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# STANDARD OPERATING PROCEDURE
for

# TOTAL CYANIDES AND CYANIDES AMENABLE TO CHLORINATION

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Approved by: _____ Supervisor — 1/4/12 Date

_____ QA Manager — 1/4/12 Date

_____ Laboratory Director — 1/4/12 Date

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# TOTAL CYANIDES AND CYANIDES AMENABLE TO CHLORINAITON

## 1. SCOPE AND APPLICATION

1.1. This procedure is applicable to cyanides, either as free cyanide, in simple soluble salts or in metal complexes, as well as cyanides amenable to chlorination. This procedure is applicable to EPA methods 335.4, 9012B and Standard Methods 4500$CN^-$ E which are applicable to drinking, surface, and saline waters and industrial wastes. Cyanide amenable to chlorination is analyzed using Standard Methods 4500-$CN^-$ G.

1.2. Oils, solids and multi-phase samples are extracted by EPA method 9013 and analyzed by method 335.4 or SM 4500$CN^-$ E. Method 9013 is not applicable to samples containing insoluble cyanide compounds.

1.3. The working range is 0.005 mg/L to 0.30 mg/L and dilutions can be made to extend this range for higher level samples. The Method Detection Limit (MDL) has been experimentally determined to be 0.003 mg/L in water for total CN and 0.003 mg/L for CN amenable to chlorination. The routine Method Reporting Limit (MRL) is 0.01 mg/L in water and 0.2 mg/kg in soil.

1.4. If total cyanide is detected below 250 mg/kg in waste, reactive cyanide is therefore considered < 250 mg/kg, and the reactive cyanide analysis is not necessary. Otherwise, use the distillation method for reactive cyanide found in section 7.3.3, Chapter 7, SW-846 to determine actual reactive cyanide.

## 2. METHOD SUMMARY

2.1. **Total/Amenable Cyanide -** Cyanide is released from cyanide complexes and converted to hydrocyanic acid (HCN) during reflux - distillation with sulfuric acid and magnesium chloride ($MgC1_2$) and absorbed in a scrubber containing a sodium hydroxide solution.

2.2. **Total/Amenable Cyanide -** The cyanide ion is then converted to cyanogen chloride (CNCl) by reaction with chloramine-T at a pH less than eight without hydrolyzing to the cyanate. After the reaction is complete, color is formed with the addition of pyridine barbituric acid reagent. The absorbance is read at 570 nm on the Lachat Automated Ion Analyzer.

2.3. **Amenable Cyanide –** A portion of the sample is chlorinated at a pH >11 to decompose the cyanide. Cyanide levels in the chlorinated sample are then determined by the method for Total Cyanide. Cyanides amenable to chlorination are then calculated by the difference.

## 3. DEFINITIONS

3.1. Analysis Sequence - Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration (initial or continuing verification) followed by sample extracts interspersed with calibration standards (CCBs, CCVs, etc...) The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria indicate an out-of-control situation.

3.2. Independent Calibration Verification (ICV) - Initial calibration verification standards which are analyzed after initial calibration with newly prepared standards but prior to sample analysis, in order to verify the validity of the standards used in calibration. The ICV standards are prepared from a materials obtained from a source different from that used to prepare calibration standards. The ICV is equivalent to the Quality Control Sample (QCS) in method 335.4.

3.3. Matrix Spike/Duplicate Matrix Spike (MS/DMS) Analysis - In the matrix spike analysis, predetermined quantities of target analytes are added to a sample matrix prior to sample preparation and analysis. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the method used for the analysis. Samples are split into duplicates, spiked, and analyzed as a MS/DMS pair. Percent recoveries are calculated for each of the analytes detected. The relative percent difference (RPD) between the duplicate spikes (or samples) is calculated and used to assess analytical precision. The concentration of the spike should be at 0.10 mg/L or at levels specified by a project analysis plan.

3.4. Laboratory Duplicates (DUP) – Duplicates are additional replicates of samples that are subjected to the same preparation and analytical scheme as the original sample. The relative percent difference (RPD) between the sample and its duplicate is calculated and used to assess analytical precision.

3.5. Standard Curve - A standard curve is a calibration curve which plots concentrations of a known analyte standard versus the instrument response to the analyte. A linear calibration model is used. (Elaborate if needed). The appropriate criteria for assessing the validity of the calibration curve must be followed prior to quantitation of target analytes in actual sample analyses.

3.6. Method Blank (MB) - The method blank is an artificial sample composed of analyte-free water or solid matrix and is designed to monitor the introduction of artifacts into the analytical process. The method blank is carried through the entire analytical procedure.

3.7. Laboratory Control Samples (LCS) – The LCS is an aliquot of analyte free water or analyte free solid to which known amounts target analytes are added. The LCS is prepared and analyzed in exactly the same manner as the samples. The percent recovery is compared to established limits and assists in determining whether the batch is in control.

3.8. Continuing Calibration Verification Standard (CCV) - A mid-level standard analyzed at specified intervals. Used to verify that the initial calibration curve is still valid for quantitative purposes.

3.9. Instrument Blank (CCB) - The instrument blank (also called continuing calibration blank) is a volume of clean solvent analyzed on each column and instrument used for sample analysis. The purpose of the instrument blank is to determine the levels of contamination associated with the instrumental analysis itself, particularly with regard to the carry-over of analytes from standards or highly contaminated samples into subsequent sample analyses.

3.10. Cyanide is defined as cyanide ion and complex cyanides converted to hydrocyanic acid by reaction in a reflux system of a mineral acid in the presence of magnesium ion.

