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Rubber compounding ingredients — Silica — Oil absorption of precipitated silica

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National foreword

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Rubber compounding ingredients — Silica — Oil absorption of precipitated silica

Ingrédients de mélange du caoutchouc — Silice — Absorption d'huile des silices précipitées

Reference number
ISO 19246:2016(E)

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Ch. de Blandonnet 8 • CP 401
CH-1214 Vernier, Geneva, Switzerland
Tel. +41 22 749 01 11
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Contents

Page

Foreword

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The committee responsible for this document is ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 3, *Raw materials (including latex) for use in the rubber industry*.

Introduction

Due to health and environmental safety precautions, the determination of DOA absorption number has been worked out to substitute the determination of the DBP absorption number.

Dibutylphthalate (DBP) and dioctylphthalate (DOP) were commonly used in the past for determining the absorption capacity of pigments and extenders, like carbon black and silica. In the meantime, both substances have been banned as carcinogenic, mutagenic, reprotoxic substances (CMR) in different countries.

The search of a suitable alternative for DBP and DOP, especially for measuring the absorption capacity of polar pigments and extenders, like silica, calcium silicates and sodium aluminium silicates has been carried out in a task group of the Association of Synthetic Amorphous Silica Producers (ASASP) between 2004-2008. Out of different tested liquids, like linseed oil, paraffinic oil, etc., DOA was found as the most suitable alternative which leads to evaluated absorption numbers close to DBP measurement.

INTERNATIONAL STANDARD ISO 19246:2016(E)

Rubber compounding ingredients — Silica — Oil absorption of precipitated silica

1 Scope

This International Standard specifies a general method for determining the liquid absorption capacity of a pigment and extender by using di-(2-ethylhexyl) adipate (DOA, CAS 103-23-1). The determination of the DOA absorption number is performed by means of an absorptometer which is equipped with a torque measurement and processing system. The DOA absorption number provides an indication of the void volume formed by the aggregates and agglomerates of the pigments and extenders.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 787-2, *General methods of test for pigments and extenders — Part 2: Determination of matter volatile at 105° C*

ISO 787-11, *General methods of test for pigments and extenders — Part 11: Determination of tamped volume and apparent density after tamping*

ISO 15528, *Paints, varnishes and raw materials for paints and varnishes — Sampling*

3 Principle

For the determination of the DOA absorption number, a defined amount of pigment or extender shall be transferred to the mixer chamber of the absorptometer.

Under permanent kneading, DOA shall be added with a constant rate. The indication is the torque of the kneaders. While the torque is low at the beginning, it increases rapidly near the point of liquid absorption of the sample and decreases after reaching the maximum torque. The mixture changes from a free-flowing state to one of a pasty consistency.

On basis of the raw data torque curve and the settings, a polynom shall be calculated. The value for 70 % of the maximum torque of this third order polynomial (smoothed curve) shall be used for the evaluation of the DOA absorption number.

4 Materials

4.1 Di-(2-ethylhexyl)adipate (DOA), which density is approximately 0,925 5 g/cm^3 at 20 °C and which refractive index n(D, 20 °C) is approximately 1,447.

4.2 Pigment or extender, as powder or micro-perls.

It can be added directly to the absorptometer chamber. In case of testing granulated materials, the determination is performed using a granular size fraction of between 1,0 mm and 3,15 mm, that is received by pre-sieving.

5 Equipment

5.1 Absorptometer, with burette and system for measurement, storage and evaluation of torque data of the kneader.

The following pieces of equipment[1)] may be used:

— Absorptometer E, Fa. Brabender, Duisburg (equipped with extended functionality/evaluation unit);

— Absorptometer C, Fa. Brabender, Duisburg;

— Hitec DBP-Absorptometer, Fa. Hitec, Luxembourg.

5.2 Beaker.

5.3 Sieves, one with mesh width of 1,0 mm, another one with mesh width of 3,15 mm.

5.4 Sieve pan.

5.5 Plastic or soft metal spatula and brush, for cleaning the kneading chamber.

5.6 Precision balance, accuracy of 0,01 g.

5.7 Oven, capable of being maintained at 105 °C ± 2 °C.

6 Sampling

Take a representative sample of the material to be tested according to ISO 15528.

