INTERNATIONAL STANDARD

Vulcanized rubber — Determination of free sulfur by gas chromatography (GC) and high performance liquid chromatography (HPLC)

Caoutchoucs vulcanisés — Dosage du soufre libre par chromatographie en phase gazeuse (CG) et chromatographie en phase liquide haute performance (HPLC)

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Contents

Foreword

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

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.

Vulcanized rubber — Determination of free sulfur by gas chromatography (GC) and high performance liquid chromatography (HPLC)

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 chromatographic methods for the determination of the inorganic free sulfur (Sx) not consumed during the vulcanization of the rubber. This method is used primarily to compare the free sulfur content in different samples.

NOTE 1   In this document, "free sulfur" is used instead of "inorganic free sulfur".

NOTE 2   The residual curing agent containing sulfur is not concerned by this measure.

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 1407:2011, *Rubber — Determination of solvent extract*

3   Terms and definitions

There are no term and definition in this document.

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

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

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

4   Principle

The free sulfur is quantified following two techniques: gas chromatography/mass spectrometric detector (GC-MS) or gas chromatography/flame ionization detector (GC/FID) (method A) and high performance liquid chromatography/ultraviolet detector (HPLC/UV) (method B).

A sample of vulcanized rubber is first extracted using an appropriate solvent according to ISO 1407:2011 (Method B). A known quantity of triphenylphosphine (TPP) is added to the obtained solution. TPP reacts with free sulfur to form a stable compound, triphenylphosphine sulfide (TPPS). See Figure 1.

TPP, Triphenylphosphine
(CAS 603-35-0)

TPPS, Triphenylphosphine sulfide
(CAS 3878-45-3)
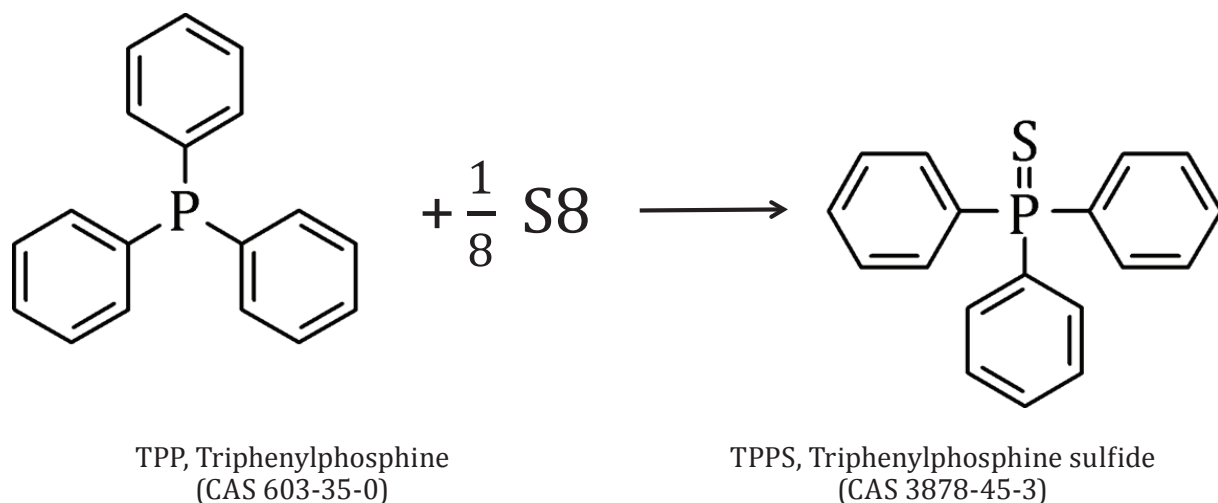
Figure 1 — TPP reaction with free sulfur for derivatization

TPPS, which contains aromatic rings, offers the following advantages:

— firstly, to have a more active chromophore in UV than sulfur, therefore being more easily detectable in HPLC/UV;

— secondly, to have sufficient thermal stability to be injected in GC.