## 4. INTERFERENCES

4.1. A number of interferences will be eliminated or reduced by using the distillation procedure in section 11.

4.2. Oxidizing agents such as chlorine decompose most cyanides. These should be removed, if possible, prior to preservation described in 6.2. If they were not removed before, they can be removed prior to distillation. Test by placing a drop of sample onto potassium iodide (KI) - starch paper wetted with 10% nitric acid. A purple color indicates the presence of oxidizing agents. Treat by adding ascorbic acid crystals, a few at a time, until a drop of sample no longer turns the KI - starch paper blue. Then add an additional 0.03 g of ascorbic acid for each 500 ml of sample.

4.3. Nitrates and nitrites can lead to high results as they can form nitrous acid during distillation, which will react with some organic compounds to form oximes. Ultimately these can decompose to generate HCN. Sulfamic acid, approximately 2 g, is added prior to addition of sulfuric acid.

4.4. Sulfides interfere with the colorimetric determination and titration procedure. Samples that contain hydrogen sulfide, metal sulfides or other compounds that may produce hydrogen sulfide during the distillation should be distilled by the optional procedure 11.4.2. Test by wetting a lead acetate test strip (8.6) in lead acetate (8.2.6). Squirt sample with 10% $HNO_3$ and hold wetted lead acetate test strip above sample. A brown color indicates the presence of sulfides.

4.5. The presence of surfactants may cause the sample to foam during refluxing. If this occurs the addition of an anti-foam agent should be added to the distillation flask to prevent the sample from foaming up into the condenser.

4.6. Some unidentified organic chemicals may oxidize or form breakdown products during chlorination, giving higher results for cyanide after chlorination than before chlorination. This may lead to a negative value for cyanides amenable to chlorination after distillation for wastes from, for example, the steel industry, petroleum refining, and pulp and paper processing. Where such interferences are encountered Method Section 4500-CN-.I for determining dissociable cyanide should be used. The Project Chemist and the client will be notified regarding this interference and the CN-WAD will be analyzed if chosen to do so.

## 5. SAFETY

5.1. All appropriate safety precautions for handling solvents, reagents and samples must be taken when performing this procedure. This includes the use of personnel protective equipment, such as, safety glasses, lab coat and the correct gloves.

5.2. Chemicals, reagents and standards must be handled as described in the CAS safety policies, approved methods and in MSDSs where available. Refer to the CAS Environmental, Health and Safety Manual and the appropriate MSDS prior to beginning this method.

5.3. Sodium Hydroxide (NaOH) is a strong caustic and a severe health and contact hazard. Use nitrile or latex gloves while handling pellets or preparing solutions.

5.4. This procedure involves the evolution of hydrocyanic acid (HCN), a highly poisonous gas. Care must be taken during distillation to prevent the release of this gas. A cyanide dosimeter is recommended for the lab bench near the distillation units.

5.5. Caution should be used when preparing and using stock standard solutions and other reagents. The MSDS for each of these should be read before handling. Specific care is listed below:

5.5.1. Potassium cyanide (KCN) and sodium cyanide (NaCN) are highly toxic and a severe health and contact hazard. Upon contact with acid they will liberate HCN, a highly poisonous gas. Use caution when preparing standards.

5.5.2. Sulfuric acid ($H_2SO_4$) is a severe health, reactivity, and contact hazard. Always wear gloves and use caution when handling.

5.5.3. Chloramine - T is a mutagen, avoid breathing dust and do not purge for an excessive period of time.

5.5.4. Pyridine is also a health hazard and its odor is very pervasive. Always prepare in a hood, wearing gloves, and keep capped tightly when transporting.

## 6. SAMPLE COLLECTION, CONTAINERS, PRESERVATION, AND STORAGE

6.1. Sample bottles can both be glass or plastic and must be thoroughly cleaned and rinsed prior to use. For macro distillation, a minimum of 250 mL of sample should be collected or 75 mL if the midi distillation is used.

6.2. Oxidizing agents such as chlorine decompose most cyanides and should be removed prior to preservation with sodium hydroxide, if possible, by the procedure described in 4.2.

6.3. Samples are to be preserved with 2 ml of a 10 N sodium hydroxide solution per liter of sample (to a pH $\geq$ 12) at time of collection.

6.4. Samples must be stored refrigerated at 4 ± 2°C and analyzed within the specified maximum holding time of 14 days from date of sample collection.

## 7. APPARATUS AND EQUIPMENT

7.1. For midi distillation, reflux distillation apparatus as shown in Figure 1. The Easy-Still unit will accommodate up to 20 distillations at one time with the following equipment.

- Boiling tube
- Reagent inlet adapter
- Cold-finger condenser and jacket
- Fritted bubbler, bubbler vessel, and clip
- Vacuum source and cooling water supply

7.2. Laboratory glassware including: graduated cylinders, 25, 50, 250, and 500 ml sizes, volumetric flasks, 10, 25, 50, 100, 250, 500, and 1000 ml sizes with stoppers, a range of volumetric pipettes, class A, and calibrated eppendorf pipettes in a range of volumes.

7.3. Lachat brand Quick Chem, Automated Ion Analyzer, and related equipment including:

7.3.1. Autosampler.
7.3.2. Peristaltic pump.
7.3.3. Six-way valve and cyanide manifold.
7.3.4. Flow cell with 570 nm filter.
7.3.5. Printer, Panasonic, KX-P2123.
7.3.6. Data system, IBM personal System/2 with keyboard.
7.3.7. Borosilicate glass sample tubes.
7.3.8. Reagents, sample, and manifold tubing.
7.3.9. Tumbler.
7.3.10. Buchner funnels with vacuum flask.
7.3.11. Glass fiber filters to fit the Buchner funnel.
7.3.12. Balance
7.3.13. Separatory funnel.

