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CERTIFICATION REPORT

The certification of particle size distribution of corundum: ERM®- FD069

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Joint Research Centre
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Contact information
Reference materials sales
Address: Retieseweg 111, 2440 Geel, Belgium
E-mail: jrc-rm-distribution@ec.europa.eu
Tel.: +32 (0)14 571 705

JRC Science Hub
https://ec.europa.eu/jrc

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Abstract

This report describes the production of ERM-FD069, which is a corundum material certified for the particle size distribution as determined by laser diffraction (ISO 13320) and optical microscopy (ISO 13322). This material was produced following ISO Guide 34:2009 and is certified in accordance with ISO Guide 35.
Two grades of commercial corundum were mixed, repeatedly divided and packed into glass bottles. These bottles are equipped with three flow-breakers made of glass to allow thorough homogenisation of the material inside the bottle.
Between unit-homogeneity was quantified and stability during dispatch and storage was assessed in accordance with ISO Guide 35:2006. The minimum sample intake was determined as the lowest amount that gave repeatable results in the characterisation study.
The material was characterised by an interlaboratory comparison of laboratories of demonstrated competence and adhering to ISO/IEC 17025. Technically invalid results were removed but no outlier was eliminated on statistical grounds only.
Uncertainties of the certified values were calculated in accordance with the Guide to the Expression of Uncertainty in Measurement (GUM) and include uncertainties related to possible inhomogeneity, instability and characterisation.
The material is intended for the quality control and assessment of method performance. As with any reference material, it/they can be used for establishing control charts or be used in validation studies. The CRMs is available in glass bottles containing at least 40 g of corundum powder. The minimum amount of sample to be used is 100 mg.

The certification of particle size distribution of corundum: ERM®- FD069

Thomas Linsinger, Jean Charoud-Got, Vikram Kestens, Tsvetelina Gerganova

European Commission, Joint Research Centre
Directorate F – Health, Consumers and Reference Materials
Geel, Belgium

Disclaimer

Certain commercial equipment, instruments, and materials are identified in this paper to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the European Commission, nor does it imply that the material or equipment is necessarily the best available for the purpose.

Summary

This report describes the production of ERM-FD069, which is a corundum material certified for the particle size distribution as determined by laser diffraction (ISO 13320) and optical microscopy (ISO 13322). This material was produced following ISO Guide 34:2009 [1] and is certified in accordance with ISO Guide 35 [2].

Two grades of commercial corundum were mixed, repeatedly divided and packed into glass bottles. These bottles are equipped with three flow-breakers made of glass to allow thorough homogenisation of the material inside the bottle.

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The following certified values were assigned:

Volume-weighted equivalent spherical diameter Laser diffraction, Fraunhofer approximation			Volume-weighted equivalent spherical diameter Laser diffraction, Mie theory			Number-weighted area-equivalent circular diameter Optical microscopy		
Diameter[1)]	Certified value [4)] [µm]	U [5)] [µm]	Diameter[2)]	Certified value[4)] [µm]	U [5)] [µm]	Diameter[3)]	Certified value[4)] [µm]	U [5)] [µm]
$x_{5,3}$	13.9	0.6	$x_{5,3}$	15.0	0.6	$x_{5,0}$	12.4	2.9
$x_{10,3}$	17.4	0.4	$x_{10,3}$	18.1	0.5	$x_{10,0}$	15.8	2.9
$x_{25,3}$	24.90	0.30	$x_{25,3}$	25.1	0.8	$x_{25,0}$	19.9	2.5
$x_{50,3}$	36.8	0.4	$x_{50,3}$	36.7	1.5	$x_{50,0}$	23.9	2.6
$x_{75,3}$	52.3	0.6	$x_{75,3}$	52.8	2.2	$x_{75,0}$	30	4
$x_{90,3}$	68.6	0.9	$x_{90,3}$	70.5	2.7	$x_{90,0}$	40	6
$x_{95,3}$	79.8	1.7	$x_{95,3}$	82	3	$x_{95,0}$	46	8

1) As defined by ISO 13320 applying the Fraunhofer approximation and applicable to both dry and wet dispersion

2) As defined by ISO 13320 applying the Mie theory using a complex refractive index of 1.77 -0i and applicable to both dry and wet dispersion

3) As defined by the application of optical microscopy for image analysis according to ISO 13322

4) Certified values are values that fulfil the highest standards of accuracy. The given values represents the unweighted mean value of the means of accepted sets of data, each set being obtained in a different laboratory and/or with a different instrument. The certified value and its uncertainty are traceable to the International System of Units (SI)."

5) The uncertainty is the expanded uncertainty of the certified value with a coverage factor k = 2 (Laser diffraction, Fraunhofer) and k = 2.57 (Laser diffraction, Mie and optical microscopy), respectively, corresponding to a level of confidence of about 95 % estimated in accordance with ISO/IEC Guide 98-3, Guide to the Expression of Uncertainty in Measurement (GUM:1995), ISO, 2008. "

Table of contents

Glossary

α	significance level
ANOVA	Analysis of variance
BCR®	One of the trademarks of CRMs owned by the European Commission; formerly Community Bureau of Reference
CI	Confidence interval
CLSI	Clinical & Laboratory Standards Institute
CRM	Certified reference material
Δ_{meas}	absolute difference between mean measured value and the certified value
d	In connection with laboratory code: dry dispersion (e.g. L1d)
d_i	Distance travelled at point *i*
$\bar{d}$	mean of all d_i
d_{tt}	chosen transport distance (500 km) for the calculation of u_{sts}
EC	European Commission
ERM®	Trademark of European Reference Materials
GUM	Guide to the Expression of Uncertainty in Measurements (ISO/IEC Guide 98-3:2008)
IEC	International Electrotechnical Commission
ISO	International Organization for Standardization
JRC	Joint Research Centre of the European Commission
k	Coverage factor
LD	Laser diffraction
LOD	Limit of detection
$MS_{between}$	Mean of squares between-unit from an ANOVA
MS_{within}	Mean of squares within-unit from an ANOVA
$\nu_{MSwithin}$	Degrees of freedom of MS_{within}
n	Mean number of replicates per unit in the homogeneity study
N	Number of samples (units) analysed
n.a.	Not applicable
n.c.	Not calculated
n.d.	Not detectable
NIST	National Institute of Standards and Technology (USA)
p	Number of number of technically valid datasets in the characterisation study
QC	Quality control
QCM	Quality control material
$Q_j(x)$	Cumulative distribution of particles smaller than x. j=0: number weighted; j=3: volume weighted.
rel	Index denoting relative figures (uncertainties etc.)
RM	Reference material
RSD	Relative standard deviation
s	Standard deviation; an additional index "rel" is added when appropriate
s_{bb}	Between-unit standard deviation; an additional index "rel" is added when appropriate
$s_{between}$	Standard deviation between groups as obtained from ANOVA; an additional index "rel" is added as appropriate
se	Standard error
SI	International System of Units
SRM	Trademark used for CRMs from NIST

s_{within}	Standard deviation within groups as obtained from ANOVA; an additional index "rel" is added as appropriate
s_{wb}	Within-unit standard deviation
$t_{\alpha, df}$	Critical *t*-value for a *t*-test, with a level of confidence of 1-α and df degrees of freedom
u	standard uncertainty
U	expanded uncertainty
u^*_{bb}	Standard uncertainty related to a maximum between-unit inhomogeneity that could be hidden by method repeatability/intermediate precision select as appropriate; an additional index "rel" is added as appropriate
u_{bb}	Standard uncertainty related to a possible between-unit inhomogeneity; an additional index "rel" is added as appropriate
u_c	combined standard uncertainty; an additional index "rel" is added as appropriate
u_{char}	Standard uncertainty of the material characterisation; an additional index "rel" is added as appropriate
u_{CRM}	Combined standard uncertainty of the certified value; an additional index "rel" is added as appropriate
U_{CRM}	Expanded uncertainty of the certified value; an additional index "rel" is added as appropriate
u_Δ	Combined standard uncertainty of measurement result and certified value
U_Δ	Expanded uncertainty of the absolute difference between mean measured value and the certified value
u_{lts}	Standard uncertainty of the long-term stability; an additional index "rel" is added as appropriate
u_{meas}	Standard measurement uncertainty
U_{meas}	Expanded measurement uncertainty
u_{rec}	Uncertainty estimated from a rectangular distribution; an additional index "rel" is added as appropriate
u_{sts}	Standard uncertainty of the short-term stability; an additional index "rel" is added as appropriate
w	In connection with laboratory code: wet dispersion (e.g. L1w)
$x_{,i,j}$	i- th percentile of a distribution of quantity j with j=0: number; j=3: volume
$\bar{\bar{x}}$	mean of all laboratory means
$\bar{y}$	Mean of all results in the homogeneity study

1 Introduction

1.1 Background

The particle size of materials is often crucial for their properties and for their useful application. Examples include sand (for making cement), cement itself, gypsum, metal powders, coffee, cocoa, dispersions of pigments etc. Therefore, reliable methods of particle size characterisation are required to ensure constant product quality in many fields. Unreliable measurements can hamper the flow of goods and are therefore regarded as non-tariff barriers.

The term "particle size" is vague: only monodisperse materials consisting of perfect spheres can be characterised by a single parameter (the diameter). This simplification is not possible for virtually any technically relevant material, which usually are polydisperse and/or of an irregular particle shape. Various size characterisation methods are available that probe different particle properties, which, in turn, are usually translated into the diameters of perfect spheres which would have the same properties ("equivalent diameter"). These equivalent diameters are therefore method defined properties [4], i.e. only meaningful in connection with a specific method and can only be reproduced using this method. To ensure the same application of such methods, the International Organization for Standardization (ISO) has issued documentary standards for many of these particle characterisation methods. However, demonstration of correct application of the methods requires the use of a certified reference material [5].

In laser diffraction as described in ISO 13320 [6], a sample is dispersed in either compressed air (dry method) or liquid (wet method) and a beam of monochromatic light is passed through this dispersion. The light is scattered at the various particles in all directions. Scattered light from each individual particle follows an intensity pattern depending on the particle size (as well as particle shape and optical properties of the particle). The light scattered from all particles is recorded by multiple detectors and transformed into a particle size distribution using an appropriate optical model. Current instruments apply either Mie theory or the Fraunhofer approximation.
The Mie theory provides a rigorous solution of the complete pattern that is valid for all sizes of spheres. However, precise knowledge of the refractive indices of medium and particle are required. The Fraunhofer approximation does not require any knowledge of the optical properties of the material or medium, but requires that the particles are large compared to the wavelength of the laser light. Both approaches give equivalent results for all particles above 50 μm and for opaque particles above 2 μm. The actual agreement for particles in the size range between 2 μm and 50 μm between the two evaluation methods depends on the relative real part and imaginary part of the complex refractive index.
Regardless of the model, the results of laser diffraction measurements are expressed as diameters of volume weighted equivalent spheres, $x_{a,3}$, with “a” being the cumulative percentage of particles smaller than the given diameter a (hence $x_{50,3}$ would be the median particle size). Many instruments also allow the possibility to convert the result into number weighted equivalent diameters $x_{a,0}$.
Laser diffraction is a method that does not require calibration of the measurement signal response by the user, but it does require verification of proper functioning and handling.

