
**Rubber and rubber products —
Determination of chlorine and
bromine content**

*Caoutchouc et produits à base de caoutchouc — Détermination de la
teneur en brome et en chlore*

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Contents

Page

Foreword.....	iv
Introduction.....	v
1 Scope.....	1
2 Normative references.....	1
3 Terms and definitions.....	1
4 Principle.....	1
5 Sample preparation.....	2
5.1 Sampling.....	2
5.2 Sample solutions.....	2
6 Method A — Ion chromatography.....	2
6.1 Reagents.....	2
6.2 Apparatus.....	3
6.3 Determination.....	3
6.3.1 Setting up the ion chromatograph.....	3
6.3.2 Preparation of the calibration curve.....	3
6.3.3 Measuring blank solutions and sample solutions.....	3
6.4 Calculation.....	4
7 Method B — Potentiometric titration.....	4
7.1 Reagents.....	4
7.2 Apparatus.....	5
7.3 Determination.....	5
7.4 Calculation.....	6
8 Precision.....	7
9 Test report.....	7
Annex A (normative) Preparation of sample solutions by the tubular furnace combustion method.....	8
Annex B (normative) Preparation of sample solutions by the oxygen combustion flask method.....	11
Annex C (normative) Preparation of sample solutions by the oxygen combustion bomb method.....	14
Annex D (informative) Conditions for ion chromatography.....	16
Annex E (informative) Precision results from an interlaboratory test programme.....	18
Bibliography.....	20

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.

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).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of 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 www.iso.org/iso/foreword.html.

The committee responsible for this document is ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 2, *Testing and analysis*.

This second edition cancels and replaces the first edition (ISO 7725:1991), which has been technically revised. The main changes compared to the previous edition are as follows:

- the ion chromatography method has been added in [Clause 6](#);
- the titration procedure has been improved in [Clause 7](#);
- the tubular furnace combustion method for sample preparation has been added in [Annex A](#);
- the oxygen combustion flask method for sample preparation has been improved in [Annex B](#);
- the oxygen combustion bomb method for sample preparation has been added in [Annex C](#);
- mercury nitrate and hydrazine are no longer used due to their hazardous properties.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

The two test methods in this document for quantitative analysis can be used for any type of rubbers (i.e. raw rubber, vulcanized rubber or unvulcanized rubber) containing chlorine and/or bromine in any form of existence, such as an element of polymer chain, chemical additives or a part of contaminations.

Three combustion methods are given for preparation of sample solution, i.e. tubular furnace combustion method, oxygen combustion flask method and oxygen combustion bomb method. After sample solutions are prepared, a content determination procedure, i.e. either ion chromatography or potentiometric titration, follows. The most convenient and efficient method from the testing time and safeness points of view, is the combination of tubular furnace combustion and ion chromatography, as ion chromatography is widely used in quality control of polymer/rubber products or in environmental analysis.

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Rubber and rubber products — Determination of chlorine and bromine content

WARNING 1 — Persons using this document should be familiar with normal laboratory practice. This document does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicability of any other restrictions.

WARNING 2 — Certain procedures specified in this document might involve the use or generation of substances, or the generation of waste, that could constitute a local environmental hazard. Reference should be made to appropriate documentation on safe handling and disposal after use.

1 Scope

This document specifies methods for the determination of chlorine and/or bromine present in raw rubber as well as vulcanized or unvulcanized rubber compounds.

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

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2 Normative references (standards.iteh.ai)

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 1795, *Rubber, raw natural and raw synthetic — Sampling and further preparative procedures*

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 4661-2, *Rubber, vulcanized — Preparation of samples and test pieces — Part 2: Chemical tests*

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:

- ISO Online browsing platform: available at <http://www.iso.org/obp>
- IEC Electropedia: available at <http://www.electropedia.org/>

4 Principle

A sample solution is obtained by combustion of a test piece either burnt in a tubular furnace with a stream of oxygen-containing gas and passed into a prepared solution or burnt in an oxygenic atmosphere in a flask or a bomb which contains a solution to absorb the combustion gas. The sample solution is then analysed by ion chromatography (method A) or potentiometric titration (method B) to determine the content of chlorine and/or bromine in a sample.

For rubber samples of very low halogen content, method A is preferable since the inflection point might not be obtained by method B.

5 Sample preparation

5.1 Sampling

For raw rubber, carry out sampling in accordance with ISO 1795.

For rubber compounds, carry out sampling in accordance with ISO 4661-2.

