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**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*



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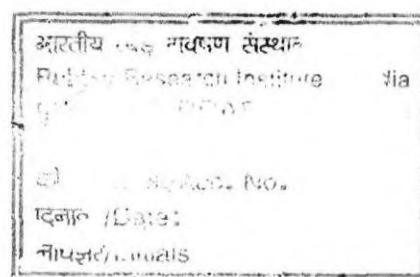
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## Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this part of ISO 1431 may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 1431-3 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 2, *Physical and degradation tests*.

ISO 1431 consists of the following parts, under the general title *Rubber, vulcanized or thermoplastic — Resistance to ozone cracking*:

- *Part 1: Static strain test*
- *Part 2: Dynamic strain test*
- *Part 3: Reference and alternative methods for determining the ozone concentration in laboratory test chambers*

Annexes A, B and C form a normative part of this part of ISO 1431.



## 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 must 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 part of ISO 1431 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<sup>[3]</sup>, 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, whilst 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 part of ISO 1431 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 normative documents contain provisions which, through reference in this text, constitute provisions of this part of ISO 1431. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this part of ISO 1431 are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 1431-1:1989, *Rubber, vulcanized or thermoplastic — Resistance to ozone cracking — Part 1: Static strain test.*

ISO 1431-2:1994, *Rubber, vulcanized or thermoplastic — Resistance to ozone cracking — Part 2: Dynamic strain test.*

ISO 13964:1998, *Air quality — Determination of ozone in ambient air — Ultraviolet photometric method.*

### 3 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.

### 4 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 5.

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 and -2.

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

### 5 Calibration

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

### 6 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.

### 7 Expression of results

Generally, the ozone concentration  $\phi_{O_3}$  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  $\text{mg/m}^3$  or in mPa. The expression  $\text{mg/m}^3$  indicates the number of ozone molecules in the volume which is available for ozone cracking and depends on both pressure and temperature.

For conversion purposes, the following equation is valid:

$$\varphi_{\text{O}_3} [\text{mg} / \text{m}^3] = 5,78 \times 10^{-3} \times \frac{p}{T} \times \varphi_{\text{O}_3} [\text{pphm}]$$

where  $p$ , the atmospheric pressure, is in hPa and  $T$  is in K.

In terms of the partial pressure of ozone:

$$p_{\text{O}_3} [\text{mPa}] = 10^{-3} p \varphi_{\text{O}_3} [\text{pphm}]$$

where  $p$ , the atmospheric pressure, is in hPa.

At 1013 hPa and 273 K, 1 pphm = 1,01 mPa.

## 8 Test report

The test report shall contain the following information:

- a) a reference to this part of ISO 1431, 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  $\text{mg}/\text{m}^3$  or mPa partial pressure of  $\text{O}_3$ , corrected if necessary by a calibration factor;
- e) the date of the test.



## Annex A (normative)

### The 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  $T$ :

$$p_{O_3} = n_{O_3} \frac{RT}{V}$$

where

$p_{O_3}$  is in mPa;

$T$  is in K;

$V$  is in m<sup>3</sup>;

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

NOTE Under standard conditions of temperature (273 K) and pressure (1 atm., 760 torr or 1 013 hPa), 1 ppm = 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<sup>[3]</sup> 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

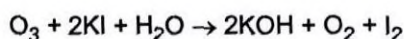
#### B.1 Electrochemical method

##### 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]).

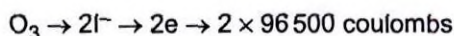
The stoichiometry is:



At the cathode:  $\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-$

At the anode:  $2\text{I}^- - 2\text{e}^- + 2\text{Hg} \rightarrow \text{Hg}_2\text{I}_2$

By Faraday's Law:



##### 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 d.c. 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 litre of chloride-free and sulfate-free distilled water:

Potassium iodide (KI)	1,50 g
Sodium monohydrogen phosphate ( $\text{Na}_2\text{HPO}_4$ )	1,50 g
Potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ )	1,40 g

