



Designation: D8301 – 21

Standard Test Method for Determination of the Content of Nitroxide Radical (4-Hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl) in Butadiene, Styrene and Isoprene by Cyclic Voltammetry Method¹

This standard is issued under the fixed designation D8301; 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 is designed to determine the content of nitroxide radical 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (H-Tempo) in butadiene, isoprene, and styrene.

1.2 This test method is applicable to samples with nitroxide radical 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (H-Tempo) with concentrations to 100 mg/kg. The limit of detection (LOD) is 0.47 mg/kg for nitroxide radical 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (H-Tempo) and the limit of quantitation (LOQ) is 1.6 mg/kg nitroxide radical 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (H-Tempo).

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

1.4 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.*

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

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

2.2 Other Documents:

OSHA Regulations, 29 CFR, paragraph 1910.1000 Air Contaminants³

OSHA Regulations, 29 CFR, paragraph 1910.1200 Hazard Communication³

3. Summary of Test Method

3.1 A sample of butadiene is dissolved in acetonitrile. Butadiene is separated by evaporation. The intensity of the cathode current signal is compared in the cyclic voltammetry (CV) with that produced by the known concentration of the H-Tempo.

3.2 A sample of isoprene and styrene is dissolved in acetonitrile. The intensity of the cathode current signal is compared in the cyclic voltammetry (CV) with that produced by the known concentration of the H-Tempo.

4. Significance and Use

4.1 Nitroxide radicals (H-Tempo, O-Tempo (4-oxo-2,2,6,6-tetramethylpiperidine-1-oxyl), etc.) are widely used as inhibitors of thermopolymerization in the processes of transportation, storage, and separation of monomers (isoprene, butadiene, styrene, etc.). This test method provides a procedure for assaying nitroxide radicals in monomers.

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 D16.07 on Styrene, Ethylbenzene and C9 and C10 Aromatic Hydrocarbons.

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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 U.S. Government Printing Office, Superintendent of Documents, 732 N. Capitol St., NW, Washington, DC 20401-0001, <http://www.access.gpo.gov>.

4.2 This procedure can be used for determination of the content of nitroxide radicals (H-Tempo, O-Tempo, etc.) in other solvents (dimethyl formamide, DMSO etc.).

5. Interferences

5.1 The N-phenyl-p-phenylenediamine derivatives in concentrations of 1 mg/kg interfere with the determination of the nitroxide radical concentration by this procedure.

5.2 Do not use rubber stoppers as antioxidants on the surface of the rubber contaminate acetonitrile solution. These antioxidants at concentrations of 1 mg/kg interfere with determination of the nitroxide radical concentration.

6. Apparatus

6.1 Laboratory balances with maximum weighing capacity of 200 g and 500 g, capable of determining 0.0001 g and 0.01 g.

6.2 Potentiostat-galvanostat capable of providing the device parameters for the experiment noted in [Annex A2](#).

6.3 PC with the operating system set up and potentiostat control program.

6.4 *Electrochemical Cell*:

6.4.1 *Working Electrode*—Platinum electrode, standard type, ID - 3 mm.

6.4.2 *Reference Electrode*—Ag/AgCl/KCl, $E_0 = 207 \text{ mV}$ (25 °C).

6.4.3 *Auxiliary (counter) Electrode*—Platinum rod, dia. 0.5 mm, 50 mm long.

6.4.4 *Salt Bridge* (U-form tube filled with electrolytic saline filler).

7. Reagents and Materials

7.1 *Potassium Chloride* (KCl, CAS 7447-40-7)—Analytical reagent grade.

7.2 *Acetonitrile* (CH_3CN , CAS 75-05-8)—Analytical reagent grade.

7.3 *Water*—Shall be understood to mean Type I or Type II reagent water conforming to Specification [D1193](#).

7.4 *Sodium Perchlorate* (NaClO_4 , CAS 7601-89-0)—Analytical reagent grade.

7.5 *Nitroxide Radical Standard* (4-Hydroxy-2,2,6,6-tetramethylpiperidine-l-oxyl, min. 98 %, CAS 2226-96-2).

7.6 *Powdered Agar-agar*.

