



A Honeywell Company

Carbonyl Number by Chemical Analysis

UOP Method 624-14

Scope

This method is a spectrophotometric determination of the carbonyl number, present as ketone or aldehyde carbonyl, and defined as “milligrams of carbonyl function per liter of sample using acetophenone as the standard.” The color intensity of the reaction product is determined both by concentration and the type of R-group presenting the carbonyl function. This method applies to aqueous solutions, and hydrocarbons and alcohols in the C₅ to C₁₇ range. The typical analysis range for carbonyl number is 1 to 100 mg/L carbonyl. Results of this analysis are primarily used as an indication of the oxygen exposure of UOP Parex[®] and Molex[®] feedstocks.

Reference

UOP Method 79, “Fractionation of Petroleum Distillates,” www.astm.org

UOP Method 999, “Precision Statements in UOP Methods,” www.astm.org

Outline of Method

A known volume of sample is reacted with an acidic solution of 2,4-dinitrophenylhydrazine at 55 °C to form a phenylhydrazone. Alcoholic potassium hydroxide is added to convert the yellow phenylhydrazone to a red compound, and the absorbance is measured spectrophotometrically at 480 nm. The amount of carbonyl is read directly from a calibration curve, and divided by the volume of sample used, to obtain the carbonyl number.

Apparatus

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

Adapters, distillation, Reliance Glass Works, Cat. No. UOP 79

Balance, analytical, readable to 0.0001 g

Bottle, serum, 60-mL (2-oz), Wheaton, with stopper, Fisher Scientific, Cat. Nos. 06-406H and 06-406-11B, respectively

Bottle, amber, storage, 4-L, Fisher Scientific, Cat. No. 02-912-276

Cells, spectrophotometric, matched set, 10-mm path length

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. SAFETY DATA SHEETS (SDS) OR EXPERIMENTAL SAFETY DATA SHEETS (ESDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

© COPYRIGHT 1965, 1967, 1974, 1994, 2014 UOP LLC. All rights reserved.

Nonconfidential UOP Methods are available from ASTM International, 100 Barr Harbor Drive, P.O. Box C700, West Conshohocken, PA 19428-2959, USA. The UOP Methods may be obtained through the ASTM website, www.astm.org, or by contacting Customer Service at service@astm.org, 610.832.9555 FAX, or 610.832.9585 PHONE.

Column, distillation, Oldershaw, one-inch, glass, bubble plate, Reliance Glass Works, Cat. No. UOP 79

Cylinder, graduated, 100-mL, borosilicate glass, Fisher Scientific, Cat. No. 08-549-5E

Filter paper, Whatman No. 40, Fisher Scientific, Cat. No. 09-845C

Flask, distillation, Reliance Glass Works, Cat. No. UOP 79

Flask, volumetric, Class A, 25-mL, Fisher Scientific, Cat. No. 10-210-5A, several required

Flask, volumetric, Class A, 100-mL, Fisher Scientific, Cat. No. 10-210-5C

Funnels, 50- and 100-mm, Fisher Scientific, Cat. Nos. 10-326A and 10-326D, respectively

Ice bath, water ice

Pipet, adjustable, capable of pipeting one to 10 mL, Electronic Digital Pipette, Rainin Instrument, Cat. No. E4-10MLXLS

Receiver, distillation, 200-mL, Reliance Glass Works, Cat. No. UOP 79

Refrigerator, 0.6 to 7.2 °C, explosion proof, Fisher Scientific, Cat. No. 97-950-1

Spatula, micro, Fisher Scientific, Cat. No. 21-401-15

Spectrophotometer, capable of reading absorbances at 480 nm

Stabilizer, lead donut, 3.5-cm diameter, Glas-Col, Cat. No. 108B LD-4B

Stirrer, magnetic, Fisher Scientific, Cat. No. 11-500-4S

Stirring bar, magnetic, teflon-coated, Fisher Scientific, Cat. No. 14-513-61

Syringe, 3-mL, disposable, with needle, Fisher Scientific, Cat. No. 14-826-82 and 14-826-5B, respectively

Water bath, capable of maintaining a constant temperature of 55 °C, Fisher Scientific, Cat. No. 15-462-S3SQ

Wire, copper

Reagents and Materials

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used. References to water mean deionized or distilled water. Unqualified references to solutions mean aqueous solutions.