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

### B.1.4 Cell calibration

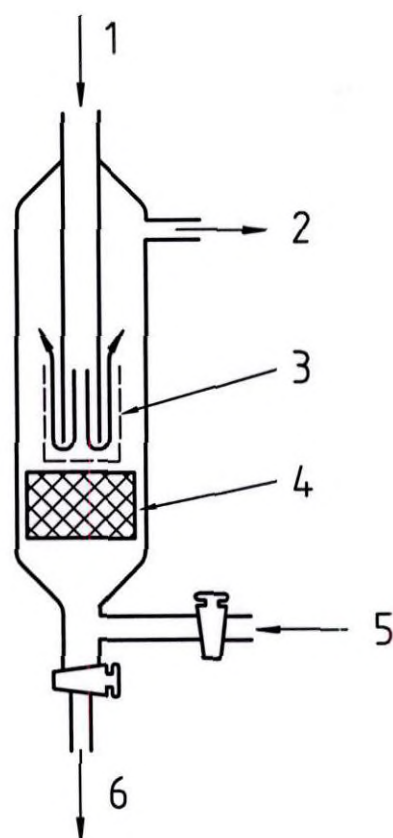
Assuming a gas flow rate of  $150 \text{ cm}^3/\text{min}$  measured at STP and an ozone content of 100 pphm, the size of the current is:

$$\frac{100 \times 10^{-8} \times 150 \times 2 \times 96,500 \times 10^6}{22,400 \times 60} = 21,55 \mu\text{A}$$

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

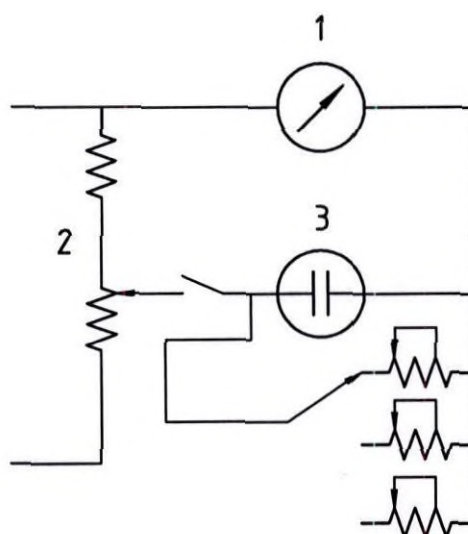
In chemiluminescence instruments, ozonized air is passed through a chamber where it comes into contact with a stream of ethylene, and the two gases undergo a chemiluminescence reaction with the emission of photons at about 430 nm. This emission of energy is measured by a photomultiplier and converted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



**Key**

- |   |                    |   |          |
|---|--------------------|---|----------|
| 1 | Air/O <sub>3</sub> | 4 | Anode    |
| 2 | Air                | 5 | Solution |
| 3 | Cathode            | 6 | To waste |

**Figure B.1 — Analyser**



**Key**

- |   |                    |
|---|--------------------|
| 1 | Micro-ammeter      |
| 2 | Stable d.c. source |
| 3 | Cell               |

**Figure B.2 — Simple analyser circuit**

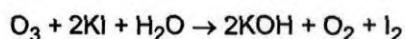


## Annex C (normative)

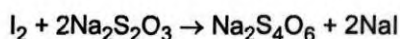
### Wet-chemical methods

#### C.1 General theory

**C.1.1** The absorption of ozone in an buffered neutral aqueous KI solution yields free iodine by oxidation:



The addition of sodium thiosulfate solution to the KI solution prior to the absorption causes an immediate reaction between the free iodine and the thiosulfate:



Thus one  $\text{O}_3$  is equivalent to  $2\text{Na}_2\text{S}_2\text{O}_3$ .

**C.1.2** Three alternative procedures are available, I, II and III, any of which may be used.

**C.1.2.1** Procedure I is the well established technique by which  $\text{O}_3$  is absorbed in a buffered KI solution with excess  $\text{Na}_2\text{S}_2\text{O}_3$ , for a fixed length of time, followed by titration of the excess  $\text{Na}_2\text{S}_2\text{O}_3$  in the usual way with a standardized  $\text{I}_2$  solution to an electrometric end-point.

**C.1.2.2** Procedure II is a modification of procedure I and uses a recorder to monitor the voltage across the electrodes of an electrometric end-point detection device. A smaller quantity (more dilute solution) of  $\text{Na}_2\text{S}_2\text{O}_3$  is added to the buffered KI solution and the absorption process is continued until the  $\text{Na}_2\text{S}_2\text{O}_3$  is totally consumed. At this point, the voltage abruptly rises. From the chart record the total elapsed time for the completion of the reaction is easily determined, and this is used to calculate the ozone concentration.

**C.1.2.3** Procedure III is a further variant using a constant-current electrolysis apparatus in conjunction with the electrometric end-point detector.

#### C.2 Procedure I

##### C.2.1 Reagents

###### C.2.1.1 Buffered potassium iodide solution

A solution of KI in a 0,1 mol/l phosphate buffer is used. This is prepared by dissolving in 1 litre of distilled water:

17,8 g of crystalline disodium hydrogen phosphate dihydrate ( $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ ) or the corresponding amount of another hydrate of disodium hydrogen phosphate;

13,6 g of potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ );

30 g  $\pm$  2 g of potassium iodide (KI).

