INTERNATIONAL STANDARD

ISO 1431-3

Second edition
2017-06

Rubber, vulcanized or thermoplastic — Resistance to ozone cracking —

Part 3:
Reference and alternative methods for determining the ozone concentration in laboratory test chambers

Caoutchouc vulcanisé ou thermoplastique — Résistance au craquelage par l'ozone —

Partie 3: Méthode de référence et autres méthodes pour la détermination de la concentration d'ozone dans les enceintes d'essai de laboratoire

Reference number
ISO 1431-3:2017(E)

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html

This document was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 2, *Testing and analysis*.

This second edition cancels and replaces the first edition (ISO 1431-3:2000), which has been technically revised.

The main changes compared to the previous edition are as follows:

- a calculation error has been corrected in the formula in B.1.4;
- the value of gas constant has been corrected in the formulae in C.2.4 and C.3.4.
- Annex A has been changed from normative to informative, and a citation has been added to Clause 8.

A list of all parts in the ISO 1431 series can be found on the ISO website.

Introduction

A number of techniques exist for the analysis of gaseous ozone/air mixtures used for ozone crack testing of rubbers. These include wet-chemical procedures, electrochemical cells, UV absorption and chemiluminescence with ethylene.

In principle, the wet-chemical, electrochemical and UV absorption methods are all absolute, but in practice they do not in general yield the same results.

Wet-chemical methods, which usually consist of the absorption of ozone in a potassium iodide solution and titration of the iodine released with sodium thiosulfate, were traditionally used in the rubber industry and were specified in national standards. They are not suitable for continuous operation or control and hence are less desirable in practice than instrumental methods. The results obtained have been shown to be sensitive to small variations in test procedures and the concentration and purity of reagents, and there has been much controversy over the stoichiometry of the reaction.

Electrochemical methods are widely used in the rubber industry and found to be convenient in continuously monitoring and controlling ozone. Chemiluminescence methods have also been used.

More recently, UV absorption analysers, which have the same monitoring and controlling ability, have been increasingly used. Most important, this technique has been adopted by all major environmental agencies as the standard and is regarded by them to be absolute.

Consequently, this standard UV absorption method is adopted as the reference technique against which all others are intended to be calibrated. Like any measurement instrument, the accuracy of any particular UV instrument is dependent on the calibration and maintenance of its components, and hence even UV analysers should be checked against acknowledged standard instruments. Studies are being undertaken in several countries to propose a primary-standard apparatus.

Although this document is concerned with ozone analysis, it also draws attention to the influence of atmospheric pressure on the rate of cracking of rubber at constant ozone concentrations as normally expressed in terms of parts by volume. As established by interlaboratory tests conducted in North America[3], the variation in ozone resistance that can result between laboratories operating at significantly different atmospheric pressures can be corrected by specifying ozone concentration in terms of the partial pressure of ozone (see Annex C).

Attention is drawn to the highly toxic nature of ozone. Efforts should be made to minimize the exposure of workers at all times. In the absence of more stringent or contrary national safety regulations, it is recommended that 10 parts of ozone per hundred million parts of air of the surrounding atmosphere by volume be regarded as an absolute maximum concentration, while the maximum average concentration should be appreciably lower.

Unless a totally enclosed system is being used, an exhaust vent to remove ozone-laden air is recommended.

Rubber, vulcanized or thermoplastic — Resistance to ozone cracking —

Part 3:
Reference and alternative methods for determining the ozone concentration in laboratory test chambers

1 Scope

This document describes three types of method for the determination of ozone concentration in laboratory test chambers.

Method A — UV absorption: this is the reference method, and is used as the means of calibration for the alternative methods B and C.