## 8. STANDARDS, REAGENTS, AND CONSUMABLE MATERIALS

8.1. Reagent grade chemicals shall 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 lowering the accuracy of the determination.

8.2. The preparation of all reagents and standards are recorded in a logbook following the procedures defined in the SOP *Reagent Login and Tracking* (ADM-RTL).

8.3. Reagents

8.3.1. Sodium hydroxide solution, 0.5N: dissolve 20 g of NaOH pellets in distilled water, dilute to one liter. (See safety section 5).
8.3.2. Sulfuric acid: Concentrated $H_2SO_4$. (See safety section 5).
8.3.3. Magnesium chloride solution: Dissolve 510 g of $MgCl_2 \cdot 6H_2O$ into distilled water and dilute to one liter.
8.3.4. Sulfamic acid, crystals from macro distillation. Dissolve 20g in deionized water and dilute to 500mL for midi distillation.
8.3.5. Ascorbic acid: crystals.
8.3.6. Lead acetate: Dissolve 30 g of Pb $(C_2H_3O_2)_2 3H_2O$ in 950 ml of distilled water. Adjust the pH to 4.5 with acetic acid. Dilute to 1 liter.
8.3.7. Calcium Hypochlorite solution: Dissolve 5 g of calcium hypochlorite ($Ca(OCl)_2$) in 100 ml of distilled water.
8.3.8. Sodium Hydroxide solution (1.25N): Dissolve 50 g of sodium hydroxide (NaOH) in distilled water and dilute to 1 L.
8.3.9. Potassium Iodide-starch test paper.
8.3.10. Lead acetate test paper
8.3.11. Reagent water : Laboratory DI Water
8.3.12. Sodium Hydroxide, 10N: Dissolve 400g of reagent grade sodium hydroxide in reagent water and take to a 100mL final volume with reagent water.
8.3.13. n-Hexane, $C_6H_{14}$.

8.4. Standards and QC Samples:

8.4.1. Stock cyanide solution: A 1000mg/L stock standard is purchased from Inorganic Ventures. Keep refrigerated (See safety section 5). The vendor-assigned expiration date is used.

8.4.2. Working standard cyanide solution: Dilute 1 ml of stock cyanide solution and 20 ml of 1.25 NaOH to 100 ml final volume with distilled water, 1 ml = 10 µg (10 mg/L). Prepare fresh monthly.

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8.4.3. Stock NaCN solution: Carefully weigh 0.189g NaCN (dried in a desiccator) and 0.16g NaOH. Dissolve in distilled water and dilute to 100 ml. This standard is verified against an independently purchased second source.

8.4.4. Working NaCN solution: Dilute 1 ml of stock NaCN solution and 20 ml of 1.25N NaOH to a 100 ml final volume with distilled 1 ml = 10 µg (10 mg/L). Prepare fresh monthly.

8.4.5. Standard silver nitrate solution, 0.0192 N: 1 ml = 1 mg $CN^-$ for standardization of cyanide standard solutions.

8.4.5.1. Purchased as a prepared 0.0192 N AgNO3 standard.

8.4.5.2. Prepare by crushing approximately 5 g $AgNO_3$ crystals and drying to constant weight at 40°C. Allow to cool in a desiccator and carefully weigh out exactly 3.2647 g of dried $AgNO_3$ and dissolve in one liter.

8.4.6. LCS Standard Water: Purchased from Inorganic Ventures. Preserve with NaOH and make according to manufacturer's directions. Equivalent LCS standards may be purchased from other vendors.

8.4.7. LCS Standard Soils: Purchased from ERA, Certified Reference Material

8.5. Semi-Automated Spectrophotometer Reagents:

8.5.1. Sodium hydroxide solution, 0.25 N: dissolve 10 g of NaOH pellets in distilled water and dilute to one liter.

8.5.2. Phosphate Buffer Solution: Dissolve 97g $KH_2PO_4 \cdot H_2O$ in distilled water and dilute to one liter.

8.5.3. Chloramine-T solution: dissolve 1.0 g chloramine -T in distilled water and dilute to 250 ml. Prepare fresh daily. (See safety section 5).

8.5.4. Pyridine - barbituric acid solution: **ALWAYS IN A HOOD**, dissolve 15 g barbituric acid in 100 ml distilled water and 75 ml pyridine in a one liter volumetric flask. Add 15 ml concentrated HCl and mix, dilute to one liter with distilled water. Transfer to an amber, one liter, stopper bottle. (See safety section 5).

8.5.5. In HCl Rinse solution: Dilute 62.5 ml concentrated HCl to one liter with distilled water.

8.6. Consumables:

Other equipment includes: Lead acetate and KI - starch test strips, funnels, tygon tubing and vacuum hosing for distillation, pipette bulbs, eppendorf pipette tips, stir bars, stir plates, gloves, and screw type clamps.

## 9. RESPONSIBILITIES

9.1. It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. Final review and sign-off of the data is performed by the department supervisor/manager or designee.

9.2. It is the responsibility of the department supervisor/manager to document analyst training. Documenting method proficiency, as described in the SOP *Documentation of Training* (ADM-TRANDOC).

## 10. PREVENTIVE MAINTENANCE

10.1. No specific maintenance steps are needed other than normal cleaning and inspection of apparatus.

10.2. In case of problems encountered with distillation, check vacuum pump performance, apparatus connections, and plugs in tubing. Record any maintenance performed in CN logbook.

10.3. For problems encountered with Lachat operation, see Lachat troubleshooting guide.

10.4. The timers on the Easy Still are verified each quarter by timing the start and end times of a distillation. The verified times are recorded in the maintenance log book.