Optical microscopy measurements investigate the particles directly under a microscope. The particle is dispersed either by compressed air or by liquid on a microscopic slide and pictures are taken, which are subsequently analysed according to ISO 13322 [7]. Usually, a digital image is captured and evaluated using image analysis software that ensures that touching particles or particles at the edge of the image are not counted. Contrary to laser diffraction which simultaneously measures a multitude of particles, the number of particles investigated

by image analysis is usually much smaller. The higher the polydispersity of a material, the more particles need to be counted to obtain reliable estimate of the true particle size distribution for each percentile.
In this report, the results of the image analysis are expressed as diameters of circles that have the equivalent projected area. These can be volume weighted ($x_{a,3}$) or number weighted ($x_{a,0}$).
Optical measurements require calibration of the magnification. This is usually performed with certified gratings that convert a known distance into a number of pixels.

To allow laboratories demonstration of the correct application of particle sizing methods, the European Commission funded a project for the production of two certified reference materials (CRMs) based on quartz for particle size characterisation according to the sedimentation method using the Andreasen cylinder in 1980 (BCR-066 (0.4 μm - 4 μm) and BCR-069 (14 μm - 90 μm); [8]), which is rarely used nowadays. In addition, the materials were becoming exhausted.

Therefore, the European Commission's Joint Research Centre (JRC) decided to launch a project to replace and improve upon BCR-069 by a new material ERM-FD069.

1.2 Choice of the material

BCR-069 consists of quartz particles of equivalent diameters between 14 μm and 90 μm. Quartz, however, has some disadvantages: it is carcinogenic when inhaled. Quartz is also transparent, which can cause problems for imaging methods. Therefore it was decided to produce the material with a material based on corundum (Al_2O_3), an opaque, non-hazardous material with roughly the same particle size distribution. Isoelectric points for α-Al_2O_3 around pH=9 have been reported [9], meaning that the surface will be positively charged at neutral and acidic pH.

1.3 Design of the CRM project

The project consisted of processing of a corundum material and subsequent testing for homogeneity and stability. The particle size was characterised by laser diffraction applying both wet and dry methods and evaluation by Mie theory and the Fraunhofer approximation as well as optical microscopy in an interlaboratory comparison among laboratories of demonstrated competence. Method specific values were calculated for selected percentiles of the material.

The volume-weighted percentiles ($x_{a,3}$) were chosen for laser diffraction whereas number-weighted percentiles ($x_{a,0}$) were selected for optical measurements.

2 Participants

2.1 Project management and data evaluation

European Commission, Joint Research Centre, Directorate F – Health, Consumers and Reference Materials, Geel, BE
(accredited to ISO Guide 34 for production of certified reference materials, BELAC No. 268-RM)

2.2 Processing

Aokin AG, Berlin. DE

European Commission, Joint Research Centre, Directorate F – Health, Consumers and Reference Materials, Geel, BE
(accredited to ISO Guide 34 for production of certified reference materials, BELAC No. 268-RM)

2.3 Homogeneity study

European Commission, Joint Research Centre, Directorate F – Health, Consumers and Reference Materials, Geel, BE
(accredited to ISO Guide 34 for production of certified reference materials, BELAC No. 268-RM; measurements under the scope of ISO/IEC 17025 accreditation BELAC No. 268-TEST)

Umicore, Analytical Competence Center, Olen, BE
(measurements under the scope of ISO/IEC 17025 accreditation BELAC No. 401-TEST)

2.4 Stability study

European Commission, Joint Research Centre, Directorate F – Health, Consumers and Reference Materials, Geel, BE
(measurements under the scope of ISO/IEC 17025 accreditation BELAC No. 268-TEST)

Umicore, Analytical Competence Center, Olen, BE
(measurements under the scope of ISO/IEC 17025 accreditation BELAC No. 401-TEST)

Sympatec GmbH, Clausthal-Zellerfeld, DE

2.5 Characterisation

Agfa-Gevaert, Research and Development Materials, Mortsel, BE

AQura GmbH, Marl, DE

Delft Solids Solutions B.V, Barendrecht, NL

Escubed Ltd., Leeds, UK
(measurements under the scope of ISO/IEC 17025 accreditation UKAS 8467)

European Commission, Joint Research Centre, Directorate F – Health, Consumers and Reference Materials, Geel, BE
(measurements under the scope of ISO/IEC 17025 accreditation BELAC No. 268-TEST)

Federal Institute for Materials Research and Testing (BAM), Berlin, DE
(measurements under the scope of ISO/IEC 17025 accreditation DAkks D-PL-11075-16-00z)

Industrial Technology Research Institute (ITRI), Shinchu, TW

MVA Scientific Consultants, Duluth, US
(measurements under the scope of ISO/IEC 17025 accreditation A2LA 2096.01)

National Institute of Metrology (NIM), Beijing, CN

National Institute of Standards and Technology (NIST), Gaithersburg, US
National Measurement Institute Australia (NMIA), Lindfield, AU
Particle Analytical ApS, Hørsholm, DK
Solvias AG, Kaiseraugst, CH
Sympatec GmbH, Clausthal-Zellerfeld, DE

3 Material processing and process control

3.1 Processing

One bag of 25 kg each of white fused corundum grinding powder grit size F240 (nominal mean particle size 50 μm), F320 (mean particle size 30 μm) and F400 (mean particle size 18 μm) were purchased from IMEXCO Ullrich GmbH (Saarbrücken, DE). The incoming material was checked by laser diffraction and the volume-weighed modal diameters, $x_{50,3}$, were confirmed as 52 μm, 35 μm and 21 μm respectively.

A scheme of the processing is shown in Figure 1. Twenty four kg of each bag was taken, combined and pre-mixed in an overhead shaker for 8 hours and was mixed again for half an hour before taking 7 kg batches for further processing. This pre-mixed material was divided into two batches of 35 kg and 37 kg, respectively. Each batch was then divided into 8 lots using a sample-divider PT100 (Retsch GmbH, Haan, DE). These 2 x 8 lots were mixed three times on the PT100 sample divider mixing lot 1, 3, 5, 7 from the first batch with lot 2, 4, 6, 8 from the second batch, obtaining finally 16 lots of 4494 g each.

Four of the final lots were combined and subdivided into 16 lots of 1123 g. To each lot of 4494 g one lot of 1123 g was added, homogenised split into 16 lots of 351 g each (the remaining 4 lots of 1123 g are discarded).

Each of the 351 g lots was again homogenised and split into 8 lots of 44 g each and filled into amber-brown glass bottles equipped with flow breakers (glass strips glued to the bottle with silicone and dried for at least 24 h). These flow breakers should prevent de-mixing upon shaking. A total of 1536 bottles were filled.

3.2 Process control

A limited homogeneity study with few samples only was performed to check for major inhomogeneity before continuing with the project. Bottles number 187, 576, 810, 1008 and 1253 were taken and analysed by optical microscopy in duplicate (approximately 5-10 images per replicate, representing about 1000 particles). The $x_{5,0}$, $x_{10,0}$, $x_{25,0}$, $x_{50,0}$, $x_{75,0}$, $x_{90,0}$ and $x_{95,0}$ were determined. The significance of the between-bottle difference of the median was evaluated using one-way analysis of variance (ANOVA). No significant difference was detected.

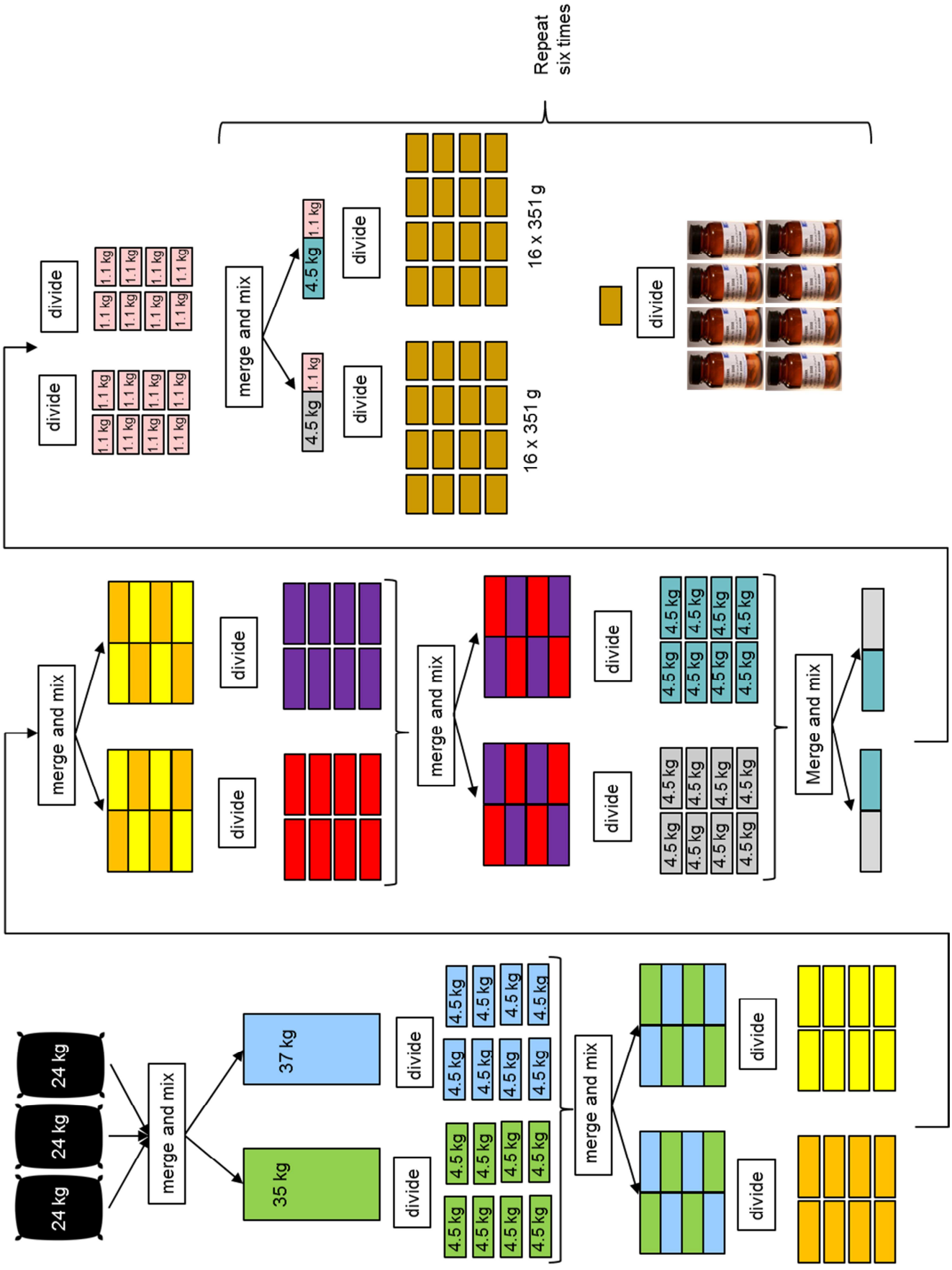

Figure 1: Flowchart of the processing of ERM-FD069

The material is polydisperse and consists of irregularly-shaped particles. A micrograph of ERM-FD069 is shown in Figure 2.

