate paper to check the sample for the presence of sulfide. A positive test is indicated by a black color on the paper. If positive, treat 25 mL more of the stabilized sample (pH $\geq$ 12) than required for the determination with powdered cadmium carbonate (this can be done in a beaker). Yellow cadmium sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate paper. Filter the solution through a dry filter paper into a dry beaker, and from the filtrate, measure the sample to be used for distillation.

c) Check for the presence of NO_3/NO_2 with test strips. If >10 ppm NO_3/NO_2, treat with sulfamic acid prior to distillation.

d) Use potassium iodide paper to check the sample for the presence of chlorine. A positive test is indicated by a dark blue color on the paper. Treat positive samples with ascorbic acid (Section H.2).

2) Place 50 mL of aqueous sample, or an aliquot diluted to 50 mL, into the digestion reflux tube along with 3 to 4 boiling chips. For soils, add 3 to 4 boiling chips to the digestion reflux tube with the weighed and mixed sample. Place the tube into the heating block hole at the back of the distillation unit (see Fig. 2). For matrix spikes, add 500 μL (or predetermined amount) of the spiking solution (G.9) to the sample in the reflux tube.

3) Measure 50 mL of absorber solution (Section G.2) into the absorber tube and place the tube into the hole in front of the distillation unit.

4) Place a reflux impinger (gas outlet facing to the rear of the unit) into the reflux sample tube. Place an absorber impinger (gas inlet facing to the rear) into the absorber tube. Connect the absorber impinger gas inlet tube to the reflux impinger gas outlet tube.

5) Connect the absorber impinger vacuum tube to the valve tube.

6) Place a cold finger condenser, with water ports facing to the rear, into the reflux impinger tube. Turn on the cooling water.

7) Repeat Sections K.2.b.1 through K.2.b.5 for each sample to be run, including the quality control samples.

8) Vacuum valves should be off. Check to make sure an excess gas trap is connected to the vacuum line. Turn on the vacuum to the unit and adjust each valve to give a flow of 2-3 bubbles/second in each reflux tube. Allow the vacuum to draw for five minutes.

9) For samples testing >10 for NO_3/NO_2 (Section K.3.b.1.c), add 5-mL sulfamic acid solution (Section G.13) through the air inlet tube. Rinse with DI water. Allow solutions to mix for three minutes.

10) Slowly add 5-mL 1:1 H_2SO_4 (Section G.14) through the air inlet tube. Rinse with DI water. Allow to mix for three minutes. Add 2-mL magnesium chloride (Section G.16) through the air inlet

tube. Rinse with DI water.

11) Turn on the heating unit, and turn on the timer for 105 minutes. This timing allows 15 minutes heat-up time and 90 minutes of reflux time. The heating unit is preset to 125°C. The unit will turn off automatically. Check the air flow and adjust as necessary.

12) After 105 minutes, allow the apparatus to cool for 15 minutes before turning off the cooling water and vacuum. Close each valve and disconnect the absorber gas inlet tube from the reflux impinger. Remove the absorber impinger. Seal the absorber tube and store at 4°C until analysis.

13) Remove the glassware and clean with DI water. If necessary, use glassware cleaner and a brush. If clogged, clean the absorber impinger Frit with 10% hydrochloric acid. **Never let the frit soak in acid longer than 20 minutes.** Rinse with distilled water at least three times after the acid treatment.

3. Analysis

a. Set up the cartridge as described in Lachat's QuickChem Method 10-204-00-1-A (section 17.3) in a well-ventilated area. Turn power on to all units. Begin pump flow with sampler wash line in DI.

b. Place all reagent lines in the appropriate reagents and the sample line in the sample wash receptacle. Allow reagents to flow through the system until a stable baseline is achieved.

c. On the computer, click on the Omnion icon to call up the operating software. Select the cyanide method. Build the sample table using the standards and check samples listed in the method table.

d. Load the sampler tray with calibrants, blanks, samples, and QC in the same order as listed in the sample table.

e. On the computer, select the **Start** button to begin analysis. QC samples listed in the method table will end a run if recovery is outside the defined range.

f. When analysis is complete, print out the Custom Report. This report contains all the calibration and sample information.

g. After analysis is complete, switch reagent lines to DI water. After 5 minutes, remove lines from DI and pump air through the lines to clean and dry the system. Turn off pump and release platens.

