**Designation: D4575 – 09 (Reapproved 2015)**

# Standard Test Methods for Rubber Deterioration—Reference and Alternative Method(s) for Determining Ozone Level in Laboratory Test Chambers[1]

This standard is issued under the fixed designation D4575; 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 ($\varepsilon$) indicates an editorial change since the last revision or reapproval.

## INTRODUCTION

Numerous techniques exist for the analysis of gaseous ozone in ozone-air mixtures used for ozone crack testing of rubber. These include wet chemical procedures, electrochemical cells, UV absorption, and chemiluminescence with ethylene. See Refs (**1-4**).[2]

Wet chemical methods (the absorption of ozone in a potassium iodide solution and titration of the iodine released with sodium thiosulfate) have been in traditional use in the rubber industry, but they are not suitable for continuous operation, and in recent years they have been shown to be sensitive to small variations in test procedures and concentration and purity of reagents. Interlaboratory tests have indicated that different procedures do not give equivalent results, and most of them differ from an absolute UV method. Frequently, wet chemical methods yield higher ozone concentrations due to the oxidizing capacity of other components of the ozone-air mixture.

Certain nonreference instrumental methods are amenable to automatic operation and for this reason they are included in this standard. They may be used for routine testing once calibrated against the reference UV method.

UV absorption is adopted as the reference method against which the others shall be calibrated. It is an absolute test method and is in common use by environmental protection agencies for the determination of pollutant ozone in air (see 2.3).

Although these test methods are concerned with ozone analysis, it also draws attention to the influence of atmospheric pressure on the rate of cracking of rubber at constant ozone concentration as normally expressed in terms of parts by volume. As described in Appendix X2, the variation in ozone resistance that can result between laboratories operating at significantly different atmospheric pressures can be eliminated by specifying ozone concentration in terms of the partial pressure of ozone.

## 1. Scope

1.1 These test methods cover the following three types of methods for the determination of ozone content in laboratory test chambers. Method A (UV absorption) is specified for reference or referee purposes and as a means of calibration for the alternative methods; Method B, instrumental device (electrochemical or chemiluminescence); and Method C, wet chemical techniques (see Appendix X1). These methods are primarily intended for use with tests for determining rubber ozone cracking resistance and thus are applicable over the ozone level range from 25 to 200 mPa.

NOTE 1—Prior to 1978, ozone concentrations were expressed in ASTM D11 Standards in parts per hundred million (pphm) of air by volume. See Appendix X2 for an explanation of the change to partial pressure in millipascals (mPa).

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *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 and health practices and determine the applicability of regulatory limitations prior to use. For a specific hazard statement, see Note 2 and 5.1.*

NOTE 2—**Warning—Ozone is a hazardous chemical.**

---

[1] These test methods are under the jurisdiction of ASTM Committee D11 on Rubber and are the direct responsibility of Subcommittee D11.15 on Degradation Tests.

Current edition approved July 1, 2015. Published September 2015. Originally approved in 1986. Last previous edition approved in 2009 as D4575 – 09. DOI: 10.1520/D4575-09R15.

[2] The boldface numbers in parentheses refer to the list of references at the end of this standard.

## 2. Referenced Documents

2.1 *ASTM Standards:*[3]

D518 Test Method for Rubber Deterioration—Surface Cracking (Withdrawn 2007)[4]

D1149 Test Methods for Rubber Deterioration—Cracking in an Ozone Controlled Environment

D1171 Test Method for Rubber Deterioration—Surface Ozone Cracking Outdoors or Chamber (Triangular Specimens)

D3395 Test Methods for Rubber Deterioration—Dynamic Ozone Cracking in a Chamber (Withdrawn 2007)[4]

2.2 *ISO Standard:*[5]

ISO-1431/I, II and III Rubber Ozone Testing; Static, Dynamic and Analysis Methods (respectively)

2.3 *Federal Standard:*[6]

Code of Federal Regulations (Protection of Environment) Title 40 Parts 1 to 51, July 1, 1984, Appendix D (Ozone in Atmosphere) pp. 550–562

## 3. Summary of Methods

3.1 This standard includes the following three types of independent methods.

3.1.1 *Method A Reference Method (UV Instrument)*—For UV absorption instruments, the ozonized air is passed through a flow cell. UV energy (wavelength 254 nm) passes through the cell and the resultant energy is detected at the other end. The degree of absorption is dependent on the number of ozone molecules in the path. The absorption is compared to the absorption with zero ozone and the difference in energy received at the detector is converted into an electrical output and measured. See Appendix X2 for more details and information.

3.1.2 *Method B—Secondary Method (Instrumental Devices):*

3.1.2.1 For chemiluminescent instruments, the ozonized air is passed through an analysis chamber, it contacts a stream of ethylene and the two gases undergo a chemiluminescent reaction with the emission of photons at about 430 nm. This emission is measured on a photomultiplier and converted to an electrical output.

3.1.2.2 For electrochemical methods, the ozonized air is bubbled at a fixed rate through a coulometric (Pt-Hg) cell containing a buffered solution of potassium iodide. The iodine liberated from the solution is ionized at the cathode and is transported to the anode by turbulence. At the anode, insoluble HgI is formed with the release of ionic charges equivalent to the ozone content of the $O_3$-air stream.

3.1.3 *Method C—Secondary Method (Wet Chemical Technique):*

3.1.3.1 *Procedure C-1*—An ozonized air sample is passed through an efficient absorption device containing an aqueous buffered solution of KI. After a fixed absorption time, the $I_2$ released is titrated with $Na_2S_2O_3$ and the ozone concentration is calculated from the thiosulfate consumed.