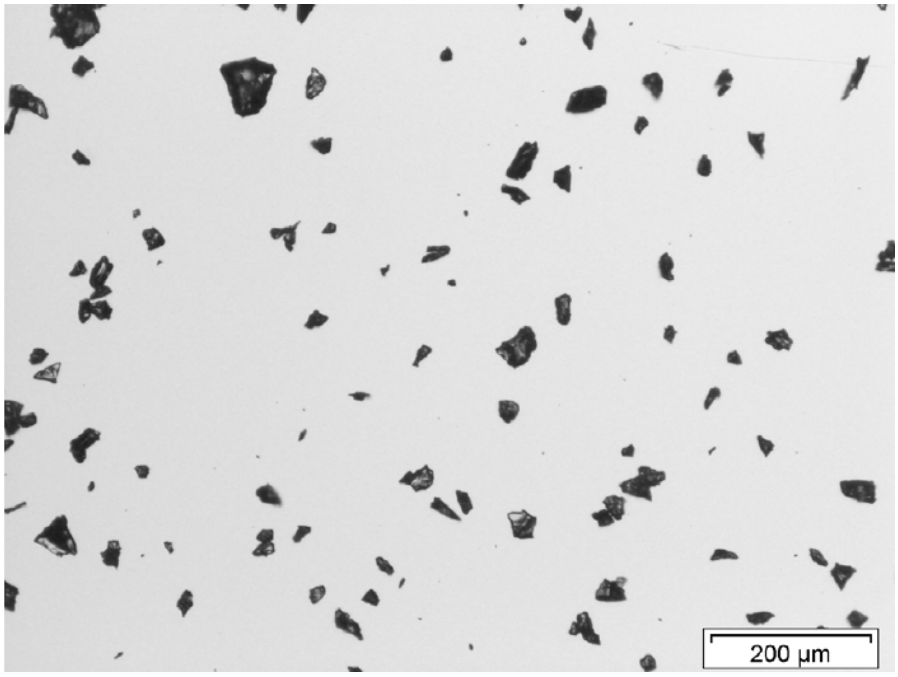

Figure 2: Micrograph of ERM-FD069

4 Homogeneity

A key requirement for any reference material aliquoted into units is equivalence between those units. Usually, several replicate measurements are performed on several units of the material. The relevant criterion for the homogeneity assessment is whether the (potential) between-unit variation is significant compared to the uncertainty of the certified value. This between-unit variation is a material property and independent of the analytical variation (variation of the results in each unit). Depending on the repeatability of the method applied, the same between-unit variation can be significant or not significant compared to the analytical variation. It is therefore irrelevant whether the between-unit variation is significant compared to the analytical variation observed in a study. Consequently, ISO Guide 34 [1] requires RM producers to quantify the between unit variation to assess whether between-unit variation contributed to the uncertainty of the certified value. This aspect is covered in between-unit homogeneity studies.

The within-unit inhomogeneity does not influence the uncertainty of the certified value when the minimum sample intake is respected, but determines the minimum size of an aliquot that is representative for the whole unit. Quantification of within-unit inhomogeneity is therefore necessary to determine the minimum sample intake.

4.1 Between-unit homogeneity

The between-unit homogeneity was evaluated to ensure that the certified values of the CRM are valid for all units of the material, within the stated uncertainties.

The number of bottles selected corresponds to approximately the cubic root of the total number of bottle produced. Fifteen bottles were selected using a random stratified sampling scheme covering the whole batch for the between-unit homogeneity test. For this, the batch was divided into 15 groups with a similar number of bottles and one bottle was selected randomly from each group. Three independent samples were taken from each selected bottle, and analysed according to ISO 13320 (laser diffraction) using the wet method (Sympatec HELOS with a QUIXEL liquid dispersion cell, Sympatec GmbH, Clausthal-Zellerfeld, DE) as well as the dry method (Instrument Sympatec HELOS with a RODOS dry dispersion cell, Sympatec GmbH, Clausthal-Zellerfeld, DE).

The measurements were performed under repeatability conditions. The order of the samples for each replicate was changed to allow detection of an instrument drift and in a randomised manner to be able to separate a potential analytical drift from a trend in the filling sequence. The results are shown as graphs in Annex A.

Regression analyses were performed to evaluate potential trends in the analytical sequence as well as trends in the filling sequence. The significance of the trend in the analytical sequence was tested on a 95 % confidence level, the one for the filling sequence on a 99 % confidence level. The reason for this difference is that trends in the analytical sequence can be corrected, as long as the analytical and filling sequences are not correlated. Furthermore, the correction of biases, even if they are statistically not significant, was found to combine the smallest uncertainty with the highest probability to cover the true value [10]. This means, false positive results have less impact on the evaluation of analytical trends than of filling trends.

For the dry method, a clear trend in the filling sequence was visible for the $x_{95,3}$. As statistically significant, it was decided to include the trend in the combined uncertainty. A trend in the filling sequence was visible for $x_{10,3}$. This trend was caused by a clear outlier in the result of the first sample measured and resulted also in the respective bottle average to be flagged as an outlier. It was decided to retain the data as a conservative measure.

There was a clear trend in the filling sequence for all percentiles in the wet method except for $x_{90,3}$ and $x_{95,3}$. However, tentative removal of the three outliers in these percentiles would also

have resulted in a significant trend, indicating that also these percentiles are affected by a trend.

The datasets were assessed for consistency using Grubbs outlier tests at a confidence level of 99 % on the individual results and on the unit means. Some outlying individual results and outlying unit means were detected. Since no technical reason for the outliers could be found, all the data were retained for statistical analysis.

Quantification of between-unit inhomogeneity was undertaken by analysis of variance (ANOVA), which separates the between-unit variation (s_{bb}) from the within-unit variation (s_{wb}). The latter is equivalent to the method repeatability if the samples are representative for the whole bottle.

Evaluation by ANOVA requires mean values per bottle, which follow at least a unimodal distribution and results for each bottle that follow unimodal distributions with approximately the same standard deviations. The distribution of the mean values per bottle was visually tested using histograms and normal probability plots. Too few data are generally available for each bottle to make a clear statement of the distribution. Therefore, it was checked visually whether all individual data follow a unimodal distribution using histograms and normal probability plots. Minor deviations from unimodality of the individual values do not significantly affect the estimate of between-unit standard deviations, but major deviations like bimodality show that evaluation by ANOVA is not appropriate and another evaluation must be chosen (see below). The results of all statistical evaluations are given in Table 1.

Table 1: Summarised results of the statistical evaluation of the homogeneity studies by laser diffraction. . The significance of the trends was tested on a 95 % confidence level for the analytical sequence and on a 99 % confidence level for the filling sequence

	Measurand	Significant trend on a 95 % confidence level		Outliers on a 99 % confidence level		Distribution	
		Analytical sequence	Filling sequence	Individual results	Unit means	Individual results	Unit means
Laser diffraction, dry	$x_{5,3}$	no	no	1	no	unimodal	unimodal
	$x_{10,3}$	yes	no	1	1	unimodal	unimodal
	$x_{25,3}$	no	no	no	no	normal	normal
	$x_{50,3}$	no	no	no	no	normal	normal
	$x_{75,3}$	no	no	no	no	normal	normal
	$x_{90,3}$	no	no	no	no	normal	bimodal
	$x_{95,3}$	no	yes	no	no	normal	bimodal
Laser diffraction, wet	$x_{5,3}$	no	yes	1	no	unimodal	unimodal
	$x_{10,3}$	no	yes	1	no	unimodal	unimodal
	$x_{25,3}$	no	yes	no	no	unimodal	unimodal
	$x_{50,3}$	no	no	1	no	unimodal	unimodal
	$x_{75,3}$	no	no	2	no	unimodal	unimodal
	$x_{90,3}$	no	no	3	no	unimodal	unimodal
	$x_{95,3}$	no	no	3	no	unimodal	unimodal

It should be noted that $s_{bb,rel}$ and $s_{wb,rel}$ are estimates of the true standard deviations and are therefore subject to random fluctuations. Therefore, the mean square between groups ($MS_{between}$) can be smaller than the mean squares within groups (MS_{within}), resulting in negative arguments under the square root used for the estimation of the between-unit variation, whereas the true variation cannot be lower than zero. In this case, u^*_{bb}, the maximum inhomogeneity that could be hidden by method repeatability, was calculated as described by Linsinger *et al.* [11]. u^*_{bb} is comparable to the LOD of an analytical method, yielding the maximum inhomogeneity that might be undetected by the given study setup.

Method repeatability ($s_{wb,rel}$), between–unit standard deviation ($s_{bb,rel}$) and $u^*_{bb,rel}$ were calculated as:

$$s_{wb,rel} = \frac{\sqrt{MS_{within}}}{\bar{y}} \qquad \textit{Equation 1}$$

$$s_{bb,rel} = \frac{\sqrt{\frac{MS_{between} - MS_{within}}{n}}}{\bar{y}} \qquad \textit{Equation 2}$$

$$u^*_{bb,rel} = \frac{\sqrt{\frac{MS_{within}}{n}\sqrt[4]{\frac{2}{v_{MSwithin}}}}}{\bar{y}} \qquad \textit{Equation 3}$$

MS_{within} mean of squares within-unit from an ANOVA

$MS_{between}$ mean of squares between-unit from an ANOVA

$\bar{y}$ mean of all results of the homogeneity study

n mean number of replicates per unit

$v_{MSwithin}$ degrees of freedom of MS_{within}

A different approach was adopted for parameters for which outlying unit means were detected. In these cases between-unit inhomogeneity was modelled as a rectangular distribution limited by the largest outlying unit mean, and the rectangular standard uncertainty of homogeneity was estimated by:

$$u_{rec} = \frac{\left|outlier - \bar{y}\right|}{\sqrt{3} \cdot \bar{y}} \qquad \textit{Equation 4}$$

$\bar{y}$ mean of all results of the homogeneity study

For bimodal distributions or where a trend in the filling sequence was significant at least at 95 % confidence level, the uncertainty was assessed in a different way. Here, u_{rec} was estimated using a rectangular distribution between the highest and lowest unit mean. The corrected uncertainty in those cases where there was a significant trend in the filling sequence is given in:

$$u_{rec} = \frac{\left|highest\ mean - lowest\ mean\right|}{2 \cdot \sqrt{3} \cdot \bar{y}} \qquad \textit{Equation 5}$$

The results of the evaluation of the between-unit variation are summarised in Table 2. The resulting values from the above equations were converted into relative uncertainties.