This solution shall have a pH of 6,8. Before using it, check for free iodine. For this purpose, take 10 ml of the solution and determine that no colour change occurs when a few drops of 2 mol/l HCl are added together with 0,5 ml of starch paste. Keep the prepared solution in a stoppered brown bottle in a cool place, away from light.

**C.2.1.2 Sodium thiosulfate solution,  $c(\text{Na}_2\text{S}_2\text{O}_3) = 0,1 \text{ mol/l}$** 

This solution can be easily prepared by using a commercially available standard solution (e.g. Titrisol®, Merck). Store this solution away from light in a cool place. Under these conditions the titre will remain stable for 6 months.

**C.2.1.3 Sodium thiosulfate solution,  $c(\text{Na}_2\text{S}_2\text{O}_3) = 0,002 \text{ mol/l}$** 

Prepare this solution freshly on the day of analysis from the 0,1 mol/l solution by appropriate dilution with distilled water. For example, pipette 5 ml of the 0,1 mol/l solution into a 250 ml volumetric flask and make up to the mark with freshly boiled distilled water.

**C.2.1.4 Iodine solution,  $c(\frac{1}{2}\text{I}_2) = 0,1 \text{ mol/l}$** 

This solution can be easily prepared by using a commercially available standard solution (e.g. Titrisol®, Merck). Store this solution away from light in a cool place. Under these conditions, the titre will remain stable for 6 months.

**C.2.1.5 Iodine solution,  $c(\frac{1}{2}\text{I}_2) = 0,002 \text{ mol/l}$** 

Prepare from solution C.2.1.4 in the same way as C.2.1.3.

**C.2.2 Apparatus****C.2.2.1 Equipment for preparation of reagents****C.2.2.1.1 250 ml and 1 000 ml volumetric flasks.****C.2.2.1.2 5 ml pipette.****C.2.2.1.3 Balance, accurate to 5 mg.****C.2.2.2 Ozone-absorption apparatus**

Material in contact with the ozonized air shall not noticeably absorb ozone. All glass equipment shall be exposed to the ozone for some hours before use. Connection tubes shall be as short as possible and shall have a diameter of at least 4 mm. Connection tubes which cannot be avoided shall have the smallest possible contact area with the ozone.

**C.2.2.2.1 Two 100 ml glass gas-absorption bottles, connected up as shown in Figure C.1.**

**CAUTION — Do not use bottles with a sintered-glass bubbler, since this interferes with the determination.**

**C.2.2.2.2 Flow meter, accurate to 1 %.****C.2.2.2.3 Thermometer, graduated at intervals of 0,5 °C.****C.2.2.3 Titration equipment****C.2.2.3.1 100 ml measuring flask.****C.2.2.3.2 2 ml pipette.****C.2.2.3.3 2 ml burette, accurate to 0,005 ml.****C.2.2.3.4 250 ml beaker.**

**C.2.2.3.5 100 ml measuring cylinder.**

**C.2.2.4 End-point detection circuit (see Figure C.2)**

**C.2.2.4.1 Two platinum electrodes**, 2,5 mm in diameter and 25 mm long, mounted in glass tubes with electrical connections provided. Instead of two separate electrodes, a pair of electrodes mounted together a short distance apart (double electrode) can be used. In the latter case, the diameter of each electrode shall be 1 mm and the length 6 mm. At the end of each shall be a ball 1,5 mm in diameter. The distance between the balls shall be 0,7 mm. When the double electrode with its smaller surface is used, the sensitivity of the micro-ammeter used shall be increased by a factor of at least 10.

**C.2.2.4.2 Micro-ammeter**, range 0 to 20  $\mu$ A.

**C.2.2.4.3 Two resistances**, wired in series, one a variable resistance which can be increased to 1 000  $\Omega$ , the other a fixed resistance of 30 000  $\Omega$ .

**C.2.2.4.4 1,5 V cell.**

**C.2.3 Procedure**

**C.2.3.1 Ozone absorption**

Aspirate a specified volume of the air-ozone mixture through the two absorption bottles connected in series, each containing about 100 ml of buffered potassium iodide solution and exactly 2,00 ml of 0,002 mol/l sodium thiosulfate solution. The gas throughput rate shall be between 1 l/min and 3 l/min and gas shall be passed through for at least 10 min. Record the time to  $\pm 1$  s.

**C.2.3.2 Titration**

Transfer the solution from the two absorption bottles to a beaker. Titrate the excess sodium thiosulfate with a 0,002 mol/l iodine solution using the end-point indication method described in C.2.3.3.