## 11. PROCEDURE

11.1. Drinking Water, Surface Water and Aqueous Waste Sample Preparation: Method 335.4 and SM 4500 $CN^-$ E

11.1.1. Measure 50 ml of aqueous sample or an aliquot diluted to 50 ml into the MIDI distillation boiling flask. The pH of samples should be taken and noted if other than 12.

11.1.2. Interference should be tested and treated for as described in Section 4.

11.1.3. Proceed to section 11.4

11.2. Sample Preparation for cyanides amenable to chlorination: SM 4500 $CN^-$ G

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11.2.1. Two sample aliquots are required to determine cyanides amenable to chlorination. To one 50 ml aliquot or a volume diluted to 50 ml, add calcium hypochlorite dropwise while agitating and maintaining the pH between 11 and 12 with sodium hydroxide. **CAUTION:** The initial reaction product of alkaline chlorination is the production of very toxic gas, cyanogen chloride. This reaction **MUST** be performed in a hood.

**Note:** If analysis of total cyanide on the untreated sample gives a value less than the MRL/MDL then a treated sample need not be analyzed in order to determine cyanide amenable to chlorination. In this case, when using the equation for cyanide amenable to chlorination (section 13.1.2) and the unchlorinated result is a ND value, the amenable cyanide must also be ND.

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

11.2.3. After one hour, add 0.5 g portions of ascorbic acid until the KI-starch paper shows no residual chlorine. Add an additional 0.5 g of ascorbic acid to insure the presence of excess reducing agent.

11.2.4. Test for total cyanide in both the chlorinated and unchlorinated aliquots. The difference in the CN- concentrations found in the chlorinated and unchlorinated aliquots is expresses as cyanides amenable to chlorination.

11.2.5. Proceed to section 11.4

11.3. Solids, Tissue and Multi-Phase Samples Procedure: Method 9013

11.3.1. Weight approximately 2.5 g of sample and add to the distillation flask. Add 50 ml of DI water. Analyte free matrix sand is used for the method blank. A certified reference material is used for the LCS.

11.3.2. If the sample does not separate or settle in the distillation flask using a Teflon coated magnetic stirring bar but mixes so that the solids are entirely suspended, then proceed to (without an extraction step) Section 11.4.

11.3.3. If the sample contains a free aqueous phase, filter the sample through a Buchner funnel using a pre-weighed glass fiber filter to remove the liquid layer from the solid portion of the sample. Determine the volume and analyze separately.

11.3.4. The solid portion along with the filter is weighed to determine the weight of the sample, subtracting the weight of the pre-weighed filter from the total weight of solid sample and filter.

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11.3.5. Place the solid sample and filter in a 1-liter bottle suitable for tumbling.

11.3.6. Add 500mL reagent water and 5mL 10N NaOH to the bottle. Also, if heavy oil is present, add 50mL n-hexane. Cap the bottle.

11.3.7. The pH of the extract must be maintained above 10 throughout the extraction procedure. After initial addition of the extraction fluids, shake the bottle for one minute. Check the pH using test strips. If the pH is below 12 add 10N NaOH in 5mL increments until the pH is at least 12. Recap the bottle and repeat the procedure until the pH no longer drops. Record total volume of NaOH used along with the 500 mL of reagent water.

11.3.8. Place bottles on the tumbler and tumble for 16 hours.

11.3.9. Filter the extract through a glass fiber filter and Buchner funnel. The entire volume of extract does not need to be filtered.

11.3.10. If the extract contains an oil phase, transfer extract to a separatory funnel, allow the water and oil phases to separate and draw off the water phase for extraction. Discard the oil phase.

11.3.11. Results for both the solid portion and free aqueous portions are analyzed and reported separately.

11.4. Midi Distillation Procedure:

11.4.1. The reflux - distillation apparatus should be assembled as in Figure 1. Up to 20 stills can be setup with cooling water flow through six condensers in a train.

11.4.2. A vacuum trap flask, to which tubing is connected, again in a train of six, each tube fitted with a screw-down clamp to connect to each absorber. The absorbers are not yet connected to the condenser, vacuum should be closed.

11.4.3. When preparing standards, treat the standards the same as the samples, adding all of the same reagents. Do not adjust volumes for distilled standards to match sample volumes. Sample volumes are accounted for in data calculations and reporting (see Sec13.2).

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11.4.4. For samples without sulfides

11.4.4.1. Place 25 mL of 0.25N NaOH (8.4.1) in bubbler vessel. Place boiling tube in midi distillation unit, insert inlet adapter, install condenser. Install bubbler in vessel and secure with clip. Attach vacuum hose to scrubber and install onto condenser.

11.4.5. For samples containing sulfides, place lead acetate scrubber apparatus in series, similar to the arrangement for macro distillation.

11.4.6. For waste reactivity samples, run as Total CN-.

11.4.7. Low and high verification standards (0.05 and 0.15 mg/L) must be distilled in the same manner as the samples.

11.4.8. Set operating parameters on the Easy Still for automatic operation.
Settings for CN-

| | |
|---|---|
| Rate1: $15.0^0$C/min. | Rate2: 0 |
| Temp1: $190^o$C | Temp2: $190^o$C |
| Time1: 1.5 hr | Time2: 0 |

Press button for the desired parameters. The LED will flash corresponding to the chosen parameter. Enter the desired value using the keypad and press "enter". Repeat for each value given above.

11.4.9. Turn on the cooling water supply to condensers and open vacuum valves to give a bubble rate of approximately 2 bubbles/sec at the inlet adapter.

**Note:** If bubble rate is too low, the sample may boil out the inlet tube. If the bubble rate is too high, the sample becomes carbonated, causing interference with the Lachat analysis.

