



A Honeywell Company

Total Oxygen in Solid, Semi-solid, and High Boiling Point Liquid Hydrocarbons by Pyrolysis

UOP Method 649-10

Scope

This method is for determining total oxygen in solid, semi-solid, and high boiling point liquid hydrocarbons at concentrations ranging from approximately 0.1 to 50 mass-%. Sampling methods are described for several types of sample matrices. The method determines the total oxygen, including organic oxygen compounds, dissolved water and dissolved molecular oxygen. The contributions of oxygen from water and dissolved molecular oxygen can be measured using other methods (see *References* below) and subtracted from this result. Volatile liquid samples should be analyzed using UOP Method 730, "Total Oxygen in Liquid Hydrocarbons by Pyrolysis."

References

ASTM Method D 1364, "Water in Volatile Solvents (Karl Fischer Reagent Titration Method)," www.astm.org

ASTM Method D 4052, "Density and Relative Density of Liquids by Digital Density Meter," www.astm.org

UOP Method 481, "Water in Liquid Hydrocarbons by Coulometry," www.astm.org

UOP Method 678, "Dissolved Molecular Oxygen in Liquid Hydrocarbons by Electrochemical Detection," www.astm.org

UOP Method 730, "Total Oxygen in Liquid Hydrocarbons by Pyrolysis," www.astm.org

Outline of Method

An oxygen analyzer (CHN/O instrument) is set up and calibrated with liquid standards or solid standards, as required for the sample matrix. Liquid samples are diluted in toluene and directly injected into the pyrolysis reactor in a helium carrier. Solid or semi-solid samples are sealed in silver foil capsules before introduction into the pyrolysis reactor. Samples are pyrolyzed at a temperature in excess of 1000°C. A metalized carbon reagent helps convert all of the oxygen in the sample into carbon monoxide (CO). Acid gas is removed from the product stream with an appropriate trap material (soda lime). The pyrolysis product gas is passed through a GC column to separate the CO. The CO content is measured using thermal conductivity detection.

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).

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Apparatus

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

Balance, readability 0.1-mg

Capsule press, CE Elantech, Cat. No. 205-030-02

CHN/O Analyzer, Thermo Scientific, Model FLASH 2000, available from CE Elantech. Instrument is equipped with a liquid autosampler and/or a solids autosampler, depending on the types of samples analyzed. Follow the manufacturer's recommendations for maintaining a supply of spare parts and consumables, such as autosampler vials. Any use of an alternative instrument must be tested to determine if it provides equivalent sensitivity and precision.

Flasks, volumetric, Class A, borosilicate glass, 10-, 25-, and 50-mL, Fisher Scientific, Cat. Nos. 20-812D, 10-210-8A, and -8B, respectively

Hot plate, Fisher Scientific, Cat. No. 11-100-16H

Microbalance, readability 1- μ g, Mettler-Toledo, Model MX5. The microbalance is normally purchased with the instrument and configured to automatically transfer the sample weights to the instrument control program.

Pipet, automatic delivery with disposable plastic tips, 20 μ L, Fisher Scientific, Cat. No. 21-377-817

Pipet, volumetric, Class A, 1-, 2-, 5- and 10-mL, Fisher Scientific, Cat. No. 13-650-2B, -2C, -2F, and -2L, respectively

Pipet filler, Fisher Scientific, Cat. No. 13-681-51

Regulator, helium, two-stage, high purity, with stainless steel diaphragm, delivery pressure range 30-700 kPa (4-100 psi), Matheson, Cat. No. 3810-580

Syringe, gastight, 250- μ L, CE Elantech, Cat. No. 365-040-42

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.

The following items are required to perform the analysis. Additional reagents and materials may be required depending on the specific oxygen analyzer utilized. Where different reagents are specified in the instrument manual, follow the manufacturer's recommendations.

BBOT (2,5-Bis(5-*tert*-butyl-benzoxazol-2-yl)thiophene), CE Elantech, Cat. No. 338-352-10. For calibration, nominal oxygen content 7.43 mass-%. Certificate of Analysis sent with material.

Benzoic acid, Aldrich, Cat. No. 242381-100G. For calibration, nominal oxygen content 26.2 mass-%. Certificate of Analysis sent with material.