Table 2: Results of the homogeneity study. n.c.: cannot be calculated as MSbetween < MSwithin; n.a.: not applicable as there is either a trend or no trend in the filling sequence

	Measurand	$s_{wb,rel}$ [%]	$s_{bb,rel}$ [%]	$u^*_{bb,rel}$ [%]	$u_{rec,rel}$ [%]	$u_{bb,rel}$ [%]
Laser diffraction, dry	$x_{5,3}$	0.314	0.115	0.092	n.a.	0.115
	$x_{10,3}$	0.233	0.053	0.068	0.233	0.233
	$x_{25,3}$	0.255	n.c.	0.076	n.a.	0.076
	$x_{50,3}$	0.251	n.c.	0.074	n.a.	0.074
	$x_{75,3}$	0.256	n.c.	0.075	n.a.	0.075
	$x_{90,3}$	0.370	n.a.	0.109	0.171	0.171
	$x_{95,3}$	0.526	n.a.	0.154	0.259	0.259
Laser diffraction, wet	$x_{5,3}$	0.675	n.a.	0.198	0.595	0.595
	$x_{10,3}$	0.451	n.a.	0.132	0.401	0.401
	$x_{25,3}$	0.319	0.168	0.095	0.268	0.268
	$x_{50,3}$	0.370	0.167	0.111	0.346	0.346
	$x_{75,3}$	0.499	0.168	0.146	0.419	0.419
	$x_{90,3}$	0.661	0.121	0.194	n.a.	0.194
	$x_{95,3}$	1.282	n.c.	0.376	n.a.	0.376

For $x_{90,3}$ and $x_{95,3}$ the calculations were also performed after tentative exclusion of the outliers mentioned in *Table 1*. The uncertainties were smaller than those estimated without removal of outliers, showing that the approach chosen is sufficiently conservative.

Several outlying unit means were found and several significant trends in the filling sequence were detected. However, taking these extreme values into account, the inhomogeneity as quantified as u_{rec} is still sufficiently small to make the material useful. Therefore, u_{rec} was used as estimate of u_{bb}. Finally, the largest value of the wet or dry method was adopted as u_{bb} for both evaluation by Mie theory and Fraunhofer approximation.

Performing two-way ANOVA on the characterisation data for optical microscopy shows that for no percentile the between-bottle variation is statistically significant compared to the repeatability of a 95 % confidence level. This shows that for all laboratories, between-bottle heterogeneity is a negligible contribution to the overall uncertainty. Therefore, the uncertainties estimated for laser diffraction are also used for optical microscopy.

4.2 Within-unit homogeneity and minimum sample intake

The within-unit homogeneity is closely correlated to the minimum sample intake. Due to this correlation, individual aliquots of a material will not have the same particle size distribution. The minimum sample intake is the minimum amount of sample that is representative for the whole unit and thus should be used in an analysis. Using sample sizes equal or above the minimum sample intake guarantees the certified value within its stated uncertainty.

The minimum sample intake was determined from the results of the characterisation study, using the method information supplied by the participants. No minimum sample intake was imposed for laser diffraction, but a minimum of 5000 measured particles (250 particles per size bin of 5 %) per was imposed for optical microscopy. The smallest sample intake that still yielded results with acceptable accuracy to be included in the respective studies was taken as minimum sample intake. Using the data from Annex C, the minimum sample intake is 100 mg (laser diffraction), or 7 mg and analysis of at least 5000 particles (optical microscopy).

5 Stability

Stability testing is necessary to establish the conditions for storage (long-term stability) as well as the conditions for dispatch of the materials to the customers (short-term stability). During transport, especially in summer time, temperatures up to 60 °C can be reached and the material can be subject to extensive vibrations during road transport. Stability under these conditions must be demonstrated, if the samples are to be transported without any change of the certified parameters.

Corundum is chemically inert so the material itself will not degrade if exposed to moderately high temperatures. However, de-mixing or grinding due to vibration during transport was regarded possible, so the effect of road transport was investigated. Furthermore, it was checked whether the material was subject to change when exposed to humid atmosphere.

The stability studies were carried out using an isochronous design [12]. In this approach, samples were transported in a car for a certain distance. Afterwards, the samples were removed from the car, so no potential further de-mixing or grinding could. At the end of the isochronous storage, the samples were analysed simultaneously under repeatability conditions. Analysis of the material (after various exposure times) under repeatability conditions greatly improves the sensitivity of the stability tests [12].

5.1 Short-term stability study

For the short-term stability study, samples were transported in a car for 150 km and 1000 km, respectively (vibration during air transport is less severe than during road transport). Two bottles for each condition were selected using a random stratified sampling scheme. These samples were compared with two samples that had not undergone transport. From each bottle, three subsamples were analysed using laser diffraction in the wet method (Sympatec HELOS with QUIXEL cuvette).

In addition, two samples from each transport condition were compared to one sample that had not undergone transport using the dry method (Sympatec HELOS with RODOS sample dispersion unit). Three replicate measurements on each sample were performed under repeatability conditions

The results were screened for outliers using the single and double Grubbs test on a confidence level of 99 %. No outlier was detected.

In addition, the data were evaluated against distance travelled, and regression lines of the $x_{5,3}$, $x_{10,3}$, $x_{25,3}$, $x_{50,3}$, $x_{75,3}$, $x_{90,3}$ and $x_{95,3}$ versus distance travelled were calculated, to test for potential increases/decrease due to shipping. The slopes of the regression lines were tested for statistical significance. None of the slopes was statistically significant at a 95 % confidence level. No statistical outliers were detected.

The results of the measurements are shown in Annex B.

The material can be dispatched without further precautions under ambient conditions.

5.2 Long-term stability study

For the long-term stability study, six samples of 1 g were stored for one month at room temperature at 33 % and 75 % relative humidity. The sample mass was determined before and after the storage to check for any water uptake.

After one month, 99.9 % ± 0.6 % (1 month at 33 % humidity) and 99.5 % ± 0.3 % of the mass (1 month at 75 % humidity) were obtained (mean and 95 % confidence interval of the results), demonstrating the absence of technically significant water uptake. The material is therefore chemically stable with negligible uncertainty with respect to water uptake.

To limit liability, the validity of the certificate will be limited to 5 years after sales.

5.3 Estimation of uncertainties

Due to the intrinsic variation of measurement results, no study can entirely rule out degradation of materials, even in the absence of statistically significant trends. It is therefore necessary to quantify the potential degradation that could be hidden by the method repeatability, i.e. to estimate the uncertainty of stability. This means that, even under ideal conditions, the outcome of a stability study can only be that there is no detectable degradation within an uncertainty to be estimated.

The uncertainties of stability during dispatch and storage were estimated, as described in [13] for $x_{5,3}$, $x_{10,3}$, $x_{25,3}$, $x_{50,3}$, $x_{75,3}$, $x_{90,3}$ and $x_{95,3}$. In this approach, the uncertainty of the linear regression line with a slope of zero was calculated. The uncertainty contributions u_{sts} and u_{lts} were calculated as the product of the chosen transport time/shelf life and the uncertainty of the regression lines as:

$$u_{sts,rel} = \frac{s_{rel}}{\sqrt{\sum \left(d_i - \bar{d}\right)^2}} \cdot d_{tt} \qquad \textit{Equation 6}$$

s_{rel} relative standard deviation of all results of the stability study

d_i time elapsed at time point *i*

$\bar{d}$ mean of all t_i

d_{tt} chosen transport distance (500 km)

The following uncertainties were estimated:

- $u_{sts,rel}$, the uncertainty of degradation during dispatch. This was estimated from the transport studies. The uncertainty describes the possible change during a dispatch at 500 km.
- $u_{lts,rel}$, the stability during storage. Based on the chemical stability of corundum and the demonstrated absence of hygroscopicity for the material, this contribution is regarded negligible compared to the contributions of homogeneity, stability and characterisation.

The results of these evaluations are summarised in Table 3.

Table 3: Uncertainties of stability during dispatch and storage. $u_{sts,rel}$ was calculated for a road transport condition of 500 km

	Laser diffraction dry	Laser diffraction, wet
	$u_{sts,rel}$ [%]	$u_{sts,rel}$ [%]
$x_{5,3}$	0.07	0.11
$x_{10,3}$	0.04	0.08
$x_{25,3}$	0.05	0.07
$x_{50,3}$	0.05	0.07
$x_{75,3}$	0.07	0.07
$x_{90,3}$	0.13	0.07
$x_{95,3}$	0.19	0.13

No significant change during transport was observed even after the samples had travelled 1000 km. Therefore, the material can be transported without special precautions. Finally, the larger of the wet or dry method was adopted as u_{sts} for both evaluations by Mie theory and Fraunhofer approximation. Although the material was only tested by laser diffraction, the fact that there was negligible-effect of transport it should also hold for optical microscopy.

6 Characterisation

The material characterisation is the process of determining the property values of a reference material.

This was based on an interlaboratory comparison of expert laboratories, i.e. the size distribution of the material was determined in different laboratories to ensure the minimal measurement bias. This approach aims at randomisation of laboratory bias, which reduces the combined uncertainty.

6.1 Methods used

All laboratories used the one of the following methods:

- ISO 13320 (laser diffraction),evaluation applying the Fraunhofer approximation
- ISO 13320, (laser diffraction), evaluation applying Mie theory
- Optical microscopy, measuring at least 5000 particles and evaluating the images according to ISO 13322 (static image analysis) with respect to excluding border particles and automatic identification of touching particles.

Detailed description of the methods, the instruments used and sample preparation steps are listed in Annex C.

6.2 Selection of participants

Fourteen laboratories were selected based on criteria that comprised both technical competence and quality management aspects. Each participant was required to operate a quality system in agreement with ISO/IEC 17025 or GMP and to deliver documented evidence of its laboratory proficiency in the field. In case a laboratory did not hold a formal accreditation or GMP certification, it had to specify which sections were covered by its quality system to demonstrate that the requirements of ISO/IEC 17025 were fulfilled. In addition, the participants had to demonstrate their proficiency by either submitting data on good results of previous intercomparisons, results on CRMs or showing that the proposed measurements were within the scope of their ISO/IEC 17025 accreditation at the start of the study.