L. DATA ANALYSIS AND CALCULATIONS

1. Data Analysis

a. Five (or six if using 0.5 PPM) standards covering the range of analysis are defined in the method table. These same standards are entered into the sample table.

b. Computer software calculates the calibration line as standards are analyzed.

c. Sample concentrations are converted from raw voltages to mg/L CN.

2. Calculations

a. The computer and software generate a report which prints CN values in mg/L. CN-A is calculated on a spreadsheet (see Fig.3).

b. If the original samples were diluted, dilution parameters are entered in the sample table. Printed values are the final concentration values in mg/L.

c. CN-A is calculated on a spreadsheet (see Att. 3). Calculate the cyanide amenable to chlorination (CN-A) as follows:

$$\text{mg/L CN-A} = U - C$$

Where:

U = mg/L total cyanide in unchlorinated aliquot
C = mg/L total cyanide in chlorinated aliquot

d. Final results for soils are calculated on a spreadsheet and based on dry weight. (Att..4)

$$\frac{(\text{mg/L CN or CN-A})\ (0.05\text{L})}{(\text{wet wt. in Kg})\ (\%\ \text{solid})} = \text{mg/Kg CN (or CN-A)}$$

e. Data are reported to three significant figures or three decimal places.

M. METHOD PERFORMANCE

1. Control limits are listed in Attachment 1 and are available in R7LIMS. These limits were calculated using the old Alpkem instrument and will only be used as interim limits. When enough data from the Lachat instrument is available, the limits will be recalculated and the method updated.

2. See Attachment 2 for method detection limits.

3. According to NELAC, the validity of the reporting limit (RL) must be verified annually by the analysis of a reporting limit check (RLC) sample, which is prepared at 1-2 times the RL with results falling within the established acceptance limits for RLC samples. The LCS control limits listed in Attachment 1 will be used as interim limits until enough data is obtained to calculate control limits.

N. POLLUTION PREVENTION

1. Hydrogen cyanide is highly toxic if inhaled. All preparations, chlorinations, and neutralizations should be conducted in a laboratory exhaust hood so that any HCN gas that may escape is safely vented.

2. The midi-distillation unit uses only 10% of the acid required in the maxi-distillations.

O. WASTE MANAGEMENT

1. Original samples are held until analysis is completed. Disposal depends on the identification of hazardous constituents and their concentration (see SOP 2440.1, “Hazardous Waste Management Plan for Region 7 Science and Technology Center”).

2. After analysis is complete, collect all distillate in a large beaker. In a hood, chlorinate the distillates from the manual distillation procedure to destroy the cyanide and neutralize with H_2SO_4 to pH 5-9. Transfer to the city sewer.