3.1.3.2 *Procedure C-2*—An air sample is passed through a solution in an efficient absorption container with an electrode end point device. The solution contains buffered KI and an amount of sodium thiosulfate to permit exhaustive absorption in 20 to 30 min (total consumption of the sodium thiosulfate). At the endpoint, the voltage across the electrodes abruptly increases and the time of this increase is recorded. The time is related inversely to the ozone content.

## 4. Significance and Use

4.1 General purpose and many specialty rubbers will undergo ozone cracking when exposed to ozone containing atmospheres, when the test specimens or actual use products are under a certain degree of tensile strain. Certain additives such as antiozonants and waxes inhibit or prevent this cracking. Various rubbers and rubber formulations containing such additives are customarily evaluated under static or dynamic tensile strain in laboratory ozone chambers. This standard provides for an accurate assessment of the ozone content of such chambers used in Test Methods D518, D1149, D1171, D3395 and ISO Standard 1431 I/II/III. For additional information on ozone analysis, refer to Code of Federal Regulations; Title 40 Parts 1 to 51.

## 5. Hazards

5.1 **Warning—**Ozone is a hazardous substance. Consult and follow all applicable laws, rules, and regulations regarding exposure to ozone.

## 6. Calibration of Nonreference Methods

6.1 The secondary (sec) methods shall be calibrated with respect to one of two reference ozone systems;

6.1.1 *Reference $O_3$ System No. 1,* consisting of (*1*) stable $O_3$ generator with adjustable output in the range from 0 to 500 mPa and (*2*) a reference UV ozone analyzer (Method A type).

6.1.2 *Reference $O_3$ System No. 2,* consisting of a UV photometric $O_3$ calibration system (calibration $O_3$/air supply). This system generates reference levels of ozone, but it does not function as an analyzer. See Appendix X2 for more information.

6.2 *Apparatus Required for Reference $O_3$ System No. 1:*

6.2.1 *Adjustable Level,* stable, generator of ozonized air. This is normally a UV lamp, flow rate, and containment system.

6.2.2 *System,* permitting the output from the ozone generator to be selectively switched to inputs for (*1*) the reference UV ozone measuring device and (*2*) the (secondary) ozone measuring device to be calibrated. The tubing for the ozonized air should be clean, PTFE or glass, and be as short as possible. A PTFE cock for switching is mandatory to prevent $O_3$ decomposition.

6.3 *Calibration Procedure:*

---

[3] 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.

[4] The last approved version of this historical standard is referenced on www.astm.org.

[5] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036.

[6] Available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401.

6.3.1 Select at least three (preferably five) ozone levels that span the range of interest. Select the lowest level and adjust the generator. Allow it to become stable in output to within ±5 % variation for several measurements made in a short time span by monitoring the output ozone with the reference UV device. Record the average ozone level.

6.3.2 Switch the ozone output to the secondary ozone measuring device, and measure the ozone several times over a time period sufficient to get an average value with individual deviations no greater than ±5 %. Record the average ozone level measured with the secondary device.

6.3.3 Take care to execute 6.3.1 and 6.3.2 until the indicated repeatability (precision) of ±5 % is attained; this indicates stable output and good secondary measurement procedure.

6.3.4 Repeat the procedure of 6.3.1 and 6.3.2 for the other two (or four) levels in ascending order.

6.3.5 Plot the average concentrations, $O_3$ (Sec) versus $O_3$ (Ref), and determine linear regression parameters $b_0$ and $b_1$.

$$O_3(\text{Sec}) = b_0 + b_1 O_3\,(\text{Ref}) \tag{1}$$

$$O_3\,(\text{Ref}) = O_3(\text{Corr}) = \frac{O_3(\text{Sec}) - b_0}{b_1} \tag{2}$$

6.3.6 To obtain true or reference $O_3$ concentration in routine daily work, use Eq 2. The value as calculated from Eq 2 is called the corrected ozone concentration, $O_3$ (corr).

6.3.7 The uncertainty of the corrected routine daily ozone level or concentration as calculated from Eq 2 will depend on the number of average values, reference and secondary, used in establishing the linear regression calibration line, upon the number of measurements forming each plotted average, and upon the basic measurement error of the secondary method. If five ozone levels are used to establish the linear regression line, an estimate of the standard deviation of the corrected ozone concentration (SD, $O_3$(corr)) that is, the standard error of the estimate, with three degrees of freedom, may be obtained by the use of Eq 3.

$$SD(O_3(\text{corr})) = \left(\frac{N-1}{N-2}\left(S_y^2 - b_1^2 S_x^2\right)\right)^{1/2} \tag{3}$$

where:

$N$ = number of plotted points,

$b_1$ = slope of regression curve of Eq 1,

$S_y^2$ = variance among plotted (average) secondary method $O_3$ concentrations, and

$S_x^2$ = variance among plotted (average) reference method $O_3$ concentrations.

6.3.8 Thus the (±)90 % confidence limits on the corrected ozone concentrations are ±1.64 SD ($O_3$ (corr)) for a linear regression curve obtained with 5 reference and secondary levels of ozone.

6.4 *Apparatus Required for Reference $O_3$ System No. 2:*

6.4.1 A UV photometric ozone calibration system shall be used. Various commercial systems may be used provided they indicate ozone concentration to the same accuracy and precision as specified in 8.2 for the direct reading UV ozone analyzer.

6.5 *Calibration Procedure:*

6.5.1 Follow the general procedure as outlined in 6.3. The procedure with the No. 2 Reference System varies from the No. 1 system only in the sense that the ozone generation and reference analysis are conducted in a self-contained system.