6.3 Study setup

Each laboratory received two bottles of ERM-FD069 and was requested to provide six independent results, three per bottle. The units for material characterisation were selected using a random stratified sampling scheme and covered the whole batch. The sample preparations (if necessary) and measurements had to be spread over at least two days to ensure intermediate precision conditions. Laboratories used different set-ups to implement these conditions: For laser diffraction, three dispersions were prepared and measured on two days each. For optical microscopy, some laboratories prepared several samples on one day and did the imaging on the same day and repeated this procedure on another day; some laboratories prepared a total of six samples on two days and performed the imaging on yet another day.

Each participant received a sample of a quality control (QC) sample. The results for this sample were used to support the evaluation of the characterisation results. The following QCMs were used:

- Laser diffraction dry method: Sympatec SiC-P600. This is a SiC material with assigned values for $x_{10,3}$, $x_{50,3}$ and $x_{90,3}$ using the Sympatec Helios in connection with the Rodos system applying the Fraunhofer approximation.

- Laser diffraction wet method: NIST SRM 1982: This is a material consisting of yttria-stabilised zirconium oxide and has certified values for laser diffraction in liquid dispersion. Reference values were assigned using an intercomparison where all laboratories used instruments from the same supplier (Microtrac) and applying a specified sample preparation method, which was not used in this study and applying the Mie theory.
- Optical microscopy: Whitehouse Scientific PS315. This material consists of soda-lime glass microspheres and has assigned values for the mass-based distribution obtained by optical microscopy. The values were therefore not directly applicable to the number-based results in this study, but allowed at least a consistency check with another material.

This summary shows that none of the QCMs has reliable certified values for the methods under investigation. Nevertheless, the data on the material can be used as an additional consistency check.

Laboratories were also requested to give estimations of the expanded uncertainties of the mean value of the six results. No approach for the estimation was prescribed, i.e. top-down and bottom-up were regarded as equally valid procedures.

6.4 Evaluation of results

The characterisation study resulted in 5-8 datasets per method. All individual results of the participants, grouped per method are displayed in table format and graphic format in Annex D.

6.4.1 Technical evaluation

The obtained data were first checked for compliance with the requested analysis protocol and for their validity based on technical reasons. The following criteria were considered during the evaluation:

- appropriate validation of the measurement procedure
- compliance with the analysis protocol: sample preparations and measurements performed on two days.
- method performance, was checked twofold: One criterion was the agreement of the measurement results with the results of others with respect to the QC sample. For laser diffraction, the second criterion was the agreement with the limits for repeatability given in ISO 13320 (3 % for $x_{50,3}$; 5 % for $x_{10,3}$ and $x_{90,3}$).

For laser diffraction (wet method), L6 and L9 exceeded the repeatability limits given in ISO 13320 and were therefore not used for characterisation. One of them also differed significantly from the other laboratories for the QCM.

For the dry method, L14 generally found lower values than the other laboratories. This difference was constant in relative terms (the percentiles of laboratory 14 were 13 % lower) but increased in absolute terms from 2 µm at $x_{5,3}$ to 11 µm at $x_{95,3}$. Laboratory 14 used an optical lens that is intended for smaller particles and has a top particle size of 175 µm. L1 used the same instrument but with a different lens (upper size 350 µm) and detected a small amount of particles up to 146 µm. It is therefore likely that the instrument settings of laboratory 14 overlooked some of the larger particles but detected more of the finer particles. As the larger particles are more relevant for the volume-weighted distribution, the results of laboratory 14 were excluded from value assignment.

The data on the QCM for optical microscopy showed relative standard deviations between 47 % ($x_{5,0}$) and 17 % ($x_{95,0}$). L4 generally gave larger diameters than the other laboratories

for the individual percentiles, whereas L9 gave smaller ones. This trend, however, was not repeated for the data on ERM-FD069, where both laboratories were among the data of the other laboratories. The fact that the QCM consisted of glass beads whereas ERM-FD069 consists of opaque corundum might have led to this difference. Therefore, all data on optical microscopy were retained.

Based on the above criteria, the following datasets were identified as potentially technically invalid (Table 4).

Table 4: Invalid datasets and actions taken

Method	Lab code	Description of problem	Action taken
LD wet	L6	The relative standard deviation exceeded the criteria given in ISO 13320.	Data not used for value assignment
	L9	The relative standard deviation exceeded the criteria given in ISO 13320. The laboratory differs significantly from the other laboratories for the QCM.	Data not used for value assignment
LD dry	L14	The laboratory used an instrument setting with a too low upper size range.	Data not used for value assignment

Participants were also asked to report results from laser diffraction in number-based distributions. These data, listed in Annex E, scattered much more than the data for the volume based distribution. Typically, the results for any given percentile span more than one decade, clearly excluding any value assignment. The only exception is laser diffraction by wet dispersion and evaluation by Mie theory. But here the low number or results preclude assignment of certified values.

6.4.2 Statistical evaluation

The individual data (i.e. 6 per laboratory and method) for laser diffraction were investigated by two-way ANOVA for difference between dry and wet method and evaluation by Mie theory and Fraunhofer approximation. These tests showed that the differences were significant for several percentiles (see Table 5). Surprisingly, differences between the evaluation models are also significant at higher percentiles.

Table 5: Error probabilities of the difference between dispersion and evaluation technique

	$x_{5,3}$	$x_{10,3}$	$x_{25,3}$	$x_{50,3}$	$x_{75,3}$	$x_{90,3}$	$x_{95,3}$
Wet/dry	<0.01	<0.01	0.17	0.92	0.37	0.07	0.02
Fraunhofer/Mie	<0.01	<0.01	0.01	0.27	0.01	<0.01	0.01

As can be seen in Figure 3, the absolute differences between the measurement/evaluation modes are small and the confidence intervals overlap. Nevertheless, there is a trend towards a smaller difference between evaluation models than within dispersing methods. It was

therefore decided to pool the results from wet and dry dispersion for each of the two evaluation models.

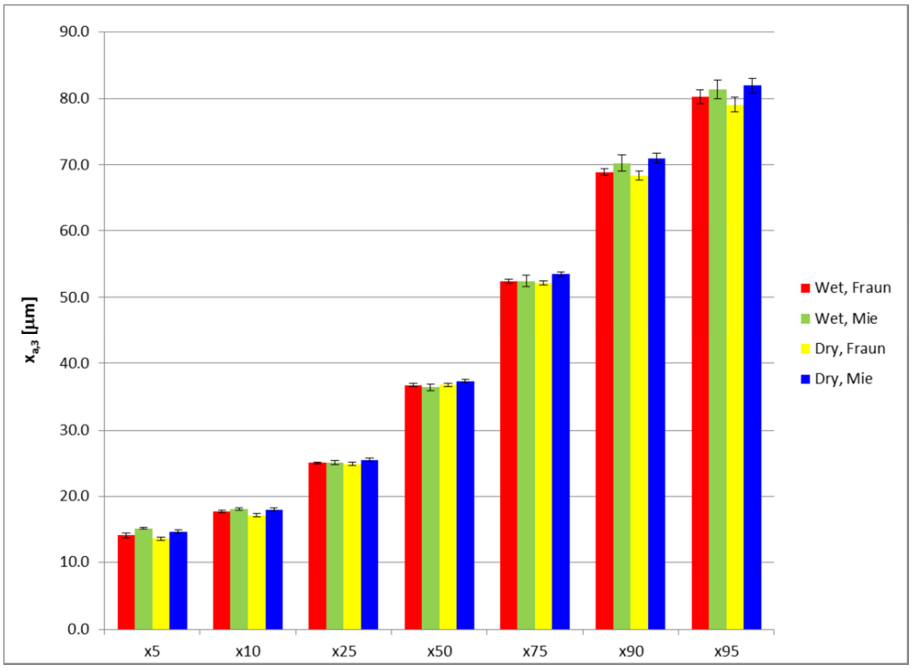

Figure 3: Averages and their 95 % confidence intervals for each of the measurement modes of laser diffraction for ERM-FD069. Fraun: Fraunhofer approximation. Averages and standard deviations are based on the mean and standard deviations of laboratory means. The same confidence interval was assigned to Dry, Mie as for Dry, Fraun, as only 2 laboratories applied Mie theory for dry measurements.

The statistical evaluation was performed by laboratory and evaluation model (Mie/Fraunhofer), meaning that results from laboratories that performed wet and dry measurements on the same instruments were not pooled. This is justified as the sample dispersion and the measurement cells differ between the two methods. Also the fact that wet and dry datasets from the same laboratory often gave quite differing results supports the decision to treat the results as independent.

The datasets accepted based on technical reasons were tested for normality of dataset means using kurtosis/skewness tests and normal probability plots and were tested for outlying means using the Grubbs test and using the Cochran test for outlying variances, (both at a 99 % confidence level). Standard deviations within (s_{within}) and between ($s_{between}$) laboratories were calculated using one-way ANOVA. The results of these evaluations are shown in Table 6.

Table 6: Statistical evaluation of the technically accepted datasets for ERM-FD069. p: number of technically valid datasets. Var - variance ; w - wet dispersion; d - dry dispersion

	Measurand	*p*	Outliers		Distribution of means	Statistical parameters			
			Means	Var.		Mean [µm]	*s* [µm]	$s_{between}$ [µm]	s_{within} [µm]
Laser diffraction, Fraunhofer approximation	$x_{5,3}$	8	0	L1w, L2d, L8d	normal	13.88	0.71	0.69	0.45
	$x_{10,3}$	8	0	0	normal	17.44	0.50	0.47	0.39
	$x_{25,3}$	8	L1d	0	not normal	24.90	0.37	0.35	0.32
	$x_{50,3}$	8	0	0	normal	36.78	0.42	0.39	0.43
	$x_{75,3}$	8	0	0	normal	52.31	0.55	0.50	0.57
	$x_{90,3}$	8	0	L13w	normal	68.62	1.17	1.12	0.89
	$x_{95,3}$	8	0	L2d	normal	79.75	2.17	2.08	1.53
Laser diffraction, Mie theory	$x_{5,3}$	6	0	L3w	normal	15.03	0.35	0.35	0.12
	$x_{10,3}$	6	0	L3w	normal	18.06	0.39	0.39	0.14
	$x_{25,3}$	6	0	L3w	normal	25.13	0.68	0.67	0.21
	$x_{50,3}$	6	0	L3w	normal	36.73	1.19	1.19	0.28
	$x_{75,3}$	6	0	L3w, L12w	normal	52.8	1.81	1.80	0.41
	$x_{90,3}$	6	0	L3w, L12w	normal	70.50	2.44	2.42	0.63
	$x_{95,3}$	6	0	L3w, L12w	normal	81.62	2.74	2.72	0.87
Optical microscopy	$x_{5,0}$	6	0	0	normal	12.38	2.75	2.71	1.15
	$x_{10,0}$	6	0	L4, L9	normal	15.83	2.76	2.71	1.18
	$x_{25,0}$	6	0	L4	normal	19.93	2.37	2.35	0.59
	$x_{50,0}$	6	0	0	normal	23.91	2.47	2.46	0.54
	$x_{75,0}$	6	0	0	normal	29.96	3.68	3.66	1.05
	$x_{90,0}$	6	0	0	normal	39.79	5.62	5.59	1.53
	$x_{95,0}$	6	0	0	normal	45.72	7.34	7.30	2.02

Laboratory 1, dry method, Fraunhofer approximation, was flagged as outlying mean on a 99 % confidence level. The value is about 1 µm below those of the other instruments and is also highly repeatable. One explanation could be the use of the autosampler, which delivers highly precise masses of samples but only from a limited location of the sample (whereas other systems automatically mix the sample). This could mean that the sampling was not representative. However, the results agree for all other percentiles with all other results, so the instrument clearly delivers comparable results with the other instruments in the study. The results were therefore retained.