P. REFERENCES

1. Test Methods for Evaluating Solid Waste, SW-846, Method 9012B.

2. Test Methods for Evaluating Solid Waste, SW-846, Method 9010C.

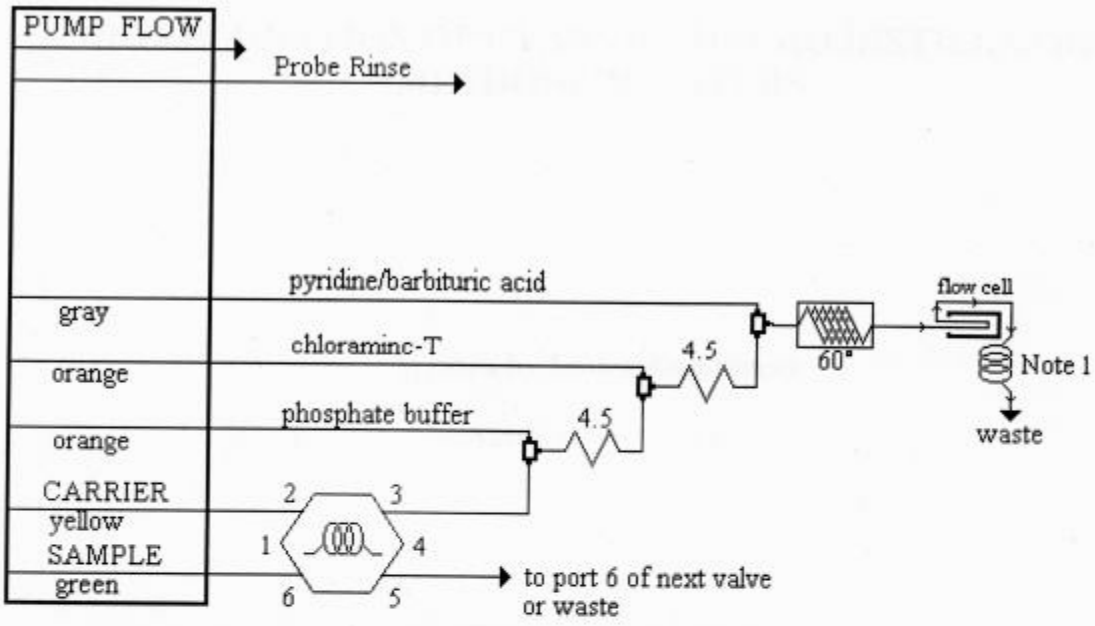
3. Methods for Chemical Analysis of Water and Wastes, EMSLC 335.4, EPA/600/R-93/100, Aug. 1993.

4. Lachat QuickChem Method 10-204-00-1-A, Omnion Software, Rev. Nov. 1, 2001.

5. EnviroPrep 1010 Midi Distillation Unit Operation Manual, Jan. 1994, Appendix A.

6. Lachat QuickChem Method 10-204-00-1-X, Omnion Software, Rev. Nov. 29, 2007.

Figure 1
CYANIDE MANIFOLD DIAGRAM



Carrier: 0.25 M sodium hydroxide solution (Reagent 1).
Manifold Tubing: 0.8 mm (0.032 in) i.d. This is 5.2 µL/cm.
AE Sample Loop: 45.5 cm x 0.8 mm i.d.
QC8000 Sample Loop: 50 cm x 0.8 mm i.d.
Interference Filter: 570 nm

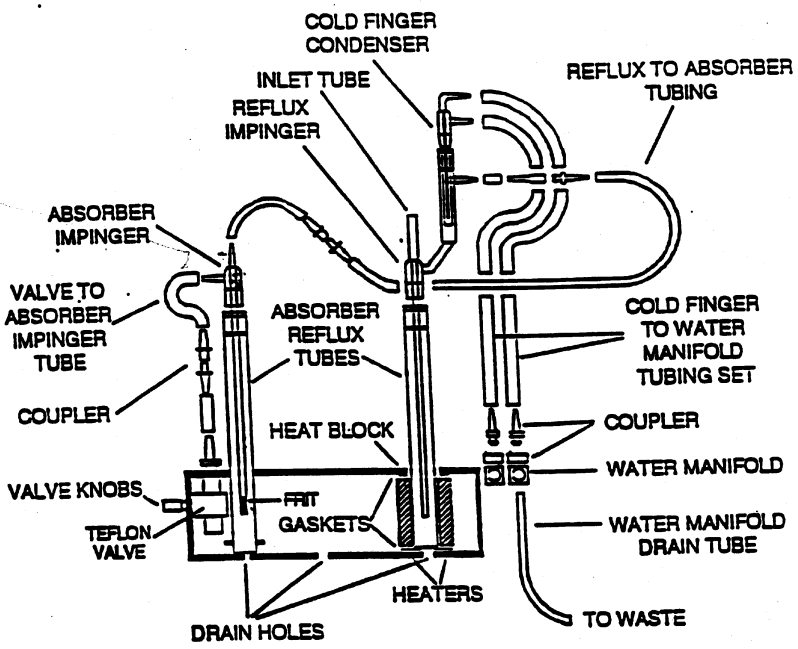
Apparatus: An injection valve, a 10 mm path length flow cell, and a colorimetric detector module is required. The  shows 650 cm of tubing wrapped around the heater block at the specified temperature.

