

Determination of Total Cyanide

Introduction

The discharge of dissolved and/or undissolved commercial and industrial waste into water supplies and the soil can result in the presence of cyanides. The cyanides can take the form of hydrogen cyanide, cyanide ions, complex cyanide compounds, organic compounds, and cyanogen chloride. Iron-cyanide complexes (Prussian Blue) and potassium-iron cyanide complexes (potassium ferricyanide) are common. Cyanides and complex cyanides are particularly common in the residual materials of production at former gas works and coking plants. They are used in the metal refining industry during metal hardening processes. This application describes the distillation of samples that contain cyanide and subsequent determination using the cyanide cuvette test TNT862. The procedure follows USEPA method 335.2 and Standard Method 4500-CN⁻ E.

Material

- MDD002 – Micro Dist Reactor Block

Or

- DRB20004 – DRB200 Reactor Block (8 x 20-mm wells)
 - LZT144 – DRB200 Adapter Sleeve for Micro Dist (8/pkg)
- A17517 – Micro Dist tubes (user filled, 50/pkg)
- A17117 – Micro Dist tubes (user filled, 100/pkg)
- 17023L – Press
- 17013L – Protective gloves, large
- 17013S – Protective gloves, small
- 21302 – Stands, collection tubes
- BBP065 – Pipet, adjustable volume, 1.0 - 5.0 mL
- BBP068 – Pipet tips, for 1.0 - 5.0 mL pipet
- 1970010 – Pipet, TenSette[®], 1.0 - 10.0 mL
- 2199796 – Pipet tips for TenSette[®], 1.0 - 10.0 mL
- TNT862 – Cyanide TNTplus reagent set

Chemicals

Releasing solution: 7.11 M H₂SO₄ / 0.79 M MgCl₂

- 1) In a fume hood, put a 500-mL beaker on a top-loading balance and zero the balance.
- 2) Add **110.8 ml** of deionized water to the 500-ml glass beaker.
- 3) Add and fully dissolve **32.2 g** of magnesium chloride hexahydrate (MgCl₂ * 6 H₂O).
- 4) Slowly add **139 g** of concentrated sulfuric acid (H₂SO₄) in increments of 40 g. Swirl and let cool between additions.
- 5) Let the solution cool to ambient temperature.
- 6) Put the solution in a closed container.

Trapping Solution: 0.1 M NaOH

- 1) Dissolve 4 g of solid NaOH in 1 liter of deionized water.

Application Note: Distillation with Micro Dist and Cyanide Determination

- 2) Let the solution cool to ambient temperature.
- 3) Put the solution in a closed container.

Procedure

Set the MICRO DIST block temperature controller to 120°C. Allow the block to warm up; it may take up to 40 min. If the DRB200 is being used for the distillation, insert the adapter sleeves into the 20-mm wells.

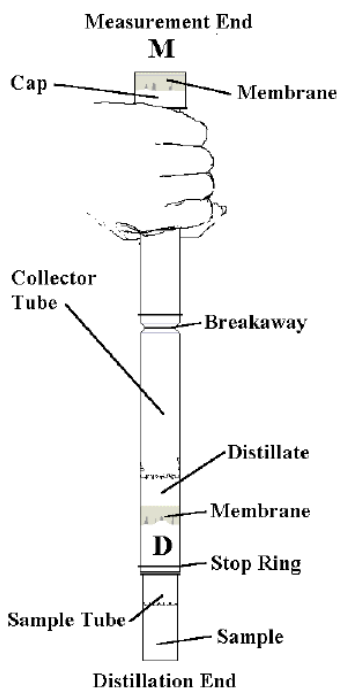


Figure 1: MICRO DIST collector tube

1) Using the User Filled cyanide tubes, fill the M (measuring) portion of the collector tube with 1.5 mL of 0.1 M NaOH for the trapping solution (Figure 1). Once the 0.1 M NaOH is added, take the loose membrane and press the cap over to seal in the trapping solution.



Figure 2: Placing sample in tubes

Application Note: Distillation with Micro Dist and Cyanide Determination

2) Place as many collector tubes as you have samples into the collector tube rack; up to 21 for one block (Micro Dist), or 8 for the DRB200. Place **6.0 mL** of sample or standard into each sample tube with a pipet (Figure 2). In this method, the standards are distilled with the samples.



