Designation: D8534 – 23

Standard Test Method for
Determination of Trace Peroxides in Liquid, Liquefied, and Reagents Soluble Hydrocarbon Streams using Flow Injection System with Ultraviolet/Visible Detector[1]

1. Scope

1.1 This test method covers the determination of trace peroxides in various hydrocarbon streams. A list of typical hydrocarbon streams can be found in Appendix X2.

1.2 This test method is applicable to the determination of peroxides in petroleum liquids including, but not limited to, 1,3-butadiene, styrene, methylcyclohexane, and alpha olefins in the range of 0.1 mg⁄kg to 100 mg⁄kg active oxygen. The limit of detection (LOD) is 0.03 mg⁄kg for active oxygen and the limit of quantitation (LOQ) is 0.11 mg⁄kg active oxygen. The upper limit has been determined by the calibration range.

NOTE 1—LOD and LOQ were calculated using data obtained during development of the method.

1.3 In determining the conformance of the test results using this method to applicable specifications, results shall be rounded off in accordance with the rounding-off method of Practice E29.

1.4 *Units*—The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Section 9.

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]
D1193 Specification for Reagent Water
D1265 Practice for Sampling Liquefied Petroleum (LP) Gases, Manual Method
D3437 Practice for Sampling and Handling Liquid Cyclic Products
D3700 Practice for Obtaining LPG Samples Using a Floating Piston Cylinder
D4790 Terminology of Aromatic Hydrocarbons and Related Chemicals
D6809 Guide for Quality Control and Quality Assurance Procedures for Aromatic Hydrocarbons and Related Materials
E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

2.2 *Other Documents:*
29 CFR 1910.1000 OSHA Regulations, Toxic and Hazardous Substances—Air Contaminants[3]
29 CFR 1910.1200 OSHA Regulations, Toxic and Hazardous Substances—Hazard Communication[3]

3. Terminology

3.1 *Acronyms:*
3.1.1 *DBP*—dibenzoyl peroxide
3.1.2 *DLP*—dilauroyl peroxide

4. Summary of Test Method

4.1 This method uses a Flow Injection System (FIS) based on High Performance Liquid Chromatography (HPLC) hardware. A sample suspected of containing peroxides is injected in a reagent stream of acidified iodide. Peroxides present in the

---

sample react with the iodide to form iodine. The formed iodine is detected using UV-Vis and is directly proportional to the peroxide content. The concentration of peroxides in the hydrocarbon sample is determined by an external calibration with dibenzoyl peroxide (DBP).

5. Significance and Use

5.1 This test method is suitable for determining the quantity of hydrogen peroxide, organic hydroperoxides, and organic peroxides as total active oxygen in various hydrocarbon streams for both quality control and quality assurance of the product.

6. Interferences

6.1 Bulk carbonyl compounds interfere by partially and/or fully reacting with the formed iodine. If the user desires to test carbonyl products for peroxides, the calibration shall be made in identical bulk material.

6.2 Samples that exhibit absorbance in the range of 350 nm to 370 nm will interfere and require a correction.

6.3 Peracids have identical reactivity to peroxides and will add to the total active oxygen.

6.4 Compounds present in samples having a higher reduction potential iodine will interfere by reacting iodide to iodine.

6.5 Double sterically hindered peroxides, like di-*tert*-butyl peroxide and di-cumyl peroxide, will not or only partially react with the iodide.

6.6 Dissolved oxygen in the sample might interfere by partially and/or fully reacting with iodide, adding to the total active oxygen.

7. Apparatus

7.1 The instrument consists of the following modules, which shall be configured in accordance with Fig. 1.

7.1.1 *HPLC System*—Any high-performance liquid chromatograph capable of delivering four liquids at flow rates between 0.5 mL/min and 3.0 mL/min. A degasser is highly recommended.

7.1.2 *Liquid Sample Injection System*—A manual and/or automated sample injection system capable of injecting sample of 10 μL (nominal) with a repeatability better than 2 %. For samples that exhibit auto-polymerization or evaporate quickly at room temperature, it is highly recommended to equip the automated sample injection system with an integrated cooler.