Acetophenone, Fisher Scientific, Cat. No. A22-500

Carbonyl standard solution. See preparation in *Procedure*.

Carbonyl stock solution. See preparation in *Procedure*.

2,4-Dinitrophenylhydrazine, Fisher Scientific, Cat. No. 241257

2,4-Dinitrophenylhydrazine solution, alcoholic. Transfer 0.1 g of 2,4-dinitrophenylhydrazine to a 100-mL volumetric flask, add about 75 mL of Formula 30, a stirring bar and stir for 1.5 hours. Remove the stirring bar. Dilute to the mark with Formula 30 and filter through Whatman 40 filter paper. Add 1 mL of concentrated hydrochloric acid to the filtrate and store in a glass-stoppered bottle or one having a polyethylene-lined cap. Refrigerate and maintain under a nitrogen blanket during use and storage. Prepare fresh solution after a period of five days.

Ethyl alcohol, UV grade, 200 proof, dehydrated alcohol, Fisher Scientific, Cat. No. A407-4

Formula 30. Weigh 10 grams of 2,4-dinitrophenylhydrazine and set aside. In a separate container, combine one gallon of ethyl alcohol, 400 mL of methanol and 200 mL of water and mix well. Add the 10 grams of 2,4-dinitrophenylhydrazine to the mixture when the sample is charged. Reflux the mixture for 2 hours and then distill the mixture as outlined by UOP Method 79, modified by the use of a one-inch glass Oldershaw column and by use of a nitrogen blanket over the column to prevent moisture and air from entering the distillate. Discard the first 200 mL of the distillate, then continue the distillation until approximately 75% of the alcohol has distilled over. *As a safety precaution, allow 10% of the original charge to remain as bottoms because there is the danger of violent decomposition of the residue if the pot is allowed to go dry.* Collect the distillate in an amber storage bottle, maintain it under a blanket of nitrogen and refrigerate.

Hydrochloric acid, concentrated, Fisher Scientific, Cat. No. A144-500

Ice, water

Isooctane, Fisher Scientific, Cat. No. O301-4

Methanol, Fisher Scientific, Cat. No. A454-4

Pipets, disposable transfer, Fisher Scientific, Cat. No. 13-711-5A

Pipet tips, 10-mL disposable, Rainin Instrument, Cat. No. RC-10ML

Potassium hydroxide, pellets, Fisher Scientific, Cat. No. P250-500

Potassium hydroxide solution, approximately 45%. Weigh approximately 45 g of potassium hydroxide pellets into a 100-mL volumetric flask. Add 75 mL of water to the flask and swirl to dissolve the pellets. Allow the flask to cool to ambient temperature. Add water to the mark, cap and invert several times to mix thoroughly.

Potassium hydroxide solution, alcoholic. Pipet 9.2 mL of 45% potassium hydroxide solution into a 100-mL volumetric flask. Add 33 mL of water to the flask and swirl to mix. Allow the flask to cool to ambient temperature and then dilute to the mark with Formula 30. Store under a nitrogen blanket and prepare a fresh solution after five days.

Sampling

Air and moisture must not be introduced into the sample during the sampling procedure. Purge the sample container with nitrogen before filling. A 60-mL (2-oz) bottle with a polyethylene-lined cap is a convenient sample container. Refrigerate the sample if it is not to be run immediately. Limited data suggest that sample carbonyl numbers increase rapidly if not stored under a nitrogen blanket at reduced temperatures.

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of spectrophotometry, and the equipment being used. Store reagents and standards under a nitrogen blanket and refrigerate when not in use. Dispose of used supplies and samples in an environmentally safe manner according to applicable regulations.