Several datasets for laser diffraction do not agree with the assigned values within the uncertainties stated by the laboratory. However, at that stage it must be borne in mind that the expanded uncertainties quoted often are significantly smaller than the limit for the repeatability standard deviation of results given in ISO 13320. These uncertainties are therefore presumably underestimated and the disagreement does not indicate significant technical differences.

Several datasets were flagged as outliers of variance. These mainly reflect the difference in repeatability obtained by the laboratories. As the data are within the repeatability limits given by ISO 13320, the data were retained.

The uncertainty of characterisation (u_{char}) has two contributions: The first one is due to the variation of laboratory means and is equivalent to the standard error of the mean of laboratory means. The second one is due to the differences between results from wet/dry measurements. This difference is only partly accounted for by the standard error of laboratory means, as the standard deviation is divided by the square root of 6 or 8 (number of datasets). The additional uncertainty $u_{rec,rel}$ was calculated as half-width of the rectangular distribution between the maximum and the minimum laboratory average wet/dry for each evaluation model as

$$u_{rec,rel} = \frac{|dry - wet|}{\bar{\bar{x}} \cdot 2 \cdot \sqrt{3}}$$ *Equation 7*

dry: mean of laboratory means using dry dispersion for the evaluation technique

wet: mean of laboratory means using wet dispersion for the evaluation technique

$\bar{\bar{x}}$: mean of all laboratory means

The uncertainty related to the characterisation is estimated as the standard error of the mean of laboratory means) combined with the uncertainty contribution reflecting the difference between wet and dry dispersion (Table 7).

Table 7: Uncertainty of characterisation for ERM-FD069. se: standard error. n.a. not applicable

	Measurand	*p*	Mean [µm]	*s* [µm]	*se* *[%]*	$u_{rec,\ rel}$ *[%]*	$u_{char,rel}$ [%]
Laser diffraction, Fraunhofer approximation	$x_{5,3}$	8	13.88	0.71	1.81	1.00	2.07
	$x_{10,3}$	8	17.44	0.50	1.01	0.97	1.40
	$x_{25,3}$	8	24.90	0.37	0.53	0.22	0.57
	$x_{50,3}$	8	36.78	0.42	0.41	0.05	0.41
	$x_{75,3}$	8	52.31	0.55	0.37	0.12	0.39
	$x_{90,3}$	8	68.62	1.17	0.60	0.23	0.65
	$x_{95,3}$	8	79.75	2.17	0.96	0.43	1.05
Laser diffraction, Mie theory	$x_{5,3}$	6	15.03	0.35	0.95	1.32	3.15
	$x_{10,3}$	6	18.06	0.39	0.88	0.91	2.01
	$x_{25,3}$	6	25.13	0.68	1.10	1.20	1.74
	$x_{50,3}$	6	36.73	1.19	1.32	0.71	1.45
	$x_{75,3}$	6	52.8	1.81	1.40	1.51	1.72
	$x_{90,3}$	6	70.50	2.44	1.41	1.44	2.25
	$x_{95,3}$	6	81.62	2.74	1.37	1.38	2.47
Optical microscopy	$x_{5,0}$	6	12.38	2.75	9.07	n.a.	9.07
	$x_{10,0}$	6	15.83	2.76	7.11	n.a.	7.12
	$x_{25,0}$	6	19.93	2.37	4.85	n.a.	4.85
	$x_{50,0}$	6	23.91	2.47	4.22	n.a.	4.22
	$x_{75,0}$	6	30.0	3.68	5.02	n.a.	5.01
	$x_{90,0}$	6	39.79	5.62	5.77	n.a.	5.77
	$x_{95,0}$	6	45.72	7.34	6.56	n.a.	6.55

7 Value Assignment

Certified, and additional information values were assigned.

Certified values are values that fulfil the highest standards of accuracy. Procedures at the JRC, Directorate F require generally pooling of not less than 6 datasets to assign certified values. Full uncertainty budgets in accordance with the 'Guide to the Expression of Uncertainty in Measurement' [3] were established.

Additional material information refers to values that were obtained in the course of the study. For example, results reported from only one or two laboratories or in cases where individual measurement uncertainty is high, would fall under this category.

7.1 Certified values and their uncertainties

The unweighted mean of the means of the accepted datasets as shown in Table was assigned as certified value for each parameter.

The assigned uncertainty consists of uncertainties relating to characterisation, u_{char} (Section 6), potential between-unit inhomogeneity, u_{bb} (Section 4.1), and potential degradation during transport, u_{sts}, and long-term storage, u_{lts} (Section 5). The uncertainty related to degradation during long-term storage was found to be negligible. These different contributions were combined to estimate the relative expanded uncertainty of the certified value ($U_{CRM,\ rel}$) with a coverage factor k given as:

$$U_{CRM,rel} = k \cdot \sqrt{u_{bb,rel}^2 + u_{sts,rel}^2 + u_{lts,rel}^2 + u_{char,rel}^2} \qquad \textit{Equation 8}$$

- u_{char} was estimated as described in Section 6.4.2
- u_{bb} was estimated as described in Section 4.1. The larger value estimated for dry or wet method was applied.
- u_{sts} and u_{lts} were estimated as described in section 5.3. The larger value estimated for dry or wet method was applied.

Applying the Welch-Satterthwaite equation [3] to calculate the effective number of degrees of freedom yields 8-20 for laser diffraction using Fraunhofer approximation and 5 for laser diffraction using Mie theory and optical microscopy. Therefore, a coverage factor k = 2 was applied for laser diffraction, Fraunhofer approximation and a coverage factor of k= 2.57 for laser diffraction, Mie theory and optical microscopy (corresponding to the student's t-table for a confidence level of 95 % and 5 degrees of freedom). The certified values and their uncertainties are summarised in Table 8.

Table 8: Certified values and their uncertainties for ERM-FD069

		Certified value [µm]	$u_{char, rel}$ [%]	$u_{bb, rel}$ [%]	$u_{sts, rel}$ [%]	U_{CRM} [1)] [µm]
Laser diffraction, Fraunhofer approximation	$x_{5,3}$	13.9	2.07	0.59	0.11	0.6
	$x_{10,3}$	17.4	1.40	0.40	0.08	0.4
	$x_{25,3}$	24.9	0.57	0.27	0.07	0.30
	$x_{50,3}$	36.8	0.41	0.35	0.07	0.4
	$x_{75,3}$	52.3	0.39	0.42	0.07	0.6
	$x_{90,3}$	68.6	0.65	0.19	0.13	0.9
	$x_{95,3}$	79.8	1.05	0.37	0.19	1.7
Laser diffraction, Mie theory	$x_{5,3}$	15.0	1.32	0.59	0.11	0.6
	$x_{10,3}$	18.1	0.91	0.40	0.08	0.5
	$x_{25,3}$	25.1	1.20	0.27	0.07	0.8
	$x_{50,3}$	36.7	1.45	0.35	0.07	1.5
	$x_{75,3}$	52.8	1.51	0.42	0.07	2.2
	$x_{90,3}$	70.5	1.44	0.19	0.13	2.7
	$x_{95,3}$	81.6	1.38	0.37	0.19	3.1
Optical microscopy	$x_{5,0}$	12.4	9.07	0.59	0.11	2.9
	$x_{10,0}$	15.8	7.12	0.40	0.08	2.9
	$x_{25,0}$	19.9	4.85	0.27	0.07	2.5
	$x_{50,0}$	23.9	4.22	0.35	0.07	2.6
	$x_{75,0}$	30	5.01	0.42	0.07	4
	$x_{90,0}$	40	5.77	0.19	0.13	6
	$x_{95,0}$	46	6.55	0.37	0.19	8

[1)] Expanded and rounded uncertainty, corresponding to a level of confidence of approximately 95 %

7.2 Additional material information

The data provided in this section should be regarded as informative only on the general composition of the material and cannot be, in any case, used as certified or indicative value.

Several participants also provided data for the mean volume-weighted mean diameter ($\bar{x}_{1,3}$.or $\overline{D}_{4,3}$). The average mean diameters of those laboratories accepted on technical ground were assigned as information values.

Table 9: Additional material information for the volume-weighted mean diameter. p: number of datasets.

	Laser diffraction, Mie theory		Laser diffraction, Fraunhofer approximation	
	p	Value [µm]	p	Value [µm]
$\bar{x}_{1,3}$	4	41.3	8	40.5

Participants were also asked to convert the volume based distribution obtained by laser diffraction into number based ones. The results show a clear difference between results from application of the Mie theory and applying the Fraunhofer approximation, especially for measurement in liquid suspensions (see Annex E). The average of the technically accepted data from wet dispersion, applying Mie theory was adopted as information value.

Two datasets from dynamic image analysis were obtained from two laboratories using the following instruments: Qicpic (Sympatec GmbH, Clausthal-Zellerfeld, DE) and Occhio Morpho 3D (Occhio s.a., Angleur, BE). The range of the two results was adopted as additional information.

The additional information values are summarised in Table 10.

Table 10: Information values for ERM-FD069

Equivalent diameter laser diffraction, wet method, application of Mie theory		Equivalent diameter dynamic image analysis	
	Diameter[1)] [µm]		Diameter[2)] [µm]
$x_{5,0}$	10.1	$x_{5,3}$	11.8-12.9
$x_{10,0}$	11.0	$x_{10,3}$	15.2-15.7
$x_{25,0}$	13.1	$x_{25,3}$	19.1-22.7
$x_{50,0}$	17.0	$x_{50,3}$	26.6-33.8
$x_{75,0}$	23.1	$x_{75,3}$	39.1-47.9
$x_{90,0}$	31.5	$x_{90,3}$	49.8-61.6
$x_{95,0}$	38.2	$x_{95,3}$	56.4-70.8

1) as obtained by following ISO 13320 applying Mie theory
2) as obtained by applying dynamic image analysis.