7.1.3 *Liquefied Sample Injection System*—A pressure station that supplies high pressure nitrogen to a suitable sample cylinder and therefore maintains sample in the liquid phases during the injection procedure. Typical nitrogen supply pressures range from 1500 kPa for 1,3-butadiene to 10 000 kPa for ethylene. The pressure station shall be connected to a sampling valve capable of injecting sample volumes of 10 μL (nominal) with a repeatability better than 2 %.

7.1.4 *Reaction Module*—A reaction module, holding the reaction coil, capable of maintaining a constant temperature ($\pm 1\,°C$) within the range from 140 °C to 180 °C with a minimum accuracy of 7 °C.

7.1.5 *Variable Wavelength Detector*—Any ultra-violet/visible detector, capable of recording the absorbance of a single wavelength in a range of 300 nm to 400 nm.

7.1.6 *Data Acquisition*—Any commercial integrator or computerized data acquisition system may be used for display of the detector signal and peak integration. Chromatographic data systems are preferred but electronic integration may be used if the user can demonstrate that the results are consistent with the precision statement.

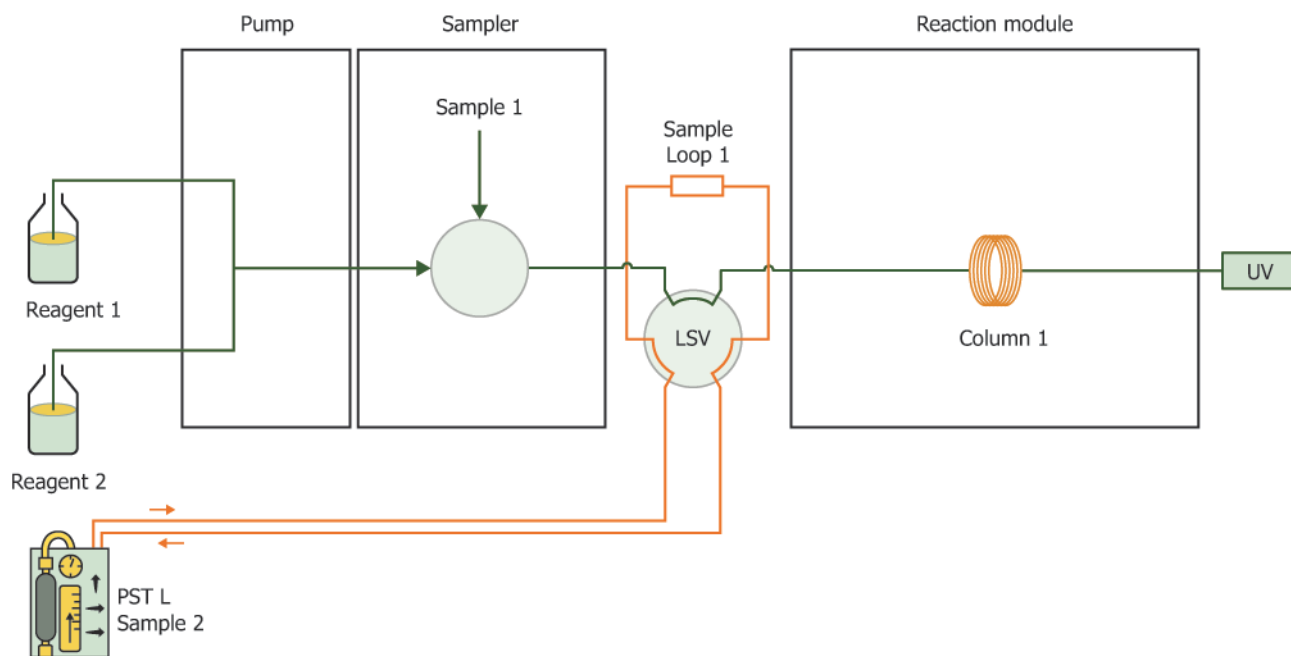7.2 *Analytical Balance,* capable of weighing to 0.1 mg precision.

FIG. 1 Schematic Overview of the Flow Injection System

7.3 *Glass Erlenmeyer Flask,* with a minimum capacity of 300 mL, with stopper.

7.4 *Weighing Boats,* paper or polystyrene.

7.5 *HPLC Bottles,* amber and transparent glass, with 1 L capacity.

7.6 *Volumetric Cylinders,* capable of measuring 500 mL or 1000 mL and 50 mL.