Figure 3: Adding the releasing solution

3) In order to both release the free cyanide as HCN (g) and to digest complexed cyanide during the digestion/distillation, add **0.75 mL** of 7.11 M sulfuric acid / 0.79 M magnesium chloride solution to the sample tube using a pipet (Figure 3).

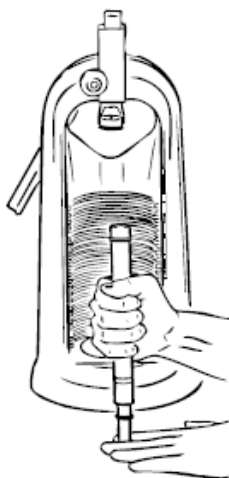


Figure 4: Starting the seal

- 4) **Immediately** push the **D** end of the collector tube over the open end of each sample tube to start the seal (Figure 4).
- 5) Place the assembly in the press (Figure 4), putting the sample tube through the hole in the white base. Before pressing, the user should grip the collector tube firmly at the breakaway point to keep the tube from shifting during the pressing procedure.
- 6) The pressing motion should be smooth constant pressure, which is just enough to slide the sample tube inside the collector tube. A jerky, forced motion may cause added strain to the tube and could potentially crack it. Press down on the handle until the stop ring on the sample tube hits the **D** end of the collector tube.
- 7) Put on the heat-resistant gloves. Push the sample tube and **D** end of each tube all the way into the

Application Note: Distillation with Micro Dist and Cyanide Determination

preheated block so that the collector tube stop ring touches the block.

8) Set the timer for **30** minutes.



Figure 5: Removing the sample tube

9) When **30** min is up, put on the heat-resistant gloves. Remove the first tube from the block and **immediately** pull off its sample tube using a downward, twisting motion as opposed to a sideways motion (Figure 5). You must pull off the sample tube **within 4 s** of removing it from the block or suck-back of the sample will occur (*if you are using the DRB200, see the troubleshooting section at the end of the note for instructions on the DRB200's timer*). Drop the sample tube and the hot solution left in it into a waste bucket reserved for this purpose.

10) Invert each collector tube and place it into the collector tube rack, now with the **D** ends up.

11) Allow tubes to cool for at least **10** min.

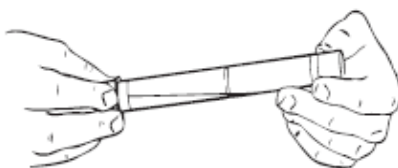


Figure 6: Rinsing the Collector tube walls

12) For each collector tube, hold the tube horizontally and rinse its walls with the distillate in order to homogenize it. Slowly roll the distillate around in the tube to gather all droplets clinging to the tube walls into the bulk of the distillate (Figure 6). Then, slowly return the collector tube to an upright position so that the **D** end is up. Stubborn drops will often fall into the **M** end when the tube is flicked with your finger or shaken down like a thermometer in a whipping motion.

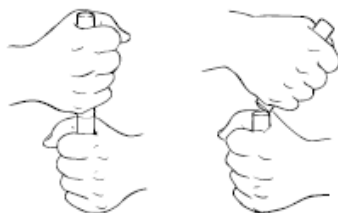


Figure 7: Breaking the 'D' End of the Collector tube

Application Note: Distillation with Micro Dist and Cyanide Determination

13) With the **D** end still up, break the collector tube in half by pulling the **D** end hard towards yourself to break it, then twisting and tearing off the **D** end (Figure 7). Discard the **D** end.

14) In the remaining **M** end of the collector tube, dilute to the 6.0 mL mark with reagent water. This results in the original sample volume in 0.025 M NaOH.



Figure 8: Shaking the tube

15) Shake the tube with a gentle whipping motion to mix in diluent water (Figure 8). Do not invert the sample. With the **M** end down; place the tube into the collector rack. **Seal both ends of the tube with Parafilm if you will not determine the sample immediately.**

16) Determine the cyanide concentration by following TNT862 cyanide procedure (refer to the working instructions in method 10265, DOC316.53.01495). Analyze a cyanide standard to determine the distillation recovery (should be >85%). Factor in the extraction rate for subsequent measurements, or for the most accurate results; create a user calibration with distilled standards.