Cystine, CE Elantech, Cat. No. 338-400-18. For calibration, nominal oxygen content 26.6 mass-%. Certificate of Analysis sent with material.

Helium, compressed gas, 99.999% minimum purity, such as Matheson Ultra High Purity.

Magnesium perchlorate (anhydrous), CE Elantech, Cat. No. 338-219-00

Methionine, CE Elantech, Cat. No. 338-352-20. For calibration, nominal oxygen content 21.5 mass-%. Certificate of Analysis sent with material.

Nickel coated carbon, CE Elantech, Cat. No. 338-238-00

Pipet, transfer, disposable plastic, 152-mm length, Fisher Scientific, Cat. No. 13-711-SA

Quartz turnings, CE Elantech, Cat. No. 338-223-10

Quartz wool, CE Elantech, Cat. No. 338-222-50

Silver capsules for liquids, CE Elantech, Cat. No. 240-051-00

Silver foil capsules, CE Elantech, Cat. No. 240-054-00

Soda lime, CE Elantech, Cat. No. 338-352-30

Toluene, anhydrous, Burdick & Jackson, Cat. No. AS347-1

Water, deionized or distilled. For calibration, oxygen content, 88.81 mass-%.

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of pyrolysis, and the equipment being used. This procedure is written for the Thermo Scientific instrument CHN/O analyzer listed in *Apparatus*. If a different instrument is used, modify the procedure as needed.

Preparation of Liquid Calibration Standards

Calibration standards can be prepared from various materials. The preparation of liquid standards using benzoic acid diluted in anhydrous toluene is described herein, and the *Calibration* and *Calculation* sections are written assuming the use of the benzoic acid in anhydrous toluene calibration standards. Alternative calibration standards may be used, with appropriate adjustments to the method.

For a benzoic acid in anhydrous toluene calibration standard, prepare a nominally 1.0 mass/volume-% oxygen (O) calibration standard as follows (see *Note 1*):

1. Weigh 0.95 ± 0.05 g of benzoic acid to the nearest 0.1 mg into a tared 25-mL volumetric flask.
2. Dilute to the mark with anhydrous toluene.
3. Calculate the concentration of oxygen, to four significant figures, in the benzoic acid stock solution using Equation 1:

$$\text{Oxygen, mass/volume-\%} = 4 M \left(\frac{31.998}{122.12} \right) \quad (1)$$

where:

M = mass of benzoic acid weighed into flask, g

4 = factor to convert to mass/volume-% (100% / 25 mL)

31.998 = atomic weight of 2 oxygen atoms per molecule of benzoic acid

122.12 = molecular weight of benzoic acid

4. Prepare additional calibration standards containing nominally 0.1-, 0.05-, and 0.01-mass/volume-% O by dilution of the stock solution with anhydrous toluene in volumetric flasks.
 - Other working solutions may be prepared if needed.
 - The 0.01 mass/volume-% solution can be prepared as a 1:10 dilution of the 0.1 mass/volume-% solution instead of a 1:100 dilution of the 1.0 mass/volume-% stock solution.
 - Use volumetric pipets and volumetric flasks to keep concentration as mass/volume-% O.
 - The solutions are stable for one week.

Preparation of Apparatus

Before starting, the instrument should be configured according to the manufacturer's recommendations. For the FLASH 2000 analyzer, the settings listed in Table 1 are recommended.

Table 1
Instrument Operating Conditions

He flow rate (analytical)	130 mL/min
He flow rate (reference)	100 mL/min
Furnace temperature	1060 °C
Column oven temperature	75 °C
Detector gain	x10
Sample size (liquid)	20-30 µL
Sample size (solid)	5-10 mg