7.7 *LC Autosampler Vials,* 1.5 mL capacity with crimp or screw cap and poly-isobutene septa.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[4] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *1-Propanol (CAS 71-23-8)*—Analytical reagent grade, containing less then 50 µg/kg active oxygen.

8.3 *Glacial Acetic Acid (CAS 64-19-7) 1-Propanol Solution (5 % v/v)*—Measure 950 mL 1-propanol in a clear HPLC bottle and add 50 mL of glacial acetic acid (100 %). Stir the solution vigorously for approximately 30 s. Alternative volumes of solutions may be prepared so long as the preparation meets the concentration specified.

8.4 *Sodium Iodide (CAS 7681-82-5) 1–Propanol Solution (1 % m/v)*—Dissolve 10 g ± 0.1 g of analytical grade (99.5 %) sodium iodide in 1000 mL of 1-propanol under gentle stirring until no more solid sodium iodide can be observed. Prepare and store the solution in an amber HPLC bottle. Alternative volumes of solutions may be prepared so long as the preparation meets the concentration specified.

8.5 *Water (CAS 7732-18-5)*—Type I reagent water conforming to Specification D1193.

8.6 *Dibenzoyl Peroxide (CAS 94-36-0)*— 73 % minimum purity, water stabilized.

8.7 *Dilauroyl Peroxide (CAS 105-74-8)*— 97 % minimum purity.

Note 2—Peroxides are reactive products and may show limited stability, observe supplier's recommendations for storage and shelf life.

9. Hazards

9.1 Consult the latest OSHA regulations, supplier's Safety Data Sheets, and local regulations regarding all materials used in this test method.

[4] *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials,* American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

10. Sampling and Handling

10.1 Collect the sample as directed in Practices D1265, D3437, or D3700.

10.2 Cool samples with tendency to auto-polymerize at room temperature.

10.3 Use amber glass for light sensitive samples.

11. Apparatus Preparation

11.1 The HPLC shall be tuned, purged, and equilibrated according to the manufacturer's recommendation.

11.2 Prior to the first use of the apparatus, the coil should be conditioned overnight, using the method described in Table 1.

11.3 To prepare the instrument after shutdown without exchanging the column, condition using the method described in Table 1 for 30 min.

11.4 Regularly flush the coil with water, to dissolve any precipitated salts (for example, before system standby). Afterwards, flush with 1-propanol to prevent algae growth.

12. Calibration

12.1 *Calibration:*

12.1.1 Weigh 0.2 g ± 0.02 g of DBP to the nearest 0.1 mg in stoppered flask and record the weight. Add 1-propanol to a total of 100 g ± 1 g to the nearest 0.1 mg and record the total weight. Add a magnetic stirring bar, stopper the flask and stir the solution for 3 h ± 0.5 h until no more DBP crystals are observed. The concentration of this stock is approximately 100 mg/kg active oxygen. Calculate the actual concentration in parts per million active oxygen (mg/kg):

$$c_{DBP} = \frac{m_{DBP} * a * M_O * 10^6}{M_{DBP} * m_{total} * 100} \tag{1}$$

where:

c_{DBP} = concentration of the calibration stock solution (mg/kg active oxygen),
m_{DBP} = total mass of the dissolved DBP (g),
a = purity of the DBP as stated in on certificate provided by the supplier (%),
M_O = molar mass of oxygen (15.9994 g/mol),
M_{DBP} = molar mass of DBP (242.23 g/mol), and
m_{total} = total mass of the solution (g).

12.1.2 Prepare a series of calibration standards by diluting the stock solution to final concentrations in the range of 0.1 mg/kg to 100 mg/kg active oxygen, with a minimum of four concentration levels. An example of a calibration series is shown in Table 2.

TABLE 1 Typical Operating Conditions

Reaction coil length	30 m
Typical injection volumes	5.0 µL to 10 µL of sample
Reactor temperature	160 °C
Flow rate	2.0 mL/min
Eluent	Acetic acid solution: Sodium iodide solution, 50:50
Typical Detector settings	360 nm, 2.5 Hz
Acquisition time	5 min

TABLE 2 Calibration Series Example

Level	Mass Stock Solution (g)	Total Mass (g)	Concentration (mg/kg active oxygen)
1	10	20	50
2	2.0	20	10
3	0.50	50	1.0
4	0.25	50	0.50

12.1.3 Establish a linear calibration curve of the obtained peak areas versus the active oxygen content. Use linear regression to obtain the best fit to the recorded data:

$$A = a*c_{peroxide} + b \tag{2}$$

where:

A = obtained peak area (mAu*s),
a = slope,
b = intercept, and
$c_{peroxide}$ = peroxide concentration (mg/kg active oxygen).