8 Metrological traceability and commutability

8.1 Metrological traceability

Identity

The certified parameters are method-defined measurands and can only be obtained by following the ISO 13320 (laser diffraction) or ISO 13322 (static image analysis). Adherence to this procedure was confirmed by agreement of the laboratories' results with the assigned value for the CRM that was used as quality control sample. The measurands are therefore operationally defined by the respective methods.

Quantity value

Traceability of the obtained results is based on the traceability of all relevant input factors. Investigation of the method and measurement details of the individual results shows that all relevant input parameters of each technically accepted dataset have been properly calibrated. All technically accepted datasets are therefore traceable to the same reference, namely the International System of Units (SI). This traceability to the same reference is also confirmed by the agreement of results within their respective uncertainties. As the assigned values are combinations of agreeing results individually traceable to the SI, the assigned quantity values themselves are traceable to the SI as well.

8.2 Commutability

Many measurement procedures include one or more steps which select specific (or specific groups of) analytes from the sample for the subsequent whole measurement process. Often the complete identity of these 'intermediate analytes' is not fully known or taken into account. Therefore, it is difficult to mimic all analytically relevant properties of real samples within a CRM. The degree of equivalence in the analytical behaviour of real samples and a CRM with respect to various measurement procedures (methods) is summarised in a concept called 'commutability of a reference material'. There are various definitions that define this concept. For instance, the CLSI Guideline C53-A [14] recommends the use of the following definition for the term *commutability*:

> "The equivalence of the mathematical relationships among the results of different measurement procedures for an RM and for representative samples of the type intended to be measured."

The commutability of a CRM defines its fitness for use and is therefore a crucial characteristic when applying different measurement methods. When the commutability of a CRM is not established, the results from routinely used methods cannot be legitimately compared with the certified value to determine whether a bias does not exist in calibration, nor can the CRM be used as a calibrant.

ERM-FD069 was produced from a commercial corundum material. The analytical behaviour will be the same as for a routine sample of corundum or similar hard materials, but the behaviour may differ from soft, biological materials.

9 Instructions for use

9.1 Safety information

The usual laboratory safety measures apply.

9.2 Storage conditions

The materials should be stored at (18 ± 5) °C. The user should close any bottles immediately after taking a sub-sample.

Please note that the European Commission cannot be held responsible for changes that happen during storage of the material at the customer's premises, especially for opened bottles.

9.3 Preparation and use of the material

Before opening a bottle, the bottle must be gently inverted several times to ensure the homogeneity of the powder. Take several sub-samples at different depths, typically top, middle and bottom of the bottle, using spatula or special sampler device (using rotating/spinning riffler).

For laser diffraction in compressed air, sub-samples should be mixed and shacked in a separate container and then the sample can be introduced in the dry dispersing system of the laser diffraction instrument.

Suspensions are prepared preferably with deionised water with addition of a surfactant like 0.1 mol/L $Na_4P_2O_7$ or isopropanol.

For optical measurements, measure at least 5000 particles.

9.4 Minimum sample intake

The minimum sample intake representative for all parameters is 100 mg (laser diffraction) and 7 mg (optical microscopy). At least 5000 particles must be counted for optical microscopy

9.5 Use of the certified value

The main purpose of these materials is to assess method performance, i.e. for checking accuracy of analytical results/calibration.

Comparing an analytical result with the certified value

A result is unbiased if the combined standard uncertainty of measurement and certified value covers the difference between the certified value and the measurement result (see also ERM Application Note 1, www.erm-crm.org [15].

When assessing the method performance, the measured values of the CRMs are compared with the certified values. The procedure is summarised here:

- Calculate the absolute difference between mean measured value and the certified value (Δ_{meas}).
- Combine the measurement uncertainty (u_{meas}) with the uncertainty of the certified value (u_{CRM}): $u_{\Delta} = \sqrt{u_{meas}^2 + u_{CRM}^2}$

- Calculate the expanded uncertainty (U_{Δ}) from the combined uncertainty ($u_{\Delta,}$) using an appropriate coverage factor, corresponding to a level of confidence of approximately 95 %
- If $\Delta_{meas} \leq U_{\Delta}$ then no significant difference exists between the measurement result and the certified value, at a confidence level of approximately 95 %.

Use in quality control charts

The materials can be used for quality control charts. Using CRMs for quality control charts has the added value that a trueness assessment is built into the chart.

10 Acknowledgments

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Annex A: Results of the homogeneity measurements

Annex B: Results of the short-term stability measurements

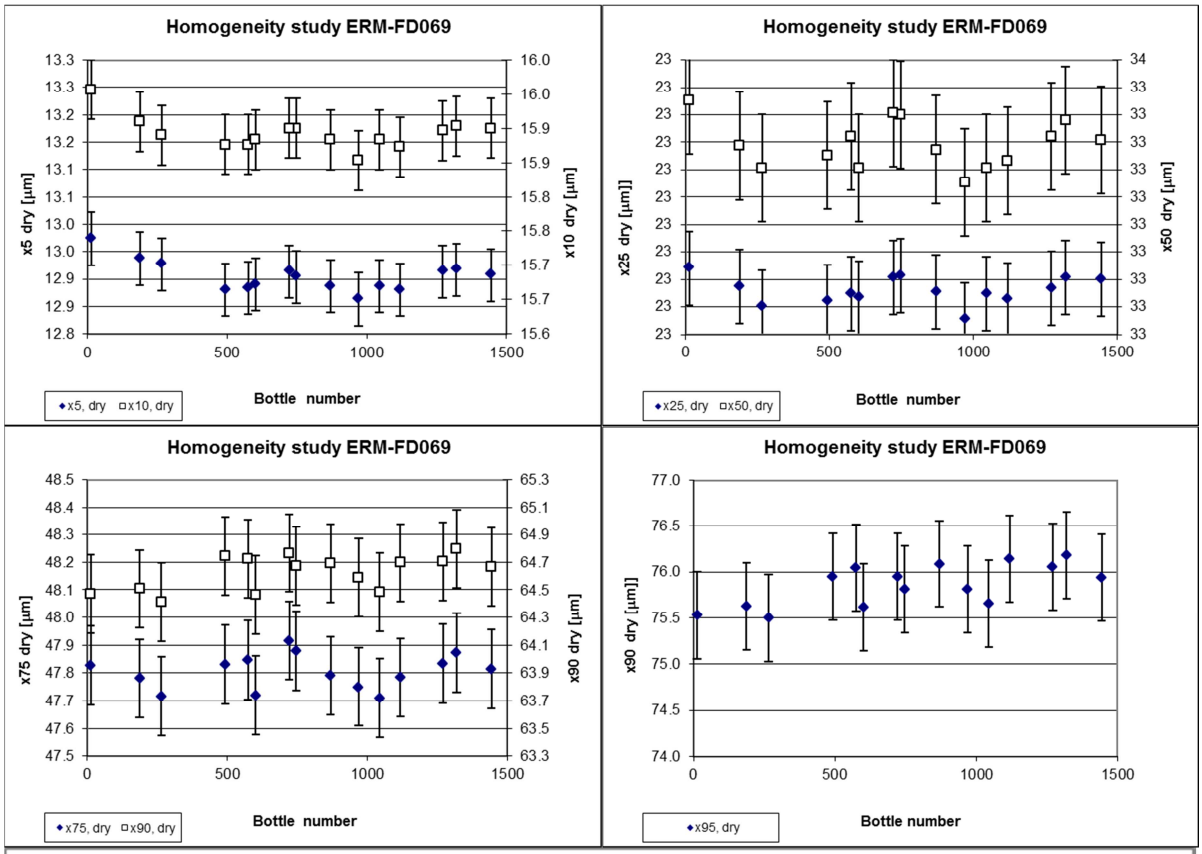
Annex C: Summary of methods used in the characterisation study

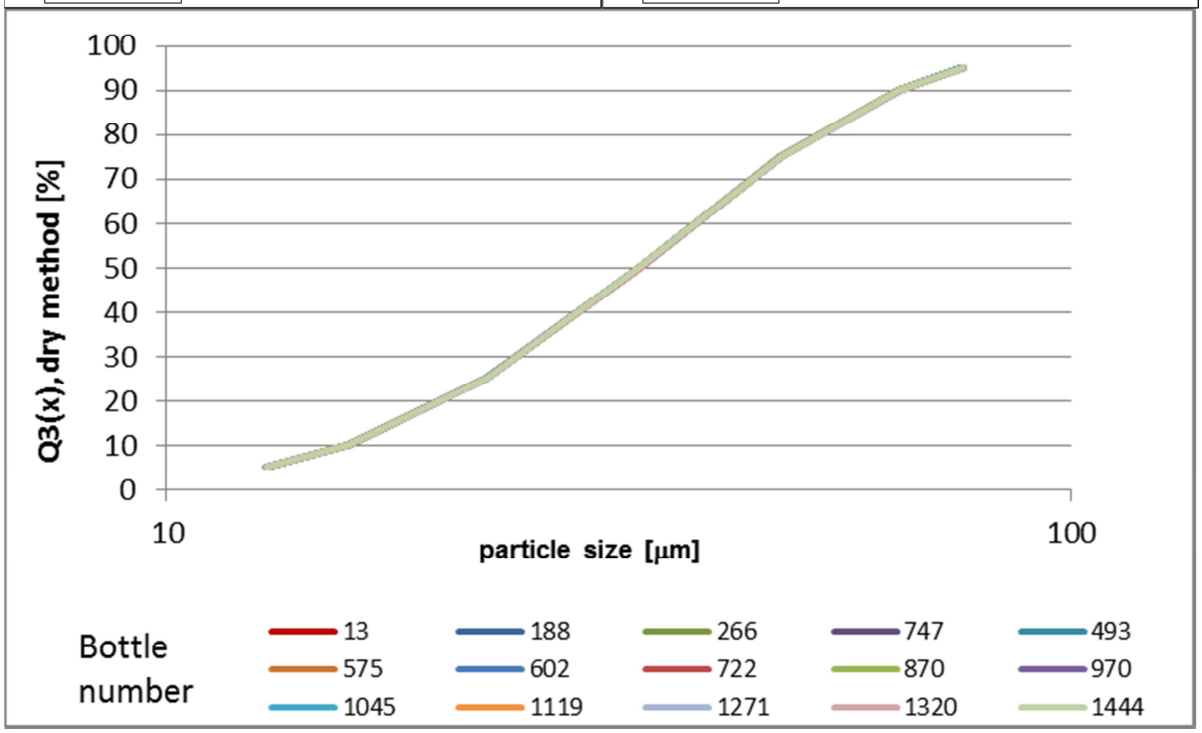
Annex D: Results of the characterisation measurements

