

***p*-PHENYLENEDIAMINE TYPE INHIBITORS IN GASOLINE**

UOP Method 374-90

SCOPE

This method is for determining UOP No. 5[®] or other *p*-phenylenediamine type inhibitors in gasoline. It is not applicable to aminophenolic or phenolic inhibitors. The method is limited to freshly-inhibited fuels since inhibitors that have been oxidized beyond an intermediate stage are not determined. Common gasoline dyes and tetraethyl lead do not interfere with this analysis. The lower limit of detection is approximately 0.2 mg/100 mL, which is approximately equivalent to 2.6 mass-ppm.

OUTLINE OF METHOD

A measured volume of gasoline is diluted with acetone and treated with acetic acid and *p*-benzoquinone. A soluble red-colored salt of the amine semiquinone is formed. The absorbance of this solution is measured in a spectrophotometer at 555 nm. The concentration of the inhibitor in the gasoline is determined by reference to a previously prepared calibration curve.

APPARATUS

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

Balance, readability 0.001-g, capacity 410 g

Bottle, amber, with TFE lined screw cap, 118-mL, Fisher Scientific, Cat. No. 03-320-4B

Cells, 10-mm light path, near-UV glass, matched pair, Fisher Scientific, Cat. No. 14-385-910A

Cylinders, graduated, 5-, 25- and 100-mL

Droppers, disposable, polyethylene, Fisher Scientific, Cat. No. 13-711-10

Flasks, volumetric, Class A, 50-, 100- and 250-mL

Pipet, Mohr, 5-mL, Fisher Scientific, Cat. No. 13-665K

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).

Pipets, volumetric, Class A, 1- and 10-mL, Fisher Scientific, Cat. Nos. 13-650-2B and 2L, respectively

Spectrophotometer, capable of measuring absorbances in the 510-560 nm wavelength

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 are available, unless otherwise specified. References to water mean deionized or distilled water.

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Acetic acid, glacial

Acetone, 99.5% minimum purity, Fisher Scientific, Cat. No. A949

p-Benzoquinone, purified, Fisher Scientific, Cat. No. Q36

Graph paper

Quinone reagent. Weight 0.15 ± 0.01 g of *p*-benzoquinone into a 100-mL volumetric flask, add approximately 50 mL glacial acetic acid and then fill to the mark. Store the benzoquinone solution in an amber bottle that is tightly capped. Prepare fresh solution weekly.

Isooctane (2,2,4-trimethylpentane), 99.9% minimum purity, Fisher Scientific, Cat. No. Q296

UOP No. 5, inhibitor, UOP

PROCEDURE

Preparation of Standard Solutions

1. Weigh to the nearest milligram 0.25 g of the UOP No. 5 inhibitor into a 250-mL volumetric flask.
 - If some other *p*-phenyldiamine type inhibitor is to be determined, use it instead of the UOP No. 5.
2. Add approximately 100 mL of isooctane and immediately mix.
 - Immediate mixing reduces oxidation of the inhibitor.
3. Dilute to volume with isooctane and invert several times to mix.
 - This solution is designated as stock "Solution A."
4. Pipet a series of 1- to 5-mL aliquots of stock "Solution A" into 5 separate 100-mL volumetric flasks.
5. Dilute each flask to volume with isooctane and invert several times to mix.
 - The resultant standard solutions contain 1, 2, 3, 4 and 5 mg of inhibitor/100 mL.
 - These standard solutions must be made just prior to preparation of the calibration curve and without interruption.
 - Protect the prepared solutions from extended exposure to light and air.

Preparation of Calibration Curve

1. Add 25 mL of acetone with a graduated cylinder to each of six 50-mL volumetric flasks.
2. Add 5 mL of glacial acetic acid with a graduated cylinder to each 50-mL flask.
3. Pipet 1 mL of the quinone solution into each 50-mL volumetric flask.
4. Dilute one of the 50-mL volumetric flasks with acetone to volume and invert several times to mix.
 - This is the reagent blank solution.
5. Fill the reference cell with the reagent blank solution and zero the spectrophotometer.
6. Pipet 10 mL of the most dilute standard solution into one of the 50-mL volumetric flasks containing the reagents.
7. Dilute to volume with acetone and mix.
8. Determine immediately the absorbance of the UOP No. 5 inhibitor solution versus the reagent blank at 555 nm.
 - If an inhibitor other than UOP No. 5 is to be determined, the wavelength at which maximum absorption occurs must be determined experimentally (see *NOTE*).
9. Repeat the procedure with 10-mL aliquots from the four remaining standard solutions.
 - Proceed sequentially from the most dilute to the most concentrated.
10. Plot the absorbances obtained vs. mg of inhibitor in 100 mL of the standard solutions.
 - Calibration should be performed once a week or when an inhibitor lot is changed.

Inhibitor in Gasoline Analysis

1. Pipet 10 mL of the gasoline sample into a 50-mL volumetric flask.
2. Add 5 mL of glacial acetic acid with a graduated cylinder, dilute to volume with acetone and mix by inverting the flask several times.
3. Fill the spectrophotometer reference cell with this sample blank and zero the instrument.
4. Add approximately 25 mL of acetone to another 50-mL volumetric flask.
5. Add 5 mL of glacial acetic acid with a graduated cylinder to the 50-mL volumetric flask.
6. Pipet 1 mL of the quinone reagent into the 50-mL volumetric flask.
7. Pipet 10 mL of the gasoline sample into the 50-mL volumetric flask.
8. Dilute to volume with acetone and mix.
9. Immediately measure the absorbance of this solution against the sample blank.

CALCULATIONS

Obtain the milligrams of inhibitor present in 100 mL of the gasoline sample directly from the calibration curve and report to the nearest 0.01 mg/100 mL.

NOTE

Measure the absorbance of the reactive mixture, prepared as indicated under *Preparation of Calibration Curve* and containing 4 mg of the *p*-phenylenediamine inhibitor in the standard solution at several wavelengths in the vicinity of 555 nm. Perform these measurements as rapidly as possible at the selected wavelengths, since the solutions tend to change, especially when exposed to light and air. Keep the 50-mL flask with the colored solution protected from light and air. Use an aliquot from this solution to replace the solution in the cell if changes are observed. Perform absorbance measurements on samples using the wavelength at which maximum absorption occurs.

PRECISION

Repeatability

Based on two tests performed by each of two analysts, on each of two days (8 tests) in one laboratory, the within-laboratory estimated standard deviation (esd) was calculated to be 0.016 at an inhibitor level of 2.63 mg/100 mL. Two tests performed in the one laboratory by different analysts on different days should not differ by more than 0.06 (95% probability) at the stated level.

Reproducibility

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

TIME FOR ANALYSIS

The elapsed time and labor requirement are identical; preparation of the calibration curve requires 2 hours and analysis of each sample, thereafter, requires 0.3 hour.

SUGGESTED SUPPLIERS

Fisher Scientific Co., 1600 W. Glenlake Ave., Itasca, IL 60143
UOP, Monirex Systems, 25 E. Algonquin Rd., Des Plaines, IL 60017-5017