



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, $E_0 = 207$ 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* (CH₃CN, 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* (NaClO₄, CAS 7601-89-0)—Analytical reagent grade.

7.5 *Nitroxide Radical Standard* (4-Hydroxy-2,2,6,6-tetramethylpiperidine-1-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 mol/dm³ KCl):

9.1.1 Transfer 111.8 ± 0.5 g of potassium chloride (KCl) to a volumetric flask with a capacity of 500 cm³. 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 mol/dm³ NaClO₄):

9.2.1 Weigh 3.06 ± 0.01 g of sodium perchlorate (NaClO₄) with an accuracy to 0.0001 g; transfer quantitatively to the volumetric flask with a capacity of 250 cm³. Add 200 cm³ of acetonitrile and stir thoroughly; make up the volume to 250 cm³ 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 cm³ 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 cm³ with an accuracy to 0.01 g; weigh 0.01 ± 0.001 g of nitroxide radical with an accuracy to 0.0001 g and quantitatively transfer it to a flask with a capacity of 250 cm³. Add 100 cm³ 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 ± 10 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 cm³ of the solution obtained in accordance with [9.5](#) and put it into a container with a ground glass stopper; pipette 9.8 cm³ 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 cm³ 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 cm³ 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

cylinder temperature to the standard temperature. The evaporation time shall not be less than 1 h under standard conditions (or up to the mass of the flask, less than the mass of the flask with acetonitrile). At the end of evaporation, weigh the flask with an accuracy to 0.01 g.

9.8 *Isoprene (or Styrene) Sample Preparation:*

9.8.1 Put 10 cm³ of acetonitrile into a glass screw-top flask, previously weighed with an accuracy to 0.01 g, and reweigh the flask with an accuracy to 0.01 g. Pipette 10 cm³ of isoprene (or styrene) sample into a flask of acetonitrile under the acetonitrile layer. Stir and weigh the flask with an accuracy to 0.01 g.

9.9 *Preparation of Test Specimen:*

9.9.1 Add 10 cm³ of sodium perchlorate solution in acetonitrile into a beaker with a working and auxiliary electrode. Then pipette 3 cm³ of the test solution.

10. Preparation of Apparatus

10.1 *Preparation of the Equipment to Measurements:*

10.1.1 Pour 15 cm³ of a solution of potassium chloride into the beaker for the reference electrode.

10.1.2 Check the electrode junction and its level of immersion into the solutions.

10.1.3 Assemble the three-electrode scheme of connecting the electrodes to a potentiostat, consisting of two beakers connected by a salt bridge. In one beaker, place the reference electrode in an aqueous solution of potassium chloride; in the other beaker of sodium perchlorate solution in acetonitrile, insert a working and auxiliary electrode.

NOTE 5—In order to avoid precipitation of reaction products on the surface of the reference electrode, it is placed into a separate beaker and is connected to the beaker with a working electrode by means of a salt bridge. The salt bridge provides contact between the reference electrode and the test solution, and allows it to minimize the junction potential.

10.1.4 *Check the Electrolytic Cell:*

10.1.4.1 Check the level of immersion of the electrodes into the solution; and

10.1.4.2 Check the tightness of the caps and elastic seals.

10.2 Connect the device to the sample cell. Make sure the connection is correct.

10.3 *Switch on the Device*

10.3.1 *Check all the Connections:*

10.3.1.1 Connection to the PC; and

10.3.1.2 Potentiostat electrical ground.

10.4 *Program Software Setting:*

10.4.1 Run the potentiostat control program on the PC;

10.4.2 Set the working program;

10.4.3 Select cyclic sweep mode;

10.4.4 Enter sweep and device parameters for the experiment (see [Annex A2](#)); and

10.4.5 Save the working program.

11. Calibration and Standardization

11.1 *Getting Started with Potentiostat Software on the PC:*

11.1.1 Run the potentiostat control program on the PC;

11.1.2 Select a work program from the saved list.

11.2 Prepare a test specimen (see [9.9](#)) and prepare electrolytic cell (see [10.1 – 10.3](#)).

11.3 Check in the software that there are no discontinuities in the system. The indicator of the absence of discontinuities is a constant value of the potential.

11.4 Run the experiment in the software.

11.5 Process the experimental results (see [Annex A3](#)).

11.6 Pour out the sample solution. Thoroughly clean and rinse the cell and the working and auxiliary electrodes.

11.7 Repeat the experiment for all solutions prepared with different concentrations of the nitroxide radical.

11.8 On the basis of the data obtained, construct the calibration dependence curve in the I_c (nA) vs. concentration (mg/kg) and find the coefficient of the calibration dependence (simple linear regression through zero) using special software, or graphically.