## TEST METHOD A

## 7. Sampling

7.1 The sampling line shall be polytetrafluoroethylene (PTFE), or glass, or PTFE-lined material, or any other demonstrably unreactive and impermeable material. The line shall be as short as practicable and, unless otherwise specified, shall be no longer than 1 m in length. The line shall be designed so as to prevent ingress of contaminants. The combination of length and bore of the sampling line should be such as to minimize residence time of the sample without producing undue pressure drop.

## 8. Preparation of Apparatus

8.1 A direct-reading UV ozone analyzer or instrument shall be used.

8.2 When the instrument is used over the 0 to 500-mPa range, the parameters shall conform to the performance requirements given in Table 1.

8.3 *Initial UV Instrument Calibration*—The calibration procedure shall be as follows:

8.3.1 Set up the instrument in accordance with the manufacturer's instructions and allow a sufficient stabilization period. Set the instrument zero using zero air produced by suitably removing contaminants with a calibration $O_3$/air supply (see X2.1). Feed the zero air directly to the instrument and adjust the zero control after allowing sufficient stabilization time. See Table 1.

8.3.2 Span the instrument measuring circuit using a self-contained calibration atmosphere system as described in 6.1.1. See also X2.2.

8.3.3 Use three to five concentrations corresponding to the spread over the measuring range. Steady indicated values shall agree to within 2 % of the calibration value.

**TABLE 1 Performance Requirements for UV Instruments Used in the Determination of Ozone in Ambient Air**

| Parameter | Requirements |
|---|---|
| Range | 0 to 500 mPa |
| Noise | 0.5 mPa |
| Lower detectable limit | 1.0 mPa |
| Interference equivalent: | |
| Each interferent | ±2 mPa |
| Total interferent | ±6 mPa |
| Zero drift, 12 h and 24 h | ±2 mPa |
| Span drift, 24 h | |
| 20 % of upper range limit | ±20.0 %, max |
| 80 % of upper range limit | ±5.0 %, max |
| Lag time | 2 min, max |
| Rise time | 2 min, max |
| Fall time | 2 min, max |
| Precision: | |
| 20 % of upper range limit | 1.0 mPa, max |
| 80 % of upper range limit | 1.5 mPa, max |

8.4 *Operational Recalibration*—The following procedure shall be carried out ideally on a daily basis, but at least weekly:

8.4.1 Check the instrument ozone level using zero air and take appropriate action, if necessary.

8.4.2 Check the span of the instrument measuring circuit as described in 8.3.2 but using a single, representative, reference test atmosphere in accordance with 6.1.2. Recalibrate the instrument through that part of the sampling system dedicated to the instrument. The indicated value shall conform proportionally to the value of span drift given in Table 1.

## TEST METHOD B

## 9. Preparation of Apparatus

9.1 A direct reading instrument shall be provided. This may be a chemiluminescence or an electrochemical device.

9.2 When the instrument is used over the range from 0 to 500 mPa, the performance requirements shall be comparable to those listed in Table 1.

## 10. Calibration

10.1 Set up the instrument in accordance with the manufacturer's instructions, and allow the instrument to stabilize.

10.2 Set the instrument to zero by the use of a calibration $O_3$/air supply.

10.3 Span the instrument measuring circuit or system using a calibration test atmosphere or $O_3$/air volume as in 8.3, and calibrate as specified in 8.3.

10.4 *Recalibration Operation*—This procedure shall be carried out ideally on a daily basis but at least weekly. See 8.4 for exact details.

10.5 *Sampling*—See 7.1 for sampling procedure.

## TEST METHOD C

## 11. General Theory

11.1 The absorption of ozone is an aqueous neutral buffered KI solution yields free iodine by oxidation.

$$O_3+2KI+H_2O \rightarrow O_2+2KOH+I_2 \tag{4}$$

11.1.1 The addition of sodium thiosulfate solution causes an immediate reaction of free iodine and thiosulfate.

$$\mathrm{I_2+2\ Na_2S_2O_3 \rightarrow Na_2S_4O_6+2NaI} \tag{5}$$

11.1.2 Thus, one $O_3$ is equivalent to 2 $Na_2S_2O_3$.

11.2 Method C contains two alternative absorption procedures, C-1 and C-2; either may be used.

## 12. Reagents

12.1 Reagent grade chemicals and distilled water shall be used in all tests.

12.2 *Buffer Solution:*

12.2.1 The recommended buffer is 0.1 M boric acid ($H_3BO_4$). This is prepared by dissolving in 1 L of distilled water; 6.18 g of $H_3BO_4$, 10 g of KI. The solution shall have a pH value of 5 ± 0.2. Before using, take 10 $cm^3$ of the buffer solution and add a few drops of (2 mol/$dm^3$ or litre alternatively or 73 mg HCl $cm^3$) HCl and 0.5 $cm^3$ of starch solution. No color should develop. Store $H_3BO_4$ buffer in a brown stoppered bottle in a cool place.

12.2.2 The second choice buffer is the customary sodium, potassium hydrogen phosphate buffer. Prepare a 0.025-M solution of anhydrous hydrogen phosphate ($Na_2HPO_4$) and a 0.025-M solution of anhydrous potassium dihydrogen phosphate ($KH_2\ PO_4$). To prepare the buffer solution having a pH of 6.7 to 7.1, add 1.5 volumes of 0.025 M $Na_2HPO_4$ solution to 1 volume of 0.025 M $KH_2PO_4$ solution. Shake thoroughly.

12.3 *Potassium Iodide* (KI)—Use pure analytical grade KI.

