

CARBONYL CONTENT OF PHENOL BY VISIBLE SPECTROPHOTOMETRY

UOP Method 804-83

SCOPE

This method is for determining carbonyl impurities in phenol by visible spectrophotometry. The test range is 1 to 200 mass/vol-ppm reported as mesityl oxide.

OUTLINE OF METHOD

The liquefied phenol sample is color-developed in a stoppered graduated cylinder by reacting it with 2,4-dinitrophenylhydrazine solution at 60 C. Alcoholic potassium hydroxide is added and the solution is brought to volume with ethanol. The absorbance of the color-developed solution is determined at 530 nm in a 5-mm cell and compared to a prepared curve of absorbance vs. known concentrations of mesityl oxide in phenol.

APPARATUS

Balance, readable to 0.1 mg

Bath, water, maintained at 60 ± 1 C

Beaker, 100-mL

Cylinder, graduated, 10-mL, glass stoppered (7 required)

Cylinder, graduated, 100-mL

Distillation equipment, as listed below for fractionation of ethanol, Reliance Glass Works, or equivalent

Column, distilling, Vigreux, 300-mm column length, $\frac{1}{2}$ 24/40 joints, Cat. No. R-3020-102

Distilling head, plain, with condenser, $\frac{1}{2}$ 24/40 joints, Cat. No. R-3051-100

Flask, round bottom, 2-L capacity, $\frac{1}{2}$ 24/40 joint, Cat. No. R-3910-110

Teflon sleeve, ground joint, $\frac{1}{2}$ joint 24/40, Cat. No. R-8100-118, or equivalent, (2 required)

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Stopper, Teflon, $\frac{3}{8}$ 10/30, Cat. No. R-6735-020

Heating mantle, hemispherical, with cordtrol, for 2-L flask, 500W, 115V, Cat. No. R-9066-116

Flasks, volumetric, 50- and 100-mL

Oven, drying

Pipets, 1-, 2-, 3-, 4-, 5- and 10-mL

Pipet, Mohr, 1- and 10-mL, graduated in tenths of a mL

Spectrophotometer, capable of measuring absorbance at 530 nm and holding a 0.5 mm cell, Beckman Instruments Inc., Model 35, or equivalent

REAGENTS AND MATERIALS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications exist, unless otherwise specified. References to water mean distilled or deionized water.

Ethanol, absolute. To prepare carbonyl free, reflux one liter of absolute ethanol with 5.00 g of 2,4-dinitrophenylhydrazine and 5 mL of concentrated hydrochloric acid for one hour. Distill using a 300-mm column. Discard the first 50 mL and 100 mL bottoms, retaining the 850-mL heart-cut.

2,4-Dinitrophenylhydrazine, 90% minimum purity, 10% water added by manufacturer, Sargent-Welch Scientific, Cat. No. EK 1866-100GM, or equivalent

2,4-Dinitrophenylhydrazine solution. Weigh 30 ± 0.5 mg of 2,4-dinitrophenylhydrazine into a 100-mL beaker. Add 0.3 mL of concentrated hydrochloric acid and 40 mL of carbonyl free ethanol. Warm in a water bath to dissolve, cool and transfer to a 50-mL volumetric flask and bring to volume with the ethanol. Prepare fresh every 6 months and store in a brown bottle.

Hydrochloric acid, concentrated

Mesityl oxide, having a maximum boiling range of 2 C and including a temperature of 127 C, Sargent-Welch Scientific, Cat. No. EKP582-001KG, or equivalent

Phenol, 99% minimum purity, low carbonyl. Manufacturers do not specify carbonyl content of phenol. Use material that does not significantly interfere with data generated at the lower end of the calibration curve. *CAUTION* Avoid skin contact, see *PRECAUTIONS*.

Potassium hydroxide, pellets, 85% minimum purity, Sargent-Welch Scientific, Cat. No. SC14201-500GM, or equivalent

Potassium hydroxide, alcoholic. Dissolve 20.00 ± 0.01 g of potassium hydroxide in 20 mL of water in a 100-mL volumetric flask. Dilute to volume with carbonyl free ethanol. Mix by inverting the flask several times. (Prepare fresh daily.)

