Determination of Total Cyanide

Distillation of water, sludge, and soil samples using Micro Dist and determination of cyanide using LCK315 cuvette tests

Application APP-PHM-0007

EN

General
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 (Berlin Blue) and potassium-iron cyanide complexes (red and yellow 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. They can also leak from hazardous waste sites (sites without adequate safety features).

Both new and old versions of the German Drinking Water Ordinance [TrinkwV] stipulate that cyanide may be present in water up to a concentration of 50 µg/l.

This application describes the distillation of samples that contain cyanide and subsequent determination using the cyanide cuvette test LCK315. As such, it is an alternative to the standard DIN 38405-D13-1-3: „Determination of cyanides (D13) through separation of hydrogen cyanide and subsequent photometric determination of cyanide ions using barbituric acid/pyridine (1-3)“.

Material

- MDI001 — Micro Dist Thermoblock, complete starter set plus
- LCK315 — Cyanide cuvette test

or

- LTV082.99.51002 — Thermostat LT200, 2 black blocks
- LZT144 — 8 adapters for 20-mm bores
- A17117 — Micro Dist tubes (to be filled by the user)
- A17070 — MicroDist Accessory Kit incl. Cap press
- LCK315 — Cyanide cuvette test

Chemicals:

- Releasing solution: 7,11 M H_2SO_4 / 0,79 M $MgCl_2$

Preparation of releasing solution:

1. First **110,8 ml** of distilled water is added to a 500-ml glass beaker.
2. Then **32,2 g** of magnesium chloride hexahydrate ($MgCl_2$ * 6 H_2O) is added and dissolved.
3. This is followed by **139 g** of concentrated sulfuric acid (H_2SO_4) which is added slowly and in small quantities.
4. **Warning: Hot! A fume extraction system is recommended as HCl can vaporize**.

- Trapping solution: 1 M NaOH
- pH adjustment: 1 M HCl
- Buffer: Phosphate buffer (0,05 M K_2HPO_4 / 0,1 M KH_2PO_4)

Preparation of the buffer:

1. Fill a 1000-ml glass beaker with **700 ml** distilled water.
2. Add **8,7 g** K_2HPO_4 and **13,6 g** KH_2PO_4 and dissolve by stirring.
3. Fill the volume up to **1000 ml**, decant into a storage bottle and store at room temperature.

Disposal information

Waste disposal must be carried out in compliance with regional and national regulations.

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Determination process

General

- Either a 6-ml liquid sample (up to 100 mg/l cyanide) or a solid sample of between 0,5 g and 1,0 g (sludge, soil) is added to the sample tubes. For solid samples, the tubes should contain 5 ml of distilled water. The sample may contain up to 600 µg of cyanide in total.
- In order to complete the determination process using cuvette test LCK315, samples with a high content (up to 100 mg/l) must be diluted after distillation to bring them into the measurement range for the cuvette test (max 0,6 mg/l).

Micro Dist work process

Prior to distillation

1. Switch on the thermostat and preheat to **120°C**.

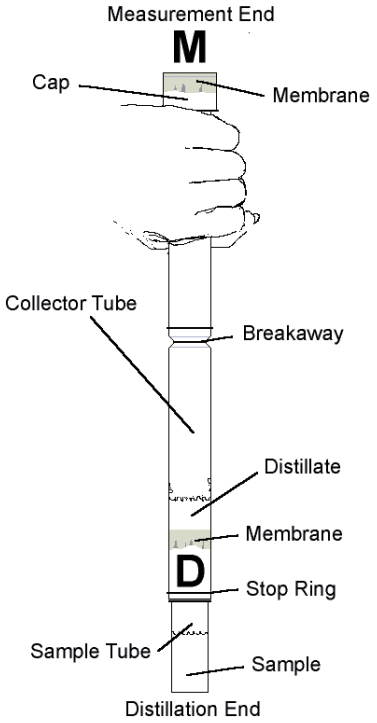

Figure 1

2. Place a **Micro Dist** (MD) collector tube (Figure 1) in a suitable holder with the **D** end facing downward and add **1,5 ml** of the trapping solution.