Glassware for this analysis must be kept separate from glassware used for other analyses. Glassware must be cleaned by rinsing thoroughly with water and finally with methanol. *Do not dry glassware with acetone. Acetone will contaminate the glassware and will produce false high results.*

Preparation of Carbonyl Stock Solution

1. Transfer about 0.020 g of acetophenone into a 100-mL volumetric flask. Record the mass (A) of the acetophenone in the flask to the nearest 0.0001 g.
2. Fill the flask to the mark with Formula 30, cap and mix well by repeated inversions until the acetophenone is completely dissolved.
 - The shelf life of this solution is one month.
3. Calculate the concentration of the carbonyl stock solution (B) to three significant figures using Equation 1:

$$B = \frac{10^6 A}{100} \quad (1)$$

where:

- A** = acetophenone added to flask, g
- B** = stock solution concentration, μg acetophenone/mL
- 100** = stock solution final volume, mL
- 10^6** = conversion factor, g to μg

Preparation of Carbonyl Standard Solution

1. Pipet 10 mL of the carbonyl stock solution into a 100-mL volumetric flask.
2. Fill the flask to the mark with Formula 30, cap and mix well by repeated inversions.
 - The shelf life of this standard is two weeks.
3. Calculate the concentration of the carbonyl standard solution (C) to three significant figures using Equation 2:

$$C = \frac{28.01 (10) B}{120.2 (100)} \quad (2)$$

where:

- B** = previously defined (Equation 1)
- C** = carbonyl standard concentration, μg carbonyl/mL
- 10** = aliquot of stock solution taken, mL
- 28.01** = molecular mass of carbonyl, g/mol
- 100** = final dilution volume, mL
- 120.2** = molecular mass of acetophenone, g/mol

Calibration

A fresh calibration is performed each time a sample set is analyzed.

1. Purge four separate 25-mL volumetric flasks with nitrogen.
2. Pipet 1-, 2-, and 3-mL aliquots of the carbonyl standard into three of the 25-mL volumetric flasks. The remaining empty flask will serve as the blank.
3. Add Formula 30 to each of the four flasks so that a total volume of 7 mL is in each flask, and then continue as described in *Sample Preparation*, beginning at Step 4.

Sample Preparation

1. Purge a 25-mL volumetric flask with nitrogen for each sample to be analyzed.
 - It is not feasible to analyze more than four samples at a time, due to the unstable developed color which must be read within a 5 minute time window.
2. Pipet 3 mL of sample into the nitrogen-filled flask.

- If the suspected carbonyl value is higher than the highest calibration standard, a smaller sample size may be used.
3. Pipet 4 mL of Formula 30 into the flask.
 - If a smaller sample size was used in Step 2, increase the Formula 30 aliquot so that the sample plus Formula 30 volume is 7 mL.
 4. Pipet 2.5 mL of 2,4-dinitrophenylhydrazine solution into each flask. Stopper and swirl each flask. Then place a lead donut stabilizer around the neck of each flask.
 5. Suspend each flask, with the stopper slightly loosened, in a water bath at 55 °C for 30 minutes.
 6. Immediately cool the flasks to room temperature by immersing the flasks in an ice water bath for about one minute.
 7. Pipet 4 mL of the potassium hydroxide solution into each flask. Stopper and swirl to mix. Let stand for about five minutes.
 - If the solution contains oil that is insoluble in the reaction mixture and forms a floating layer in the neck of the flask, draw off the oil layer with a disposable transfer pipet. If the oil does not float on top of the reaction mixture but instead remains beneath the surface, add 0.5 mL of isooctane directly into the oil phase using a disposable pipet. A very slight swirl to mix will cause the oil phase to float on top of the medium. Remove all of the oil phase.
 - If the solution is cloudy, filter the solution using Whatman No. 40 filter paper.
 8. Dilute each flask to the mark with Formula 30. Cap and mix well by repeated inversions.
 9. Zero a dual-beam spectrometer at a wavelength of 480 nm with the blank in a 10-mm cell in the sample side and air, without cell, in the reference side.
 - If a single-beam spectrometer is used, zero with the blank in the 10-mm cell.
 - Zeroing on the blank automatically subtracts the blank absorbance from the following standard and sample absorbances (Step 10), yielding the net absorbances for use in *Calculations*.
 10. Read the absorbance of each of the standard and sample solutions using a 10-mm cell at a wavelength of 480 nm, no sooner than 10, nor later than 15 minutes after addition of the potassium hydroxide.
 - The developed color is not stable and must be read within the 10 to 15 minute time window after the addition of the potassium hydroxide.

