METHOD 8

DETERMINATION OF PHENOLS IN EFFLUENTS

Ref: Reg 7-303

1. PRINCIPLE

1.1 This method is applicable to the determination of the concentration of phenolic compounds in effluents collected in 0.1 N NaOH solution.

1.2 The phenols form phenolates when absorbed in NaOH. They are hydrolyzed by acid and the concentration of each phenol compound in the sample is determined by gas chromatography.

1.3 Sample clean up, if necessary, is done by extraction using carbon tetrachloride as solvent.

1.4 Interference:

1.4.1 Butyl cellosolve and ethyl cellosolve acetate interfere with phenol and n-decane interferes with 3,4-dimethylphenol (DMP) when the primary column is used.

1.4.2 Verify the concentrations of phenol and DMP by using a confirming column.

1.4.3 p-cresol interferes with m-cresol in the confirming column (2.1.1).

1.5 The limit of detection (LOD) for this method is 1.0 μg phenolic compound per ml of sample.

2. APPARATUS

2.1 Gas Chromatograph. This unit is fitted with a flame ionization detector (FID), a glass sleeve injection port, a temperature programmer and a compatible integrator or data station. The operating parameters are as follows:

2.1.1 Primary Analytical Column: (See Fig. 1)
2 m x 2 mm ID glass column packed with Carbopack F-TA, 60/80 mesh

Initial Oven Temp.	160^0 C
Iso Time	5 min.
Program Rate	10^0 C/min.
Final Oven Temp.	220^0 C
Final Delay	5 min.
Injector Temp.	250^0 C
Detector Temp.	250^0 C

Carrier Gas	He or N_2

Carrier Gas Flow	20 ml/min.
Injection Sample Size	2 µl

2.1.2 Confirming Analytical Column: (See Fig. 2)

2 m x 2 mm ID glass column packed with 10% GP SP 2100, 100/120 in Supelcoport.

Initial Oven Temp.	110^0 C
Iso Time	15 min.
Program Rate	30^0 C/min.
Final Oven Temp.	200^0 C
Final Delay	10 min.
Injector Temp.	250^0 C
Detector Temp.	250^0 C
Carrier Gas	He or N_2
Carrier Gas Flow	20 ml/min.
Injection Sample Size	2 µl

2.2 Micro syringe, 10 µl capacity.

2.3 Volumetric flasks, various sizes as needed.

2.4 Beakers, various sizes as needed.

2.5 Test Tubes, 25 ml capacity.

2.6 Pipette, 10 ml and 1 ml capacity.

2.7 Refrigerator.

2.8 Parafilm.

2.9 Analytical Balance. Capable of weighing to 0.0001 g.

3. REAGENTS

3.1 Sodium Hydroxide (0.1 N). Add 4 grams of NAOH pellets to a 1 L volumetric flask containing approximately 600 ml of distilled water. Cap and shake the flask until all the pellets have dissolved. Add distilled water to the mark. Cap and invert the flask several times to mix the solution. Transfer the solution to a screw capped plastic bottle (NOTE 1).

NOTE 1: The ground glass parts of the flask will be cemented to each other once the droplets of the alkaline solution in the area dry up.

3.2 Sulfuric Acid (1.0 N). To about 500 ml of distilled water in a 1 L volumetric flask, slowly add 28.0 ml of concentrated sulfuric acid, cool

and dilute to the mark with distilled water. Cap and invert the flask several times to mix the solution thoroughly.

3.3 Copper Sulfate Solution (10%). To a 100 ml volumetric flask containing approximately 60 ml of distilled water, add 10 grams of anhydrous copper sulfate crystals. Cap and shake the flask until all the crystals have dissolved. Add distilled water to the mark. Cap and invert the flask several times to mix the solution well.

3.4 Carbon Tetrachloride. Reagent Grade.

3.5 pH Paper. ColorpHast pH Indicator Strips non-bleeding or equivalent. This is available from EM Science, 111 Woodcrest Road, Cherry Hill, NJ 08034-0395.

3.6 Phenol. Reagent Grade or best available grade. A minimum purity of 99% is acceptable.

3.7 o-, p-, and m-Cresol. Reagent Grade or best available grade. A minimum purity of 99% is acceptable.

3.8 3,4-Dimethyl Phenol. Reagent Grade or best available grade. A minimum purity of 99% is acceptable.

3.9 Cylinder Hydrogen.

3.10 Cylinder Helium or Nitrogen.

3.11 Cylinder Air.

4. ANALYTICAL PROCEDURE

4.1 All samples are to be refrigerated after submission to the laboratory. If samples are to be analyzed within three days, proceed with (4.2). If samples are to be stored more than three days, add 1 ml of 10% copper sulfate solution to each impinger (NOTE 2).

NOTE 2: Copper sulfate serves as a preservative.

4.2 If the sample is contaminated with heavy oil, extract the phenolic compounds using carbon tetrachloride as the extracting solvent. This procedure is not necessary if the sample is “clean”.