- Load the pyrolysis reactor according to the manufacturer's directions.
 - The order of the reagent layers and layer thicknesses stated by the manufacturer should be followed closely.
 - Do not over compress the reagents when packing since this can lead to backpressure problems and poor analytical performance. Tap the pyrolysis reactor to settle the material.
- Check the system for leaks before heating the pyrolysis reactor, following the procedures as described by the instrument manufacturer. The instrument must pass the manufacturer's leak specification before proceeding.
 - The helium should continue to flow through the reactors.
- Disconnect the pyrolysis reactor from the acid gas trap and heat the instrument to operating temperature to remove water from the nickel carbon reagent.
 - The inlet to the trap should either have dry helium flowing through it or should be capped during the pyrolysis reactor bake out.
 - The water desorbed from the nickel carbon should not be allowed to enter the GC column. It can result in a loss of CO retention time by remaining in the molecular sieve column packing. The water will also condense in the thermal conductivity detector, causing baseline drift until the detector finally stabilizes.
- The pyrolysis reactor should be kept at 1060°C for at least 2 hours for conditioning.
 - When not actively analyzing samples, the instrument is in standby at half the temperature setpoint.
- Refill the acid gas trap with magnesium perchlorate and soda lime, as per the manufacturer's instructions. Add 3 drops of water to the soda lime before reassembling the trap.
- Leak check the instrument before calibrating or analyzing samples.
 - The instrument should always pass the leak check before starting a calibration and at the beginning of the day; otherwise troubleshoot the leak before proceeding.

Calibration of Apparatus

Part A – Liquid Calibration

- Select the appropriate calibration standards for a linear calibration over the range of interest. It is recommended to include at least 3 standards and a solvent blank (anhydrous toluene). Follow instrument manufacturer's guidelines to determine maximum injectable volume.

- The linear calibration is made from injections of the same volume of standards of different concentrations.
 - It is recommended that an autosampler be used with the instrument.
 - The sample must be completely injected into the pyrolysis reactor. Small volumes and/or slow injection rates can result in a loss of sample to the walls of the pyrolysis reactor, resulting in a bias to lower results.
 - The use of larger injection volumes shortens the useful life of the pyrolysis reactor. The injection of 20-30 μL from a 250 μL syringe is the best compromise for meeting the analytical requirements while maximizing the reactor life.
2. Create a calibration program sequence in the instrument control software. The solvent blank and the standards on the calibration sequence should be analyzed in duplicate.
 - 3-5 injections of anhydrous toluene should be made before starting the calibration to condition the pyrolysis reactor.
 - The injections of the anhydrous toluene and lowest standard should repeat within 20% relative, and the standards above 0.02% O, within 10% relative. If not, check the equipment and procedures.
 3. Fill autosampler vials with the standards using disposable transfer pipets. Place the samples in the appropriate positions on the autosampler.
 4. Run the calibration sequence according to manufacturer's instructions.
 5. Once completed, check the calibration line. If a single injection of a standard is off of the calibration line (the CF reported by the data system is less than 0.99), re-analyze that standard. If the chromatograms show excessive tailing, the pyrolysis reactor will need to be repacked. See *Preparation of Apparatus*, Step 1. If tailing still occurs, consult the instrument manual for other possible causes and remedies.
 - Inspect the peaks on the chromatogram. On occasion the data system will miss or incorrectly measure the CO peak. The solvent blanks and low standards may require reintegration and recalculation.

Part B – Solid Calibration

1. Select the appropriate calibration standards for a linear calibration over the range of interest. Typically, three or more standards and a blank are run.
 - BBOT (nominally 7.43 mass-% O) is recommended for 0.1 – 10% oxygen calibration
 - Calibrations above 10% oxygen should use a high level standard, such as benzoic acid (nominally 26.2 mass-% O), methionine (nominally 21.5 mass-% O), or cystine (nominally 26.6 mass-% O) as part of the calibration set.
 - Samples containing more than 30% water should be analyzed using a calibration curve with deionized water (88.81 mass-% O) as the oxygen standard.
2. Create a calibration program sequence in the instrument control software. 2 or 3 empty silver capsules (either hard or foil) should be analyzed at the start of the calibration sequence.
 - Silver capsules serve to condition the instrument and serve as the instrument blank value.
 - The standard should repeat within 10% relative. If not, check the equipment and procedures.
3. Weigh the standard into the silver capsules over the range of 0.1 to 10 mg.
 - Solid materials are weighed in silver foil capsules.
 - For samples containing high amounts of water, the deionized water calibrant should be dispensed into tared hard silver capsules, purged with helium and then crimp sealed before weighing (see *Note 2*).