7 Procedure

7.1 Preliminary note

7.1.1 The following most important factors which affect the determination shall be pointed out.

a) Pore volume: the porosity of the material is the real cause for the absorption of liquid.

b) Moisture content: as the moisture content increases, the absorptive capacity decreases.

c) Particle size: at the same material family but different degree of milling, the particle size can influence the DOA absorption. This is to take into account for comparison. In case of extremely fine milled samples, an overload with DOA in connection with inhomogeneity of the mixture can occur that results in incorrect values.

d) Sample weight: with increasing sample weight, the specific DOA absorption number decreases.

7.1.2 Carry out the determination in duplicate.

7.1.3 To avoid erroneous results, check the feeding pipe before starting the measurement. It shall be free of air bubbles. If necessary, the pipe shall be purged and the burette refilled.

1) Examples of suitable products available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of these products.

7.1.4 The following settings should be used in the program.

7.1.4.1 Measurement settings

— Dosing rate (burette): 4,0 ml/min;

— Rotation speed

  — First blade: 125 min^{-1};

  — Second blade: 250 min^{-1};

— Temperature: 23 °C.

The temperature of 23 °C in the settings should be used as a target value. Actually, the temperature during the measurement should be in a range of 23 °C ± 5 °C.

7.1.4.2 Evaluation

a) Test end

  — Threshold: 100 mNm;

  — End time: 40 s after maximum;

  — Torque limit: 10 000 mNm.

b) Polynom

  — Start percent: 50 % of maximum torque;

  — End time: 20 s after maximum.

7.1.5 The evaluation of the aging status of the absorptometer shall be done according to Annex A.

7.2 Determination

7.2.1 Method A (powder sample, micro-perls)

7.2.1.1 The loss on drying of the sample material should not exceed 10 %. Material with a higher content of moisture should be dried to a lower value.

7.2.1.2 Weigh 12,50 g ± 0,02 g of the sample material by means of a precision balance (5.6) into a beaker (see 5.2), transfer to the kneader chamber and enter the sample weight into the program.

A sample weight of 12,5 g represents an optimum for most silica or silicates. It is advisable to use an integrated or separated funnel for filling the kneader chamber during the operation of the absorptometer. This allows also in case of material with lower tamped density (<150 g/l) to add the whole sample amount of 12,5 g at once.

In case of sample material with higher tamped density (>300 g/l), it is recommended to use a higher sample amount (preferably 20,0 g) to achieve a sufficient filling of the kneader chamber and repeatable measurements.

The tamped density shall be measured according to ISO 787-11.

Ideally, the sample amount should be designed to fill the kneader chamber sufficiently. It should neither be worked with too low sample amount (there is no sufficient increase of torque), nor the chamber

should be overfilled, that does not ensure a sufficient mixing of the sample. Any deviation of the sample weight of 12,5 g shall be documented in the test report.

7.2.1.3 Close the safety device of the equipment, bring the feeding pipe into position and start the determination.

7.2.1.4 After the determination is ended, read the DOA absorption (based on original substance) as expressed as the 70 % value of the maximum torque from the measurement report.

During the determination, however, in the range of the maximum DOA absorption, the observable silica-DOA-mixture forms a paste, that is indicated in the increase of the torque. After reaching the torque maximum, the torque decreases to lower values. The DOA absorption number based on original substance in ml/100 g is the consumption of DOA related to the sample amount at 70 % of the maximum torque of the polynom. This polynom curve is calculated automatically at the end of the determination based on the settings (see 7.1.3) using the raw data of the measured torque curve.

7.2.1.5 Refill the burette, if there is no automatic refilling mode, and clean the mixing chamber and kneader blades carefully. The DOA sample mixture is disposed conveniently, considering legal restrictions.

The DOA-sample mixture may cause difficulties during cleaning. In this case, it is recommended to add some portion of a silica powder, switch on the kneader only for a short time and then dismount the mixing chamber for cleaning.

7.2.2 Method B (granulated samples)

7.2.2.1 Prepare a granular size fraction of between 1,0 mm and 3,15 mm by means of the appropriate sieves (5.3).

7.2.2.2 The further determination shall be carried out according to method A.

7.3 Evaluation

7.3.1 Evaluation for powder and micro-perl materials

The result of the determination can be given as DOA absorption based on original substance or optional as moisture corrected DOA absorption, as based on dried substance. This result shall be specified in the test report.

The calculation of the DOA absorption number based on dried substance can be calculated on the basis of Formulae (1) and (2) and is given without decimal place.

$$DOA_{\text{orig}} = DOA_{\text{dry}} \times p \tag{1}$$

and

$$p = \frac{100}{100 - LOD} \tag{2}$$

where

DOA_{orig} is the DOA absorption based on original substance, in ml/100 g;

DOA_{dry} is the DOA absorption number based on dry substance, in ml/100 g;

p is the correction factor;

LOD is the loss on drying (2 h at 105 °C), in %.