11.4.10. Add reagents at inlet adapter as follows: 5 mL sulfamic acid solution, 2.5 mL $H_2SO_4$ (conc.) ***slowly***, and 2.0 mL $MgCl_2$ solution. Rinse inlet adapter with DI water.

11.4.11. Press "start" button. The Easy Still will automatically go through the distillation cycle set above.

**Note:** Periodic check of boiling and vacuum rate is necessary to avoid possible sample loss.

11.4.12. When the distillation cycle is complete, wait for block temperature to fall below $100^o$C to remove samples.

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11.4.13. Remove scrubber and vessel from condenser as a unit with vacuum hose attached. Remove clip and separate vessel from scrubber. Empty vessel contents into 30 mL centrifuge tube. No further dilution is required prior to initial Lachat analysis.

11.4.14. Record all samples, duplicates, spikes, and QC samples distilled volumes, spike level and any other pertinent information on bench sheet.

11.5. Semi-Automated Spectrophotometric Determination

11.5.1. Set up Lachat system and cyanide manifold as described by manufacturer and download the cyanide method. To remove carbon dioxide that has been absorbed by stored solutions, purge carrier (0.25N NaOH) and phosphate buffer with Helium for approximately two minutes.

**NOTE:** Do not purge pyridine barbituric acid solution. (See safety section 5).

11.5.2. For all analyses, enter analyst name, service request, and current LCS information in the comments section for tray being run. Next enter sample identification numbers for tray in order being run, including all QC samples being run (see section 10) into identification location.

11.5.3. Pour calibration standards, blanks, control standards and samples in tray in order being run. An analyses sequence could appear as follows.

Calibration Standards
ICV/QCS
ICB
CCV-1
CCB-1
MB
LCS
0.15mg/L dist. std.
0.05 mg/L dist. std.
Sample 1
Sample 1Dup.
Sample 1Spk.
Sample 2
Sample 3
Sample 4
CCV-2
CCB-2
Sample 5
Sample 6
Sample 7
Sample 8

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Sample 9
Sample 10
Sample 11
Sample 12
CCV-3
CCB-3

11.5.4. Calibration

11.5.4.1. The Linear Calibration Range (LCR) must be determined initially and verified every six months or whenever a significant change in instrument response is observed or expected. The initial demonstration of linearity must use sufficient standards to insure that the resulting curve falls in the linear range of the instrument. The verification of linearity must use a minimum of a blank and three standards. If any verification data exceeds the initial values by ±10%, linearity must be reestablished. If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion.

11.5.4.2. Calibration standards: When prepared as follows, the calibration standards are valid for 7 days. Prepare a blank and seven calibration standards at the following concentrations by adding 20 ml of 1.25N NaOH solution and the following amount of standard solution and making up to 100 ml with distilled water:

| ml Standard Cyanide Solution (8.3.2) 10 mg/L | Concentration mg $CN^-$/L |
|---|---|
| 0 | 0 |
| 0.1 | 0.01 |
| 0.2 | 0.02 |
| 0.5 | 0.05 |
| 1.0 | 0.1 |
| 1.5 | 0.15 |
| 2.0 | 0.2 |
| 3.0 | 0.3 |

11.5.4.3. Analyze the standards using the Lachat system as set up in Section 11.8.

11.5.4.4. The data system which accompanies the instrument uses specific functions for calibration and quantitation. The algorithm used is a linear regression calibration curve (see Appendix A). The system software calculates the calibration equation using the response or signal from the analysis of the standard to establish the calibration. No other calibration options are available to the analyst.

11.5.4.5. The correlation coefficient for each calibration is checked by the analyst to determine that the coefficient is ≥0.995. The data system will reject a calibration with a value <0.995 and will not process subsequent samples. If the criterion is not met, repeat the calibration.

11.5.4.6. An Independent Calibration Verification (ICV standard should be run as first injection of the sample tray immediately after running the calibration. The ICV is at level mid range in the calibration. The ICV is prepared from NaCN. This is a second source (source other than calibration standards), undistilled standard. The measured amount must be within 90-110% of the true value. If not, remake the standards and recalibrate.

**Note: The DoD** acceptance criteria for the ICV is 85- 115%.

11.5.4.7. Continuing Calibration Verification (CCV): A 0.100 mg $CN^-$/L. standard is analyzed after every ten samples including duplicates, spikes, MB's, etc. and at the end of the tray, at the level of the mid-range standard. The measured amount must be 90-110% of the true value. If not, remake the standards and recalibrate. Reanalyze any sample associated with a failing CCV.

11.5.4.8. Calibration blanks (ICB, CCB) are analyzed after every calibration verification (i.e., ICB after every ICV and CCB after every CCV). The measured amount must be less than the MRL or CRDL. If not, recalibrate and reanalyze any sample associated with the failing CCB.

11.5.4.9. As a check on the distillation, undistilled and distilled standards at 0.05 mg $CN^-$/L and 0.15mg $CN^-$/L are analyzed (one distilled/undistilled set at each level). The measured values of the distilled standards should be 90-110% of the measured values in the undistilled standards. If not, re-make and reanalyze the undistilled standard and apply the criteria.

**Note: DoD** acceptance criteria for distilled standards are 85-115%.

11.5.5. Sample Analysis

11.5.5.1. Analyze the samples as described in section 11.7. Observe progress of the run noting anything noteworthy about peak shapes etc. onto post run report.

11.5.5.2. Reportable sample concentrations can be no higher than the highest standard. Make dilutions as necessary and include these on the end of the tray with the proper calibration verification and QC (e.g. CCV/CCB bracket) and record these on post run report also. For dilutions, ensure normality of final solution is 0.25N, using NaOH solution.

11.6. If problems occur due to instrument malfunction, stop the run and perform any necessary service or maintenance, recording what was done in the Lachat Maintenance Log.