The following calibration methods are possible for both types of chromatography (GC and HPLC). The preparation of samples is the same for GC and HPLC.

— Standard addition method is the preferred calibration method, used to correct matrix effects and when samples contain unknown contents of free sulfur.

— External calibration is used in case of absence of matrix effect and to check known contents of free sulfur.

5 Apparatus

5.1 Balance, precision 0,01 mg.

5.2 Soxhlet extractor.

5.3 Material for gas chromatography (Method A).

5.3.1 Injector for either split or splitless injection.

5.3.2 Mass spectrometric (MS) detector or **flame ionization detector (FID)**.

5.3.3 Mass spectrometer with the following specifications:

— transfer line temperature: 300 °C;

— ionizing energy: 70 eV;

— scan range: 33 m/z to 600 m/z;

— analysis mode: full scan.

5.3.4   Data system, using an acquisition and a data processing software.

5.3.5   Apolar capillary column.

A column 5 % diphenyl-dimethylpolysiloxane of 30 m length, 0,25 mm diameter and 0,25 μm thickness film, is usually appropriate.

The use of an autosampler is recommended for a better precision.

5.4   Material for liquid chromatography (Method B).

5.4.1   Solvent pump, allowing the use of gradient.

5.4.2   Injector, allowing injection of variable volumes.

5.4.3   Ultraviolet (UV) detector.

5.4.4   Data system, using an acquisition and a data processing software.

5.4.5   Column, for example, a cartridge with C18 type silica-bound.

A column of 15 cm length, 4,6 mm diameter and 5 μm particle size, is usually appropriate.

6   Reagents and materials

6.1   Standard solutions

6.1.1   TPP, analytical grade.

6.1.2   TPPS, analytical grade.

6.1.3   Tetrahydrofuran (THF), HPLC grade.

6.2   Materials for preparation of samples

6.2.1   Single use polytetrafluoroethylene (PTFE) filters, 25 mm diameter, 0,45 μm porosity.

6.2.2   Solvent for extraction, according to ISO 1407:2011, Table A.1, or any suitable solvent (e.g. dichloromethane).

6.2.3   THF, HPLC grade.

6.3   Reagents used in GC

6.3.1   Helium, purity ≥ 99,999 % or purity ≥ 99,999 9 % quality, as carrier gas (hydrogen can also be used).

6.3.2   Air and hydrogen, purity ≥ 99,99 %.

6.3.3   Syringe rinsing solvent: cyclohexane of analytical grade (or other solvent for the sample dissolution).

6.3.4   Rinsing solvent used between each injection series: THF, HPLC grade.

6.4   Elution solvents used in HPLC

6.4.1   Water, ultrapure quality (resistivity ≥ 18 MΩ·cm) used for the preparation of ammonium acetate buffer solution (pH 6,7).

6.4.2   Acetonitrile, HPLC grade.

6.4.3   Ammonium acetate, analytical grade, used for the preparation of buffer solution, using 10^{-2} mol/l of ammonium acetate.

7   Preparation of standard solutions and calibration curves

7.1   Standard addition method

The standard solutions of standard addition method shall be prepared as specified below.

Add standard solutions varying in concentration to the sample solution into several even aliquots in separate volumetric flasks of the same volume.

The standard solutions A, B, C, D and E correspond to the concentration range from 5×10^{-4} mol/l to 5×10^{-3} mol/l of TPPS. The preparation of the standard solutions shall be carried out in accordance with Table A.1.

The concentration range shall be adapted in function of the requested quantification limit.

Add 0,5 ml of each standard solution to the sample solution (F, prepared according to Clause 8):

— G = F (0,5 ml) + A (0,5 ml);

— H = F (0,5 ml) + B (0,5 ml);

— I = F (0,5 ml) + C (0,5 ml);

— J = F (0,5 ml) + D (0,5 ml);

— K = F (0,5 ml) + E (0,5 ml).