12.4 *Sodium Thiosulfate Solution* (0.020 N)—Prepare a 10 mol/$m^3$ (0.020 N) sodium thiosulfate ($Na_2S_2O_3$) solution. This may be standardized by using a standard 0.0200 N potassium bromate ($KBrO_3$) solution to oxidize an excess quantity of potassium iodide (KI) in acid solution. Titrate the liberated iodine immediately with the $Na_2S_2O_3$ solution. The titration equipment for the Microammeter Method (or Null Method) may be used to determine the end point in this titration. Store the prepared 10 mol/$m^3$ (0.020 N) $Na_2S_2O_3$ solution in a cool dark place.

12.5 *Sodium Thiosulfate Solution* (1 mol/$m^3$)(0.0020 N)—Prepare 1 mol/$m^3$(0.0020 N) $Na_2S_2O_3$ solution for use in the ozone analysis by diluting the 10 mol/$m^3$ (0.020 N) solution 10 to 1, using a 10-$cm^3$ pipet and 100-$cm^3$ volumetric flask. Redeterminations of the normality of the 10 mol/$m^3$ (0.020 N) $Na_2S_2O_3$ solution should be carried out weekly.

## 13. Preparation of Apparatus

13.1 The arrangement of the ozone analysis train is shown in a generalized format in Fig. 1. The sequence of devices is shown and is the same for all three alternative methods or absorption devices as depicted in Figs. 2-4. The pressure differential as measured at manometer (4 of Fig. 1) shall be subtracted from the barometric pressure to obtain the air sample pressure, as follows:

$$P = P_B - P_M \tag{6}$$

1—Ozone chamber
2—Thermometer
3—Flowmeter (rotameter type)
4—Manometer (mercury)
5—Absorption device
6—Cold trap (optional)
7—(Air) Vacuum pump
8—Bleeder valve to adjust flow rate

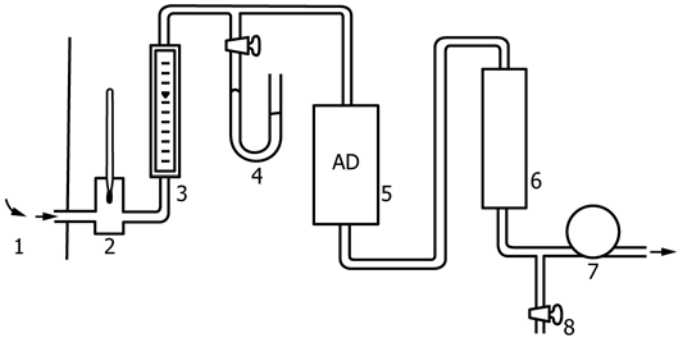

FIG. 1 Generalized Analysis Train Format

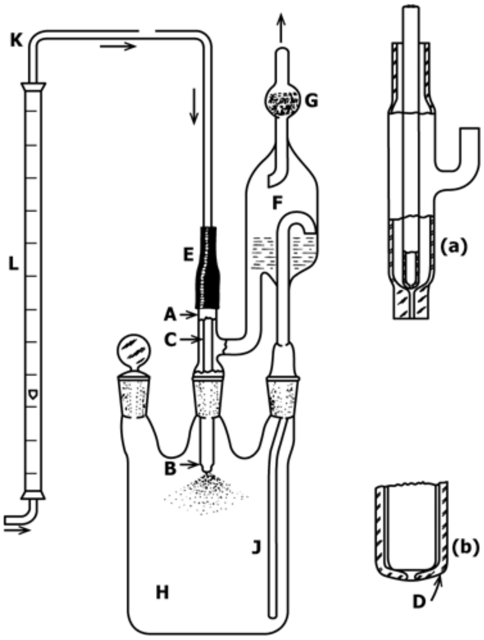

FIG. 2 Ozone Absorbing Device (Spray Jet)

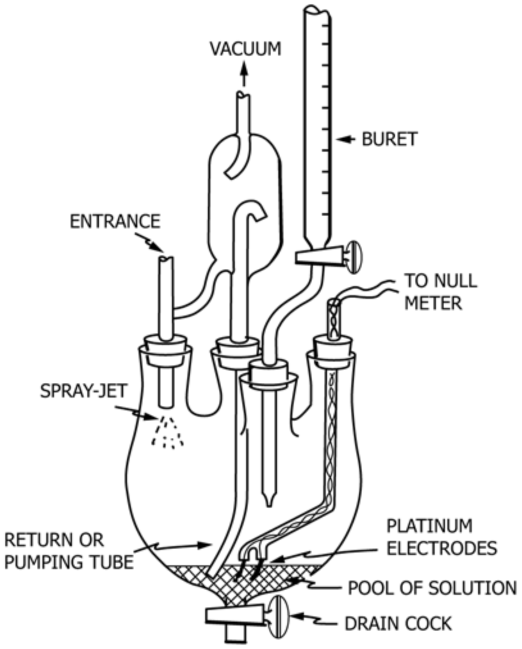

FIG. 3 Modified Spray-Jet Apparatus

where:

$P$ = air sample pressure,
$P_B$ = barometric pressure, and
$P_M$ = manometer pressure differential, all pressures in kPa (mm Hg × 0.133).

The temperature of the air sample shall be obtained from the thermometer at point 2 of Fig. 1. An alternative flowmeter (3 of Fig. 1) may be used, that is, the differential manometer type.

13.2 One of the two alternative absorption devices shall be provided. The first is the spray-jet device, and the second is the single column solution absorption device.