**C.2.3.3 End-point indication**

A low potential difference is maintained between the two electrodes immersed in the buffered solution of potassium iodide containing an excess of sodium thiosulfate. The electrodes are polarized and a very small current passes through the ammeter. At the exact moment when the added iodine no longer reacts, corresponding to moment when all the sodium thiosulfate solution has been consumed, the cathode depolarizes and a much larger current passes. The end-point is thus indicated by a sharp deflection of the ammeter needle from its lowest point.

**C.2.3.4 Blank test**

Run a blank test in exactly the same way as in C.2.3.1 to C.2.3.3, but passing ordinary air through the absorption bottles.

**C.2.4 Expression of results**

Calculate the ozone concentration  $\varphi_{O_3}$  in pphm (parts by volume of ozone per  $10^8$  parts by volume of air), using the following equation:

$$\varphi_{O_3} = \frac{5 \times 10^5 \times (V_b - V_a) \times c \times R \times T}{p \times F \times t} \text{ pphm}$$

where

$V_b$  is the volume of iodine solution used in the blank test, in ml;

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- $V_a$  is the volume of iodine solution used in the actual determination, in ml;
- $c$  is the concentration of the iodine solution, in mol/l;
- $T$  is the temperature of the air/ozone stream, in K;
- $p$  is the pressure at the input of the flow meter, in hPa;
- $F$  is the flow rate, in l/min;
- $t$  is the length of time the ozone-air stream was passed through the absorption bottles, in min;
- $R$  is the gas constant (8,315 Pa·m<sup>3</sup>·mol<sup>-1</sup>·K<sup>-1</sup>).

### C.3 Procedure II

#### C.3.1 Preparation of reagents

##### C.3.1.1 Buffered potassium iodide solution

This solution is identical to that specified in C.2.1.1.

##### C.3.1.2 Standardized sodium thiosulfate solutions

These solutions shall be prepared freshly on the day of analysis from the 0,1 mol/l solution specified in C.2.1.2. The concentration needed depends on the ozone concentration. The following concentrations are suitable:

0,000 1 mol/l for 25 pphm ozone

0,000 2 mol/l for 50 pphm ozone

0,000 5 mol/l for 100 pphm ozone

0,001 mol/l for 200 pphm ozone

The dilution with distilled water can be carried out in one or two steps by using pipettes and standard flasks.

#### C.3.2 Apparatus

##### C.3.2.1 Equipment for preparation of reagents

For general requirements, see C.2.2.1.

##### C.3.2.2 Ozone-absorption apparatus

For general requirements, see C.2.2.2.

The apparatus is illustrated schematically in Figure C.3. The absorption flask is shown in more detail in Figure C.4. If a flask of this kind is not available, a 250 ml three-neck flask is also suitable. The absorption flask is placed on a magnetic stirrer. A pair of platinum electrodes or a double electrode is inserted into the flask and connected to a chart recorder which is set to give a full-scale deflection of 50 mV or 100 mV. The chart speed shall be checked with a stopwatch.

#### C.3.3 Procedure

##### C.3.3.1 Using the by-pass, adjust the ozone/air flow rate to 1 l/min.

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**C.3.3.2** Introduce about 60 ml of buffered KI solution and, with a pipette, exactly 5 ml of the standardized  $\text{Na}_2\text{S}_2\text{O}_3$  solution into the flask. Begin vigorous stirring and start the recorder at a chart speed of preferably 10 mm/min.

**C.3.3.3** Switch the gas stream to the absorption flask and simultaneously mark that point on the recorder chart (or start a stopwatch and mark later).

**C.3.3.4** Adjust the flow rate if needed, and allow the absorption to continue until the baseline mV signal on the chart shows an abrupt increase. Measure the elapsed time either using the stopwatch or from the chart trace. In the latter case, take as the end point the point of intersection of the baseline with the steadily increasing line after the end point.

**C.3.3.5** If analytical-grade reagents are used and they are stored away from light in a cool location, a blank run is not needed.

### C.3.4 Expression of results

Calculate the ozone concentration  $\varphi_{\text{O}_3}$  as follows:

$$\varphi_{\text{O}_3} = 5 \times 10^5 \frac{V \times c \times R \times T}{p \times F \times t} \text{ ppm}$$

where

$V$  is the volume of  $\text{Na}_2\text{S}_2\text{O}_3$  solution used, in ml;

$c$  is the concentration of the  $\text{Na}_2\text{S}_2\text{O}_3$  solution, in mol/l;

$T$  is the temperature of the ozonized air, in K;

$F$  is the flow rate of the ozonized air, in l/min;

$t$  is the elapsed time, in min;

$p$  is the pressure at input of the flow meter, in hPa;

$R$  is the gas constant ( $8,315 \text{ Pa} \cdot \text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ).