4.5: 70 cm of tubing on a 4.5 cm coil support

Note 1: 200 cm backpressure loop, 0.52 mm i.d.

Figure 2
MIDI-DISTILLATION APPARATUS

2.4 Parts Diagram



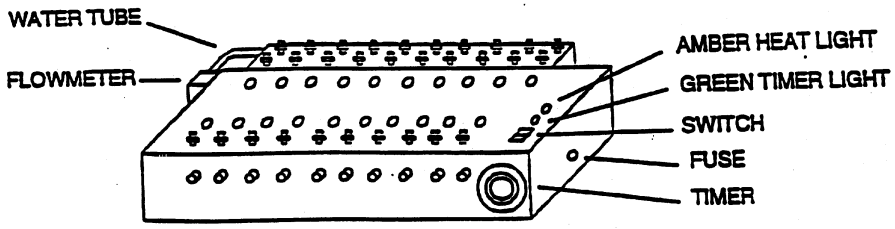


Figure 3
MICRODIST DISTILLATION DEVICE

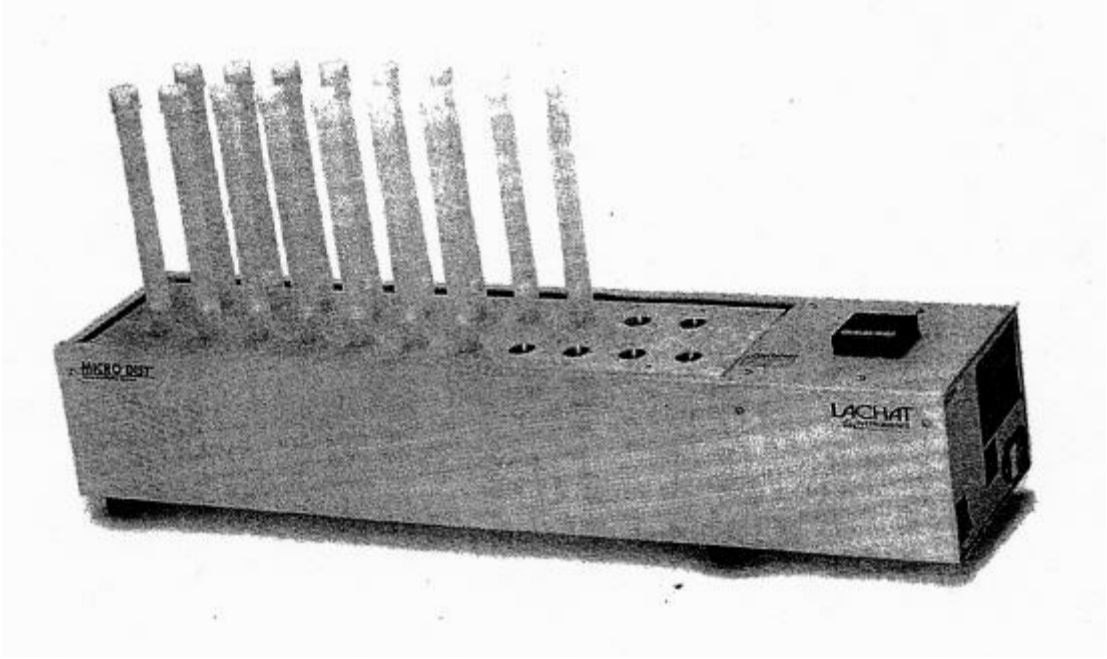
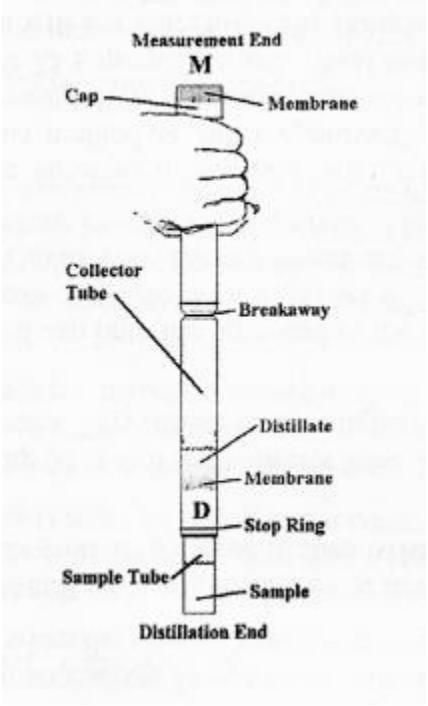


