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Rubber and rubber products — Determination of bromine and chlorine content — Oxygen flask combustion technique

Caoutchouc et produits à base de caoutchouc — Détermination de la teneur en brome et en chlore — Technique de combustion dans une fiole en présence d'oxygène

Reference number
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Foreword

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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.

International Standard ISO 7725 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*.

Annex A of this International Standard is for information only.

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Introduction

This International Standard describes an oxygen flask combustion technique for the destruction of rubber, followed by either a potentiometric titration for chlorine and bromine if they occur singly or together, or a visual titration for bromine only or chlorine only.

Mutual interference, caused by co-precipitation, can be a problem in the potentiometric titration with silver nitrate. This is largely overcome though not completely eliminated by the addition of aluminium nitrate. The problem is least when bromine is in excess. At its worst, when chlorine is in excess, the bromine concentration may appear high, to an extent of 5 % of the chlorine content. The problem may be minimized by carrying out the titration at 60 °C, and keeping the rate of addition of titrant to a minimum.

During combustion of bromine-containing compounds, a small proportion of the bromine appears as bromate instead of bromide. Bromine results can therefore be low by about 1 % of the bromine content. This can be overcome in the case of the potentiometric finish only by treating the solution obtained on combustion with hydrazine sulfate.

The potentiometric titration (see 7.2.1) is sensitive down to 6 µg of bromine or 3 µg of chlorine when these are present singly.

The visual titration (see 7.2.2) lower limits are down to 0,2 mg of bromine or 0,1 mg of chlorine. When both chlorine and bromine are present, the lower limits are 60 µg of bromine and 30 µg of chlorine. These limits are dependent on the electrical sensitivities of the individual instruments used (see 5.3 to 5.5).

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Rubber and rubber products — Determination of bromine and chlorine content — Oxygen flask combustion technique

1 Scope

This International Standard specifies methods for the determination of chlorine and/or bromine present in raw rubber, uncured mixes or vulcanizates.

The methods are applicable to natural rubbers and to the following synthetic rubbers: isoprene, styrene-butadiene, butadiene, chlorinated, butyl, halogenated butyl, nitrile, ethylene-propylene, polychloroprene and epichlorohydrin.

2 Principle

The test portion is ignited in an atmosphere of oxygen in an oxygen combustion flask containing potassium hydroxide and hydrogen peroxide. The carbon and hydrogen of any organic matter are oxidized and halogen is converted to the potassium salt. These potassium salts are titrated potentiometrically with silver nitrate solution to determine the amount of chlorine and bromine, when they occur together in a rubber sample, or are titrated visually with mercuric nitrate solution to give either chlorine or bromine, when only one halogen is present.

3 Interference

3.1 Iodine will interfere but Zn^{2+}, S, CN^- and CO_3^{2-} do not.

3.2 Bromine and chlorine contained in additives/contaminants will be determined by this method, unless previously removed by extraction.

4 Reagents and materials

WARNING — All recognized health and safety precautions shall be in effect when carrying out the operations specified in this International Standard. Failure to heed the directions contained in this International Standard or those of the manufacturer of the devices used may result in explosions.

During the analysis, use only reagents of recognized analytical reagent grade and only distilled water or water of equivalent purity.

4.1 Hydrogen peroxide, 6 % (*m*/*m*) solution.

Dilute 20 cm³ of 30 % (*m*/*m*) aqueous hydrogen peroxide solution to 100 cm³ with water.

WARNING — 30 % (*m*/*m*) hydrogen peroxide is very corrosive to the skin. Wear rubber or plastic gloves and eye protection when handling.

4.2 Potassium hydroxide, solution, $c(\text{KOH}) = 0{,}5$ mol/dm³

Dissolve 2,8 g of potassium hydroxide in 100 cm³ of water.

4.3 Nitric acid, concentrated, $\rho = 1{,}42$ Mg/m³.

4.3.1 Nitric acid, dilute, $c(\text{HNO}_3) = 2$ mol/dm³.

Dilute approximately 120 cm³ of concentrated nitric acid (4.3) to 1 dm³ with water.