## C.4 Procedure III

### C.4.1 Preparation of reagents

#### C.4.1.1 Buffered potassium iodide solution

This solution is similar to that specified in C.2.1.1. Prepare it by mixing 0,1 mol/l sodium dihydrogen phosphate solution and 0,1 mol/l potassium phosphate monobasic solution in the ratio 3:2 by volume and dissolving in it sufficient potassium iodide to give a concentration between 10 % and 20 %.

#### C.4.1.2 Standardized sodium thiosulfate solution

Prepare an approximately 0,1 mol/l sodium thiosulfate solution, transfer a suitable quantity to a volumetric flask and dilute 10 times to give a concentration of about 0,01 mol/l. Standardize this solution by a suitable method.

**NOTE** Solutions of known concentration can be obtained commercially (see C.2.1.2).

**C.4.1.3 Absorption solution**

To 300 ml of the solution prepared in C.4.1.1 add 2 ml of the sodium thiosulfate solution prepared in C.4.1.2.

**C.4.2 Apparatus****C.4.2.1 Equipment for preparation of reagents**

For general requirements, see C.2.2.1.

**C.4.2.2 Ozone-absorption apparatus**

The apparatus is illustrated in Figure C.5. Preferably use apparatus made of coloured glass. Pack it with glass beads of diameter 3 mm to 4 mm.

**C.4.2.3 End-point detector**

An example of a suitable circuit is shown in Figure C.6.

**C.4.2.4 Electrolysis equipment**

An example of a suitable circuit is shown in Figure C.6.

**C.4.2.5 Other equipment****C.4.2.5.1 Stopwatch.****C.4.2.5.2 Flow meter, size 5 ml.****C.4.2.5.3 Pipettes, capacity 5 ml and 2 ml respectively.****C.4.2.5.4 Electric stirrer.****C.4.3 Procedure**

**C.4.3.1** Pipette 7 ml of the absorption solution into the absorption apparatus.

**C.4.3.2** Connect the ozonized-air supply to the inlet of the apparatus and the flow meter to the outlet.

**C.4.3.3** Pass about 5 litres of the ozonized air through the apparatus at about 2 l/min.

**C.4.3.4** When this operation is complete, remove the inlet tube and stop the pump. Then open the stopcock, at the same time pouring 100 ml of water into the upper end of the apparatus to flush the absorption solution into a 250 ml beaker.

**C.4.3.5** Introduce the platinum electrodes of the end-point detector and those of the electrolysis equipment into the absorption solution (see Figure C.6) and apply about 0,15 V to the electrodes of the end-point detector. Confirm that the ammeter reads zero. Switch on the electrolysis equipment, and pass a current of 200  $\mu$ A between the electrodes whilst stirring the solution at a constant rate. Start the stopwatch at the same time as the electrolysis is started.

**C.4.3.6** When the ammeter of the end-point detector indicates 0,3  $\mu$ A, stop the stopwatch, switch off the electrolysis equipment and read off the time  $t_1$  required for electrolysis.

**C.4.3.7** Carry out a blank run by repeating the electrolysis using 7 ml of absorption solution (C.4.1.3), to which 100 ml of water has been added, in a clean beaker. Measure the time  $t_0$  required for the blank.