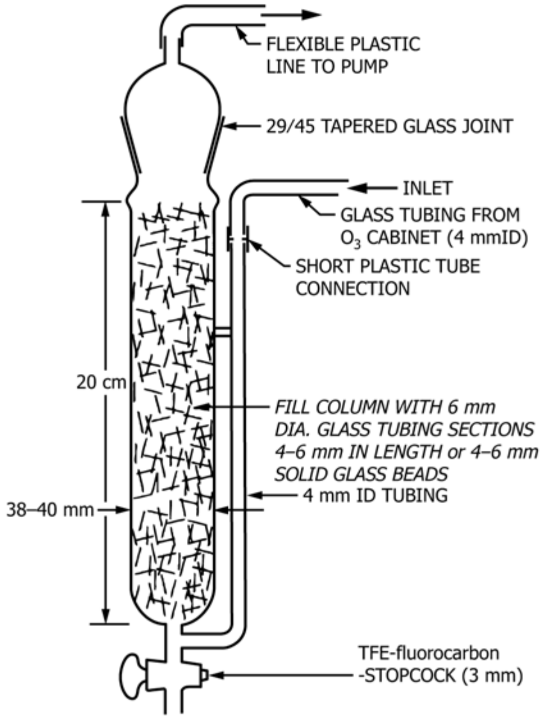

FIG. 4 Ozone Absorption Column

13.3 *Spray-Jet Device:*

13.3.1 The spray-jet device is shown in Fig. 2. The glass tube, A, is approximately 9.5 mm (0.375 in.) in diameter and 100 mm (4 in.) long, terminating at B in a short length of capillary tubing with a base of 1 to 2 mm (0.04 to 0.08 in.). Concentric within A is a smaller glass tube. C. (Fig. 2(a) is an enlarged view of this part.) The end of C is heated in a flame until the bore is reduced in size so as just to admit a wire or drill 0.75 mm (0.03 in.) in diameter. At this thickened end two flats are ground off on a sheet of fine alumina abrasive paper as at D in Fig. 2(b). When in position in tube A, end D fits snugly against the hole in capillary B. A rubber tubing connection at E holds the two tubes in position. F is a trap about 50 mm (2 in.) in diameter and 100 mm (4 in.) long, and G is an enlargement in the exit tube about 40 mm (1.5 in.) in diameter, containing glass wool to trap spray passing F. F is connected to the side tube of A. H is a 1-L three-neck round-bottom flask in which A and F are secured by standard-taper ground joints. A occupying the center opening with B protruding just below the neck and J reaching to within 13 mm (0.5 in.) of the bottom of the bottle. The third opening serves to introduce and remove the reagent. A is connected through plasticized poly(vinyl chloride) tubing and glass tubing to a rotameter[7] graduated from 0 to 1.0 $m^3$ (0 to 35 $ft^3$) of air/h. The entrance to the rotameter is connected with glass tubing to the sampling tube, and the exit of F is connected through a regulating valve to a

---

[7] The sole source of supply of the rotameter known to the committee at this time is the Fischer & Porter Rotameter, obtainable from Fischer & Porter Co., Warminster, PA. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

vacuum line. When properly regulated and a vacuum applied at F, most of the reagent enters F, furnishing a head of reagent at B, where the entering air resolves it into a fine mist that fills the entire bottle. The absorption flask shall be mounted in a light-tight box to protect it from light during the time a run is being made.

13.4 *Single Column Absorption Device:*

13.4.1 This technique uses a single absorption column that is shown in Fig. 4. The dimensions are noted on the diagram. Fill the body of the column with clean glass beads in accordance with the drawing. Stopcock greases shall not be used on the ground glass joints or on the stopcock; a TFE-fluorocarbon stopcock is used to avoid the need for such grease and water is used to lubricate and form a seal at the 29/45 standard taper joint.

13.5 *Titration Apparatus:*

13.5.1 *Microammeter Method*—The titration shall be conducted in a 250-$cm^3$ widemouth flask, or beaker of equal size. An air or magnetic stirrer should be used. The titrating equipment consists of a microburet, microammeter of 0 to 20 range, a heavy-duty dry cell of 1½ V, one 1000 and one 30 000-Ω resistor, and two platinum electrodes approximately 2.5 mm (0.1 in.) in diameter and 25 mm (1 in.) in length. The resistors are connected in series across the 1½-V battery, and the potential across the 1000-Ω resistor is applied to the electrodes. The microammeter is connected in series in this second electrode circuit, with proper consideration for polarity. The platinum electrodes are imbedded in glass tubing in the usual manner.

13.5.2 *Null Indicator Method*—A special null meter can be employed that uses a one-transistor amplification stage and represents a tenfold increase in end-point sensitivity. This null meter may be used with any ozone absorption device and the titration or timed voltage increase procedure. This potential is automatically applied by the circuitry in the null meter.

## 14. Directions for Ozone Measurement

14.1 *Spray-Jet Absorber Procedure C-1:*

14.1.1 Dissolve 15 g of KI in 75 $cm^3$ of buffer solution. Add this to the absorber flask, apply a vacuum and adjust the jet to produce a fine mist. Adjust the flow to 0.0050 $m^3$/min, or alternatively 70 to 80 $cm^3$/s (9 to 11 $ft^3$)/h. After completion of the absorption run, titrate the solution and washings with 1 mol/$m^3$ (0.0020 N) $Na_2S_2O_3$ solution. Add the $Na_2S_2O_3$ solution to the buffered solution of liberated iodine until zero current or the initial current value is reached. Add the $Na_2S_2O_3$ solution dropwise when nearing the end point, and wait between each drop to ensure complete reaction.

