

PHENOL IN LIGHT AROMATIC HYDROCARBONS AND CYCLOHEXANE BY SPECTROPHOTOMETRY

UOP Method 464-00

SCOPE

This method is for determining phenol at concentrations from 0.1 to 2.0 mass-ppm in light aromatic hydrocarbons such as benzene, ethylbenzene, cumene, toluene and xylene, as well as cyclohexane by visible spectrophotometry. Higher concentrations can be determined by diluting the sample. The presence of substituted phenols may cause a positive interference. Aldehydes, ketones, ethers, alcohols, amines, and sulfur compounds will interfere, if present.

OUTLINE OF METHOD

Phenol is extracted from the sample with 2% sodium hydroxide. The pH of the aqueous extract is adjusted to 10. The concentration of phenol is determined by measuring the coupling product of 4-aminoantipyrine and phenol in the presence of an alkaline oxidizing agent.

APPARATUS

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Absorption cells, quartz, 10-mm, matched, Fisher Scientific, Cat. No. 14-385-904C

Balance, readability 0.1-mg

Beakers, 150-mL, borosilicate glass, Fisher Scientific, Cat. No. 02-540J, 6 required

Bottle, narrow mouth, round, amber, glass-stoppered, 500-mL, Fisher Scientific, Cat. No. 03-320-1D

Calculator, capable of least squares analysis (optional)

Cylinders, graduated, 100- and 500-mL, Fisher Scientific, Cat. Nos. 08-553B and C, respectively

Flasks, volumetric, Class A, 100- (six required), 250- and 500-mL, Fisher Scientific, Cat. Nos. 10 210-5C, E, and F, respectively

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

Funnel, filter, 75-mm diameter, Fisher Scientific, Cat. No. 10-326C

Funnels, separatory, 250-, 500- and 1000-mL, Fisher Scientific, Cat. Nos. 10-437-5C, D, and E, respectively

pH meter, Fisher Scientific, Cat. No. 02-226-83

Pipet, Mohr, 1-mL with 0.1-mL graduations, Fisher Scientific, Cat. No. 13-650-4

Pipets, volumetric, Class A, 2-, 3-, 4-, 5-, 7-, 10- and 20-mL, Fisher Scientific, Cat. Nos. 13-650-2C, D, E, F, H, L, and N, respectively

Spectrophotometer, capable of reading at 510 nm

Vacuum source, a water aspirator, Fisher Scientific, Cat. No. 09-960-2 is sufficient

REAGENTS AND MATERIALS

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

4-Aminoantipyrine, 98% minimum purity, Aldrich Chemical, Cat. No. A 3,930-0

4-Aminoantipyrine solution, 2.0 mass/volume-%. Dissolve 2 ± 0.01 g of 4-aminoantipyrine in water and dilute to 100 mL. Label, date and store in an amber, glass-stoppered bottle. Prepare fresh monthly when samples are being analyzed.

Ammonium chloride, salt, 99.5 % minimum purity, Fisher Scientific, Cat. No. A661-500

Ammonium chloride solution, 5.0 mass-volume-%. Dissolve 5 ± 0.01 g of ammonium chloride in water and dilute to 100 mL.

Buffer solution, pH 10 and pH 7, Fisher Scientific, Cat. No. SB115-4 and SB 107-4, respectively

Gloves, nitrile, Fisher Scientific, Cat. No. 11-390-13B

Graph paper, for plotting calibration curve

Hydrochloric acid, concentrated, Fisher Scientific, Cat. No. A144S-500

Hydrochloric acid, approximately 2 M. Dilute 17 ± 0.1 mL of concentrated hydrochloric acid to 100 mL with water.