#### C.4.4 Expression of results

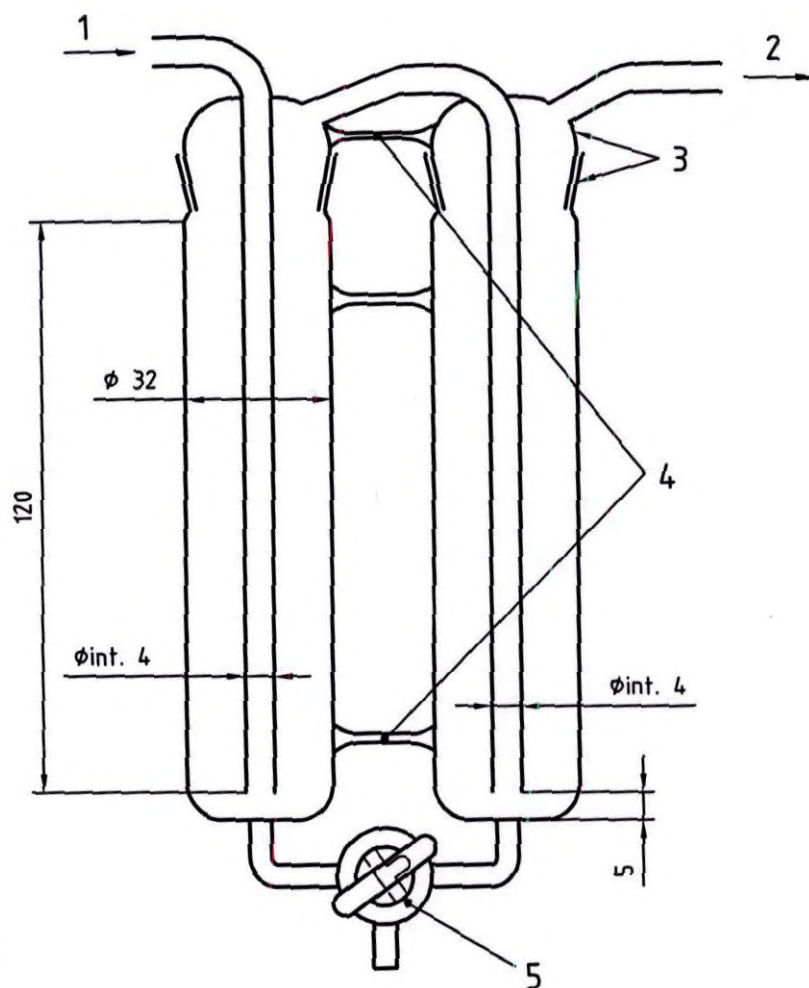
Calculate the ozone concentration  $\varphi_{O_3}$  by volume in the ozone/air mixture from the following equations:

$$\begin{aligned}\varphi_{O_3} &= \frac{200 \times 11,2 \times 760 \times (t_0 - t_1) \times T \times 10^{-6}}{96,500 \times 273 \times 5 \times p} \\ &= \frac{1,29 \times (t_0 - t_1) \times T}{p} \text{ pphm}\end{aligned}$$

where

- $t_1$  is the time taken for electrolysis of the test solution, in seconds;
- $t_0$  is the time taken for electrolysis of the blank solution, in seconds;
- $p$  is equal to  $760 - \Delta p$  in mmHg (where  $\Delta p$  is the difference between the pressure at the input of the flow meter during the actual determination and the pressure during the blank run);
- $T$  is the temperature of the solution, in K.

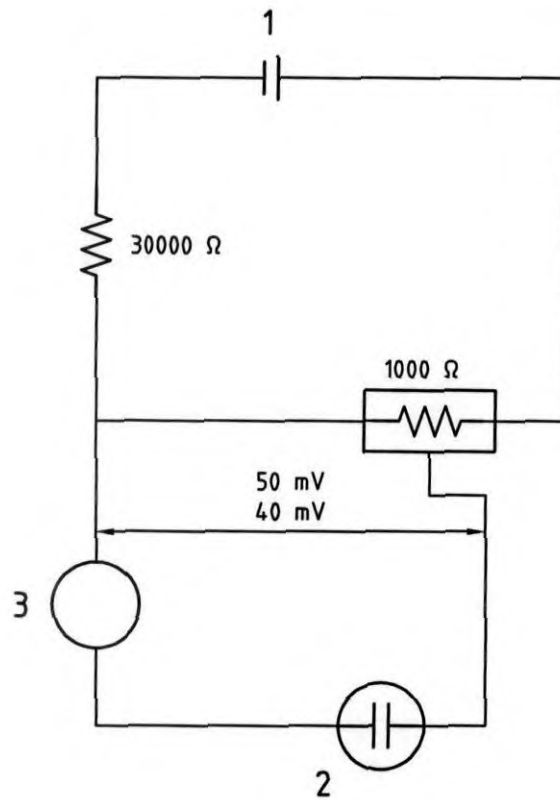
Dimensions in millimetres

**Key**

- 1 Gas in
- 2 Gas out
- 3 29/42 or 34/45 conical joint
- 4 Glass cross-pieces
- 5 3-mm-diameter 3-way PTFE stopcock