The injected volume is 1 µl in GC (Method A) and 20 µl in HPLC (Method B).

The calibration curve is obtained by plotting the peak area of G to K solutions versus the concentrations of the standards TPPS, A to E, see example in Figure 2.

In the absence of autosampler, repeat the injections three times and report the average of the three values.

7.2   External calibration method

The various solutions are prepared and correspond to the concentration range from 5×10^{-3} mol/l to 6×10^{-5} mol/l of TPPS. The preparation of the standard solutions shall be carried out in accordance with Table B.1.

The concentration range shall be adapted in function of the requested quantification limit.

The injected volume is 1 µl in GC (Method A) and 20 µl in HPLC (Method B).

The calibration curves are obtained by plotting the peak area function of the initial concentration of TPPS.

In the absence of autosampler, repeat the injections three times and report the average of the three values.

8   Preparation of samples

Weigh a test piece of vulcanized rubber (4 g is currently used), cut it into pieces and extract according to ISO 1407:2011, Method B.

Evaporate the obtained solution under partial vacuum using a rotary evaporator. Dilute the residue using 5 ml of THF.

NOTE   The use of SPE (solid-phase extractor) cartridge, having a volume capacity of approximately 2 ml or 5 ml, can improve the purification of the extract.

Introduce the solution in a flask of 10 ml; add 4 ml of solution of TPP 10^{-1} mol/l to this solution. Complete up to 10 ml with THF. Filtrate with PTFE filter.

In order to have a total derivatization, it might be necessary to use a larger volume of TPP to be in excess related to free sulfur in the sample.

The tests shall be duplicated. Two test pieces per sample are extracted and derivatizated.

9   Chromatographic procedure

9.1   Method A by GC procedure

The split ratio is 42 and the split flow is 50 ml/min.

The injector temperature is 250 °C.

The flowrate of the carrier gas (helium) is set at 1,2 ml/min.

In the case of a FID detector, the flowrate of air and hydrogen are 450 ml/min and 40 ml/min respectively. The detector temperature is 320 °C. The make-up could be adjusted.

The injected quantity is 1 μl.

The column oven temperature program is shown in Table 1.

Table 1 — Column oven temperature program

Oven ramp	°C /min	Next °C	Hold min
Initial		50	0,00
Ramp 1	25,00	150	0,50
Ramp 2	10,00	250	0,00
Ramp 3	25,00	320	10,00
Post run	—	0,00	0,00

NOTE   For information, the retention time for TPP and TPPS is 12,75 min and 16,10 min respectively.

An example of chromatogram for method A is found in Figure C.1.

9.2   Method B by HPLC procedure

9.2.1   General

Two elution solvents are used in this method.

The temperature of the column is standard laboratory temperature.

The wavelength of detection is fixed to 260 nm.

The gradient elution program used is the following:

— solvent A: buffer aqueous solution at pH = 6,7, using ammonium acetate;

— solvent B: acetonitrile;

— flowrate: 1 ml/min.

NOTE 1   Solvents can be continuously degassed.

NOTE 2   For information, the retention time for TPPS and TPP is 8,96 min and 11,96 min respectively.

An example of chromatogram for method B is found in Figure C.2.

9.2.2   Standard addition method

The operating conditions for standard solutions including the sample are given in Table 2.

NOTE   The gradient condition can be adapted depending on the sample analysed.

Table 2 — Operating conditions for sample solutions

Time t min	Solvent A %	Solvent B %
$t = 0$	50	50
$t = 12$ min	0	100
$t = 30$ min	0	100
$t = 35$ min	50	50
$t = 45$ min	50	50

9.2.3   External calibration method

The operating conditions for external calibration solutions are given in Table 3.

Table 3 — Operating conditions for external calibration solutions

Time t min	Solvent A %	Solvent B %
$t = 0$	50	50
$t = 12$ min	0	100
$t = 13$ min	50	50
$t = 20$ min	50	50

The operating conditions for the sample solution are given in Table 2.

## 10 Sample analysis and calculation

10.1 General

Check that the calibration curve is linear and the determination coefficient r^2 is greater than 0,99.

In order to obtain quantitative results, basic chromatographic rules shall be respected in term of resolution, coelution, etc.

Check in the obtained chromatogram that the derivatization reaction is complete, i.e. the TPP peak is saturated. Examples of chromatograms are given in Figure C.1 (GC) and Figure C.2 (HPLC).

10.2 Calculation using standard addition method

The concentration of TPPS shall be calculated, in mol/l, using the equation of the calibration curve typically y = a x + b, where linear regression is performed to the point on the abscissa x-axis at which y = 0. Using the slope (a) and y-intercept (b), this concentration x will be x = abscissa (-b/a).
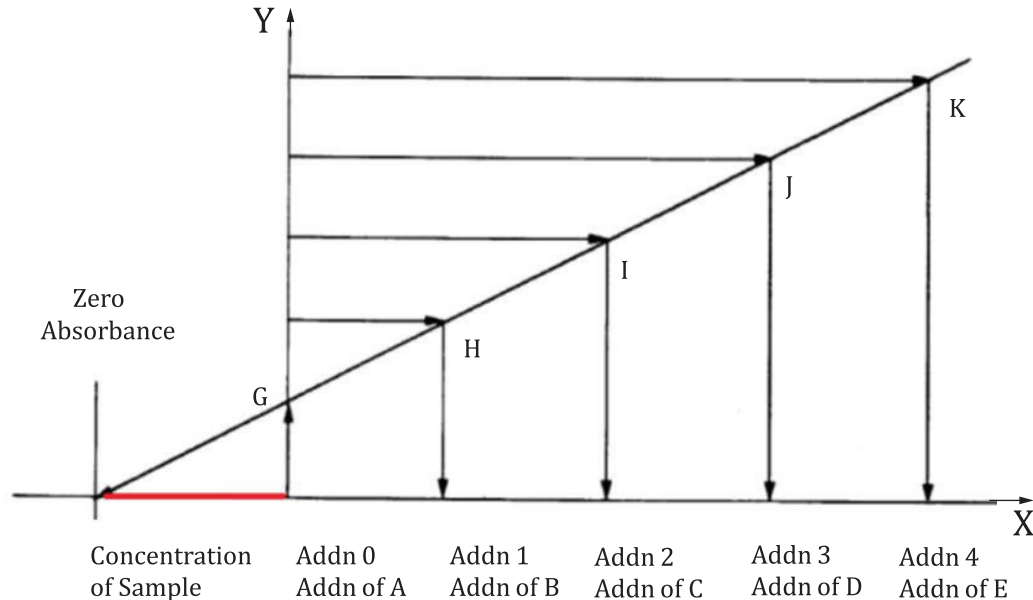
Figure 2 — Standard addition calibration curve

The content of free sulfur in the test piece shall be calculated, in µg/g (ppm), using Formula (1):

$$\text{Free sulfur content} = c_{\text{TPPS}} \times V \times M \times 10^6 \, / \, m \tag{1}$$

where

c_{TPPS} is the TPPS concentration in mol/l;

V is the volume of TPPS solution obtained after derivatization of the sample (10×10^{-3} l);

M is the atomic weight of sulfur (32,06 g/mol);

m is the mass of the test piece in g.

A test result shall be the average of two tests in either of method A or method B.

10.3 Sample analysis and calculation using external calibration method

Once the calibration system has been established, run the sample extract prepared in accordance with Clause 8 using the procedure described in 9.1 (Method A) or 9.2 (Method B).

The concentration of TPPS shall be calculated, in mol/l, using the equation of the calibration curve and the TPPS area obtained for the test piece.

The content of free sulfur in the test piece shall be calculated, in µg/g (ppm), using the Formula (1).