The loss on drying (2 h at 105 °C) shall be determined separately according to ISO 787-2.

7.3.2 Evaluation of granulated materials

The result of the determination is the DOA absorption number based on original substance that is given without decimal place.

8 Precision data

See Annex B.

9 Test report

The test report shall include the following information:

a) a reference to this International Standard, i.e. ISO 19246:2016;

b) all details necessary for the identification of the sample;

c) the method used (A or B);

d) the DOA absorption number;

e) any operations not included in this International Standard or in the International Standards to which reference is made, as well as any operation regarded as optional;

f) any unusual feature;

g) the date of the test.

Annex A
(normative)

Normalization of the mixer chamber by using reference materials

A.1 General

This annex describes the normalization of the mixing device due to the aging (abrasiveness) of the chamber and blades.

A.2 Normalization of the mixer for the determination of the DOA absorption number

A.2.1 Principle

The routine determination of the DOA absorption number as quality control parameter for precipitated silica made a problem of this test method very soon visible, the aging of the mixing chamber and blades by the more or less abrasive silica products. This effect leads to a continuous increase of the DOA absorption number values although the quality of the silica is not changed. In case the DOA absorption number is part of a specification usually with a target value and lower/upper limits, the DOA values can move slowly but continuously to the upper limit and also could lie outside of the specification. This aging of the mixing device by abrasion effects is depending from the number of measurements and also from the abrasiveness of the silica which are tested. This means that each mixer has its own abrasion characteristics and the normalization shall be carried out for every single device.

The following standard operating procedure describes the determination of the continuously changing aging status of mixers and is used for the correction of the originally found DOA absorption number values. The DOA normalized values indicate the DOA values as if they would be found when the mixing chamber and blades are new or still in good conditions.

The procedure includes the following:

— the suitability test for the mixer;

— the determination of the target values of reference materials;

— the normalization of the mixer using the reference materials.

A.2.2 Abbreviations and terms

Table A.1 — Abbreviations and terms

Abbreviation	Term
SRM	Silica reference material
IRM	ASTM silica standard acc. to ASTM D5900-13
RM (1)	Reference material with low DOA absorption
RM (2)	Reference material with medium DOA absorption
RM (3)	Reference material with high DOA absorption
DOA absorption	70 % value of the maximum torque (ml/100 g)

A.2.3 General process

First, the suitability of the available mixer shall be checked. For that, the DOA absorption shall be determined by using a silica reference material (SRM) of free choice where the DOA is already known. If such a standard material is not available, it is recommended to use the IRM 100 silica standard material according to ASTM D5900-13. The DOA absorption of this silica is known and documented by the ASTM organization.

The DOA absorption is given in ml/100 g based on the 70 % value of the maximum torque. The DOA absorption value determined by using the mixer shall lie within the tolerances for the target value of the silica reference material. Otherwise, the status of the mixer chamber and plates is insufficient for the following normalization procedure.

In the next step, the target DOA absorption values (70 % values) of three silica reference materials shall be determined. It is recommended to select three products of free choice but with DOA values in the low, medium and high DOA absorption level.

The target values determined are used for normalization of the mixer. The normalization curve obtained ($Y = a\,X + b$) is specific for the mixer tested.

A.2.4 Check of the suitability of the mixer for the initial normalization

First, the DOA absorption of the SRM shall be measured on the existing mixer (dual determination). In case the DOA absorption value, determined (70 % value) for SRM, is within the permissible tolerances which should not exceed more than 2 % of the target value of the chosen silica standard, the existing chamber and kneader blades can be used for the following determination of the target values of the three reference materials (see A.2.3).

In case of using the ASTM IRM 100 silica standard, the associated DOA target value is documented in ASTM D5900-13.

If the deviation is higher than 2 % from the used silica standard, the mixer should not be used for the subsequent defining of the targets of the normalization standards RM (1), RM (2) and RM (3). However, the mixer can be used for the normalization of the chamber under the assumption that reference materials with known target values are available (item 3).