**Figure C.1 — Ozone-absorption apparatus**

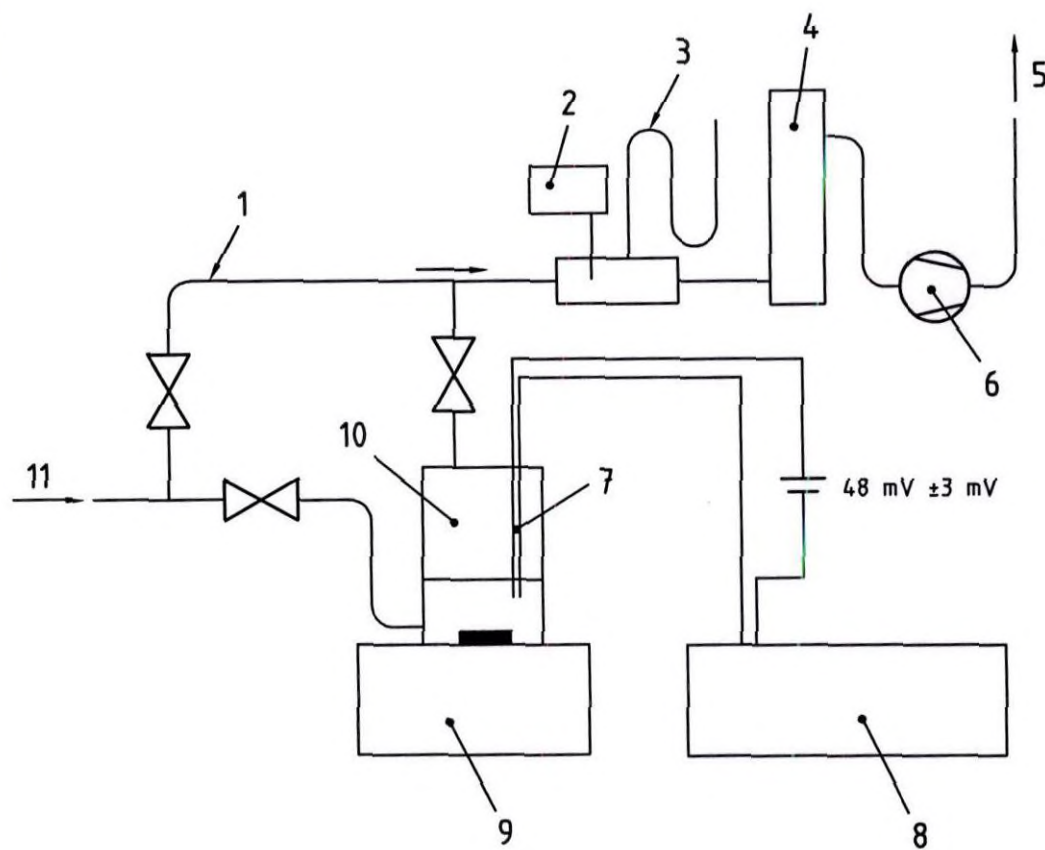




**Key**

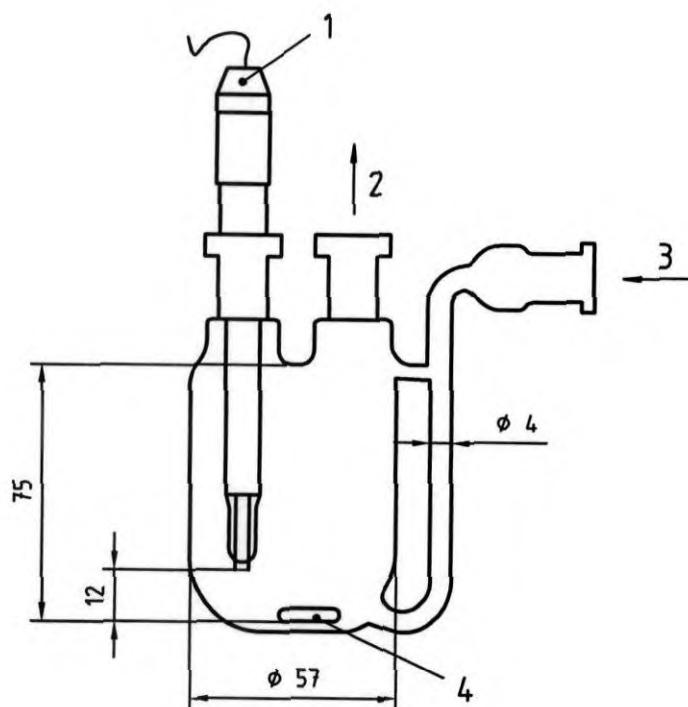
- 1 1,5 mV battery
- 2 Two platinum electrodes
- 3 Micro-ammeter

**Figure C.2 — Electrometric end-point detection circuit**

**Key**

- |   |                |    |                     |
|---|----------------|----|---------------------|
| 1 | By-pass        | 7  | Platinum electrodes |
| 2 | Thermocouple   | 8  | Recorder            |
| 3 | Pressure gauge | 9  | Stirrer             |
| 4 | Flow meter     | 10 | Absorption flask    |
| 5 | Gas out        | 11 | Gas in              |
| 6 | Pump           |    |                     |