4.3.2 Nitric acid, dilute, $c(\text{HNO}_3) = 0{,}5$ mol/dm³.

Dilute 30 cm³ of concentrated nitric acid (4.3) to 1 dm³ with water.

4.3.3 Nitric acid, dilute, 0,2% (*V*/*V*).

Dilute 2 cm³ of concentrated nitric acid (4.3) to 1 dm³ with water.

4.4 Silver nitrate, standard volumetric solution, $c(\text{AgNO}_3) = 0{,}02$ mol/dm³.

Prepare from commercial ampoules or dissolve 3,4 g of silver nitrate in 1 dm³ of water.

Standardize the silver nitrate solution as follows:

Take a measured volume of between 1 cm³ and 5 cm³ of sodium chloride solution (4.5), dilute with water to 25 cm³ in a 50 cm³ beaker, add 2 drops of sulfuric acid (4.11) along with a stirring bar, place on a stirrer (5.8) and titrate manually or with an automatic titrator (5.9). Plot the reading in millivolts versus the volume of silver nitrate to find the inflection point, or read the volume from the automatic titrator. Carry out the standardization in duplicate.

Besides determining the concentration of the silver nitrate, this operation serves to alert the analyst to the proper functioning of the millivoltmeter (5.3) and indicates the proper inflection point for chlorine.

4.5 Sodium chloride, standard reference solution, $c(\mathrm{NaCl}) = 0{,}02\ \mathrm{mol/dm^3}$.

Prepare from commercial ampoules or dissolve 1,17 g of sodium chloride in 1 dm³ of water.

4.6 Methyl orange indicator, solution.

Dissolve 0,2 g of methyl orange in 100 cm³ of water.

4.7 Aluminium nitrate, with low halide content.

4.8 Diphenylcarbazone indicator, solution.

Dissolve 1,5 g of diphenylcarbazone in 100 cm³ of ethanol. Heat to dissolve, if necessary.

4.9 Bromophenol blue indicator, solution.

Dilute 5 cm³ of a 1 g/100 cm³ ethanolic solution of bromophenol blue to 100 cm³ with ethanol.

4.10 Mercury(II) nitrate, standard volumetric solution, $c(\mathrm{Hg(NO_3)_2 \cdot 0{,}5H_2O}) = 0{,}01\ \mathrm{mol/dm^3}$.

Dissolve 3,4 g of mercury(II) nitrate in 1 dm³ of water containing 2 cm³ of 0,2 % (V/V) nitric acid (4.3.3). Adjust the pH to 1,7, using a pH-meter and adding the nitric acid dropwise.

Standardize the mercury(II) nitrate solution as follows:

Weigh and record, to the nearest 0,1 mg, 40 mg to 60 mg of potassium chloride and make up to 100 cm³ with water in a graduated flask. Transfer 10 cm³ of this solution to a 250 cm³ conical flask. Add 20 cm³ of water and 80 cm³ of ethanol (4.14) and stir magnetically at moderate speed. Add 5 drops of the bromophenol blue indicator solution (4.9) and then add 0,5 mol/dm³ nitric acid (4.3.2) dropwise until the yellow end-point is reached, plus 3 drops in excess. Add 5 drops of the diphenylcarbazone indicator solution (4.8) and titrate with the mercury(II) nitrate solution to the first appearance of a permanent pink colour. Carry out the standardization in duplicate.

Carry out a blank titration, omitting the potassium chloride.

Calculate the concentration c_1, expressed in moles of $\mathrm{Hg(NO_3)_2 \cdot 0{,}5H_2O}$ per cubic decimetre, using the equation

$$c_1 = \frac{m_1}{149{,}11(V_1 - V_2) \times 10}$$

where

m_1 is the mass, in milligrams, of potassium chloride weighed out;

V_1 is the volume, in cubic centimetres, of mercury(II) nitrate solution used for the titration of the potassium chloride;

V_2 is the volume, in cubic centimetres, of mercury(II) nitrate solution used for the titration of the blank.

4.11 Sulfuric acid, concentrated, $\rho = 1{,}84\ \mathrm{Mg/m^3}$.

4.12 Supply of oxygen.

4.13 Potassium chloride, with low bromide content.

4.14 Ethanol.

Alternatively 2-propanol may be substituted wherever ethanol is specified.