7.7 *U-shaped Glass Tube*.

8. Hazards

8.1 Consult current OSHA regulations, suppliers' Safety Data Sheets, and local regulations for all materials used in this test method.

9. Sampling, Test Specimens, and Test Units

9.1 *Preparation of Potassium Chloride Solution* ($c=3 \text{ mol/dm}^3 \text{ KCl}$):

9.1.1 Transfer $111.8 \pm 0.5 \text{ g}$ of potassium chloride (KCl) to a volumetric flask with a capacity of 500 cm^3 . Add distilled water to the volume.

NOTE 1—Commercially available solutions of the same concentration can be used instead.

9.2 *Preparation of Sodium Perchlorate Solution in Acetonitrile* ($c=0.1 \text{ mol/dm}^3 \text{ NaClO}_4$):

9.2.1 Weigh $3.06 \pm 0.01 \text{ g}$ of sodium perchlorate (NaClO_4) with an accuracy to 0.0001 g; transfer quantitatively to the volumetric flask with a capacity of 250 cm^3 . Add 200 cm^3 of acetonitrile and stir thoroughly; make up the volume to 250 cm^3 with acetonitrile and stir it.

9.3 *Preparation of a Filler for a Bridge Electrolyte*:

9.3.1 Add 5 g of powdered agar-agar a little at a time to 100 cm^3 of a potassium chloride solution at 100 °C (water bath); make sure that the solution does not foam and boil. The solution is aged at 100 °C until all the agar-agar is dissolved, and then add 10 g to 15 g of solid potassium chloride to create an excess of the solid phase.

9.4 *Preparation of a Salt Bridge*:

9.4.1 A U-shaped glass tube is filled with a hot solution prepared according to [9.3](#), with a syringe.

NOTE 2—Store the electrode junction in a water solution of potassium chloride with tube branches downwards.

NOTE 3—Other bridging electrolytes can be used.

9.5 *Preparation of a Nitroxide Radical Solution at a Concentration of 100 mg/kg*:

9.5.1 Weigh a conical flask with a capacity of 250 cm^3 with an accuracy to 0.01 g; weigh $0.01 \pm 0.001 \text{ g}$ of nitroxide radical with an accuracy to 0.0001 g and quantitatively transfer it to a flask with a capacity of 250 cm^3 . Add 100 cm^3 of acetonitrile and stir thoroughly, make up the solution to a weight of 1 000 000 times greater than the weight of the nitroxide radical ($100.0 \pm 10 \text{ g}$) with acetonitrile and stir it; close the flask.

9.6 *Preparation of Calibration Solutions with Nitroxide Radical Concentration of 2 mg/kg, 5 mg/kg, 10 mg/kg, 20 mg/kg, 30 mg/kg, 40 mg/kg, 50 mg/kg, 60 mg/kg, 80 mg/kg, 90 mg/kg*:

9.6.1 Pipette 0.2 cm^3 of the solution obtained in accordance with [9.5](#) and put it into a container with a ground glass stopper; pipette 9.8 cm^3 of acetonitrile into the same container. Stir the obtained solution with a concentration of 2 mg/kg.

9.6.2 Prepare other solutions as described above by taking the appropriate amount of the solution obtained according to [9.5](#) and the amount of acetonitrile.

9.6.3 It is acceptable to prepare solutions of nitroxide radical using other volumetric apparatus or other final volumes of solutions, or combinations thereof.

NOTE 4—Prepared solutions with nitroxide radical should be kept in tightly closed containers to avoid concentration changes of the obtained solutions, due to the evaporation of acetonitrile.

9.7 *Butadiene Sample Preparation*:

9.7.1 Put 10 cm^3 of acetonitrile into the cylinder with a well-ground stopper previously pre-weighed with an accuracy to 0.01 g, and reweigh the cylinder with an accuracy to 0.01 g. Cool the cylinder with acetonitrile to -10 °C in the cryostat or cooling mixture. Pipette 30 cm^3 of butadiene into the cylinder with acetonitrile. Stir and weigh the flask with an accuracy to 0.01 g. Evaporate the butadiene slowly by adjusting the