Calculations

Calculate the μg carbonyl function in each of the standards to three significant figures using Equation 3. Using the net absorbance readings from the standards, plot a graph of absorbance versus micrograms of carbonyl function (see Figure for a Typical Plot).

$$\mu\text{g Carbonyl Function} = CV \quad (3)$$

where:

C = previously defined (Equation 2)

V = volume of carbonyl standard solution taken, from *Calibration*, Step 2, mL

Determine the micrograms of carbonyl found in the sample by using the net absorbance of the sample and the previously prepared calibration curve. Calculate the carbonyl number using Equation 4. Report to the nearest 1 mg/L.

$$\text{Carbonyl Number, mg carbonyl/L} = \frac{R}{S} \quad (4)$$

where:

R = carbonyl function from the calibration curve, μg

S = volume of sample (from *Sample Preparation*, Step 2), mL

Precision

Precision statements were determined using UOP Method 999, "Precision Statements in UOP Methods."

Repeatability and Site Precision

A nested design was carried out for determining carbonyl number on samples by two analysts on two separate days, performing two analyses each day for a total of eight analyses. Using a stepwise analysis of variance procedure, the within-day estimated standard deviations (esd) were calculated at the concentration means listed in Table 2. Two analyses performed in one laboratory by the same analyst on the same day should not differ by more than the repeatability allowable differences shown in Table 2 with 95% confidence. Two analyses performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable differences shown in Table 2 with 95% confidence.

Table 2
Repeatability and Site Precision, Carbonyl Number, mg carbonyl/L

<u>Sample</u>	<u>Mean</u>	<u>Repeatability</u>		<u>Site Precision</u>	
		<u>Within-Day esd</u>	<u>Allowable Difference</u>	<u>Within-Lab esd</u>	<u>Allowable Difference</u>
A	4	0.1	1	0.1	1
B	10	0.1	1	0.4	2
C	14	0.2	1	1.1	6

The data in Table 2 represent short-term estimates of the repeatability of the method. When the test is run routinely, use of a control standard and a control chart is recommended to generate an estimate of long-term repeatability.

Reproducibility

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

Time for Analysis

The labor requirement for a single analysis is one hour and the elapsed time is also one hour, excluding preparation of Formula 30. Four samples can be completed in 2 hours. It is not feasible for one analyst to analyze more than 4 samples at a time using this method. Distillation of the Formula 30 takes approximately 12-14 hours.

Suggested Suppliers

Fisher Scientific, 300 Industry Dr., Pittsburgh, PA 15275, USA, 1-412-490-8300,
www.fishersci.com

Glas-Col, 11 Hulman St., Terre Haute, IN 47802, USA, 1-812-235-6167, www.glascol.com

Rainin Instrument Co., Mack Rd., Woburn, MA 01801, USA, 1-800-472-4646, www.rainin.com

Reliance Glass Division, 1455 Elmhurst Rd., Elk Grove Village, IL 60007, USA, 1-847-228-2851,
www.wilmad-labglass

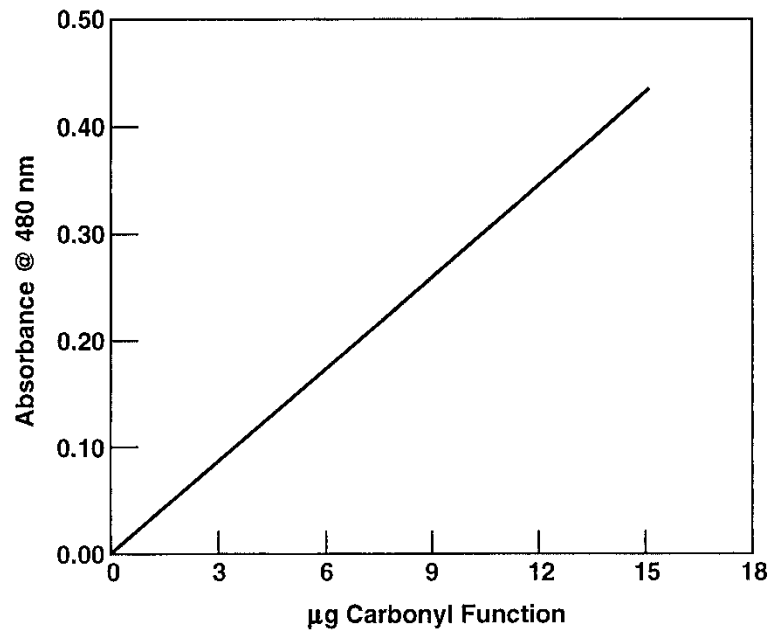


Figure
Typical Plot