4. Run the calibration sequence according to manufacturer's instructions.
5. Once completed, check the calibration line. If a single measurement of a standard is off of the calibration line (the CF reported by the data system is less than 0.99), re-analyze that standard. If the chromatograms show excessive tailing, the pyrolysis reactor will need to be repacked. See *Preparation of Apparatus*, Step 1. If tailing still occurs, consult the instrument manual for other possible causes and remedies.
 - Inspect the peaks on the chromatogram. On occasion the data system will miss or incorrectly measure the CO peak. The solvent blanks and low standards may require reintegration and recalculation.

Sample Analysis

Benzoic acid in anhydrous toluene can be used to calibrate up to 1% oxygen in samples (see *Note 1*). If the result for the diluted portion of the sample is less than 0.02% oxygen or greater than 1% oxygen, re-dilute and reanalyze.

Part A - Dilution Procedure for Liquid Samples

1. Calibrate the instrument using 1% oxygen standard as the highest point on the calibration line.
2. Using a volumetric pipet, add 2.00 mL of sample to a 10-mL volumetric flask. If diluting by mass, use approximately 2 g of sample measured to the nearest 0.1 mg.
3. Dilute the sample to the mark with anhydrous toluene and shake the flask well to mix.
4. Fill an autosampler vial with diluted sample using a disposable transfer pipet.
5. Set up the sample program to analyze the samples.
6. Follow the procedure recommended by the manufacturer for the analysis of the sample.
 - Sample analysis is generally performed at least in duplicate; 3 or 4 replicate injections are recommended. Average the results. The repeatability of the replicates should be within the precision of the method. If they are not, look for air bubbles in the syringe or other instrument malfunction.
 - The sample must be completely injected into the pyrolysis reactor. Small volumes and/or slow injection rates can result in a loss of sample to the walls of the pyrolysis reactor, resulting in a bias to lower results.
 - 1 or 2 conditioning blanks should be injected before the first sample if the instrument has been idle for longer than 30 minutes.
7. A QC sample should be analyzed before and after the set of samples to check instrument stability.
 - A benzoic acid in toluene solution made at a concentration not used for calibration can be used as a QC. This solution should be prepared each week.

Part B - Capsule Procedure for Solid Samples

1. Calibrate the instrument using solid organic standards, such as BBOT or methionine, depending on the concentration range of the samples.
2. Samples should be ground to a fine powder or chipped into small pieces.
3. Tare the capsule.
4. Add the sample to the silver foil capsule. Fold the capsule to exclude air before weighing.

- Weigh 5 – 10 mg of sample.
5. Weigh the sample in the tared capsule and enter the weight on the sample table.
 6. Repeat steps 3 – 5 for this sample for a duplicate analysis. If the sample is non-homogeneous, analyze a third portion.
 7. Repeat these steps for all remaining samples.
 8. Follow the procedure recommended by the manufacturer for the analysis of the sample.
 - Sample analysis is generally performed at least in duplicate. Average the results of all the analyses performed. The repeatability of the replicates should be within the precision of the method.
 - 1 or 2 conditioning blanks (empty silver capsules) should be analyzed before the first sample, if the instrument has been idle for longer than 30 minutes.
 9. A QC sample should be analyzed before and after the set of samples to check instrument stability.
 - The QC material should be a different compound than the one used for calibration.

Part C - Capsule Procedure for Semi-solid and Low Melting Point Solids

1. Calibrate the instrument using solid organic standards, such as BBOT or methionine, depending on the concentration range of the samples.
2. Warm the samples on a hot plate until melted, then cap and mix thoroughly.
3. Unfold the silver foil capsule until nearly flat. Tare the capsule.
4. Add a drop of the sample to the foil capsule near the center.
 - Weigh 5 – 10 mg of sample.
5. Allow the drop of sample to cool to room temperature and solidify.
6. Fold the foil in half, then fold in from each side and then finally fold down the top of the foil capsule to make a sealed packet.
7. Weigh the sample in the tared capsule and enter the weight on the sample table.
8. Repeat steps 3 – 7 for this sample for a duplicate analysis. If the sample is non-homogeneous, analyze a third portion.
9. Repeat these steps for all remaining samples.
10. Follow the procedure recommended by the manufacturer for the analysis of the sample.
 - Sample analysis is generally performed at least in duplicate. Average the results. The repeatability of the replicates should be within the precision of the method.
 - 1 or 2 conditioning blanks (empty silver capsules) should be analyzed before the first sample if the instrument has been idle for longer than 30 minutes.
11. A QC sample should be analyzed before and after the set of samples to check instrument stability.
 - The QC material should be a different compound than the one used for calibration.