4.15 Hydrazine sulfate, 20 g/dm³ solution (only for use in 7.2.1).

5 Apparatus

Ordinary laboratory apparatus, plus the following:

5.1 Oxygen combustion flask (Schöniger flask), thick-walled, 1 000 cm³ capacity, with a platinum sample carrier and a strong pinch clamp or fastening device (see 5.2, note 1).

5.2 Igniter, suitable for igniting the flammable material in which the test portion is contained in the tightly closed combustion flask. Common types are electrical and infra-red, both of which are suitable for use in this determination.

NOTE 1 There are many types of oxygen combustion flask assembly, complete with igniter, that are commercially available and that are suitable for this determination provided they are operated in accordance with the manufacturer's instructions.

5.3 Millivoltmeter, with high input impedance: e.g. a pH-meter with a millivolt scale.

5.4 Silver electrode, to be used as a measuring electrode.

WARNING — Do not coat the electrode with halogen.

5.5 Reference electrode, of the salt bridge type: mercury(I) sulfate or any other type with a potassium sulfate salt bridge.

5.6 Burette, 10 cm³ or 25 cm³ capacity.

5.7 Balance, capable of weighing to 0,01 mg.

5.8 Magnetic stirrer and **stirring bar**.

5.9 Automatic titrator.

5.10 Wrappers, of black or white paper, or **cellulose capsules**, suitable for oxygen combustion purposes. Typical paper configurations are illustrated in figure 1. The test portion is placed in the centre of the large section and the paper folded over it to enclose it completely. The narrow strip is allowed to protrude to reach a flame or the beam of an infrared igniter or an igniting electrode.

5.11 Safety chamber.

6 Selection and preparation of intermediate test portion

6.1 Selection

Cut from the sample an intermediate test portion of between 0,5 g and 2,0 g depending on the expected halogen level, if necessary from more than one place so that proper representation of the whole sample is achieved.

Dimensions are approximate and in millimetres

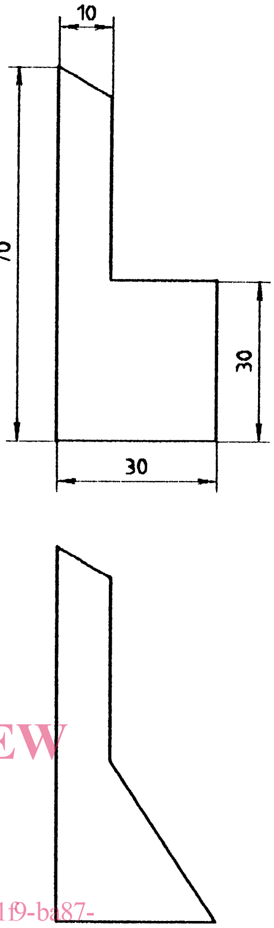


Figure 1 — Paper configurations for wrapping test portions for oxygen combustion

6.2 Preparation

Pass the intermediate test portion six times between the cold rolls of a laboratory mill set to a nip not exceeding 0,5 mm. If it is not possible to pass it through the mill, the intermediate test portion may be cut into pieces less than 1 mm per side.

7 Procedure

7.1 Combustion

7.1.1 Weigh 40 mg to 50 mg of rubber to ± 0,1 mg and place this test portion in a capsule or wrap in paper (5.10). Due to the small test portion size, the rubber and paper or capsule used for containing the test portion shall be protected from contamination. Handle with forceps or plastic gloves. The test portion shall contain at least 0,25 mmol of halogen. If it is known that the amount of halogen is small, it is advisable to combust several (maximum 4) 80 mg to 100 mg test portions of rubber in the same flask, consecutively, over the same absorbing solution (see 7.1.8).

7.1.2 Place 1,0 cm³ of the potassium hydroxide solution (4.2), 5 cm³ of the hydrogen peroxide solution (4.1) and 10 cm³ of water into the combustion flask and insert the test portion.

