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]

This standard is issued under the fixed designation D8534; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

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

[1] This test method is under the jurisdiction of ASTM Committee D16 on Aromatic, Industrial, Specialty and Related Chemicals and is the direct responsibility of Subcommittee D16.04 on Instrumental Analysis.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] Available from DLA Document Services, Building 4/D, 700 Robbins Ave., Philadelphia, PA 19111-5094, http://quicksearch.dla.mil.

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 (±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.

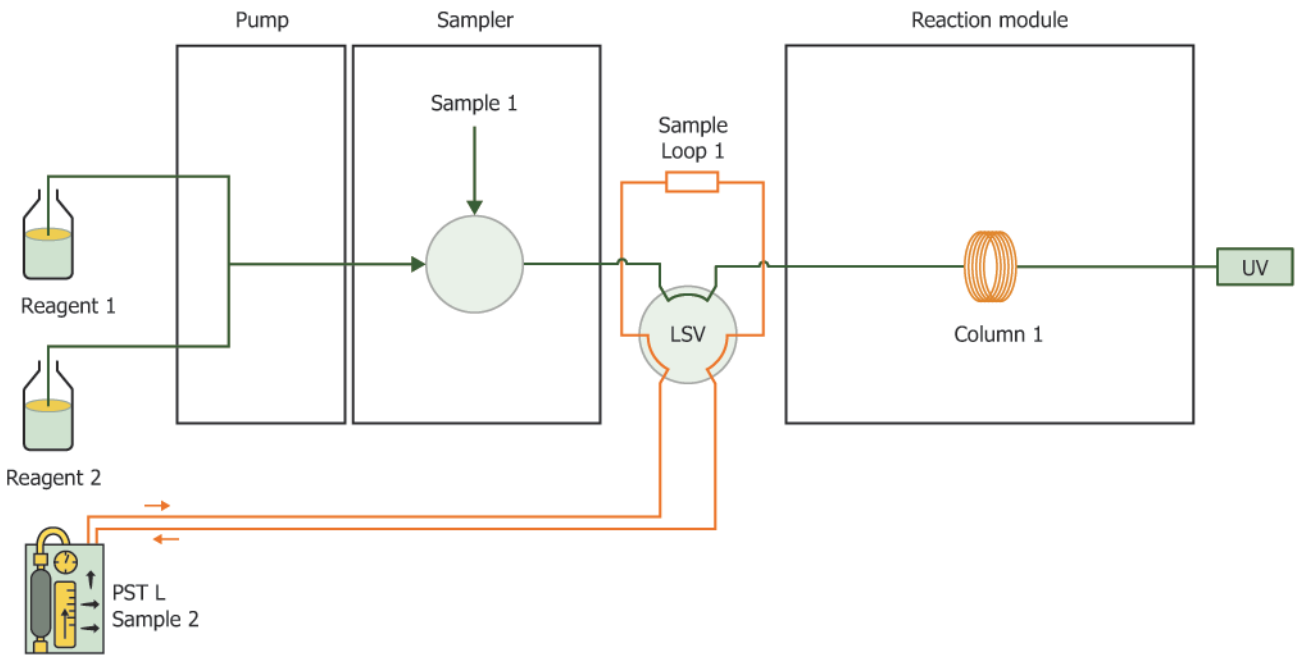

FIG. 1 Schematic Overview of the Flow Injection System