Method B — Instrumental techniques:

B1: electrochemical

B2: chemiluminescence

Method C — Wet-chemical techniques:

Procedure I

Procedure II

Procedure III

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 1431-1, *Rubber, vulcanized or thermoplastic — Resistance to ozone cracking — Part 1: Static and dynamic strain testing*

ISO 13964, *Air quality — Determination of ozone in ambient air — Ultraviolet photometric method*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— IEC Electropedia: available at http://www.electropedia.org/

— ISO Online browsing platform: available at http://www.iso.org/obp

4 Principle

An ozone/air mixture is sampled from an ozone exposure chamber and the ozone concentration is determined by the UV absorption reference method or by alternative instrumental or chemical-analysis methods calibrated against the UV absorption method.

5 Apparatus

Apparatus used for the determination of the ozone concentration shall be one of the following types:

UV absorption

Electrochemical

Chemiluminescence

Wet-chemical

The reference method is UV absorption, and all equipment shall be calibrated against the UV absorption method as specified in Clause 6.

The apparatus used for the UV absorption method shall be in accordance with ISO 13964, except that it shall be capable of measuring ozone concentrations specified in ISO 1431-1.

Descriptions of alternative methods are given in Annex B (instrumental methods) and Annex C (wet-chemical methods).

6 Calibration

Calibration of the apparatus for determining the ozone concentration shall be in accordance with the procedures given in ISO 13964.

7 Procedure

The UV method shall be carried out in accordance with ISO 13964.

Other instrumental methods shall be used in accordance with the manufacturer's instructions, attention being paid in particular to initial setting up, zero adjustment and maintaining and checking the instrument as mentioned in Annex B.

Wet-chemical methods shall be carried out in accordance with Annex C.

8 Expression of results

Generally, the ozone concentration φ_{O_3} is expressed in parts of ozone by volume per hundred million parts of air by volume (pphm).

However, the ozone concentration may also be expressed in mg/m^3 or in mPa. The expression mg/m^3 indicates the number of ozone molecules in the volume which is available for ozone cracking and depends on both pressure and temperature (see Annex A).

For conversion purposes, the following formula is valid:

$$\varphi_{\mathrm{O}_3}\left[\mathrm{mg/m^3}\right]=5{,}78\times10^{-3}\times\frac{p}{T}\times\varphi_{\mathrm{O}_3}\left[\mathrm{pphm}\right]$$

where

p is the atmospheric pressure, in hPa;

T is the temperature, in K.

In terms of the partial pressure of ozone:

$$p_{O_3}\left[\text{mPa}\right]=10^{-3}\,p\,\varphi_{O_3}\left[\text{pphm}\right]$$

where p, is the atmospheric pressure, in hPa.

At 1 013 hPa and 273 K, 1 pphm = 1,01 mPa.

9 Test report

The test report shall contain the following information:

a) a reference to this document, i.e. ISO 1431-3;

b) the method used, i.e. type of instrument or wet-chemical;

c) the measurement interval if measurement was not continuous;

d) the ozone concentration or range of concentrations measured, expressed in pphm or mg/m^3 or mPa partial pressure of O_3, corrected if necessary by a calibration factor;

e) the date of the test.

Annex A
(informative)

Effect of ambient atmospheric pressure on ozone cracking of rubber

The rate of reaction of ozone with rubber, i.e. the cracking rate, is a function of the rate of collision of the ozone molecules with the rubber surface and is therefore a function of the number of ozone molecules present, all other factors being constant.

The perfect-gas equation and Dalton's law permit the partial pressure of ozone p_{O_3} to be calculated as a function of the number of moles of ozone n_{O_3} in volume V of the ozone/air mixture, measured at temperature T:

$$p_{\mathrm{O}_3} = n_{\mathrm{O}_3} \frac{RT}{V}$$

where

p_{O_3} is the partial pressure of ozone, in mPa;

T is the temperature, in K;

V is the volume of the ozone/air mixture, in m^3;

R is the gas constant (R = 8,314 $\mathrm{Pa \cdot m^3 \cdot mol^{-1} \cdot K^{-1}}$).

NOTE Under standard conditions of temperature (273 K) and pressure (1 atm., 760 torr or 1 013 hPa), 1 pphm = 1,01 mPa.