7.1.3 Flush the flask for 1 min with oxygen (4.12), using a flow rate of at least 2 l/min.

7.1.4 Firmly close the flask with the clamps or closures recommended and place the flask in the safety chamber (5.11).

7.1.5 Ignite and burn the test portion.

WARNING — Leave the flask in the safety chamber until the last spark is extinguished. At this point, it can be removed, but since a slight vacuum is formed, hand and eye protection is recommended.

7.1.6 After removing the flask from the igniter assembly (5.2), insert a stopper and allow it to stand for 1 h or until all of the vapours have condensed into the absorbing solution. If black residual carbon is noted at this point, repeat the procedure with a smaller test portion.

7.1.7 Remove the stopper from the flask, and rinse all the stopper surfaces with water into the combustion flask.

7.1.8 If more than one test portion is to be combusted in the same flask, wrap the next test portion, insert it in the flask and repeat the operations described in 7.1.3 to 7.1.7.

7.1.9 Boil the contents of the flask for a short time to decompose the hydrogen peroxide, but do not allow the flask to boil to dryness.

7.2 Titration

7.2.1 Potentiometric titration for bromine and/or chlorine (present singly or together)

7.2.1.1 Transfer the solution obtained as described in 7.1.9 quantitatively to a 50 cm³ beaker with several washes of water. The total volume should be about 20 cm³. Place a magnetic stirring bar in the beaker and place the assembly on the magnetic stirrer (5.8). When bromine is present, add 5 drops of hydrazine sulfate solution (4.15).

7.2.1.2 Add a few drops of the methyl orange solution (4.6) and, while stirring, add 0,5 mol/dm³ nitric acid (4.3.2) until a colour change is noted, indicating that the solution is neutralized. Add a further 2 cm³ of the nitric acid (4.3.2) and 2 g of the aluminium nitrate (4.7). Continue stirring to dissolve the aluminium nitrate[1] and then add 160 cm³ of ethanol (4.14).

7.2.1.3 Insert the electrode pair (5.4 and 5.5) into the solution and titrate with the silver nitrate solution (4.4), monitoring the change in millivolts against the volume of titrant added, either manually by taking readings to produce a graph of millivolts versus volume of titrant, or with an automatic titrator (5.9).

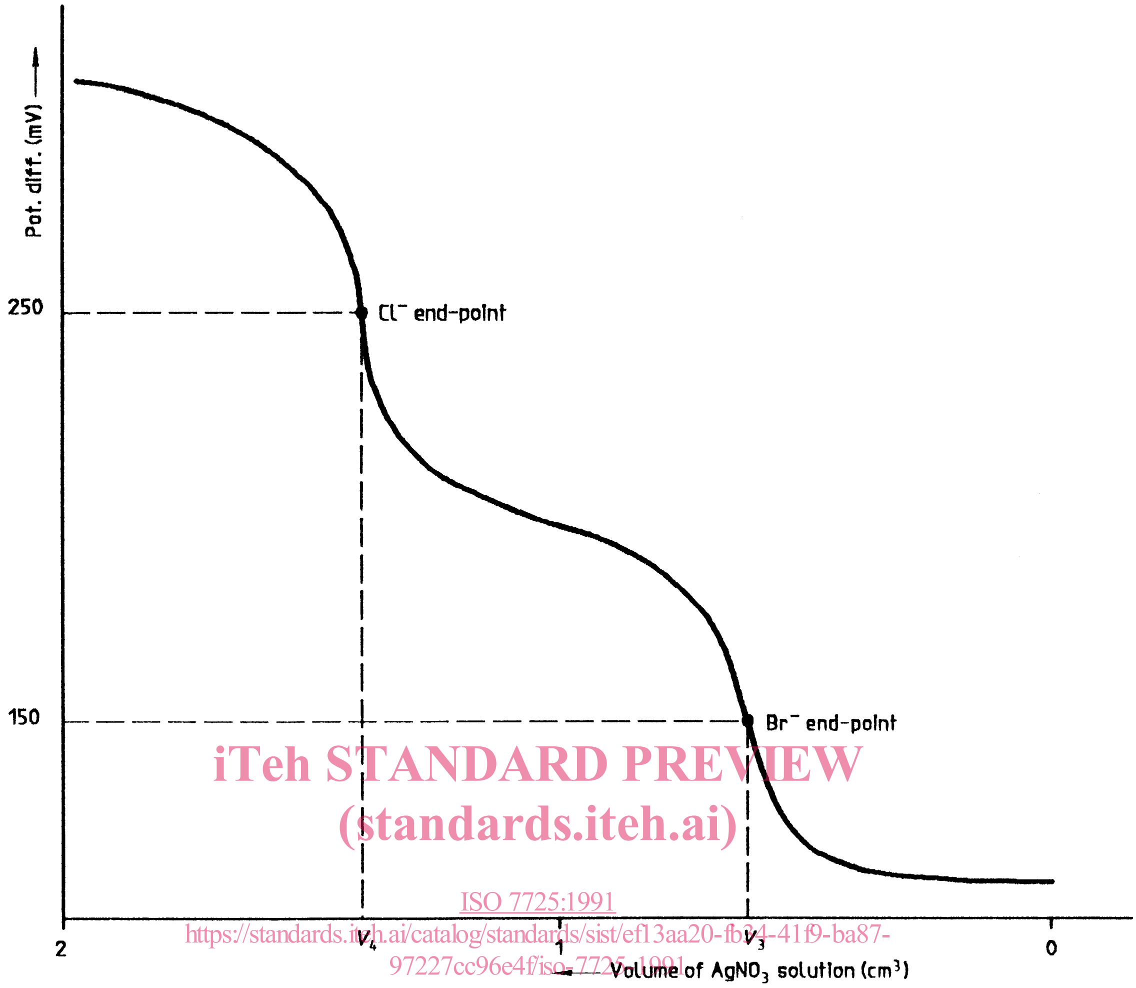
7.2.1.4 The first inflection point on the titration curve represents the bromide end point, and the second inflection represents the chloride end point. If bromine or chlorine is present singly, the inflection point for bromide occurs at about 150 mV, that for chloride at about 250 mV. A typical titration curve is given in figure 2.