11.7. When run is complete, pump in HCl rinse solution and then distilled water through all reagent lines, including carrier, for approximately ten minutes. Clean up sample tubes etc.. Drain lines of liquid.

11.8. Print out the following forms: Post-run report, calibration report, and calibration statistics. Record the slope and intercept of the calibration curve. Date and initial post run report.

## 12. QA/QC REQUIREMENTS

**Note:** When performing work on samples from **DoD** project, refer to the SOP ADM-DoD for general DoD QC requirements.

12.1. Initial Precision and Recovery Validation

12.1.1. Initial demonstration of capability must be validated before analysis of samples, or whenever significant changes to the procedures have been made. The ability of each analyst/instrument to generate acceptable accuracy and precision must be documented prior to sample analysis by performing 4 replicate LCS analyses and calculating average recovery and %RSD. Method criteria must be met for these results. This must be completed before analysis of samples, or whenever significant changes to the procedures have been made.

12.2 Method Detection Limits, LOD and LOQ

12.2.1 Method detection limit (MDL), Limits of Detection (LOD) and Limits of Quantification (LOQ) must be determined before analysis of samples can begin. Refer to the SOP for the *Performing Method Detection Limit Studies and Estimation of Limits of Detection and Quantitation (ADM-MDL).*

| | | | MDL | MRL | |
|---|---|---|---|---|---|
| 335.4 | Cyanide, Total | Water | 0.003 | 0.01 | mg/L |
| SM4500 CN-E | Cyanide, Total | Water | 0.003 | 0.01 | mg/L |
| 9010B/9012B | Cyanide, Total and Amenable | Soil | 0.06 | 0.2 | mg/Kg |
| 9010B/9012B | Cyanide, Total and Amenable | Water | 0.002 | 0.01 | mg/L |
| SM4500 CN G | Cyanides Amenable to Chlorination | Water | 0.002 | 0.01 | mg/L |
| SM4500 CN I | Cyanides, Weak Acid Dissociable | Water | 0.003 | 0.01 | mg/L |

12.3 Ongoing QC Samples required are described in the CAS-Kelso Quality Assurance Manual and in the SOP for Sample Batches. Additional QC Samples may be required in project specific quality assurance plans (QAPP). For example projects managed under the DoD ELAP must follow requirements defined in the DoD *Quality Systems Manual for*

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*Environmental Laboratories.* General QA requirements for DoD QSM are defined in the laboratory SOP, Department *of Defense Projects – Laboratory Practices and Project Management (ADM-DOD).* General QC Samples are:

12.4 Method Blanks

12.4.1 A method blank is extracted and analyzed with every batch of 20 (or fewer) samples to demonstrate that there are no method interferences. If the method blank shows any hits above the reporting limit, corrective action must be taken. Corrective action includes recalculation, reanalysis, system cleaning, or re-extraction and reanalysis.

12.4.2 **DoD QSM Method Blank Requirements**– The Method Blank will be considered contaminated if:

- The concentration of any target analyte in the blank exceeds ½ the reporting limit and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).
- The concentration of any common laboratory contaminant in the blank exceeds the reporting limit and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).
- The blank result otherwise affects the samples results as per the test method requirements or the project-specific objectives.

12.5 Sample Duplicates

12.5.1 One duplicate sample should be distilled for every twenty samples or less of a particular matrix (i.e. water, soil, etc.) and concentration if known (i.e. low, high). The first sample on a service request should be chosen sample QC unless another is specifically designated. Samples designated as field blanks are not to be used. The acceptance criteria is $\leq$ 20% RPD (for sample and duplicate results $\geq$ 5x MRL. If either or both sample replicate is < 5x MRL, then RPD is not applicable).

12.6 Laboratory Control Sample

12.6.1 The LCS, or laboratory control sample, is a purchased standard used to check the performance of the analytical system. LCS recovery must be acceptable before samples can be analyzed. Method 335.4 requires LCS recoveries between 90-110%. Control limits for methods SM 4500 CN and 9012B are statistical limits based upon laboratory results. See the following table for QC limits.

12.7 Matrix Spike (MS)

12.7.1 One matrix spike should be performed for every twenty samples or less of a particular matrix (i.e. water, soil, etc.). Spike should also be the first sample on a

service request, and preferably the same sample chosen for the duplicate unless another is designated. Field blanks should not be used, if designated as such. Method 335.4 requires MS recoveries between 90-110%. Control limits for methods SM 4500 CN and 9012B are statistical limits based upon laboratory results. See the following table for QC limits.

12.7.2 If the recovery falls outside the recovery range and the laboratory performance for that analyte is shown to be in control (LCS acceptable), the recovery problem with the MS is judged to be either matrix or solution related, not system related. No reanalysis is necessary.

**Note:** For method 9012B analyses, the method of standard additions shall be used for the analysis of all samples that suffer from matrix interferences such as samples which contain sulfides.

**Note:** Duplicate samples are routinely analyzed, however all **DoD** projects require a MSD with every preparation batch. The MSD sample is prepare as described above. The RPD criterion for duplicates is 20% RPD. For **DoD** QSM work, MS recoveries are assessed using the QSM LCS control limits.

| Method | LCS Water (%Rec) | LCS Soil (%Rec) | MS Water (%Rec) | MS Soil (%Rec) |
|---|---|---|---|---|
| | | | | |
| 335.4 | 90-110 | NA | 90-110 | NA |
| 9012B | 82-116 | 62-128 | 38-145 | 10-171 |
| SM 4500 CN E | 84-115 | NA | 23-148 | NA |
| SM 4500 CN G | 53-147 | NA | 10-180 | NA |

## 13. DATA REDUCTION, REVIEW AND REPORTING

13.1. Calculations

13.1.1. Calculate the concentrations of samples and standards from distillate concentrations taking into account any dilutions made at the instrument and the initial sample volume and final distillate volume.

$$e.g. CN^{-} mg/L = \frac{AxBxC}{D}$$

Where A = mg $CN^{-}$/L read from Lachat Report
B = dilutions made
C = final distillate volume (e.g. 100 ml)
D = sample size (e.g. 200 ml)

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13.1.2. Calculate the cyanide amenable to chlorination as follows:

CN, mg/L = A – B

Where:

A = mg/L total cyanide in unchlorinated aliquot.
B = mg/L total cyanide in chlorinated aliquot.