11.9 The correlation coefficient of the calibration dependence shall be at least 0.99.

11.10 The calibration dependence is established at least once every six months or when replacing parts of the electrochemical system: replacement or cleaning of the main electrode surface; replacement of the reference electrode; replacement of potentiostat; repair of the potentiostat or its parts.

11.11 The stability of the calibration dependence is verified according at least once every two months to the current peak height values for at least three standard nitroxide radical solutions (with known concentration). The results of the determination in all standard solutions shall not exceed 5 % of the previously established calibration dependence.

12. Procedure

12.1 Put 10 cm³ of sodium perchlorate solution in acetonitrile (background electrolyte) and 3 cm³ of sample solution into the electrolytic cell. Carry out measurement in accordance with the procedure described in [11.1](#) to [11.6](#).

12.2 If necessary, dilute or concentrate the sample solution in accordance with the requirements of the specified analytical procedures.

12.3 Repeat the measurement at least two times.

13. Calculation or Interpretation of Results

13.1 Determine the content of nitroxide radical C_0 in the test solution according to the constructed calibration dependence or according to calibration dependence formula:

$$C_0 = \frac{I_{\text{average}}}{k} \quad (1)$$

where:

I_{average} = average value of peak height according to the current I_c for 3 cycles, and

k = calibration dependence coefficient.

13.2 *Processing of the Results for Butadiene Sample:*

13.2.1 Calculate the content of nitroxide radical (C) in butadiene according to the formula:

$$C = \frac{C_0 \cdot (m_3 - m_0)}{(m_2 - m_1)} \quad (2)$$

where:

- C_0 = content of nitroxide radical in the test solution, mg/kg;
- m_0 = weight of the flask, g;
- m_1 = weight of the flask with acetonitrile, g;
- m_2 = weight of the flask with acetonitrile and butadiene sample, g; and
- m_3 = weight of the flask with sample solution after butadiene evaporation, g.

13.2.2 The result of measurement of the content of nitroxide radical in butadiene (mg/kg) is taken as the average value of the results of two parallel determinations, the difference between which should not exceed the limit of repeatability (see [Table 1](#)).

13.2.3 If the repeatability limit is exceeded, the values are considered invalid, and the experiment is repeated.

13.3 Processing of the Results for Isoprene Sample:

13.3.1 Calculate the content of nitroxide radical (N) in isoprene (or styrene) according to the formula:

$$N = \frac{C_0 \cdot (m_2 - m_0)}{(m_2 - m_1)} \quad (3)$$

where:

- C_0 = content of nitroxide radical in the test solution, mg/kg;
- m_0 = weight of the flask, g;
- m_1 = weight of the flask with acetonitrile, g; and
- m_2 = weight of the flask with acetonitrile and isoprene (or styrene) sample, g.

TABLE 1 Range and Repeatability

Component	Range	Repeatability (r)
nitroxide radical (H-Tempo) in butadiene	of 1 mg/kg to 100 mg/kg	0.45
nitroxide radical (H-Tempo) in isoprene (or styrene)	of 1 mg/kg to mg/kg	0.45

13.3.2 The result of measurement of the content of nitroxide radical in isoprene (styrene) (mg/kg) is taken as the average value of the results of two parallel determinations, the difference between which should not exceed the limit of repeatability (see [Table 1](#)).

13.3.3 If the repeatability limit is exceeded, the values are considered invalid and the experiment is repeated.

14. Report

14.1 Report the following information as the assay value of nitroxide radical in monomer rounded to the nearest 0.1 mg/kg. The LOD is 0.47 mg/kg.

15. Precision and Bias

15.1 *Precision*—A single sample with the component near the lower limit of detection was analyzed 20 times by one person using one instrument over the shortest practical time (see [Annex A1](#)).

15.2 *Repeatability*—Results should not be suspect unless they differ by more than shown in [Table 1](#). Results that differ by less than r have a 95 % probability of being correct.

15.3 Reproducibility has not been determined and will be determined within five years.

15.4 *Bias*—Since there is no accepted reference material suitable for determining the bias for the procedure in this test method for measuring H-TEMPO in monomers, bias has not been determined.

16. Keywords

16.1 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl; butadiene; cyclic voltammetry method; H-TEMPO; isoprene; nitroxide radical; styrene

ANNEXES

(Mandatory Information)

A1. RESEARCH REPORT OF REPEATABILITY

A1.1 See [Fig. A1.1](#).