14.1.2 Calculate the ozone partial pressure in millipascals in accordance with Eq 8.

14.2 *Modified Spray-Jet Device Procedure C-2:*

14.2.1 A modification of the spray-jet method is in current use. This involves absorbing the ozone in a buffered potassium iodide solution that contains a measured amount of standard sodium thiosulfate solution. The time for the sodium thiosulfate to be consumed by reaction with iodine is measured. This has the advantage over the unmodified spray-jet method, in that no iodine is volatilized, and no empirical factor is therefore necessary to correct for this loss. To use this modified method, it is necessary to alter slightly the equipment shown in Fig. 2. A round-bottom flask with a bottom drain cock shall be used with four necks or outlets. Two of these are used as depicted in Fig. 2 to house the spray-jet and the upper reservoir return tube, and the other two contain a pair of platinum electrodes and a buret for adding sodium thiosulfate solution. The modified apparatus is shown in Fig. 3.

14.2.2 A sufficient quantity of buffer solution containing 15 g of potassium iodide is added so that a pool of solution fully immerses the electrodes when an air stream is drawn through the apparatus. As iodine is liberated, the current increases and the null indicator or microammeter will indicate this increase. A reference point on the scale is chosen, and as soon as the indicator reaches this point a stop watch is started. Immediately after a known volume of 0.0020 N sodium thiosulfate solution is added from the buret and the time for the current to again reach its original or reference value is noted. For low ozone levels, 1 to 2 $cm^3$ of sodium thiosulfate solution accurately added are sufficient; for higher ozone levels correspondingly more shall be added. This is the preferred absorption method when using the spray-jet to remove ozone from the air-ozone stream.

14.2.3 For the modified spray-jet apparatus, calculate the ozone partial pressure in accordance with Eq 9.

14.3 *Alternative Single Column Absorption Device Procedure C-1:*

14.3.1 Prepare 100 $cm^3$ of buffer solution containing 15 g of KI.

14.3.2 Insert the column in the analysis train. Close the stopcock and fill the column approximately ⅓ full with the KI solution. Place the 29/45 standard taper joint top on the column, lubricating the contacting ground glass surfaces with distilled water prior to firm contact. Turn on the pump and adjust the bleeder valve to obtain the desired flow rate. Record this flow rate, the temperature, and manometer reading. Continue the flow for a sufficient time to produce a satisfactory titration volume.

14.3.3 Stop the test (turn off pump) and drain the solution in the column into a clean 250-$cm^3$ beaker. Remove the top of the column and wash down with 25 $cm^3$ of distilled water. Allow this to drain into the titration beaker with 0.002 N standard $Na_2S_2O_3$ using the technique described in 11.6 to detect the end point.

14.3.4 Calculate the ozone partial pressure in millipascals in accordance with Eq 9.

14.4 *Rotameter Flowmeters:*

14.4.1 A rotameter-type flowmeter is often used. When such a device is used it is necessary that the true flow rate be obtained. Such flowmeters are calibrated at a specific temperature and pressure. The true flow rate is given by the following equation:

$$F = F_1 \sqrt{\frac{Pc}{P}\frac{T}{Tc}} \quad (7)$$

where:

$F$ = true flow rate at P and T, $m^3/s$, (or $m^3/min$),
$F_1$ = indicated flow rate on the meter during analysis, $m^3/s$, or $m^3/min$
$Pc$ = calibration pressure, kPa (0.133 × mm Hg),
$P$ = pressure during analysis, kPa,
$Tc$ = calibration temperature,°K, and
$T$ = temperature during analysis, °K.

14.4.2 Use the true flow rate in Eq 8 and Eq 9.

14.5 *Blank Analysis:*

14.5.1 A blank ozone analysis run shall be made when new batches of reagents are prepared and at any time when the quality of reagents is in doubt. A blank run shall be made under conditions identical to those of the ozone analysis as to time of sampling, rate of sampling, and general procedure. However, the air sample for the blank run shall be obtained from de-ozonized air. See Appendix X2. Ambient air that has been drawn through an absorption tube or absorption tower containing a minimum gas path length of 125 mm and a minimum diameter of 25 mm filled with Linde 13 X molecular sieves or equivalent will also suffice. The entrance and exit of this absorber shall contain fritted glass disks or be packed with glass wool. The efficiency of the sieves after some use may be tested by drawing air from an active ozone chamber through the absorber and analyzing the stream. Active molecular sieves should allow no ozone to pass into the analysis apparatus as determined by a comparison of the result obtained with that obtained with ambient air and fresh molecular sieves, taking into consideration the repeatability of the measurement.

14.6 Expressions for ozone content for the three alternative types of analysis devices are as follows:

14.6.1 *Spray-Jet Device:*

$$P(O_3),\ \text{mPa} = \frac{(Va - Vb) \times M \times T \times 9.247}{F \times t} \qquad (8)$$

where:

$Va - Vb$ = effective volume of $Na_2S_2O_3$ used, $cm^3$, = actual volume − blank,
$M$ = molarity of $Na_2S_2O_3$, $kmol/m^3$ ($mol/dm^3$),
$T$ = temperature, K,
$F$ = true flow rate, $m^3/s$, or $m^3/min$, and
$t$ = total analysis time, s or min if $m^3/min$ used above.

14.6.2 *Modified Spray-Jet Device and Single Column Absorption Device:*

$$P(O_3),\ \text{mPa} = \frac{(Va - Vb) \times M \times T \times 8.314}{F \times t} \qquad (9)$$

where:

($Va - Vb$), $M$, $F$, and $t$ are defined as in 14.6.1.

## 15. Test Report

15.1 When reporting ozone analysis results using this standard the following information shall accompany the report.

15.1.1 Method used (A, B, or C).

15.2 If Method B or C are used to measure the ozone concentration, the following information shall be reported.

15.2.1 The type of instrument used if an instrumental method is employed.

15.2.2 The concentration (in mPa partial $O_3$ pressure) expressed in terms of the UV method equivalent, i.e., the actual measured $O_3$ concentration converted by the calibration correction equation into a Method A value. This is designated $O_3$(corr), see 6.3.6.