**Note**: If analysis of total cyanide on the untreated sample gives a value less than the MRL/MDL then a treated sample need not be analyzed in order to determine cyanide amenable to chlorination. In this case, when using the equation for cyanide amenable to chlorination and the unchlorinated result is a ND value, the amenable cyanide must also be ND.

13.2. Data Review and Reporting

13.2.1. It is the analyst's responsibility to review analytical data to ensure that all quality control requirements have been met for each analytical run. Results for QC analyses are calculated and recorded as specified in this SOP. All data will be initialed, dated and attached to required data quality worksheet.

13.2.2. Following primary data interpretation and calculations, all data is reviewed by a secondary analyst. Following generation of the report, the report is also reviewed. Refer to the SOP (ADM-DREV) *LABORATORY DATA REVIEW PROCESS.*

13.2.3. Reports are generated in the CAS LIMS by compiling the SMO login, sample prep database, instrument date, and client-specified report requirements (when specified). This compilation is then transferred to a file which LIMs uses to generate a report. The forms generated may be CAS standard reports, DOD, or client-specific reports. The compiled data from LIMS is also used to create EDDs deliverables.

13.2.4. As an alternative, reports are generated using Excel© templates located in R:\WET\FORMS. The analyst should choose the appropriate form and QC pages to correspond to required tier level and deliverables requirements.

13.2.5. Reporting units are mg $CN^-$/L for liquids and mg $CN^-$ /Kg for solids.

13.2.6. Include copy of the cyanide bench sheet and instrument reports (run time, post run, calibration report and calibration stats) with the report forms.

## 14. CORRECTIVE ACTION

14.1. Refer to the SOP for Corrective Action (ADM-CA) for procedures for corrective action. Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected.

14.2. Handling out-of-control or unacceptable data

14.2.1. On-the-spot corrective actions that are routinely made by analysts and result in acceptable analyses should be documented as normal operating procedures, and no specific documentation need be made other than notations in laboratory maintenance logbooks, runlogs, for example.

14.2.2. Documentation of a nonconformity must be done using a Nonconformity and Corrective Action Report (NCAR) when:

- Corrective action is not taken or not possible
- Corrective action fails to correct an out-of-control problem on a laboratory QC or calibration analysis.
- Reanalysis corrects the nonconformity but is not a procedurally compliant analysis.

## 15. METHOD PERFORMANCE

15.1. This method was validated through single laboratory studies of accuracy and precision. Refer to the reference method for additional method performance data available.

15.2. The method detection limit (MDL) is established using the procedure described in the SOP for *Performing Method Detection Limit Studies and Limits of Detection and Quantitation (ADM-MDL).* Method Reporting Limits are established for this method based on MDL studies and as specified in the SOP ADM-MDL.

## 16. POLLUTION PREVENTION

16.1. It is the laboratory's practice to minimize the amount of solvents, acids and reagent used to perform this method wherever feasible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site. The threat to the environment from solvent and reagents used in this method can be minimized when recycled or disposed of properly.

## 17. WASTE MANAGEMENT

17.1. The laboratory will comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the CAS EH&S Manual.

17.2. This method uses acid. Waste acid is hazardous to the sewer system and to the environment. All acid waste must be neutralized to a pH of 2.5-12 prior to disposal down the drain. The neutralization step is considered hazardous waste treatment and must be

documented on the treatment by generator record. See the CAS EH&S Manual for details.

17.3. This method uses a base. Waste base is hazardous to the sewer system and to the environment. All waste must be neutralized to a pH of 2.5-12 prior to disposal down the drain. The neutralization step is considered hazardous waste treatment and must be documented on the treatment by generator record. See the CAS EH&S Manual for details.

## 18. TRAINING

18.1. Refer to the SOP for Documentation of Training for standard procedures.

18.2. Training outline

18.2.1. Review literature (see references section). Read and understand the SOP. Also review the applicable MSDS for all reagents and standards used. Following these reviews, observe the procedure as performed by an experienced analyst at least three times.

18.2.2. The next training step is to assist in the procedure under the guidance of an experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

18.2.3. Perform initial precision and recovery (IPR) study as described above for water samples. Summaries of the IPR are reviewed and signed by the supervisor. Copies may be forwarded to the employee's training file. For applicable tests, IPR studies should be performed in order to be equivalent to NELAC's Initial Demonstration of Capability.

18.3. Training is documented following the SOP for Documentation of Training.

NOTE: When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

## 19. METHOD MODIFICATIONS

19.1. There are no known modifications in this laboratory standard operating procedure from the reference method.

## 20. REFERENCES

If this SOP is accessed electronically, it is an uncontrolled copy and will not be updated.



