Determination of Phenol

Introduction

Phenols may be present in domestic and industrial wastewaters, natural waters, and potable water supplies. Phenols are used in household products and are used as starting materials to manufacture industrial products like plastics, explosives and pharmaceuticals. Phenol analysis for exhaust air (after absorption and condensates) formed during the manufacturing and processing of benzene, petroleum products, glass and mineral fibers, hardboard, coke, oil shale, hazardous waste, town gas, coal as well as brown coal products, tar, asphalt, and bitumen.

This application describes the distillation of samples that contain phenol and subsequent determination using the phenol cuvette test TNT868. The procedure follows USEPA method 420.1 and adapted from Standard Methods for the Examination of Water and Wastewater 20th Edition, Section 5530.

Materials:

- 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
- 17012 – Stands, collection tubes
- 21302 – Stands, sample tubes
- 1970010 – Pipet, TenSette®, 1.0 - 10.0 mL
- 2199796 – Pipet tips for TenSette®, 1.0 - 10.0 mL
- TNT868 – Phenol TNTplus reagent set

Chemicals

These reagents are used to adjust the pH of the sample to an approximate pH of 4 prior to the distillation. The phenol distillation does not use trapping or releasing solutions.

1) 1 M NaOH
2) 10% H_2SO_4

Procedure

Set the Micro Dist block temperature controller to 130°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.

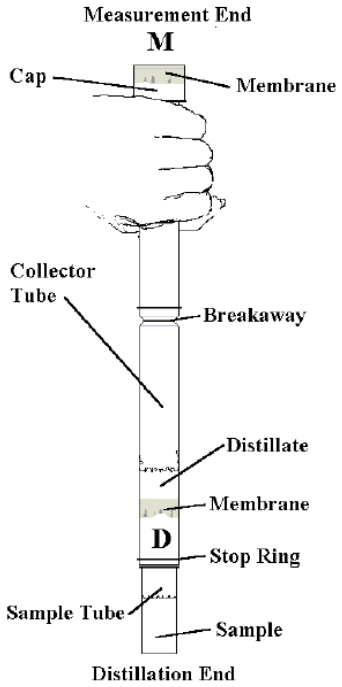

Figure 1: Micro Dist collector tube

1) Using the User Filled phenol tubes, take the loose membrane and press the cap over to seal the collector tube; the phenol distillation does not use a trapping solution.

Figure 2: Placing sample in tubes

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). Adjust the pH of the sample and standards to a pH of approximately 4 with 1 M NaOH or 10% H_2SO_4. In this method, the standards are distilled with the samples.

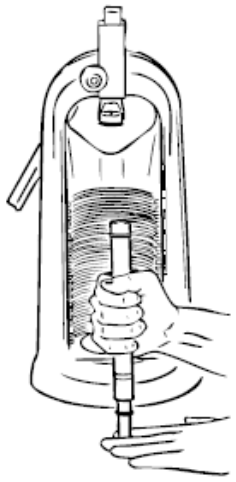

Figure 3: Starting the seal

3) **Immediately** push the **D** end of the collector tube over the open end of each sample tube to start the seal (Figure 3).

4) Place the assembly in the press (Figure 3), 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.

5) 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.

6) Put on the heat-resistant gloves. Push the sample tube and **D** end of each tube all the way into the preheated block so that the collector tube stop ring touches the block.

7) Set the timer for **90** minutes.

Figure 4: Removing the sample tube

8) When **90** 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 4). 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.

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

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

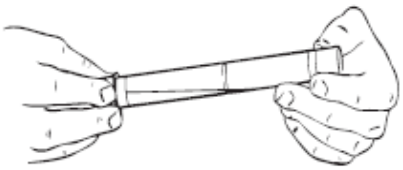

Figure 5: Rinsing the collector tube walls

11) 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 5). 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.

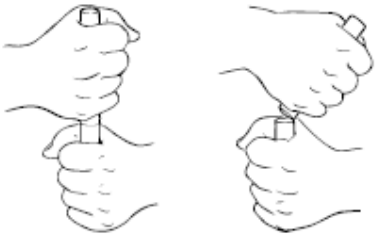

Figure 6: Breaking the 'D' end of the collector tube

12) 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 6). Discard the **D** end.

13) In the remaining **M** end of the collector tube, dilute to the 6.0 mL mark with reagent water.

Figure 7: Shaking the tube

14) Shake the tube with a gentle whipping motion to mix in diluent water (Figure 7). 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**.

15) Determine the phenol concentration by following TNT868 phenol procedure (refer to the working instructions in method 10266, DOC316.53.01496). Analyze a phenol 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 = 50 mg/L, measured standard concentration = 43 mg/L
50 mg/L / 43 mg/L = 1.163 factor → 43 mg/L x 1.163 = 50 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 = 43 mg/L, standard concentration = 50 mg/L
43 mg/L / 50 mg/L = 0.86 x 100 = 86%

Troubleshooting – DRB200 Time 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 90-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:

$A = C \times ((1\ L / l000\ mL) \times V)$

B = A divided by (W × 1000 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 it would be recommended to use 4-5 mL of water versus 6 mL.

● 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.

Conclusion

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 TNT868 phenol procedure (method 10266, DOC316.53.01496).

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