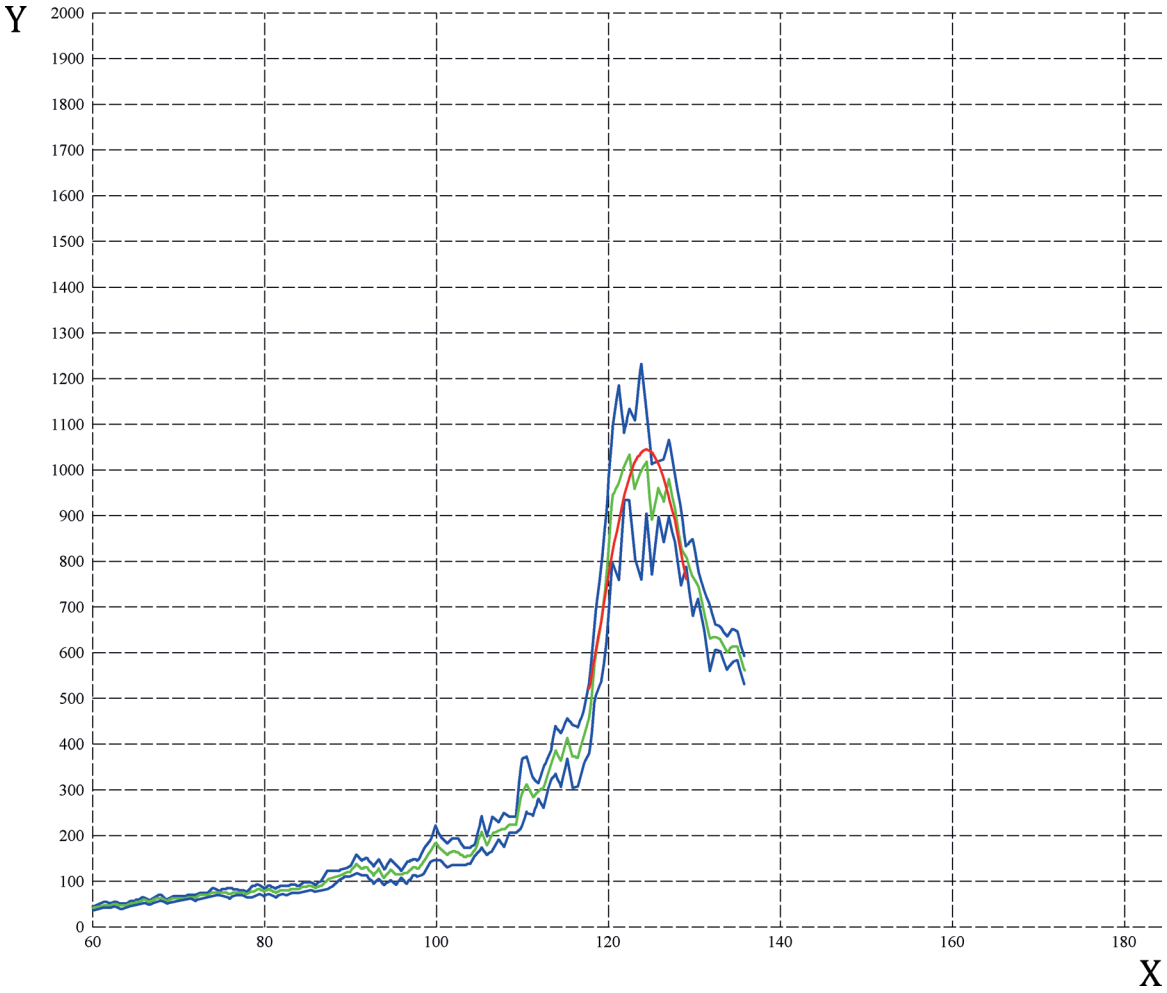
A.2.5 Determination of the target values of DOA absorption of the reference materials for the normalization process

The three reference materials RM (1), RM (2) and RM (3) with different DOA absorptions shall be first tested by multiple determinations (minimum five data records per reference material).

The DOA absorption average values are calculated.

The averages shall be stored in the software as target values. These values shall be fixed for the three standards and valid for all future normalizations, independent from the used mixing device. In case a standard is replaced by a new one, the same procedure shall be carried out again.

The following examples show torque curves of the three reference materials RM (1), RM (2) and RM (3) with the data on DOA absorption (70 % value).