20.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. EPA SW-846, 3rd Edition, Final Update IV, 9012B, November 2004.
20.2. Determination of Total Cyanide by Semi-Automated Colorimetry, Rev 1.0 August 1993, Environmental Monitoring Systems Laboratory, Office of Research and Development, Environmental Protection Agency, Method 335.4
20.3. Cyanide Extraction Procedure for Solids and Oils , EPA method 9013, Rev 0, July 1, 1992.
20.4. USEPA Contract Laboratory Program, document Number ILMO 4.0, Method for Total Cyanide Analysis by MIDI Distillation #335.4 CLP-M.
20.5. Methods 4500C,E, 4500-CN- G Standard Methods for the Examination of Water and Wastewater, 20th Edition.
20.6. DoD Quality Systems Manual for Environmental Laboratories Version 4.2
20.7. Operation Manual - Lachat
20.8. Quick Chem Methods
20.9. Troubleshooting guide - Lachat
20.10. Easy-Still Environmental Methods Manual

## 21. CHANGES SINCE THE LAST REVISION

21.1. Sec 6.4 – remove the word *distilled.* HT is 14 days from collection not distillation
21.2. Sec 8.4.5 – added purpose of silver nitrate solution
21.3. Sec 11.5.1 –removed chloramine and edited second sentence
21.4. Sec 12.7 – removed *LCS* from MS section
21.5. Sec 12.7.2 – updated table
21.6. Sec 19 is new

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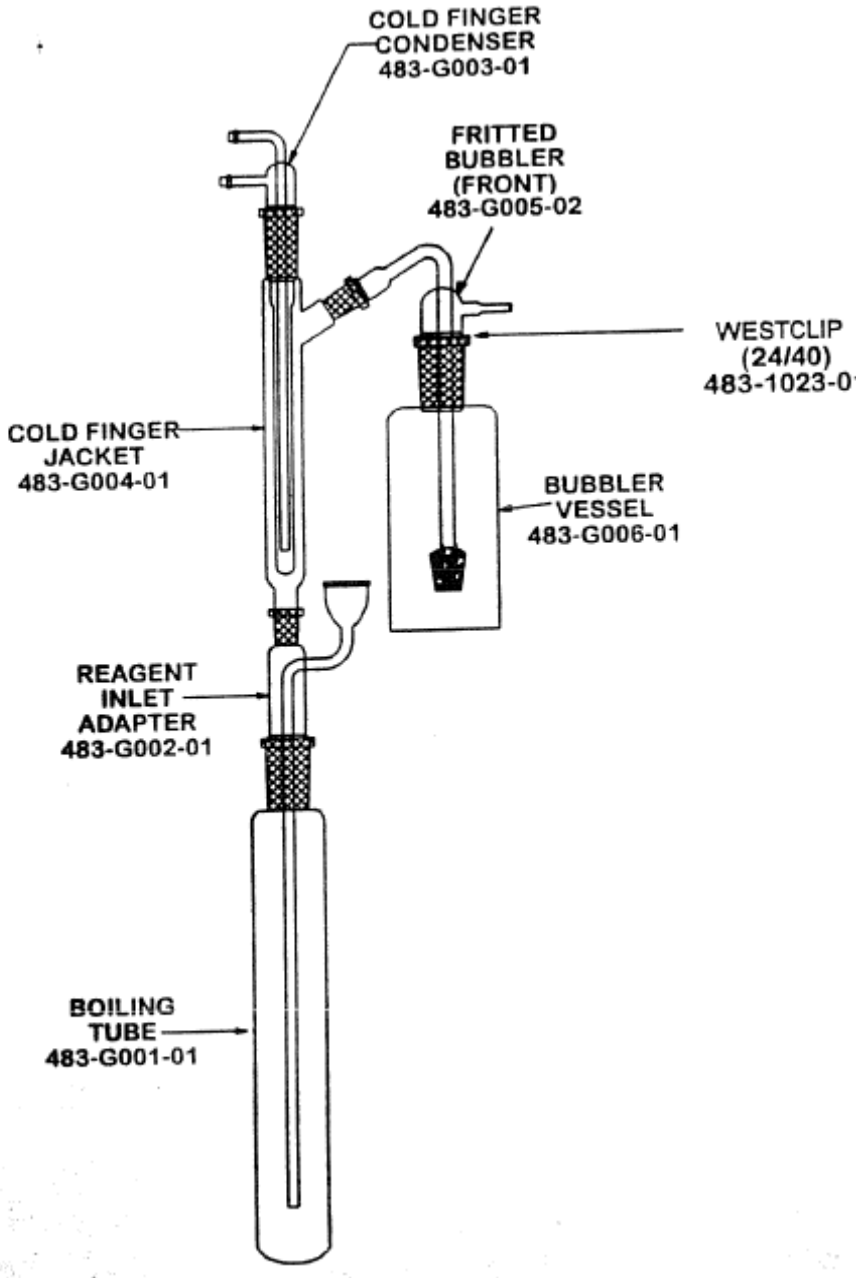
**FIGURE 1**

**CYANIDE DISTILLATION APPARATUS (MIDI)**



# APPENDIX A

The calibration is determined using a linear regression that best fits the line of the X:Y pairs. The quality of the fit is determined by calculating the coefficient of determination ($R^2$), also called the correlation coefficient.

The line of regression is calculated as follows:

Start with the equation for a line, y = mx + b. From here the line of regression can be determined.

$$m = \frac{n\sum(xy) - \sum x \sum y}{n\sum(x^2) - \left(\sum x\right)^2}$$

$$b = \frac{\sum y - m\sum x}{n}$$

Where:

$x$ = the values of the x variables.
$y$ = the values of the y variables.
$n$ = the number of data points.

Once the line of regression has been determined then the coefficient of determination can be calculated.

$$r^2 = \frac{\left(\sum xy - n\bar{x}\bar{y}\right)^2}{\left(\sum x^2 - \bar{x}\sum x\right) * \left(\sum y^2 - \bar{y}\sum y\right)}$$