Phenol, 99+ % minimum purity, Aldrich Chemical, Cat. No. 43,151-6

Phenol stock solution, 0.025 mg phenol/mL. Weigh 0.25 ± 0.01 g, to the nearest 0.1 mg, of phenol. Dissolve in water and dilute to 500 mL in a volumetric flask, and label as Phenol Starting Solution. Pipet 5 mL of this solution into a 100 mL volumetric flask, dilute to the mark with water, and label as Phenol Stock Solution. Calculate the exact phenol concentration in this stock solution using Eq. 1 under *CALCULATIONS*. Prepare the Phenol Stock Solution fresh daily when in use. *CAUTION*: Phenol is a highly toxic, corrosive compound that is readily absorbed through the skin, and it should be handled with care and the appropriate personal protective equipment (PPE), including gloves.

Potassium ferricyanide, salt, 99+% minimum purity, Aldrich Chemical, Cat. No. 39,351-7

Potassium ferricyanide solution, 2.0 mass/volume-%. Dissolve 2 ± 0.01 g of potassium ferricyanide in water and dilute to 100 mL. Prepare fresh daily when samples are being analyzed.

Sodium hydroxide solution, 2.5-*M* (10%), aqueous, Fisher Scientific, Cat. No. SS414-1

Sodium hydroxide solution, 2.0%. Dilute 50 mL of the 10% solution to 250 mL with water in a volumetric flask, stopper and mix.

Water, distilled

CALIBRATION

1. Using a graduated cylinder, place approximately 20 mL of 2% sodium hydroxide solution into six 150-mL beakers.
2. Pipet 2, 4, 7, 10 and 13 mL of the 0.025 mg/mL phenol stock solution into the 150-mL beakers, leaving the last beaker for preparation of a reference solution.
 - Standards prepared in this fashion will contain 2, 4, 7, 10 and 13 times the concentration of phenol in the phenol stock solution per 100 mL of standard.
3. Pipet 5 mL of 5% ammonium chloride solution into each beaker and swirl to mix.
4. Adjust the pH of each standard and the reference to 10-10.2 by slowly adding 2-*M* hydrochloric acid. Standardize the pH meter with the pH 10 buffer solution before each set of samples.
 - pH meters that offer two point calibration should be standardized with pH 7 and pH 10 buffers.
5. Transfer, quantitatively with water, each standard and the reference to 100-mL volumetric flasks using a funnel.
6. Using a Mohr pipet, add 0.6 mL of 2% aminoantipyrine solution to each flask and mix.
7. Add 2 mL of 2% potassium ferricyanide solution by pipet to each flask and again mix.
8. Dilute each flask to volume with water and allow to stand 3 to 5 minutes for the color to develop.
 - The absorbance must be read within 5 minutes of the color development.
9. Fill a matched pair of 10-cm absorption cells with the reference solution and place them in their respective beam paths. Zero the spectrophotometer at 510 nm.
10. Empty the sample cell, rinse it with water, and dry it using vacuum.
11. Transfer the first standard solution into the cell and return it to the sample beam. Measure the absorbance at 510 nm against the reference solution.
12. Repeat Steps 10 and 11 to determine the absorbance of the remaining standard solutions.
13. Plot, on graph paper, mg of phenol/100 mL of solution vs. absorbance. A calibration curve prepared in this fashion should be linear. If not, check the instrument and/or calibration standards and repair and/or re-calibrate as needed.

Alternatively, a least square analysis can be performed to obtain the slope and the correlation coefficient, Q, using a calculator or computer. The correlation coefficient should be 0.99 or higher. If the value of Q is less than 0.99 the calibration has not been performed correctly and must be repeated. The slope is expected to be between 0.7 to 0.8 mg phenol/ absorbance unit. However, it is somewhat instrument dependent and is expected to vary.

PROCEDURE

1. Determine the density of the sample by ASTM Method D 4052, or equivalent.
2. Using a graduated cylinder, measure the suggested amount of sample (Table 1) into a separatory funnel. Using a graduated cylinder, add 20-mL of 2% sodium hydroxide solution. Cap the funnel and shake vigorously for 2 to 3 minutes. Vent the funnel at intervals to avoid pressure build-up.