CALIBRATION

Preparation of Standards

Weigh 100 ± 0.1 mg of mesityl oxide into a 50-mL volumetric flask. Melt the low carbonyl phenol in a water bath and add approximately 30 mL of the molten phenol to the flask. Swirl the flask to mix and then place the flask in a hot water bath at 60 C for about 5 minutes. Dilute to volume with phenol at 60 C and mix by inverting the stoppered flask several times. This stock solution contains 2000 μg of mesityl oxide per mL.

Using previously warmed pipets, transfer 1, 2, 3, 4 and 5 mL of the warm mesityl oxide stock solution successively into five separate 50-mL volumetric flasks. Dilute the contents of each flask to volume with molten phenol at 60 C. These flasks contain 40, 80, 120, 160 and 200 μg of mesityl oxide per mL.

Color Development

Transfer by a previously warmed pipet one milliliter of each of these solutions, which are maintained at 60 C, to separate 10-mL graduated cylinders. Prepare a reference blank by pipeting one milliliter of molten phenol into a sixth graduated cylinder. Color develop by adding one milliliter of 2,4-dinitrophenylhydrazine solution to each of the 6 graduated cylinders and stopper loosely. Swirl to mix and then place in a water bath at 60 C. After one minute, secure the stoppers and allow to remain in the bath for 50 ± 1 minutes. Cool them in room temperature water for two minutes then add 7.5 mL of alcoholic potassium hydroxide. Swirl to mix and bring up to volume with carbonyl free ethanol. Allow the flasks to sit three minutes and then read the absorbance of the standards vs. the blank in a 5-mm cell at 530 nm as soon as possible.

Prepare a calibration graph by plotting μg of mesityl oxide in the 10-mL graduated cylinders vs. absorbance.

PROCEDURE

Place the sample in a 60 C water bath to melt the phenol. When fluid, invert the container several times to mix contents. Transfer one milliliter of the sample from the container with a pipet, previously warmed in an oven for several minutes at 60 ± 10 C, into a 10-mL graduated cylinder. Prepare a blank by pipeting one milliliter of molten phenol used to prepare the calibration curve into a second graduated cylinder.

Continue the analysis as described under *Color Development*. Read the absorbance of the sample against the blank at 530 nm. If the absorbance is greater than 1.1, dilute a portion of the sample solution to 50 mL by pipeting one milliliter into a 50-mL volumetric flask and bringing to volume with carbonyl free ethanol.

From the calibration curve determine the μg of mesityl oxide in the sample solution.

CALCULATIONS

Calculate the carbonyl content of the phenol sample, expressed as mesityl oxide as follows:

If no additional dilution of the 10-mL sample solution was required:

$$\text{Mesityl oxide, mass/vol-ppm} = G$$

where:

G = mesityl oxide from the calibration curve, μg

If the carbonyl content is high and additional sample dilution was required:

$$\text{Mesityl oxide, mass/vol-ppm} = \frac{50G}{10}$$

where:

G = previously defined

10 = volume to which the sample was originally diluted, mL

50 = final volume of sample solution, mL

PRECAUTIONS

Carry out all operations in a hood, except for reading the absorbance of the color-developed solutions.

Avoid skin contact with the melted phenol. Wear plastic gloves where possible.

PRECISION

Based on 6 replicate determinations, the estimated standard deviation (esd) for carbonyl as mesityl oxide at the 90 mass/vol-ppm level was calculated to be 1.7 ppm. Duplicate results by the same operator should not differ by more than 6.0 mass/vol-ppm (95% probability) at the stated level.

TIME FOR ANALYSIS

The elapsed time for a single analysis is 2.75 hours. The labor requirement is 1.25 hours.

SUGGESTED SUPPLIERS

Beckman Instruments Inc., Scientific Instruments Div., 2500 Harbor Blvd., Fullerton, CA 92634

Reliance Glass Works, Inc., 17 Gateway Rd., Bensenville, IL 60106

Sargent-Welch Scientific Co., 7300 N. Linder Ave., Skokie, IL 60077