## 16. Precision and Bias

16.1 Since these test methods do not involve the testing of materials or items that can be sent to a number of laboratories in the customary inter-laboratory test program sense, the concept of reproducibility (laboratory-to-laboratory variation) cannot be applied.

16.2 A program to assess repeatability of the three test methods as stipulated in this standard will be organized and results published when available.

16.3 As stated in the Introduction, the UV reference method is an absolute method, and for properly calibrated UV instruments, the test bias is negligible, that is, less than 1 mPa.

## 17. Keywords

17.1 chemical; deterioration; ozone measurement; rubber test; ultraviolet

# APPENDIXES

## (Nonmandatory Information)

## X1. THE EFFECT OF AMBIENT ATMOSPHERIC PRESSURE ON OZONE CRACKING OF RUBBER

### INTRODUCTION

The rate of ozone reaction with rubber (the cracking rate) is a function of the collision rate of ozone molecules with the rubber surface, all other factors constant. A change in barometric pressure, at constant temperature, will alter this collision rate even if the ozone content in the chamber is maintained constant on a volume (ozone) per unit volume (air) basis. Therefore, ozone concentration cannot be unambiguously expressed on a volume per volume basis in situations where differences in atmospheric pressure are likely. A method of expressing ozone content that is free of this limitation must be used.

This problem was addressed in 1973. The results of an ASTM interlaboratory program conducted to provide firm evidence of the atmospheric pressure effect have been recently published (**3**). Section X1.1 summarizes the published work from 1973 (**4**). Section X1.2 decribes the more recent published work (**3**) and correction to the problem inherent in the original process.

## X1.1 Simple Analysis of Test Results

X1.1.1 The expected effect of a reduction in pressure when the ozone concentration is maintained constant, pphm by volume, is a reduction in the collision rate (or partial pressure) of ozone molecules with the rubber surface. The ratio of air or total pressures will also be the same ratio as the $O_3$ partial pressures, under two different pressures.
Therefore:

$$\text{Expected Effect Ratio} = \frac{P_2}{P_1} \qquad (X1.1)$$

where:

$P_1$ = lower pressure, and
$P_2$ = higher pressure.

X1.1.2 The expected effect ratio refers to the rate of cracking or to the extent of cracking for a fixed exposure time under two different pressure conditions. In the two laboratories participating in the ASTM testing program, the nominal difference in barometric pressure was 100 torr (13 kPa); 736 versus 636 torr. Therefore, the expected effect ratio would be as follows:

$$\text{Expected Effect Ratio} = \frac{736}{636} = \frac{98.1\ \text{kPa}}{84.8\ \text{kPa}} = 1.16 \qquad (X1.2)$$

X1.1.3 A16 % increase in cracking rate or degree of cracking at a fixed ozone chamber exposure time is to be expected at the higher atmospheric pressure test laboratory.

X1.1.4 The extent of ozone cracking was quantitatively estimated by a technique previously published (**4**). In this technique, the extent of ozone cracking is determined by microscopic measurement of typical ozone crack dimensions. The product of the length and width is called the severity of ozone cracking abbreviated by the letters, SOC. A quantitative estimate of degree of ozone cracking is required if an experimental expected effect ratio is to be compared to the theoretical value obtained from the simple analysis outlined above.

X1.1.5 The published paper (**4**) contains many details on the interlaboratory program, but the work may be summarized by the data in Table X1.1. The Effect Ratio is the ratio of log (SOC) at the high atmospheric pressure to log (SOC) at the low pressure. It was found that log (SOC) was essentially linear with $O_3$ concentration, and it is used as the parameter that estimates the damage due to ozone cracking.

**TABLE X1.1 Effect Ratio Measured at 4-h Exposure and at the Listed $O_3$ Concentrations at Both Laboratories** [A]

| Compound | 30 pphm | 50 pphm | 70 pphm |
|---|---|---|---|
| A(SBR-1502) | 1.14 | 1.11 | 1.16 |
| B(SBR-1502) | 1.28 | 1.16 | 1.15 |
| C(SBR-1708) | 1.11 | 1.14 | 1.14 |
| D(SBR-1708) | 1.25 | 1.17 | 1.12 |
| Average | 1.19 | 1.15 | 1.14 |
| Grand average | 1.16 | | |

[A] The grand average experimental Effect Ratio is 1.16 which agrees with the theoretical derived value of 1.16. Thus the data strongly substantiate the simple theoretical analysis on collision rates and show that although nominal ozone concentrations (pphm by volume) as measured by the current ozone analysis technique are equal, ozone attack or cracking will not be equivalent if atmospheric pressures and consequent $O_3$ partial pressures are not equal.

## X1.2 Correcting the Problem (3)

X1.2.1 One pphm assumes one volume of ozone in $10^8$ volumes of air at normal atmospheric pressure and at any test temperature. While the test temperatures (within) between laboratories can be held constant, the atmospheric pressure varies day-to-day within a laboratory and more importantly consistently between laboratories at different elevations above sea level. The number of ozone molecules in a fixed geometric volume (of space) varies directly with the atmospheric pressure. To have the same number of ozone molecules in this fixed volume at any atmospheric pressure, the partial pressure due to ozone, must be kept constant.