Table 1
Suggested Sample Size

<u>Expected Phenol Concentration, mass-ppm</u>	<u>Suggested Sample Size, mL</u>
<0.4	500 or more
0.5 to 1.0	200
1.0 to 2.0	100

If the sample contains more than 2 mass-ppm phenol, use a smaller sample volume so that the measured phenol concentration is between 0.4 and 2.0 mass-ppm.

3. Allow the layers to separate. Drain the aqueous (lower) layer into a 150 mL beaker.
4. Add another 20-mL of 2% sodium hydroxide solution, cap, shake, vent, separate, and drain as above, into the same 150-mL beaker
5. Prepare the reference solution by placing 40 mL of 2% sodium hydroxide solution in a 150-mL beaker. Follow Steps 3 through 11 under *CALIBRATION*.
6. Obtain the mass of phenol from the calibration curve or least squares analysis.

CALCULATIONS

Calculate the actual concentration of phenol in the phenol stock solution to three significant figures using Eq. 1:

$$P = 0.1M \quad (1)$$

where:

M = mass of phenol weighed to prepare stock solution, g

P = phenol concentration in stock solution, mg/mL

$$0.1 = (1000 \times 5)/(500 \times 100)$$

where:

5 = aliquot taken from first dilution, mL

100 = volume of stock solution, mL

500 = volume after first dilution, mL

1000 = conversion factor, g to mg

Calculate the mass-ppm phenol in the sample, to two significant figures. If using the plotted calibration curve, use Eq. 2. If using a least squares analysis, use Eq. 3.

$$\text{Phenol, mass - ppm} = 1000 \frac{A}{BD} \quad (2)$$

where:

A = phenol mass obtained from calibration curve, mg

B = volume of sample selected for extraction, mL

D = density of sample, g/mL

1000 = conversion factor, mg to μg

or,

$$\text{Phenol, mass - ppm} = 1000 \frac{ES}{BD} \quad (3)$$

where:

E = absorbance of phenol in the sample, absorbance units

S = slope of the calibration curve, mg / absorbance unit

B, D and 1000 = previously defined

PRECISION

The precision statements were determined using UOP Method 999.

ASTM Repeatability

A nested design was carried out for determining phenol in toluene with two analysts in one laboratory. Each analyst carried out tests on two separate days, performing two tests each day. The total number of tests was 8. Using a stepwise analysis of variance procedure, the within-day estimated standard deviation (esd) was calculated and is listed in Table 2. Two tests performed by the same analyst on the same day should not differ by more than the ASTM allowable difference shown in Table 2 with 95% confidence.

UOP Repeatability

A nested design was carried out for determining phenol in toluene with two analysts in one laboratory. Each analyst carried out tests on two separate days, performing two tests each day. The total number of tests was 8. Using a stepwise analysis of variance procedure, the within-day estimated standard deviation (esd) was calculated and is listed in Table 2. Two tests performed in one laboratory by different analysts on different days should not differ by more than the UOP allowable difference shown in Table 2 with 95% confidence.

The data in Table 2 is a short-term estimate of repeatability. When the test is run routinely, a control standard and chart should be used to develop a better estimate of the long-term repeatability.

Reproducibility

There is insufficient data to calculate the reproducibility of the test at this time.

Table 2
ASTM and UOP Repeatability, mass-ppm

Mean Concentration	ASTM Repeatability		UOP Repeatability	
	Within-Day esd	Allowable Difference	Within-Lab esd	Allowable Difference
0.53	0.007	0.03	0.007	0.03

TIME FOR ANALYSIS

The elapsed time and labor requirement for a single analysis are identical, 0.9 hour.

REFERENCES

ASTM Method D 4052, www.astm.org
UOP Method 999, "Precision Statements in UOP Methods"

SUGGESTED SUPPLIERS

Aldrich Chemical Co., 1001 West Saint Paul Avenue, Milwaukee, WI 53233 (414-273-3850)
www.sigma-aldrich.com
Fisher Scientific, 50 Fadem Rd., Springfield, NJ 07081-3193 (973-467-6400) www.fishersci.com