Figure 4
MICRODIST DISTILLATION TUBE



Attachment 1
CONTROL LIMITS

Matrix Analyte Name	Default Rep Flag	MS/MSD LCL	MS/MSD UCL	MS/MSD PCL	LCS LCL	LCS UCL	LD PCL
Water							
Cyanide (amenable)	Yes	10	222	202	10	208	**29**
Cyanide (total)	Yes	36	143	53	46	124	29
Solid							
Cyanide (amenable)	Yes	**38**	**131**	**31**	**30**	**147**	**38**
Cyanide (total)	Yes	38	131	31	30	147	38
Waste							
Cyanide (amenable)	Yes	**38**	**131**	**31**	**30**	**147**	**38**
Cyanide (total)	Yes	**38**	**131**	**31**	**30**	**147**	**38**

Note: These limits were calculated using the old Alpkem instrument and will only be used as interim limits. When enough data from the Lachat instrument is available, the limits will be recalculated.

RLAB Method 3135.2I

Attachment 2
METHOD DETECTION LIMIT

SAMPLE ID	RAW DATA (mg/L)	TRL mg/L	Final Result mg/L
MDL MB	0	0.003	0.00
MDL 1	0.00789		0.00789
MDL 2	0.00673		0.00673
MDL 3	0.00464		0.00464
MDL 4	0.00665		0.00665
MDL 5	0.00612		0.00612
MDL 6	0.00643		0.00643
MDL 7	0.00631		0.00631
MDL 8	0.0074		0.00740
TV	0.01		0.0100
Average			0.00652
Sample Std Deviation			0.000961
Students T for 8 Replicates	2.99795		
MDL			0.00288
Avg/MDL			2.26
TV/MDL			3.47

RLAB Method 3135.2I

Attachment 3

Spreadsheet for CN - A calculations

Parameter: Cyanide - Amenable
Date : 6/19/2006

Analyst: _____ Reviewer: _____

Sample ID	Total CN ppm	-	Chlorinated ppm	=	CN-A PPM	code	%rec
2843 13	0.001	-	0.194	=	0.000	U	
2843 15	0.001	-	0.050	=	0.000	U	
2843 11	0.001	-	0.046	=	0.000	U	
2843 11 MS	0.302	-	0.131	=	0.171		122.0%
SPIKE	0.339	-	0.199	=	0.140		
2843 11 MSD	0.264	-	0.111	=	0.153		109.0%
SPIKE	0.339	-	0.199	=	0.140		
2843 21 FB	0.000	-	0.000	=	0.003	U	
SPIKE	0.100	-		=	0.100		
2843 901 LCS	0.284	-	0.022	=	0.262		150.0%
True Value	0.424	-	0.249	=	0.175		
2843 901 MB	0.002	-					
SPIKE	0.100	-		=	0.100		
2843 905 LCS	0.350	-	0.103	=	0.247		141.0%
True Value	0.424	-	0.249	=	0.175		
2843 903 MB	0.002	-		=	0.003	U	

Method Detection Limit = 0.003 MG/L

Control Limits for LCS (Absolute55132 lot 031005) = 0.297 - 0.55 for Total CN(70-130%)
and 0.000 - 0.56 for CN-A (0% - 400%)
Control Limits for Laboratory Matrix Spikes = 10 - 229 %.
Precision from Duplicate Spikes = 41 PLC