**Figure C.3 — General arrangement of apparatus for procedure II**

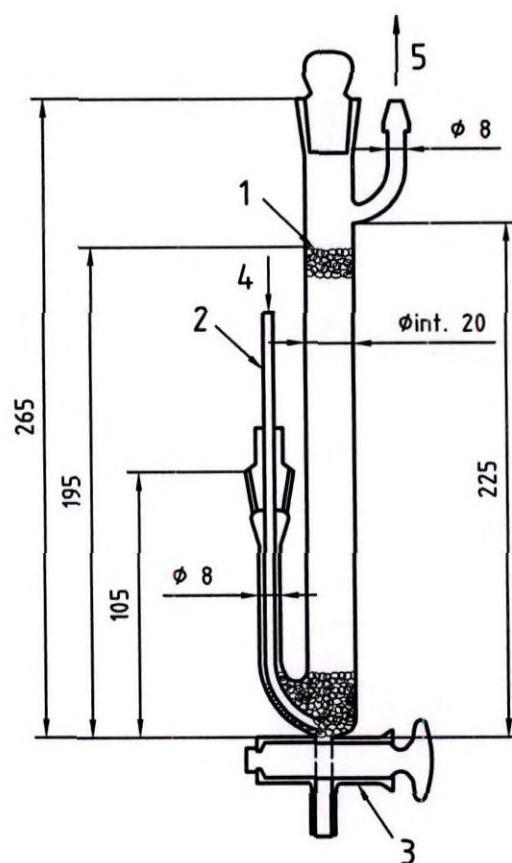


**Key**

- 1 Platinum electrodes
- 2 Gas out
- 3 Gas in
- 4 Stirrer bar

**Figure C.4 — Ozone-absorption flask for procedure II**

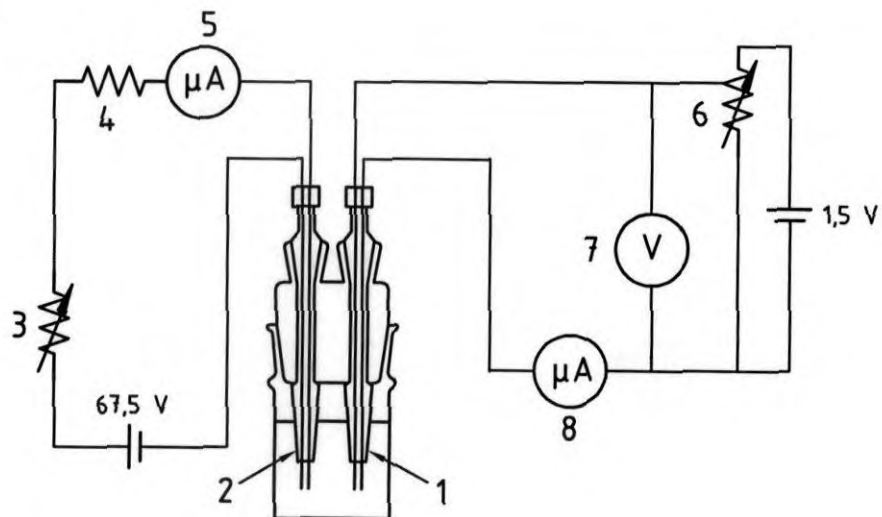
Dimensions in millimetres

**Key**

- 1 Glass beads, diameter 3 mm to 4 mm
- 2 PTFE tube, diameter 2 mm to 3 mm
- 3 Stopcock, diameter 3 mm
- 4 Gas in
- 5 Gas out

**Figure C.5 — Ozone-absorption apparatus for procedure III**

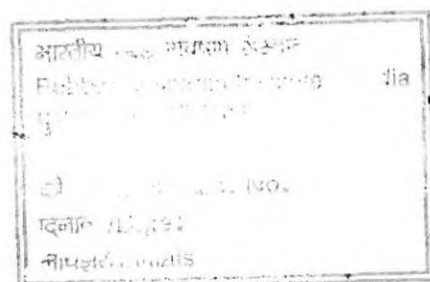




**Key**

- |   |  |   |  |
|---|--|---|--|
| 1 | Electrodes of end-point detector   | 5 | Micro-ammeter, full-scale deflection 200 $\mu$ A |
| 2 | Electrodes of electrolysis equipment                                     | 6 | 2 k $\Omega$ variable resistance                 |
| 3 | Variable resistance, switchable between 30 k $\Omega$ and 500 k $\Omega$ | 7 | Voltmeter, full-scale deflection 0,5 V           |
| 4 | 60 k $\Omega$ resistance   | 8 | Micro-ammeter, full-scale deflection 10 $\mu$ A  |

**Figure C.6 — Example of suitable electrolysis and detector circuits**



## Bibliography

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