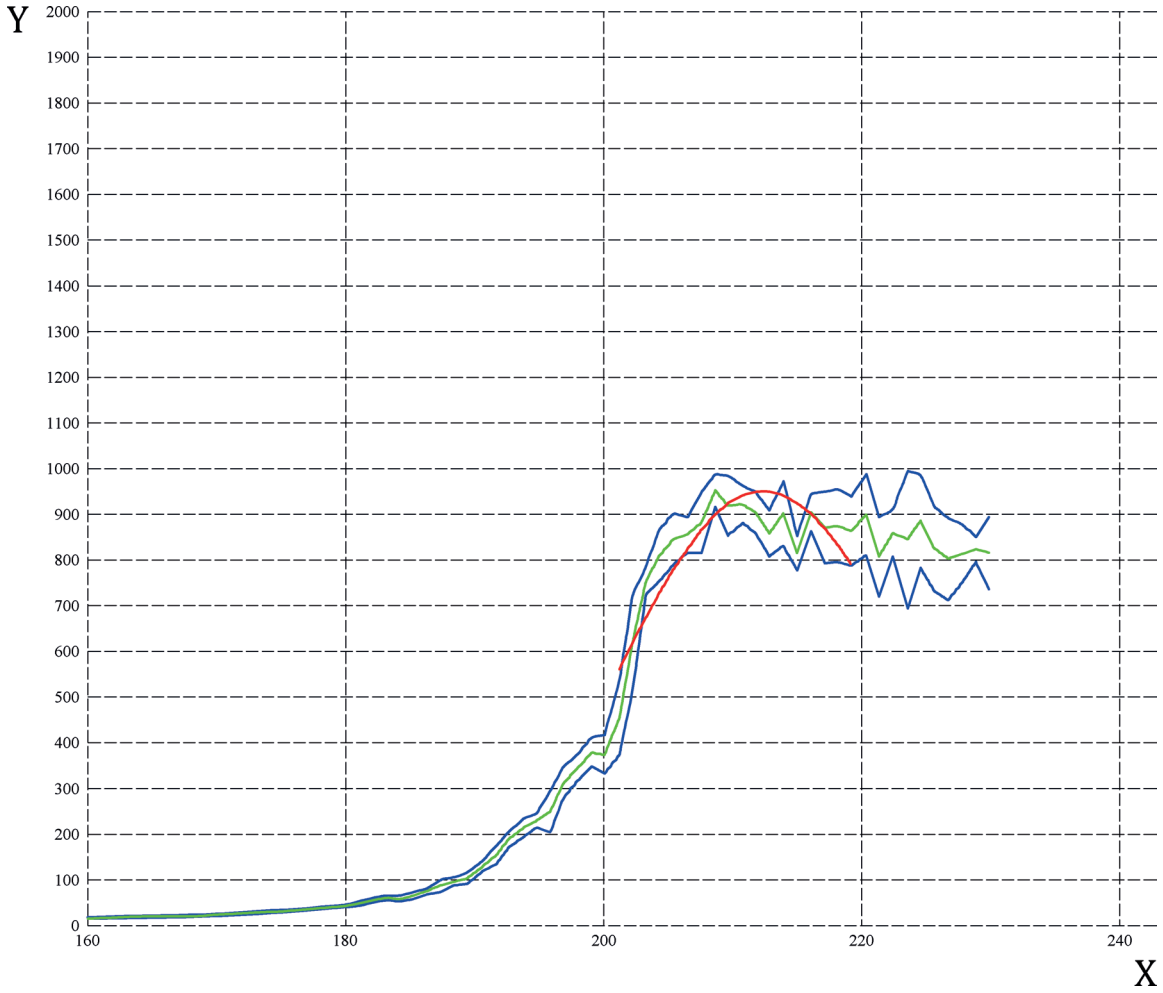


Key

X DOA absorption (ml/100 g)

Y torque (mNm)

Figure A.1 — Torque curve of the reference material RM (1)