It can be demonstrated that, for the same ozone content, by volume, of the ozonized air, measured at the same temperature but at different atmospheric pressures, the partial pressure of ozone and the number of moles of ozone vary in the same ratio as the atmospheric pressure.

The results of an interlaboratory test programme conducted in North America[3] prove the effect of ambient pressure on the cracking rate at a constant volumetric ozone content.

Therefore, the expression of the ozone concentration in laboratory test chambers on a volume per volume basis is inappropriate where differences in atmospheric pressure are likely to exist.

The effect of these variations can be corrected for by working at a constant test chamber pressure or by varying the volumetric ozone content of the ozone/air mixture in an inverse ratio to the atmospheric pressure. The effect can also be overcome by expressing the ozone concentration as the partial pressure of the ozone in ozonized air.

Annex B
(normative)

Alternative instrumental methods

B.1 Electrochemical method

B.1.1 Principle

Ozonized air is bubbled at a fixed rate through a coulometric cell containing a buffered solution of potassium iodide and having a platinum cathode and a silver (preferred) or mercury anode.

The ozone reacts with the potassium iodide to liberate free iodine which is ionized at the cathode and removed at the anode to produce silver or mercury iodide. Two units of charge are produced for each ozone molecule and the resultant current is proportional to the ozone concentration. The net emf of the cell is cancelled by an applied back emf and corrections made for ambient temperature and pressure (see Reference [1]).

The stoichiometry is:

$$O_3 + 2KI + H_2O \rightarrow 2KOH + O_2 + I_2$$

At the cathode: $I_2 + 2e \rightarrow 2I^-$

At the anode: $2I^- - 2e + 2Hg \rightarrow Hg_2I_2$

By Faraday's Law:

$$O_3 \rightarrow 2I^- \rightarrow 2e \rightarrow 2 \times 96\ 500 \text{ coulombs}$$

B.1.2 Apparatus

The analyser shall include a coulometric cell of the general type shown in Figure B.1. Standard models are available commercially.

The cathode is in the form of a platinum basket through which the ozonized air is bubbled. The anode can take the form of one of the following, although b) is the preferred type:

a) a pool of mercury;

b) a silver mesh spiral.

The iodine liberated from the solution by the ozone is ionized at the cathode and is transported to the anode by the liquid circulation induced in the direction of the arrows by the bubbling action. At the anode, insoluble silver iodide or mercurous iodide is formed with the release of ionic charges which are exactly equivalent to the ozone introduced by the air stream.

The cell shall be connected to an analyser circuit of the general type shown in Figure B.2.

A stabilized DC voltage source is provided as a means of opposing the standard potential which appears at the cell terminals when ozone-free air is passed through the cell. This standard potential will depend on the anode material.

B.1.3 Reagents

Prepare a buffered solution of potassium iodide as follows.

Weigh out the following analytical-reagent quality chemicals and dissolve in 1 l of chloride-free and sulfate-free distilled water:

Potassium iodide (KI)	1,50 g
Sodium monohydrogen phosphate (Na_2HPO_4)	1,50 g
Potassium dihydrogen phosphate (KH_2PO_4)	1,40 g

This should give a solution buffered at pH 6,5 to pH 6,8.

B.1.4 Cell calibration

Assuming a gas flow rate of 150 cm^3/min measured at standard temperature and pressure and an ozone content of 100 pphm, the size of the current is:

$$\frac{100\times10^{-8}\times150\times2\times96{,}500\times10^{6}}{22{,}400\times60}=21{,}54\ \mu\text{A}$$

Thus, in the typical circuit shown in Figure B.2, the analyser can be calibrated directly by relating cell current to ozone concentration.

B.2 Chemiluminescence

In chemiluminescence instruments, ozonized air is passed through a chamber where it comes into contact with a stream of ethylene, and the two gases undergo a chemiluminescence reaction with the emission of photons at about 430 nm. This emission of energy is measured by a photomultiplier and converted to an electrical output which is proportional to the ozone concentration.