4.3 Measure and record the total liquid volume in each impinger. Transfer a 9.0 ml aliquot to a 25 ml test tube and add 1 ml of 1 N sulfuric acid. Cover the test tube with parafilm, invert and mix well. Check the pH of the solution using a pH paper. The solution must be acidic, (pH ~ 1).

4.4 Set up the gas chromatograph as described in Section 2.1.

4.5 Prepare a blank by adding 1 ml of 1N H2SO4 to 9 ml of 0.1 N NaOH solution in a 25 ml test tube. Cover the test tube with a parafilm, invert and mix well. Check the pH of the solution using a pH paper. The solution must be acidic, (pH ~ 1)

4.6 Inject 2 µl of (4.5) into the gas chromatograph.

4.7 Keep on injecting the blank until the column is cleared and a stable baseline is obtained.

4.8 Inject 2 µl of (4.3) into the gas chromatograph.

4.8 Record the retention time and peak area of the phenolic compounds found in the sample. Retain the chromatogram.

5. STANDARDIZATION

5.1 Standard Phenol Stock Solution Preparation.

5.1.1 Weigh 0.1 to 0.11 g (± 0.0001 g) of each reagent grade phenol, o-, p- and m-cresol and 3, 4 dimethylphenol using a plastic weighing tray.

5.1.2 Quantitatively, transfer (5.1.1) to a 1 L volumetric flask containing approximately 500-600 ml of 0.1 N NaOH solution. Cap and shake the flask until all the phenolic compounds have dissolved.

5.1.3 Add 0.1 N NaOH to the mark and mix the solution well by inverting the flask several times This solution contains approximately 100 µg/ml of each phenol. If kept refrigerated this solution is stable for, at least, one month. (NOTE 4).

NOTE 4: p-Cresol interferes with m-Cresol when the confirming column (2.1.1) is used.

5.1.4 Transfer the phenol stock solution (5.1) to a 1 L glass bottle with a screw cap (Note 1).

5.2 Standard Phenol Working Solution Preparation.

5.2.1 Pipette 10 ml of the phenol stock solution (5.1) into a 100 ml volumetric flask and add 0.1 N NaOH to the mark.

5.2.2 Cap and invert the flask several times to mix the solution thoroughly. This solution contains 10 µg/ml of each phenolic compound. Prepare the working standard fresh prior to use.

5.3 To 9.0 ml of the phenol working standard (5.2) add I.0 ml of 1N H_2SO_4. Check the pH of the solution using a pH paper. The solution must be acidic (pH ~ 1).

5.4 Inject 2 µl of (5.3) into the gas chromatograph (2.1) using a 10 µl syringe. Record the retention time and the peak area of each phenolic compound. Retain the chromatogram. (NOTE 4).

NOTE 4: Rinse the syringe with acidified NaOH solution between injections.

6. CALCULATION

6.1 Compare the chromatogram obtained in (4.6) to that obtained in (5.5) to confirm the identity of the phenol, o-cresol, p-cresol, m-cresol and 3,4-dimethylphenol. Determine the concentration of each phenolic compound in the sample using the following equations:

6.1.1 Total µg of Phenol per impinger $= \frac{\text{Total } V_{(S)} \times PA_{(S)} \times Concn_{(STD)}}{PA_{(STD)}}$

Where:

$\text{Total } V_{(s)}$ = Total Volume of Sample in the Impinger

$PA_{(S)}$ = Peak Area of the phenolic compound in the Sample

$Concn_{(STD)}$ = µg/ml of the individual phenolic compound in the Standard

$PA_{(STD)}$ = Peak Area of the phenolic compound in the Standard

Total µg of phenol in the sample = µg in the 1st Impinger + µg in the 2nd Impinger

Total µg of o-, p-, and m-cresol in the sample = µg in the 1st Impinger + µg in the 2nd Impinger

Total µg of DMP in the sample = µg in the 1st Imp + µg in the 2nd Impinger

$$\text{ppm Phenol} = \frac{\text{Total µg Phenol in the Sample}}{(f^*) \times \text{Sample Volume (liters)}}$$

Where:

(f*) = 3.84 for phenol; 4.42 for o-, p-, and m-cresol; and 4.99 for DMP.

The (f*) values are µg/µl of the individual phenol at 25^{o}C and 760 mm Hg.

Total ppm Phenols = ppm Phenol + $\sum$(ppm Cresols) + ppm 3, 4 DMP

7. REFERENCE

7.1 Standard Test Method for Tar Acid Composition by Gas-Liquid Chromatography. ASTM Book of Standards, Vol 06.04, ASTM Designation: D 3626-85 (Reapproved 1990).