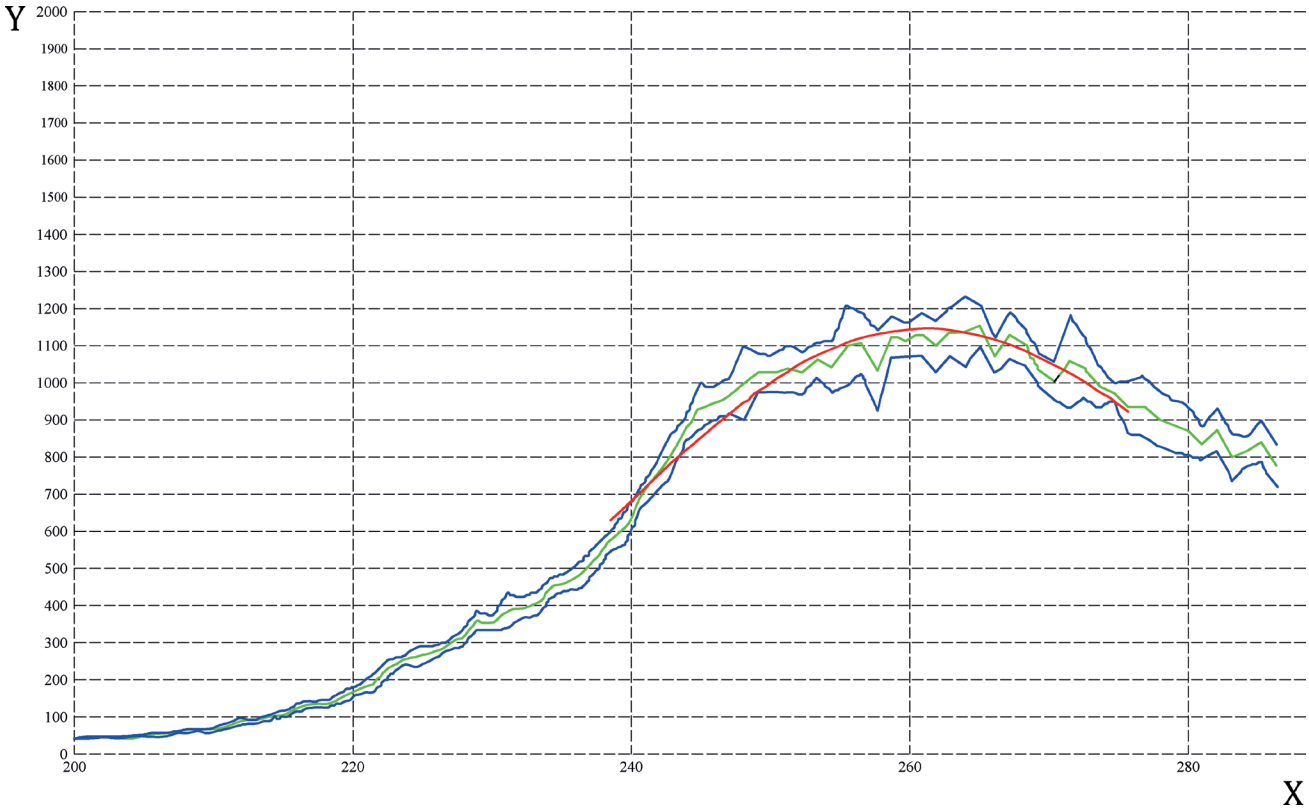


Key

X DOA absorption (ml/100 g)

Y torque (mNm)

Figure A.2 — Torque curve of the reference material RM (2)



Key

X DOA absorption (ml/100 g)

Y torque (mNm)

Figure A.3 — Torque curve of the reference material RM (3)

A.2.6 Normalization of the mixer using reference materials with known target values

For the first normalization of an individual mixer, each of the three reference materials with known or previously determined target values shall be tested four times. For each reference material, the average value shall be calculated and brought into a correlation to the respective target values. The resulting curve/formula describes the actual status of an individual mixing device and is the basis of the normalization (correction) for the routine silica DOA measurement.

EXAMPLE

$$Y = 0,977\ 0\ X + 4,354\ 1$$

where

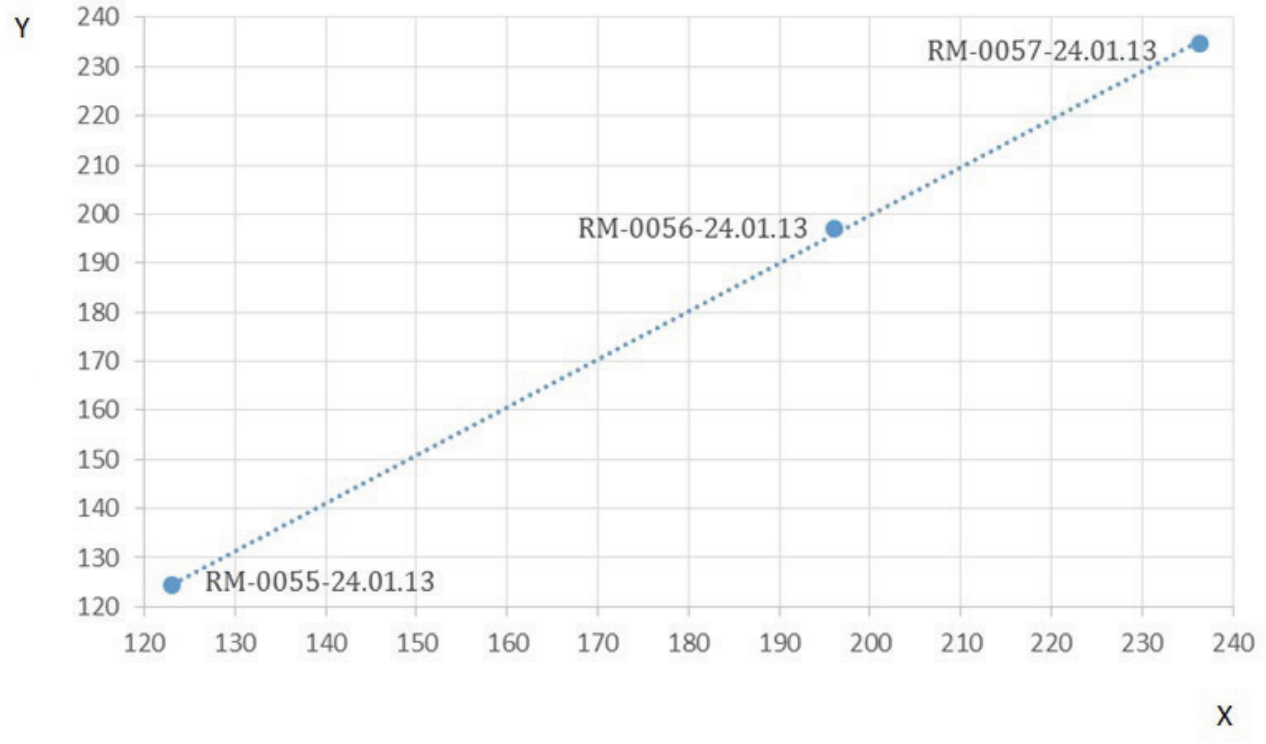
Y is the DOA absorption, norm;

X is the DOA absorption.

For example, DOA absorption is 250 ml/100 g.

$$Y = \frac{0,977\ 0 \times 250}{100} + \frac{4,354\ 1}{100} = 248,6\ \text{ml/100 g}$$

Y = 0,977 0 × 250 ml/100 g + 4,354 1 ml/100 g = 248,6 ml/100 g



Key

X average (ml/100 g)

Y target (ml/100 g)

RM-0055-24.01.13		RM-0056-24.01.13		RM-0057-24.01.13	
Time	Value	Time	Value	Time	Value
24.01.2013 11:06:31	124,2	24.01.2013 13:19:03	194,3	24.01.2013 15:32:56	237,0
24.01.2013 10:40:26	123,6	24.01.2013 13:33:24	195,2	24.01.2013 14:59:22	233,8
24.01.2013 10:22:10	120,4	24.01.2013 13:17:33	197,6	24.01.2013 14:42:29	237,2
24.01.2013 09:58:33	124,3	24.01.2013 11:28:37	197,2	24.01.2013 14:10:27	237,2
Average	123,1	Average	196,1	Average	236,3
Target	124,3	Target	196,9	Target	234,6

Figure A.4 — Example

After a reasonable time, depending from the number of DOA measurements and the type of samples, the normalization of the mixing device shall be updated. For that each reference material shall be tested once and the result shall be added to the normalization table while the earliest value shall be removed. Based on the latest four test results, the average value shall be calculated and brought again into correlation with the known target values. The new curve is now the basis for the normalization (correction) of the routine DOA measurements.

Annex B
(informative)

Precision data

B.1 General

This annex describes a statistical study which shows the influence of the normalization procedure versus the original DOA test results.

B.2 Statistical evaluation of data according to DOA normalized versus DOA original — Cross check study

B.2.1 Test sample

EXP 7137-1

Precipitated silica powder.

B.2.2 Participants

12 laboratories, globally.

B.2.3 Test plan

Five tests in each laboratory on homogenized material were carried out. The test results are evaluated as “original” and “original, normalized”. “Original” means that the result is referred to original substance and not moisture corrected. “Normalized” is referred to the arithmetical correction of the kneading chamber’s aging status.

B.2.4 Evaluation

Table B.1

Sample	Average OAN original	Within laboratory			Between laboratories		
		s_r	r	(r)	s_R	R	(R)
	ml/100 g	ml/100 g	ml/100 g	%	ml/100 g	ml/100 g	%
EXP 7137-1	257,3	1,0	2,0	0,8	7,2	14,5	5,6
EXP 7137-1	248,8	1,4	2,8	1,1	2,4	4,8	1,9

s_r is the within-laboratory standard deviation (in measurement units).

r is the repeatability (in measurement units).

(r) is the repeatability (in percent of mean level).

s_R is the between-laboratory standard deviation (for total between-laboratory variation in measurement units).

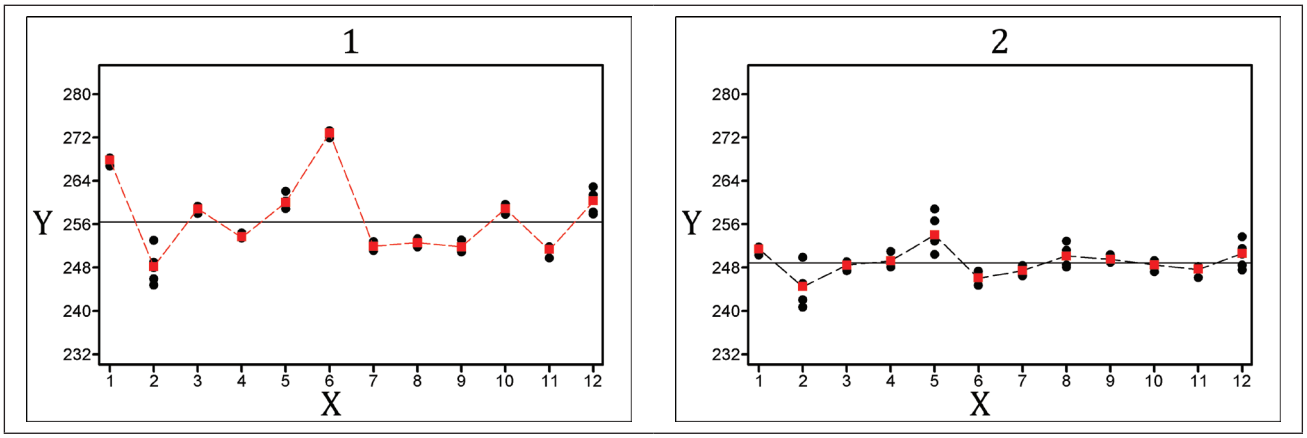
R is the reproducibility (in measurement units).

(R) is the reproducibility (in percent of mean level).

B.2.5 Precision data

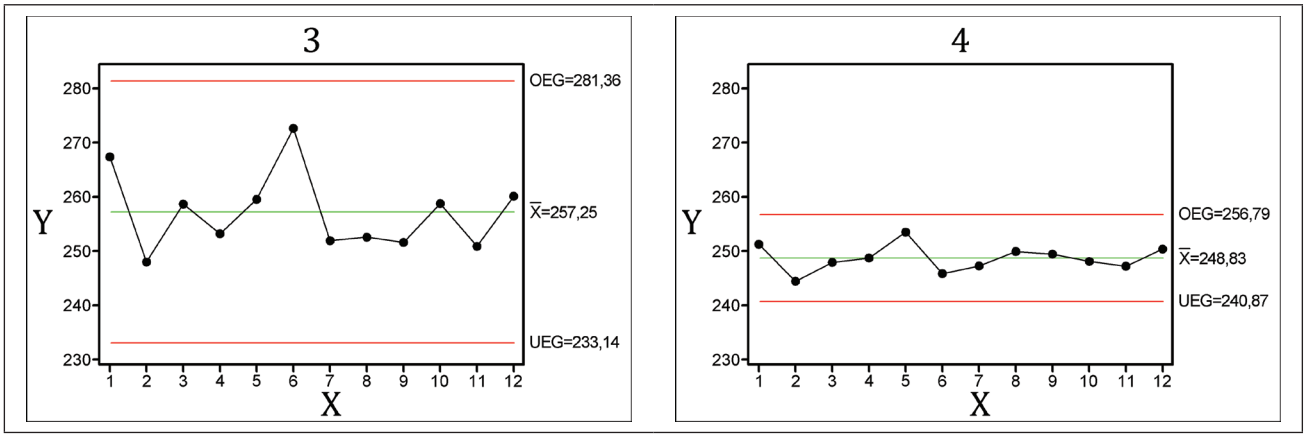
Assumption: the average value is the correct value.

Simplified calculations of R&R - > 2s/xq



a) Control chart DOA original (individual results per laboratory)

b) Control control chart DOA original, normalized (individual results per laboratory)



c) Control chart DOA original (average values)

d) Control chart DOA original, normalized (average values)

Figure B.1 — Illustrations of the test results

Bibliography

[1] ASTM D5900-13, *Standard Specification for Physical and Chemical Properties of Industry Reference Materials (IRM)*

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