Calculations

The instrument software will calculate the sample results for solid samples as mass-% oxygen directly. For liquid samples, the results are calculated on a volume basis (since the injection volume remains constant) unless the sample mass is entered into the sample table. Some instruments will allow the user to enter the sample density to convert the results to mass-% oxygen. In that case, use 0.866 as the density of the toluene standards and dilutions.

For diluted liquid samples, calculate the oxygen concentration of the original sample in mass-% using Equation 2:

$$\text{Oxygen, mass-\%} = \frac{C}{D} \left(\frac{B}{A} \right) \quad (2)$$

where:

- A** = volume of sample diluted, mL (2.0 mL, from *Sample Analysis, Dilution Required*, Step 2). If the sample was taken by mass, then **A** = **sample mass / density** (from ASTM D4052 or similar)
- B** = total volume of first dilution, mL (10 mL, from *Sample Analysis, Dilution Required*, Steps 2 and 3)
- C** = concentration of oxygen measured, mass/volume-%
- D** = density of the solvent, g/mL

Report diluted samples to one decimal place after calculation.

Notes

1. Benzoic acid solutions in toluene will reach a solubility limit at ~10% benzoic acid (approximately 2.6% O). All benzoic acid/toluene solutions at or above 1% oxygen should be checked for precipitate formation before use.
2. Low vapor pressure liquid standards and samples (e.g. water, C₁₆ hydrocarbons) can be analyzed by sealing in crimped hard silver capsules. The capsules are tared before dispensing the sample. After the sample is introduced, the capsules are purged with helium before sealing. It is recommended to install an indicating flow controller (such as a rotameter) on the purge helium supplied to the press.

Precision

The precision data listed below was generated using a Thermo Flash EA1112 CHN/O Analyzer. The instrument was renamed the FLASH 2000 in 2009. If another instrument is to be used, confirm its precision and accuracy at the oxygen concentrations to be measured. Precision statements were determined using UOP Method 999.

Repeatability and Site Precision

A nested design was carried out for determining the oxygen content of three samples with two analysts in one laboratory. Each analyst carried out tests on two separate days, performing four tests on each sample each day. The total number of tests was 48. The precision data are summarized in Table 2. Two tests performed by the same analyst on the same day should not differ by more than the repeatability allowable difference with 95% confidence. Two tests performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable difference with 95% confidence.

The data in Table 2 are 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 reproducibility of the test at this time.

Table 2
Repeatability and Site Precision, oxygen, mass-%

<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>
Diluted Liquid	0.22	0.005	0.02	0.013	0.06
Vacuum Gas Oil	0.30	0.018	0.06	0.022	0.08
Organic Solid	21.5	0.28	0.9	0.41	1.5

Time for Analysis

The elapsed time for one analysis, including calibration, is approximately 1.5 hours. Each succeeding analysis requires 0.3 hour. Preparation of the calibration standards requires approximately 0.5 hour of labor. Analysis of each standard or sample requires 0.1-0.2 hour of labor (transferring or diluting samples, creating the sample table, reviewing the chromatograms, and recalculating when necessary).

Suggested Suppliers

Aldrich, 1000 West Saint Paul Avenue, Milwaukee, WI 53233 (414-273-3850) www.sigma-aldrich.com

Burdick & Jackson, 1953 S. Harvey St., Muskegon MI 49442 (231-726-3171)
www.burdickandjackson.com

CE Elantech, 170 Oberlin Avenue North, Suite 5, Lakewood, NJ 08701-4548 (732-370-5559)
www.ceelantech.com

Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219-4785 (412-490-8300) www.fishersci.com

Matheson Tri-Gas, 166 Keystone Drive, Montgomeryville, PA 18936 (215-641-2700)
www.mathesontrigas.com

Mettler-Toledo, 1900 Polaris Parkway, Columbus, OH 43240 (614-438-4511) www.mt.com

Thermo Fisher Scientific, 81 Wyman Street, Waltham, MA 02454 (781-622-1000)
www.thermo.com