RLAB Method 3135.2I

Attachment 4
Sample Spreadsheet for Soil Calculations

QC DATA CYANIDE IN SOIL Activity # 2920

DATE: 03/24/06 ANALYST= _____ _____

SOP #3135.7C REVIEWER= _____ _____

Instrument: Lachat 8500

SAMPLE NUMBER	VALUE MG/L	VOL. L	WET WT. G	% SOLID	DRY WT. KG	MG/KG	% REC.	% RPD
2920 300	0.0127	0.050	21.80	2.2	0.00048	1.34		
2920 300MS	0.0458	0.050	20.93	2.2	0.00046	4.97	16.7	
SPIKE	0.2000	0.050	20.93	2.2	0.00046	21.72		
								119.9
2920 300MSD	0.0259	0.050	21.90	2.2	0.00048	2.69	13.0	
SPIKE	0.1000	0.050	21.90	2.2	0.00048	10.38		
2920 954 MB	0.0001	0.050	11.50	100.0	0.01150	0.00		
2920 953 LCS	2.7100	0.050	0.74	100.0	0.00074	183.11	87.2	
true value	3.1080	0.050	0.74	100.0	0.00074	210.00		
		0.050		100.0				
2920 952 LFB	0.0715	0.050	5.29	100.0	0.00529	0.68	71.5	
true value	0.1000	0.050	5.29	100.0	0.00529	0.95		

2920 954MB= CLEAN SAND

2920 953LCS= ERA SOIL 51 True Value 210 MG/KG Acceptance Limits D.L.-318 MG/KG.

Method Detection Limit = 0.068MG/KG based on using a 2.5g sample.

Control Limits for Laboratory Matrix Spikes =38-134%

Precision from Duplicate Spikes AL%RSD = 39%

RLAB Method 3135.2I

Attachment 5

Data Quality Assessment Record **ASR:** _____ **Analysis:** *CYANIDE - TOTAL*

Method: 3135.2I **Matrix:** water

Project ID / Desc: _____

Laboratory: EPA x ESAT _____ Other (specify) _____

Signature: _____ _____ _____

Peer-Reviewer EPA Program Manager

Date: _____ _____ _____

Sample Numbers: All / Part of the samples for this ASR

	Yes	N/A	No	RevCk
1. Overview of Analytical Services:				
Is a copy of the ASR and SRN included?	X			
Did customer request specific reporting limits?	X			
If so, were the requested reporting limits met?	X			
Did customer specify other DQOs?	X			
If so, were these DQOs met?	X			
If not, was the supervisor or PM notified?		X		
Were all requested analyses performed?	X			
2. Sample Receipt/ Prep:				
Were all samples properly preserved and stored?	X			
Were all samples analyzed within the 14-day holding time?	X			
3. Initial Calibration:				
Was a plot and summary of the Initial Calibration included?	X			
Was a sequence list included?	X			
Was the correlation coefficient > 0.995?	X			
4. Continuing Calibration:				
Was a CCV analyzed at the beginning of the run?	X			
Was a CCV analyzed at the end of the run?	X			
Was a CCV analyzed every 20 samples or less?	X			
Were the recoveries above all acceptable (90 – 110%)?	X			
5. Quality Control Samples:				
Method Blank:				
Were blank analyses performed?	X			
Were the blanks clean and free of contaminants?	X			
If not, were blank rules applied to the data?		X		
Matrix Spike/Matrix Spike Duplicate:				
Were matrix spike/m.s. duplicate analyses performed?	X			
Were acceptable recoveries obtained?	X			
Were precision recoveries acceptable?	X			
Laboratory Control Sample:				

Was an LCS analyzed with the samples?	X			
Were acceptable recoveries obtained?	X			
6. Raw Data Evaluation:				
Is supporting documentation included?	X			
Were samples free of interferences?	X			
7. Final Review:				
Are all LIMS reports signed/initialed?	X			
Are all other required documents present?	X			
Are results rounded to the correct number of significant figures?	X			
Were data reported without qualification?	X			
Did data meet customer's DQOs?	X			
If not, was supervisor or PM notified?		X		
Are all exceptions properly documented?	X			

Additional Comments: