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Rubber, raw — Determination of residual monomers and other volatile low-molecular-mass compounds by capillary gas chromatography — Thermal desorption (dynamic headspace) method

Caoutchouc brut — Détermination des monomères résiduels et autres composés volatils de masse moléculaire faible par chromatographie en phase gazeuse sur colonne capillaire — Méthode par désorption thermique (espace de tête dynamique)

Reference number
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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 2.

The main task of technical committees is to prepare International Standards. 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 document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 17052 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 2, *Testing and analysis*.

This International Standard was produced after lengthy collaboration between ISO/TC 45/SC 2/WG 5 and the International Institute of Synthetic Rubber Producers. Experts from eight different producing companies located in five countries took part and the standard incorporates the sum of their best practices and experience.

Introduction

Nowadays, with the ever-increasing amount of legislation on emissions of volatile organic chemicals to the workplace and the environment in general, there is a need to know the nature and amounts of these materials in raw rubber down to trace levels.

Therefore, this International Standard has been produced, describing an advanced method for the determination of residual monomers and other volatile organic compounds in raw rubber.

Rubber, raw — Determination of residual monomers and other volatile low-molecular-mass compounds by capillary gas chromatography — Thermal desorption (dynamic headspace) method

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This standard 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 ensure compliance with any national regulatory conditions.

CAUTION — Certain procedures specified in this International Standard may 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 International Standard specifies a method for the determination of residual monomers and other volatile low-molecular-mass compounds in raw rubber by capillary column gas chromatography using a thermal desorption (also known as dynamic headspace) method. It includes a generic section that is applicable to all types of raw rubber and two annexes specific to particular rubber types.

This method has the advantages of not requiring a solvent, of concentrating the volatile compounds and of introducing them to the chromatograph in a very precise manner.

The compounds found in the raw rubber which are to be determined are defined as residual monomers, solvents and other low-molecular-mass compounds in the boiling point range of C4 to C12 hydrocarbons.

NOTE The limit of detection is 1 µg/g.

2 Normative references

The following referenced documents are indispensable for the application 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 2393, *Rubber test mixes — Preparation, mixing and vulcanization — Equipment and procedures*

ISO 23529, *Rubber — General procedures for preparing and conditioning test pieces for physical test methods*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
relative response factor
RRF
ratio of the response of the compound under test to the response of a calibrant compound

4 Principle

A test piece is heated to a specified temperature in a stream of carrier gas for a specified period of time. The stream passes through a cold trap maintained at a specified temperature where the volatile compounds are held. Subsequently, the trap is rapidly heated in a specified manner, transferring the volatile compounds into a gas chromatograph equipped with a capillary column and a suitable detector. The separated compounds are determined via an external-standard calculation method.

5 Reagents

All chemicals used for the procedure shall be of analytical grade. All chemicals used for determining response factors and retention times shall be of known purity.

5.1 Carrier gas: dry nitrogen, helium or hydrogen of high purity.

6 Apparatus

Ordinary laboratory equipment, together with the following:

6.1 Laboratory two-roll mill, as specified in ISO 2393.

6.2 Gas chromatograph, equipped with a capillary column capable of providing sufficient resolution, a flame ionization detector, a thermal desorption system and data-handling equipment.

6.3 Analytical balance, accurate to 0,000 1 g.

6.4 20 ml glass flasks, which can be properly sealed by a septum (for instance headspace vials with crimp caps or screw thread vials).

6.5 Microvolume syringe, capacity 1 µl, capable of containing the sample in the needle (“needle in needle” syringe), accuracy 0,01 µl.

7 Preparation of apparatus

7.1 Prepare the chromatograph in accordance with normal practice and the manufacturer’s instructions.

7.2 Establish the instrumental conditions as described in either Annex A or Annex B, depending on the type of rubber that is being analysed.

8 Calibration

8.1 General

The compound used for calibration (the calibrant) shall be either the compound that is to be determined or a substitute compound. If a substitute compound is used, the response factor of the substitute compound relative to the residual monomer or residual compound of interest shall be determined using Equation (1):

$$\mathrm{RRF} = \frac{A_\mathrm{s} \times m_\mathrm{m}}{A_\mathrm{m} \times m_\mathrm{s}} \qquad (1)$$

where

RRF is the response factor of the substitute compound (calibrant) relative to the residual monomer or residual compound of interest;

A_m is the peak area of the residual monomer or residual compound of interest;

A_s is the peak area of the substitute compound;

m_m is the mass of residual monomer, in grams, to the nearest 0,000 1 g;

m_s is the mass of the substitute compound, in grams, to the nearest 0,000 1 g.

Alternatively, a theoretical approach can be used (see References [1], [2] and [3] in the Bibliography).

8.2 Preparation of stock solutions

In order to avoid systematic errors, two solutions shall be prepared. These solutions shall contain 1 % and/or 5 % of calibrant(s). The chosen concentration of the stock solution will depend on the expected concentration range of residual monomers or residual volatile compounds of interest in the polymer; if the expected concentration range is between 1 ppm and 100 ppm, two stock solutions of 1 % shall be used. If the range is between 100 ppm and 1 000 ppm, two stock solutions of 5 % shall be used. If it is around 100 ppm, it is recommended that both the 1 % and the 5 % stock solutions be prepared. Stock solutions shall be prepared in 20 ml glass flasks (6.4).

8.3 Preparation of working solutions

Working solutions are solutions with accurately known concentrations of calibrants. These can either be the stock solutions themselves, or specific dilutions of the stock solution(s).

8.4 Calibration of the dynamic headspace system

Initially, a five-point calibration is recommended. This shall be done to check the linearity of the detector in the respective concentration range. Prepare five working solutions with different concentrations of calibrant(s). The concentration range shall cover the range of expected concentration of the residual monomer or volatile compound of interest in the polymer. If the expected concentration range is completely unknown, a “full” calibration between 1 µg/g and 1 000 µg/g shall be performed.

1 µl of the respective calibration solution shall be injected, using a microvolume syringe (6.5), into a desorption tube containing an appropriate packing and then processed through the dynamic headspace system.

Determine the slope of the calibration curve which gives the response area per µg of calibrant.

The five-point calibration need only be performed once. For subsequent analyses, it is sufficient to perform a one-point calibration. The concentration of the working solution for this single calibration point shall be as close as possible to the expected concentration in the polymer of the compound under analysis. The difference between the result obtained from the single-point analysis and the expected result from the calibration curve shall be < 10 %. If not, the five-point calibration shall be repeated.

NOTE Great care must be taken when preparing stock solutions of volatile calibrants.

9 Procedure

9.1 Conditioning of the system

Run a blank test under the conditions specified for the rubber to be determined. If the blank is not satisfactory, purge the system and repeat the blank test.

9.2 Preparation of the test sample

Take a test sample of 250 g ± 5 g from the centre of a laboratory sample prepared in accordance with ISO 1795. For rubber in chip or powder form, take a similar quantity at random from the package.

NOTE For rubbers that can be conveniently massed on a laboratory mill, it has been shown that test repeatability is improved if the following procedure is carried out. Mass the test sample, prepared as above, on a laboratory mill as specified in ISO 2393, following the procedure given in ISO 1795 but with the mill rolls at standard laboratory temperature, as specified in ISO 23529, using a nip width of 3,5 mm ± 0,5 mm and only six mill passes.

9.3 Determination of residual monomers and other volatile compounds

Take a test piece weighing about 0,25 g from the centre of the test sample. Cut into small pieces of approximate dimension 0,5 mm, and weigh approximately 0,05 g, to the nearest 0,000 1 g, into a suitable container, e.g. a desorption tube. For samples in powder form, weigh approximately 0,05 g, to the nearest 0,000 1 g, and transfer to the container.

Any other preparative process, such as cryogenic grinding, is unnecessary and may have a deleterious effect on the results. The preparative process may also have a significant effect on the results. Therefore, for comparison purposes between laboratories, the storage and conditioning of the sample, the timing of the test and the preparative process shall be agreed and closely controlled.

Start cooling the trap. When the trap reaches the specified temperature, slide the container into the oven so that it is heated under a stream of inert carrier gas at the specified temperature (the desorption temperature).

After the specified time (the desorption time) has elapsed, heat the cold trap as rapidly as possible to the specified temperature so that the trapped compounds are transferred to the gas chromatograph.

NOTE These operations are often performed automatically by the equipment.

For comparison purposes between laboratories, the same type of equipment should preferably be used.

9.4 Calculation of compound concentration

Calculate the concentration of the compound under analysis from the resultant chromatogram using Equation (2). Usually, this calculation is performed automatically.

$$C = \frac{\mathrm{RRF} \times A \times C_\mathrm{c} \times V}{A_\mathrm{c} \times m} \qquad (2)$$

where

C is the concentration of the compound under analysis, in µg/g;

C_c is the concentration of the calibrant in the calibration solution, in µg/ml;

V is the volume of the calibration solution injected (1 µl);

A is the peak area of the compound under analysis;

A_c is the peak area of the calibrant;

m is the mass, in grams, of the test piece;

RRF is the response factor of the compound under analysis relative to the calibrant.

For unknown compounds and minor components, assume the relative response factor to be 1.

9.5 Check for complete desorption

Repeat the procedure on the same test piece in its original container to check that complete desorption has occurred, i.e. that no peak of the compound under analysis is observed.

10 Precision

See Annex C for details of the precision of the test method for residual monomer.

11 Test report

The test report shall include at least the following information:

a) sample details:
   1) a full description of the sample and its physical nature, e.g. bale, pellet, powder, etc.,
   2) the method of preparation of the test piece and whether the optional massing procedure given in 9.2 was carried out;

b) a full reference to the test method used, i.e. the number of this International Standard;

c) test details:
   1) the time and temperature of conditioning of the system,
   2) identification of the equipment used,
   3) details of any procedures not specified in this International Standard;

d) test results:
   1) identification of the residual monomers and other volatile compounds tested for,
   2) the amount found on each desorption (the result is the sum of the amounts from each desorption),
   3) duplicate test results, expressed as µg/g (ppm);

e) the date of the test.

Annex A
(normative)

Test details for rubber types containing butadiene (specifically BR, SBR, NBR)

A.1 Calibrant solutions

Cyclohexane has been shown to be a suitable solvent.

NOTE Great care must be taken in making up and storing the calibration solutions because of the volatility of the calibrants, particularly isoprene which boils at 34 °C.

A.2 Desorption conditions for different calibrants

Type of rubber	BR	SBR		NBR	
Monomer to be analysed for	Butadiene	Butadiene	Styrene	Butadiene	Acrylonitrile
Calibrant	Isoprene	Isoprene	Styrene	Isoprene	Acrylonitrile
Desorption temperature, °C	125	125		125	
Desorption time, min	30	30		30	

Annex B
(normative)

Test details for rubber types that do not contain butadiene (specifically EPDM, EOM)

B.1 Calibration solutions

Cyclohexane has been shown to be a suitable solvent.

B.2 Desorption conditions for different calibrants

Type of rubber	EPDM	EOM
Monomer to be analysed for	Ethylidene norbornene (ENB) (both isomers)	Octene (all isomers)
Calibrant	ENB	1-octene
Desorption temperature, °C	200	150
Desorption time, min	10	10

Annex C
(informative)

Precision for residual monomer

C.1 General

Two interlaboratory test programmes (ITPs) were conducted to evaluate the precision of the method for residual monomer content, the first in 2003 and the second in 2005, in both cases using the precision procedures and guidelines as described in ISO/TR 9272:2005, which was under ballot review at the time.

C.2 ITP No. 1 (2003)

C.2.1 The first, or 2003, ITP was conducted using two groups of polymers as listed below with the residual monomer indicated for each polymer. The polymers are divided into two groups on the basis of monomer concentration.

Group 1 lists seven polymers (designated as “materials” using the usual precision evaluation terminology) that had measured residual monomer levels above 1 ppm for most of the laboratories. There are two different grades or types of NBR, EPDM and EOM as indicated by the suffixes 1 and 2.

Group 2 polymers had residual monomer levels for butadiene and styrene that were below 1 ppm.

NOTE The same polymers can appear in both groups, depending on the residual monomer being measured.

Group 1:

Material 1 = NBR-1, acrylonitrile measured

Material 2 = NBR-2, acrylonitrile measured

Material 3 = SBR, styrene measured

Material 4 = EPDM-1, ethylidenenorbornene measured

Material 5 = EPDM-2, ethylidenenorbornene measured

Material 6 = EOM-1, isomers of octene measured

Material 7 = EOM-2, isomers of octene measured

Group 2:

Material 1 = NBR-1, butadiene measured

Material 2 = NBR-2, butadiene measured

Material 3 = SBR, butadiene measured

Material 8 = SBC, butadiene measured

Material 8 = SBC, styrene measured

Eight laboratories participated in the 2003 ITP and a type 1 precision was evaluated. A test result represents a single determination of residual monomer content as evaluated on each of three different test days.

C.2.2 The precision results for the 2003 ITP may not be applied to acceptance or rejection testing for any group of materials or products without documentation that the results of this precision evaluation actually apply to the products or materials tested.

C.2.3 Precision results — ITP No. 1 (2003): The precision results for residual monomer are given in Parts A, B and C of Table C.1. Part A is for the Group 1 materials. The precision results given in Part A were obtained using the outlier replacement procedures and outlier deletion procedures as described in ISO/TR 9272:2005. General statements for the use of the precision results are given below. These are given in terms of the absolute precision, r and R, and also for relative precision, (r) and (R) (see additional discussion below). Parts B and C of Table C.1 refer to Group 2 materials.

The 2003 ITP repeatability and reproducibility statements are as follows for Part A:

Repeatability: The repeatability, or local domain precision, for each of the monomers has been established by the values found in Part A of Table C.1 for each of the materials as listed in the table. Two single test results (obtained by the proper use of this International Standard) that differ by more than the tabulated values for r, in measurement units, or (r), in percent, should be considered as suspect, i.e. to have come from different populations. Such a situation suggests that some appropriate investigative action be taken.

Reproducibility: The reproducibility, or global domain precision, for each of the monomers has also been established by the values found in Part A of Table C.1 for each of the materials as listed in the table. Two single test results obtained in different laboratories (by the proper use of this International Standard) that differ by more than the tabulated values for R, in measurement units, or (R), in percent, should be considered as suspect, i.e. to have come from different populations. Such a situation suggests that some appropriate investigative action be taken.

C.2.4 Additional analysis comments on the 2003 ITP: The last column of Part A of Table C.1, the number of laboratories that were included in the database used for the final precision calculations, indicates that a substantial number of data values were deleted as outliers. On an overall basis (for all seven materials), the repeatability parameter r was reduced by a reduction factor ($r_{\text{orig}}/r_{\text{final}}$) of 0,56 after all repeatability outlier data were deleted. On the same overall basis, the reproducibility parameter R was reduced by a reduction factor ($R_{\text{orig}}/R_{\text{final}}$) of 0,66 after all reproducibility data outliers were deleted (see Table C.2 for individual reduction factors). Individual laboratories may show poor agreement in repeatability or poor agreement in reproducibility, or both.

Repeatability r is a good linear function of residual monomer content over the range evaluated in this ITP. Relative repeatability increases as the residual monomer content decreases, and it was found that a plot of $1/(r)$ had a negative linear slope when plotted against log residual monomer content. Reproducibility R did not show the same good positive linear slope when plotted against residual monomer content (over the whole range of this ITP). However, for residual monomer levels up to 150 ppm, a good linear relationship, R vs residual monomer, was obtained. The relative reproducibility (R) was found to have a negative linear slope when plotted against log residual monomer. It is noted for both this 2003 ITP and the 2005 ITP (see below) that the numerical value of the relative precision, (r) and (R), may be quite high because the mean level of the measured value for each material is so low. It is better to use the actual precision parameters r and R for comparison purposes.

C.3 ITP No. 2 (2005)

C.3.1 The precision obtained from the first, or 2003, ITP was considered to be rather poor and not representative of the test method itself. It is possible that sample preparation and residual monomer inhomogeneity were contributing to the overall scatter. Therefore a second ITP was carried out to try to eliminate these effects. Two polymers, SBR and NBR, were used and a type 1 ITP was conducted. For SBR, the residual monomer was styrene and for NBR the residual monomer was ACN. There were two data sets for NBR, one for testing in 2005 and, as a complement, a data set obtained in 2004. Results for both are reported.

The NBR sample was supplied as a powder. This form was chosen in order to eliminate the sample preparation stage, apart from weighing and transfer to the desorption tube. Thus the results should give a true representation of the precision of the instrumental part of the test method.

The SBR sample was supplied in bulk form. However, it had been homogenized to ensure an even distribution of the residual styrene. Thus the results should give a true representation of the precision of the test method, i.e. sample preparation and the instrumental procedure.

Seven laboratories participated in the SBR testing, and five labs participated in both of the NBR testing programmes. A test result represents the mean of three individual determinations of residual monomer content. Test results (means of three determinations) were obtained on each of three different test days, several days apart. All data analysis has been conducted on the basis of test results. Precision for both the 2003 and the 2005 programmes are reported on the basis of test results for each of the two ITPs.

C.3.2 The precision results for this 2005 ITP may not be applied to acceptance or rejection testing for any group of materials or products without documentation that the results of this precision evaluation actually apply to the products or materials tested.

C.3.3 Precision results — ITP No. 2 (2005): For each of the two materials (polymers), the precision results for residual monomer are as given in Table C.3. The precision results were obtained using the outlier replacement or deletion procedures as described in ISO/TR 9272:2005. General statements for the use of the precision results are given below. These are given in terms of the absolute precision, r and R, and also for relative precision, (r) and (R).

The 2005 ITP repeatability and reproducibility statements are as follows:

Repeatability: The repeatability, or local domain precision, for each of the monomers has been established by the values found in Table C.3 for each of the materials listed in the table. Two single test results (obtained by the proper use of this International Standard) that differ by more than the tabulated values for r, in measurement units, or (r), in percent, should be considered as suspect, i.e. to have come from different populations. Such a situation suggests that some appropriate investigative action be taken.

Reproducibility: The reproducibility, or global domain precision, for each of the monomers has been established by the values found in Table C.3 for each of the materials listed in the table. Two single test results obtained in different laboratories (by the proper use of this International Standard) that differ by more than the tabulated values for R, in measurement units, or (R), in percent, should be considered as suspect, i.e. to have come from different populations. Such a situation suggests that some appropriate investigative action be taken.

C.4 Bias

Bias is the difference between a measured average test result and a reference or true value for the measurement in question. Reference values do not exist for this test method and therefore bias cannot be evaluated.