NOTE Chlorine and bromine contained in additives or contaminants can be detected by these sampling methods, unless previously removed by extraction.

5.2 Sample solutions

To prepare sample solutions by the tubular furnace combustion method, follow the method specified in [Annex A](#). Repeat the procedure to create two solutions for each sample.

To prepare sample solutions by the oxygen combustion flask method, follow the method specified in [Annex B](#). Repeat the procedure to create two solutions for each sample.

To prepare sample solutions by the oxygen combustion bomb method, follow the method specified in [Annex C](#). Repeat the procedure to create two solutions for each sample.

If incomplete combustion, such as soot generation during combustion, is expected by the oxygen combustion flask method, it is preferable to use the tubular furnace combustion method or the oxygen combustion bomb method.

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6 Method A — Ion chromatography (standards.iteh.ai)

6.1 Reagents

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6.1.1 **Water**, of grade 1 or higher. It shall be as specified in ISO 3696.

6.1.2 **Chloride ion standard stock solution**, of a commercial standard solution with a certified chloride ion concentration, e.g. 1 000 mg/l of chloride, traceable to national standards. Comply with the manufacturer's expiration date or recommended shelf-life.

6.1.3 **Chloride ion calibration solution**, prepared by diluting the chloride ion standard stock solution (6.1.2) with water (6.1.1). Prepare at least four solutions of different concentration of chloride ion covering the expected concentration from the sample. The solutions shall be prepared every analytical day.

6.1.4 **Bromide ion standard stock solution**, of a commercial standard solution with a certified bromide ion concentration, e.g. 1 000 mg/l of bromide, traceable to national standards. Comply with the manufacturer's expiration date or recommended shelf-life.

6.1.5 **Bromide ion calibration solution**, prepared by diluting the bromide ion standard stock solution (6.1.4) with water (6.1.1). Prepare at least four solutions of different concentration of bromide ion covering the expected concentration from the sample. The solutions shall be prepared every analytical day.

6.1.6 **Mixed calibration solution**, for measuring chloride ion and bromide ion at the same time, prepared by mixing chloride ion (6.1.2) and bromide ion (6.1.4) with water (6.1.1). Prepare at least four solutions of different concentration of chloride ion and bromide ion covering the expected concentration from the sample. The solutions shall be prepared every analytical day.

6.1.7 **Eluent solution**, capable of eluting chloride ion and bromide ion to a proper retention time in selected column. Follow the column manufacturer's instructions.

NOTE Some examples of eluent are provided in [Annex D](#).

6.2 Apparatus

6.2.1 Ion chromatograph, consisting of a pump to supply eluent, a sample injector, a column and a conductivity detector specified as follows:

- pump: capable of delivering a constant flow within the range of 0,1 ml/min to 2,0 ml/min;
- sample injector: capable of injecting a constant volume of solution;
- column: filled with anion exchange resin suitable for resolving chloride ion and bromide ion from other inorganic anions;
- suppressor: used for reducing the conductivity of high ionic eluent;
- detector: for detecting conductivity.

NOTE Some examples of commercially available column are provided in [Annex D](#).

An ion chromatograph fitted with a suppressor as [Figure 1](#) is suitable for sensitive analysis. The suppressor is attached between a column and a detector.

An ion chromatograph without a suppressor as [Figure 2](#) may also be selected.



Figure 1 — Example of basic ion chromatography system with suppressor

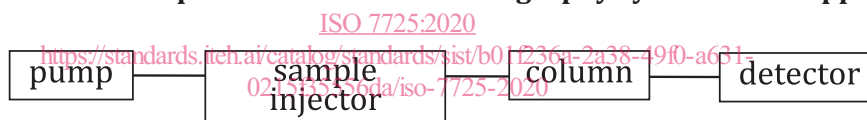


Figure 2 — Example of basic ion chromatography system without suppressor

6.3 Determination

6.3.1 Setting up the ion chromatograph

Set up the ion chromatograph in accordance with the manufacturer's instructions.

6.3.2 Preparation of the calibration curve

Inject the calibration solutions in increasing order of concentration and measure the conductivity of chloride ion and bromide ion peak area in each solution. Determine the correlation formula (calibration curve) by plotting the peak area as a function of concentration by means of linear regression.

6.3.3 Measuring blank solutions and sample solutions

Inject the blank solution and sample solutions (created in [5.2](#)) to measure the peak areas in sequence. Then determine the chloride ion and bromide ion concentration of the blank (C_{B1} and C_{B2} , respectively) as well as the concentration of the individual sample solution (C_{S1} and C_{S2} , respectively) by using the calibration curve determined in [6.3.2](#).