Figure 2

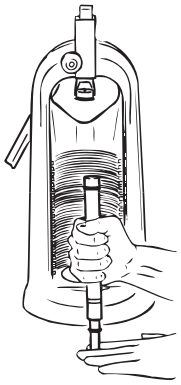

Figure 3

3. Seal the **measurement end (M** end**)** of the MD tube using a Teflon membrane and a cap.

4. Add a **6,0-ml** sample/**0,5 – 1,0-g** soil sample plus **5 ml** of distilled water to the sample tube (Figure 2).
Add a suitable standard to a tube as a sample and process it simultaneously.

5. Add **0,75 ml** of releasing solution to the sample.

6. Immediately afterward, insert the sample tube into the collector tube and seal with the press (Figure 3).

7. Insert the MD tube in the pre-heated thermostat (120°C) (warning: wear heat-resistant protective gloves) and distill for **30 minutes**.

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After distillation (30 minutes)

1. Remove the MD tube from the thermostat after 30 minutes (wear protective gloves) and ***immediately*** separate the sample tube from the collector tube.
2. Discard the sample tube and dispose of the content correctly (the content is acid).
3. Place the collector tube in a suitable holder with the **M** end facing downward and allow to cool (10 minutes).

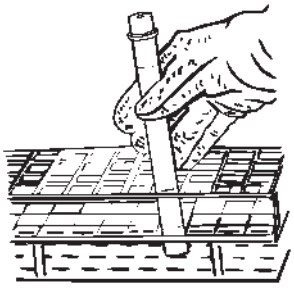

Figure 4

4. Collect the distillate by tilting and rotating the tube.

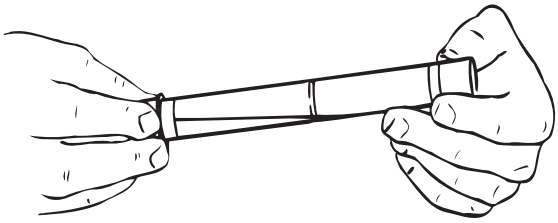

Figure 5

5. Position the collector tube with the **M** end facing downward and break off the **D** end.

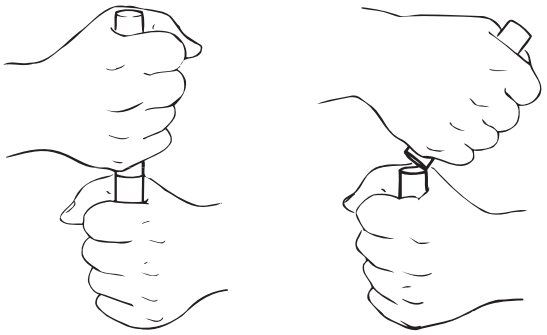

Figure 6

6. Acidify the distillate with **1,5 ml** of HCl and then immediately top up to **6 ml** using a phosphate buffer.
7. Insert the distillate for measurement using LCK315 (refer to the work instructions for the LCK315 for the work process).
8. Determine extraction using the measured standard (should be > 80%). Factor in the extraction rate for subsequent measurements.

Calculation:

$$\text{Sample result} = \text{result read off} \times \frac{\text{standard concentration (target)}}{\text{measured standard concentration}}$$

The measurement results must be subjected to plausibility checks (dilute and/or spike the sample).

The Micro Dist manual provides further details.

Trouble shooting – 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 scummy organic material caking the membrane or actually oozing through the membrane as this causes 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 sample. If the sample is low in organic content, one can 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 MicroDist manual.

Calculating the amount of sample in mg/kg after analysis:
Multiply the determined concentration in mg/l by the volume in the tube (in ml, normally 6 ml) and divide then with 1000 (conversion l/ml) to get the amount of analyte in mg.
Divide the content of analyte in mg by the weight of original sample (in g) and multiply then with 1000 (conversion g/kg) to get the result as mg analyte / kg sample.

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 it would be recommended that 4-5 ml of water be used 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.

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