Application Notes and Troubleshooting

Calculation for Extraction Rate Factor

Sample results = Standard Concentration / Measured Standard Concentration

For example: Standard concentration = 0.5 mg/L, measured standard concentration = 0.43 mg/L
 $0.5 \text{ mg/L} / 0.43 \text{ mg/L} = 1.163$ factor $\rightarrow 0.43 \text{ mg/L} \times 1.163 = 0.5 \text{ mg/L}$

Note: Only use this factor for non-reporting purposes

Calculation for % Recovery Rate

Sample results = Measured Standard Concentration / Standard Concentration

For example: Measured standard concentration = 0.43 mg/L, standard concentration = 0.5 mg/L
 $0.43 \text{ mg/L} / 0.5 \text{ mg/L} = 0.86 \times 100 = 86\%$

Stock cyanide standards should be prepared in a 0.025 M NaOH solution. Too high of a sodium hydroxide molarity concentration will cause low recovery with the TNTplus cyanide reagent. The reagent's buffer is not strong enough to overcome high alkaline samples and/or standards.

Application Note: Distillation with Micro Dist and Cyanide Determination

Troubleshooting – DRB200 Timer and Membrane Suck-Back Issues

The DRB200 has a timer built into the block. Once the timer expires on the block, the temperature on the will start to decrease. The decreasing temperature of the block can be problematic if the distillation tubes are not removed immediately after the distillation time expires. Once the block temperature starts to decrease, a pressure difference will develop between the sample and the distillate causing the distillate to be sucked-back into the sample tube, ruining the distillate sample. To keep the digestion block from cooling off after the distillation has finished, **do not start the timer on the DRB200 and track the 30-minute distillation time period off-line.**

Troubleshooting – Membrane Caking

When solid samples or sludges are distilled, foam comes up through the membrane, or scum cakes over the underside of the membrane causing it to be pushed up. This occurs when the sample has a lot of organics in it such as grease or oils. The scum or foam is organic surfactants which wet the hydrophobic membrane. This causes it to lose its hydrophobicity and thus not function properly. The placement of the membranes on all collector tubes is elevated such that the matrix foam normally will not come into contact with the membrane. Be careful of organic material caking the membrane or actually coming through the membrane as this will cause pressure to build up in the sample tube. The pressure is not large but it is sufficient to cause spattering of the hot sample when the sample tube is removed. In some cases the distillation membrane may pop out of the ring.

Running Solid Samples with Micro Dist

The Micro Dist is capable of handling many different kinds of solid samples from sands to sludges. As a general guideline, if the sample is high in organic content use only 0.5 g or less of sample. If the sample is low in organic content, use up to 1 g of sample. Experiment with samples to determine the best weight of sample to add for each matrix type. The sample will be diluted with DI water (5 to 6 mL) per the Micro Dist manual. Calculating the amount of sample in mg/kg after analysis:

$$A = C \times ((1 \text{ L} / 1000 \text{ mL}) \times V)$$

$$B = A \text{ divided by } (W \times 1000 \text{ g/kg})$$

Where:

A = mg of analyte in the sample

B = mg of analyte per kg of sample (mg/kg)

C = determined concentration (mg/L)

V = dilution volume in tube (mL)

W = weight of the original sample (g)

If foaming or caking of the membrane continues to be a problem even with reduced sample weights of 0.5 g, try the following:

- Add activated charcoal so it covers the surface of the solid and then fill the remaining void space with glass wool. When trying this procedure its recommended to use 4-5 mL of water versus 6 mL.
- For soil or organic samples containing cyanide, Biobeads™, manufactured by BIO-RAD, part number SM-2, have proven effective in laboratories.
- Test a known standard with one of these procedures and a spiked sample of the foaming or caking matrix to conclude whether these solutions will work.

Application Note: Distillation with Micro Dist and Cyanide Determination

For more information on the Micro Dist block, the distillation tubes and troubleshooting, see the Lachat Micro Dist User Manual, DOC022.97.80305. For more information on interferences, please see TNT862 cyanide procedure (method 10265, DOC316.53.01495).

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