The correlation coefficients for all the fitted calibrations shall be greater than 0.995.

12.2 *Quality Control Standard:*

12.2.1 Weigh 0.2 g ± 0.02 g of DLP to the nearest 0.1 mg in stoppered flask and record the weight. Add 1-propanol to a total of 80 g ± 1 g to the nearest 0.1 mg and record the total weight. Add a magnetic stirring bar, stopper the flask and stir the solution for 3 h ± 0.5 h until no more DLP crystals are observed. The concentration of this stock is approximately 100 mg/kg active oxygen. Calculate the actual concentration in parts per million active oxygen (mg/kg):

$$c_{DLP} = \frac{m_{DLP}*a*M_O*10^6}{M_{DLP}*m_{total}*100} \tag{3}$$

where:

c_{DLP} = concentration of the quality control stock solution (mg/kg active oxygen),
m_{DLP} = total mass of the dissolved DLP (g),
a = purity of the DLP as stated in on certificate provided by the supplier (%),
M_O = molar mass of oxygen (15.9994 g/mol),
M_{DLP} = molar mass of DLP (398.62 g/mol), and
m_{total} = total mass of the solution (g).

12.2.2 Dilute the stock solution 100 times to obtain and 1.0 mg/kg active oxygen DLP solution.

13. Procedure

13.1 Prepare and equilibrate the system as described in 11.1.

13.2 Analyze the samples using the typical operating conditions in Table 1.

13.2.1 After a system startup, start the sample sequence with 3 1-Propanol blanks.

13.2.2 During calibration, run the calibration standards in increasing order of concentration to minimize possible carry-over.

13.3 Calculate the peroxide content of a sample as follows:

$$c_{peroxide} = \frac{(A - b)*D_{std}}{a*D_{sample}} \tag{4}$$

where:

A = obtained peak area (mAu*S),
a = slope,
b = intercept,
$c_{peroxide}$ = peroxide concentration (mg/kg active oxygen),
D_{std} = relative density 60/60F of the calibration standards (0.8111 for 1-propanol), and
D_{sample} = relative density 60/60F of the sample.

After a successful calibration, analyze the Quality Control Standard and calculate the recovery. The recovery shall be greater than 95 % but lower than 105 %.

13.4 Liquid samples can be analyzed without any preparation.

13.5 Present liquefied samples in a suitable cylinder, by placing it in a pressure station connected to a liquid sampling valve.

13.6 For solid samples, apply the following procedure:

13.6.1 Place a 1.5 mL LC autosampler vial onto the balance and tare. Use a spatula and add 0.2 g ± 0.02 g of the solid sample to the nearest 0.0001 g. Using a dropping pipette, add 1-propanol to fill the autosampler vial, and note the exact weight. Homogenize the solution sample vial and ensure the sample dissolves completely by shaking. Do not apply heat.

13.6.2 If 1-propanol proves to possess insufficient solubility, another solvent may be used given it contains peroxides at a concentration level below 0.1 mg/kg active oxygen.

14. Report

14.1 Report the following information, in no particular order:

14.1.1 Report the determined peroxide content to the nearest 0.1 mg/kg active oxygen.

14.1.2 For results below 0.1 mg/kg active oxygen, report as "< 0.1 mg/kg active oxygen".

14.1.3 A reference to this standard.

14.1.4 The type and complete identification of the product tested.

14.1.5 Any deviation, by agreement or otherwise, from the procedure specified.

14.1.6 The date of the test.

14.1.7 The date of the most recent calibration.

15. Precision and Bias

15.1 *Precision*—The repeatability standard deviation from a single operator has been determined to be 0.06. A single sample with components near the limit of detection was analyzed 20 times by one operator using one instrument under repeatability.

NOTE 3—An interlaboratory study of this test method is being conducted and a complete precision statement is expected to be available on or before 2028.

15.2 *Bias*—Since there is no accepted reference material suitable for determining the bias in this test method, bias has not been determined.

16. Quality Guidelines

16.1 Laboratories shall have a quality control system in place.