7.2.1.5 Determine the volume of the silver nitrate solution required to titrate a blank to the same inflection points, using the same quantities of reagents as for the test solution, but omitting the test solution.

7.2.2 Visual titration for bromine or chlorine (present singly)

7.2.2.1 Transfer the solution obtained as described in 7.1.9 quantitatively to a 150 cm³ beaker with small washes of water. The final volume should be about 20 cm³. Add enough ethanol (4.14) to make the solution approximately 80 % alcoholic, by volume. Add the magnetic stirring bar and place the assembly on the magnetic stirrer (5.8). Titrate as in the standardization of mercury(II) nitrate solution (4.10), beginning with "Add 5 drops of the bromophenol blue..." up to "permanent pink colour".

7.2.2.2 Determine the volume of the mercury(II) nitrate solution required to titrate a blank, using the same quantities of reagents as for the test solution, but omitting the test solution.



NOTE — When it is not known which halide is present in the sample, the inflection point can be used to identify whether it is bromine or chlorine.

Figure 2 — Typical titration curve

8 Expression of results

8.1 For bromine and/or chlorine (present singly or together), using the potentiometric titration, the bromine content $w(\mathrm{Br})$, expressed as a percentage by mass, is given by the equation

$$w(\mathrm{Br}) = \frac{V_3 c_2 \times 79{,}9 \times 100}{m_2}$$

and the chlorine content $w(\mathrm{Cl})$, expressed as a percentage by mass, is given by the equation

$$w(\mathrm{Cl}) = \frac{(V_4 - V_3) c_2 \times 35{,}45 \times 100}{m_2}$$

where

V_3 is the volume, in cubic centimetres, of silver nitrate solution (4.4) required to titrate to the first inflection point, as found by plotting millivolts versus volume of silver nitrate solution or as read from the automatic titrator, minus the volume used in the blank titration (see 7.2.1.5);

V_4 is the volume, in cubic centimetres, of silver nitrate solution (4.4) required to titrate to the second inflection point, as found by plotting millivolts versus volume of silver nitrate solution or as read from the automatic titrator, minus the volume used in the blank titration (see 7.2.1.5);

c_2 is the concentration, in moles per cubic decimetre, of the silver nitrate solution (4.4);

m_2 is the mass, in milligrams, of the test portion (see 7.1.1).