7.2 Levaggi, D.A., Feldstein, M., "Determination of Phenols and Trimethylamine in Industrial Effluent." AIAA Library No. 71-1115, 750 3rd Avenue, New York, N.Y. 100

7.3 Phenols - EPA Test Method 604: Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, (U.S.) Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

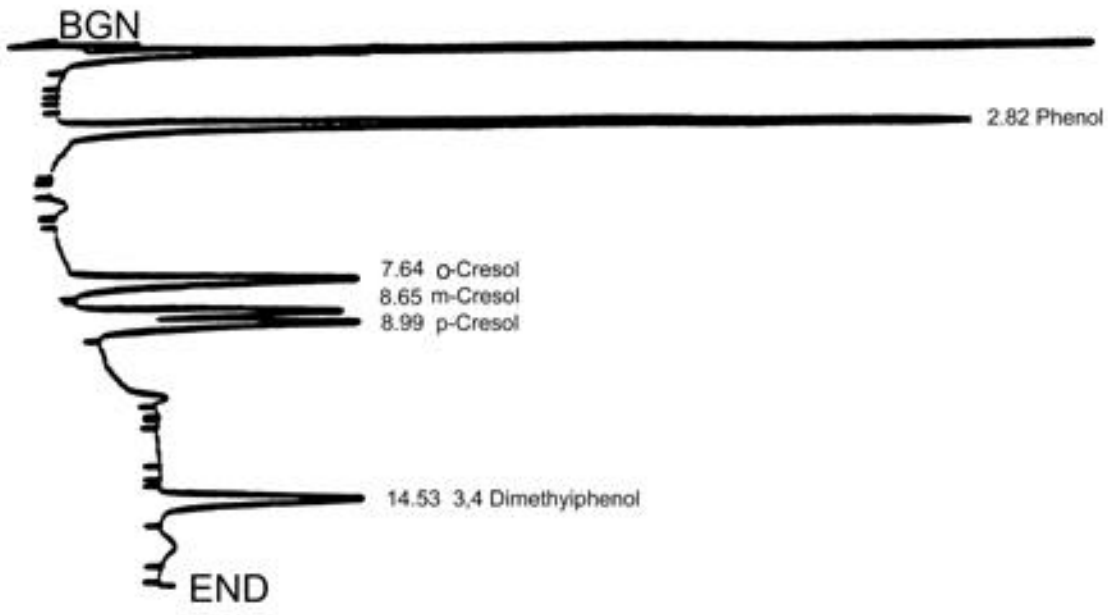

FIGURE 8-1

A Typical Chromatogram Using the Primary Column
(2m x 2mm ID glass column packed with Carbopack F-TA, 60/80 mesh)

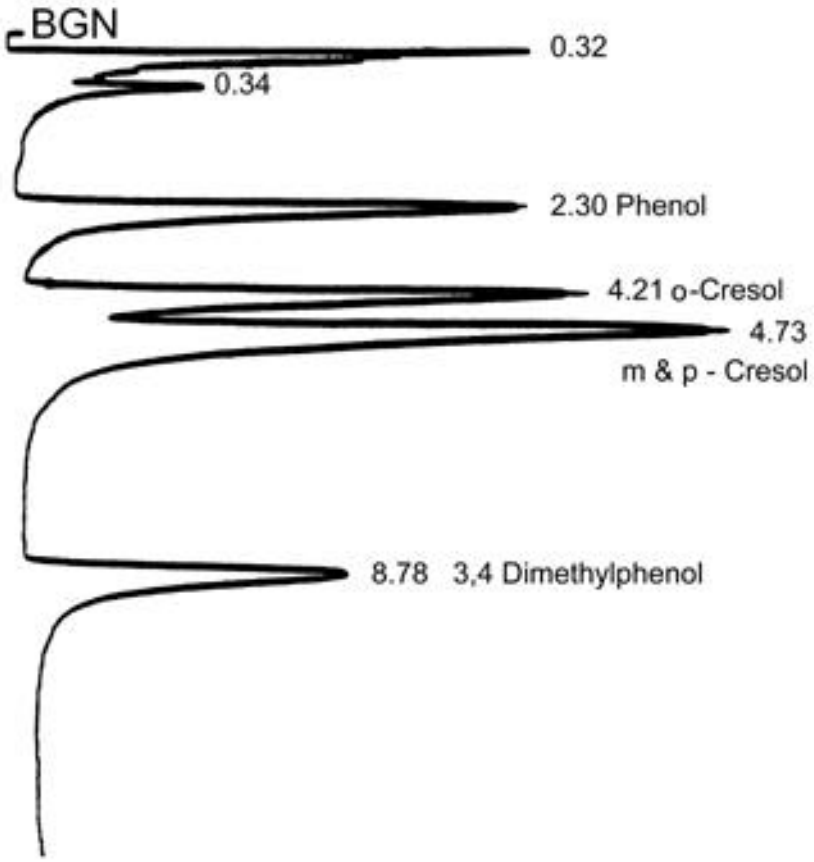

FIGURE 8-2

A Typical Chromatogram Using the Confirming Analytical Column
(2m x 2mm ID glass cloumn packed with 10% GP SP 2100, 100/200 mesh Supelcoport)