6.4 Calculation

Calculate the chlorine content (w_1) and/or bromine content (w_2), in percentage by mass, by [Formulae \(1\)](#) and [\(2\)](#), using the two determination values in [6.3](#). Average the results and round to the second decimal place.

$$w_1 = \frac{(C_{S1} - C_{B1}) \times V}{W \times 1000} \times 100 \quad (1)$$

$$w_2 = \frac{(C_{S2} - C_{B2}) \times V}{W \times 1000} \times 100 \quad (2)$$

where

W is the mass of the test piece, in mg (see [A.4.2](#), [B.4.1](#) or [C.4.1](#));

C_{S1} is the chloride ion concentration of the sample solution, in mg/l;

C_{B1} is the chloride ion concentration of the blank solution, in mg/l;

C_{S2} is the bromide ion concentration of the sample solution, in mg/l;

C_{B2} is the bromide ion concentration of the blank solution, in mg/l;

V is the fixed amount of the solution, in ml (see [A.4.5](#), [B.4.9](#) or [C.4.8](#)).

7 Method B — Potentiometric titration

7.1 Reagents

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7.1.1 Water, of grade 1 or higher. It shall be as specified in ISO 3696.

7.1.2 Nitric acid, concentrated, $\rho = 1,42 \text{ g/cm}^3$.

7.1.3 0,5 mol/l Nitric acid, $c(\text{HNO}_3) = 0,5 \text{ mol/l}$, obtained by diluting 30 ml of concentrated nitric acid ([7.1.2](#)) to 1 000 ml with water ([7.1.1](#)).

NOTE Commercially available 0,5 mol/l nitric acid can be used.

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

Standardize a silver nitrate solution obtained by dissolving 3,4 g of silver nitrate in 1 000 ml of water ([7.1.1](#)) as follows:

Take a measured volume (between 1 ml and 5 ml) of sodium chloride solution ([7.1.5](#)), dilute with water ([7.1.1](#)) to 25 ml in a 50 ml beaker, and add 2 ml of 0,5 mol/l nitric acid ([7.1.3](#)) along with a stirring bar. Place the solution on a stirrer ([7.2.2](#)) and titrate with the silver nitrate solution ([7.1.4](#)) using an automatic titrator ([7.2.3](#)). Read the volume from the automatic titrator. Determine the factor (f) from the averaged result in duplicating the same procedure.

Commercially available 0,02 mol/l silver nitrate standard volumetric solution and its guaranteed factor (f) can be used.

7.1.5 Sodium chloride solution, traceable to national standards. $c(\text{NaCl}) = 0,02 \text{ mol/l}$.

Alternatively, dissolve 1,168 g of sodium chloride in 1 000 ml of water ([7.1.1](#)).

7.1.6 Aluminium nitrate, of analytical reagent grade.

NOTE Aluminium nitrate is used to minimize the mutual interference caused by co-precipitation of chloride and bromide.

7.1.7 Ethanol, of analytical reagent grade.

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

7.2 Apparatus

7.2.1 Electronic balance, capable of weighing to the nearest 0,01 mg.

7.2.2 Magnetic stirrer and a stirring bar.

7.2.3 Automatic titrator.

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

7.2.5 Reference electrode, of the salt bridge type.

NOTE It is possible to use a combined electrode instead of the silver electrode and the reference electrode.

7.3 Determination

7.3.1 Transfer the blank solutions and sample solutions (created in [5.2](#)) obtained quantitatively to a 300 ml beaker each with several washes water. Place a magnetic stirring bar in the beaker and place the assembly on the magnetic stirrer ([7.2.2](#)).

7.3.2 Add 2 ml of the 0,5 mol/l nitric acid ([7.1.3](#)) and 2 g of the aluminium nitrate ([7.1.6](#)). Continue stirring to dissolve the aluminium nitrate, then add 160 ml of ethanol ([7.1.7](#)).

7.3.3 Insert the electrode pair ([7.2.4](#) and [7.2.5](#)) into the solution and titrate with the silver nitrate solution ([7.1.4](#)) with an automatic titrator ([7.2.3](#)).

NOTE The problem is least when bromine is in excess. At its worst, when chlorine is in excess, the bromine concentration might appear high, to an extent of 5 % of the chloride ion content. The problem can be minimized by carrying out the titration at 60 °C and keeping the rate of addition of titrant to a minimum^[2].