X1.2.2 A resolution to the volume per volume expression of ozone content can be accomplished by the application of Dalton's Law and the gas equation. The ozone partial pressure is used to express ozone content or activity. The partial pressure of ozone in the mixture with air, $P(O_3)$, is given in megapascals by the following equation:

$$P(O_3) = n(O_3)RT/V \qquad (X1.3)$$

where:

$n\ (O_3)$ = number of moles of $O_3$ (in volume V),
$R$ = gas constant, (8.312 mPa $m^3$/K),
$T$ = temperature, K,
$V$ = volume of air-ozone mixture sampled, $m^3$, and
$P\ (O_3)$ = partial pressure of $O_3$, mPa.

X1.2.3 The evaluation of $n(O_3)$ is made on the basis of any of the analytical methods cited. Temperature is directly measured and the volume sampled is evaluated from time multiplied by the flowmeter reading suitably corrected for ambient atmospheric pressure since this affects the flowmeter reading.

X1.2.4 This particular mode of expressing ozone content, which is responsive to variations in atmospheric pressure, yields a good correspondence to nominal pphm values under standard conditions of temperature and pressure.
Thus:

1 pphm = 1.01 mPa at 1 atmosphere pressure 101 kPa (sea level)
At 85 kPa, 1 mPa = 1.18 pphm.

NOTE X1.1—One atmosphere (standard) = 101.32 kPa; one atmosphere (meteorological) = 100.000 kPa, and one atmosphere (technical) = 98.067 kPa.

## X2. BRIEF DESCRIPTION OF A TYPICAL UV OZONE MEASUREMENT DEVICE AND AUTOMATIC OZONE CALIBRATOR

### X2.1 UV Ozone Measurement Device

X2.1.1 These devices typically operate on the following basis. Sample gas is continually supplied to the sample chamber and the intensity of the UV beam traversing the sample cell is attenuated in proportion to the concentration of ozone in the sample (Beer's Law). This signal is detected and electronically processed for the readout system.

X2.1.2 Two reference subsystems correct for variations in source intensity, optical path transmittance, and detector response. Self zeroing and interference removal is accomplished by comparison of sample and reference readings, that is, no span or zero drift.

X2.1.3 The light attenuation is not affected by other substances provided they do not change from one measurement to the next. It is not affected by flow or temperature and pressure since the absorption depends only on the nature of the ozone molecule.

X2.1.4 Three subsystems make up the monitor: optical, gas flow, and electronics. The optical sub-system consists of the UV source, folded absorption cell, and two photodiode detectors. The sample detector measures attenuation due to the presence of ozone. The control detector is positioned near the UV lamp and measures variations in its light output correcting the signal that comprises the ozone reading.

X2.1.5 The gas flow subsystem includes the inlet/exhaust ports, the absorption cell, flowmeter, a gas switch, a selective ozone filter, and a sample pump. The switch directs the input gas through the filter where ozone is selectively removed, then to the absorption cell; after a given time, the sample is sent directly to the absorption cell. Alternately measuring the current (light level) at the sample detector with the ozone removed, and then with the ozone present, gives the ozone measurement.

### X2.2 Automatic Ozone Calibrator

X2.2.1 An automatic ozone calibration consists of two subsystems, a calibration air supply and the automatic calibrator proper.

X2.2.2 *Calibration Air Supply:*

X2.2.2.1 The calibration air supply is a source of interferent free air for ambient analyzer calibration. It supplies low humidity zero air at high flow rates for flow dilution.

X2.2.2.2 Components in the system, provide for clean air (oxygen concentration at a constant 21 %). The requirements for zero air (calibrate ambient air monitors) are met by an optional catalytic air cleaner. A pre-ozonator converts NO to $NO_2$, which is then removed along with $H_2S$, $SO_2$ and excess $O_3$ in an activated charcoal scrubber. Excess moisture is removed by compressing the incoming air then passing it through a coalescing filter. The carrier/purge air can be further dried with an optional or user supplied desiccant system. Regulators, gages, and a flowmeter are provided for setting pressures and monitoring flows.

X2.2.3 *Automatic Calibrator:*

X2.2.3.1 Ozone is generated when oxygen is exposed to short wavelengths in the UV, typically 185 nm and is emitted from a variable intensity mercury lamp through which a supply of clean, dry air flows. The output of the generators contains a level of ozone proportional to the light output of the generator lamp.

X2.2.3.2 The ozone level is measured by a UV photometer by measuring the proportional intensity changes of a UV beam as it traverses a fixed path containing the ozone.

X2.2.3.3 The UV wavelength used for measuring the ozone is 254 nm (the absorptivity peak of ozone) emitted from a mercury lamp. The shorter ozone-generating wavelengths are filtered out by a vycor outer shield over the inner quartz lamp. The photodetectors measure the UV with a narrow response peaked at around 250 nm, thereby rejecting the low level, longer wavelengths produced by the mercury lamp. The combined filtering effects produce a light measurement which is monochromatic to better than 0.5 %.

The sample temperature and pressure affect the measurement when determining parts per million ozone. Temperature and pressure measurements are made on the sample and entered into the computation of the displayed result.

## REFERENCES

(1) CSI Ozone Monitor, Model 1100, Columbia Scientific Corp., P.O. Box 9908, Austin, TX 78766 (USA).

(2) OREC Ozone Monitors, Ozone Research Equipment Company, 221 Beaver St., Akron, OH 44304.

(3) Veith, A. G., and Evans, R. L., "The Effect of Atmospheric Pressure on Ozone Cracking of Rubber," *Journal of Polymer Testing*, Vol 1, January 1980, pp. 27–38.

(4) Veith, A. G., "A Rapid Quantitative Method for Measuring Ozone Cracking," *Rubber Chemistry and Technology*, Vol 45, 1973, p. 293.

*ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.*

*This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.*

*This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org). Permission rights to photocopy the standard may also be secured from the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, Tel: (978) 646-2600; http://www.copyright.com/*