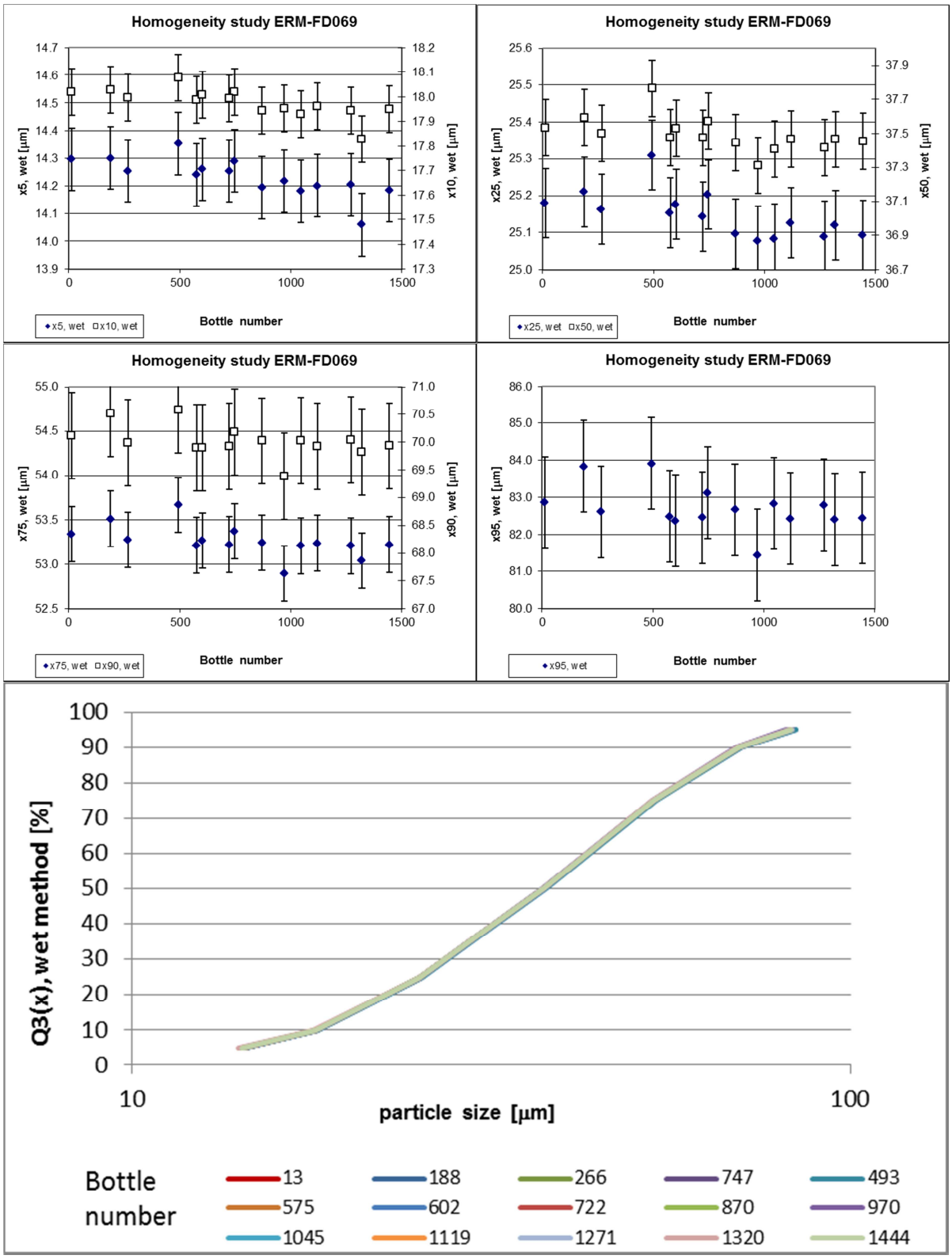
Annex E: Results for number based distribution and dynamic image analysis

Annex A: Results of the homogeneity study

Shown are the average percentiles for each bottle. The error bars represent the 95 % confidence interval of the percentile for each bottle, based on the within-bottle standard deviation as obtained from ANOVA. Also given is one graph compiling all cumulative distributions Q3(x) of all bottles (the individual lines overlap, giving the impression of a single line).

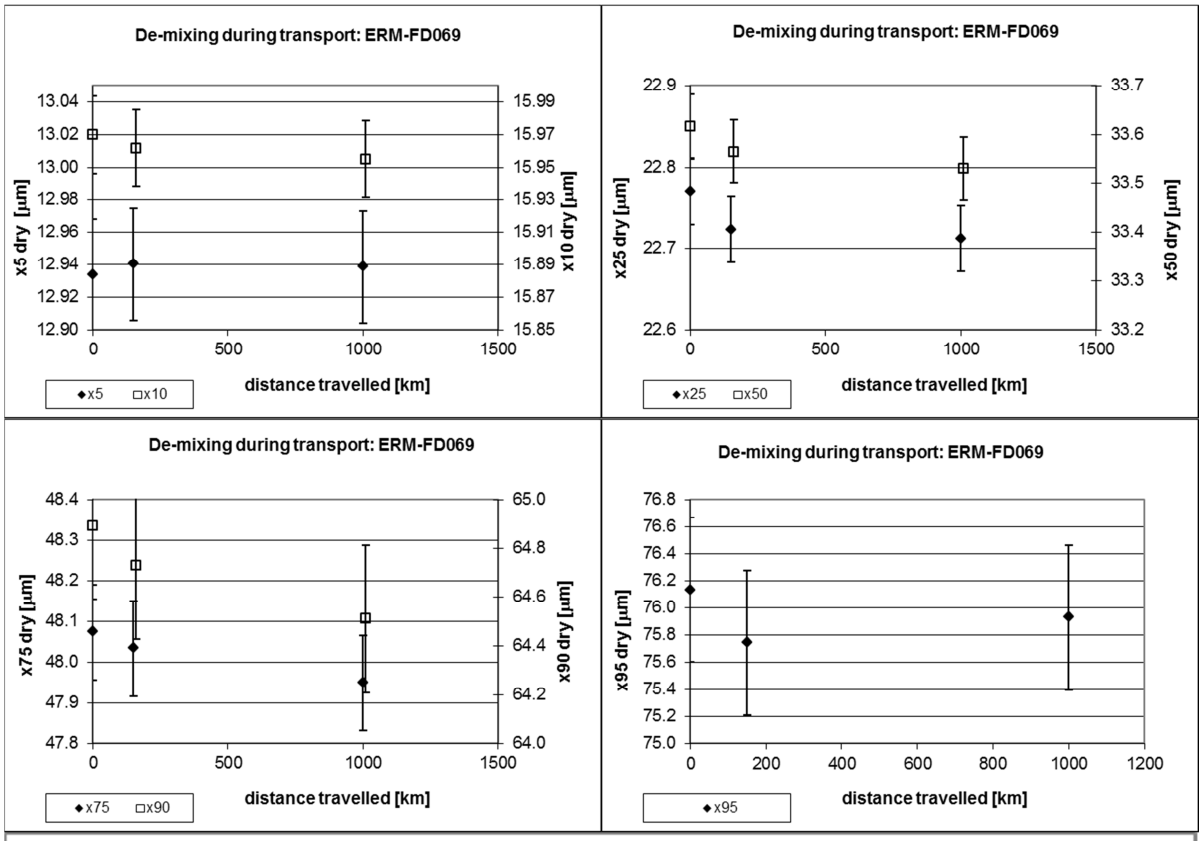


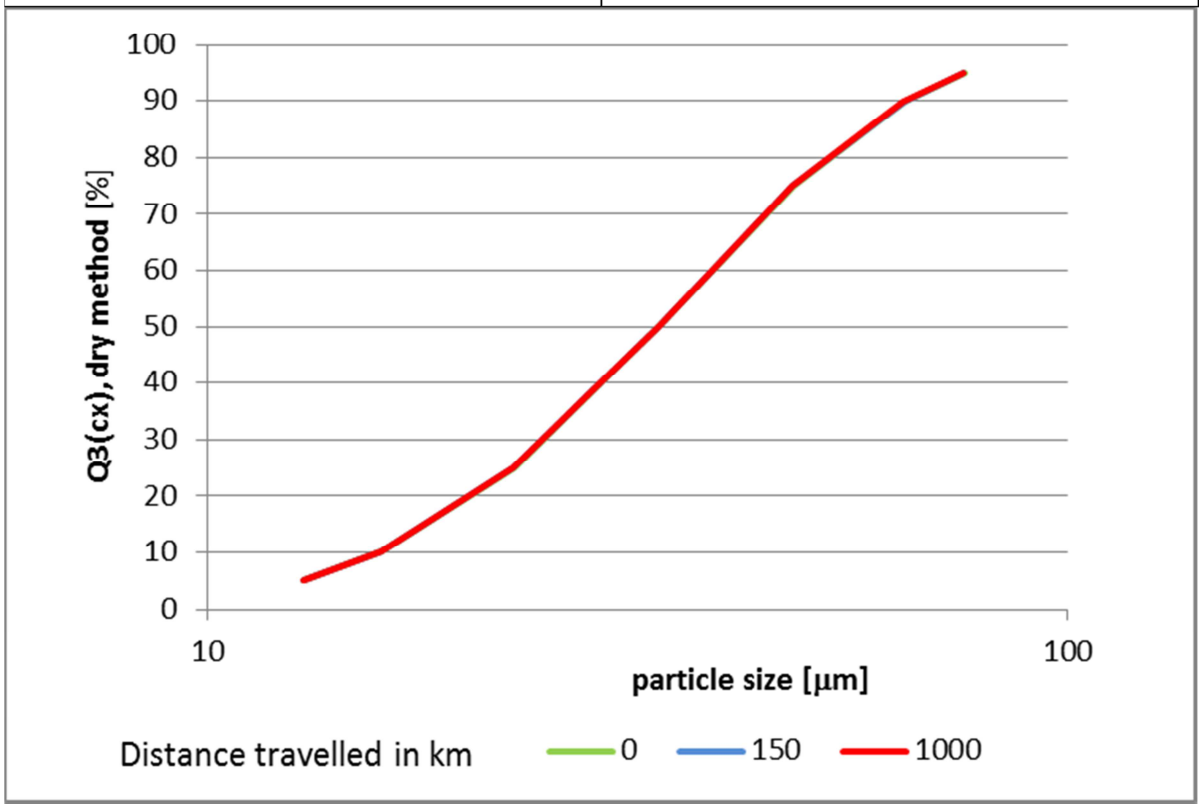


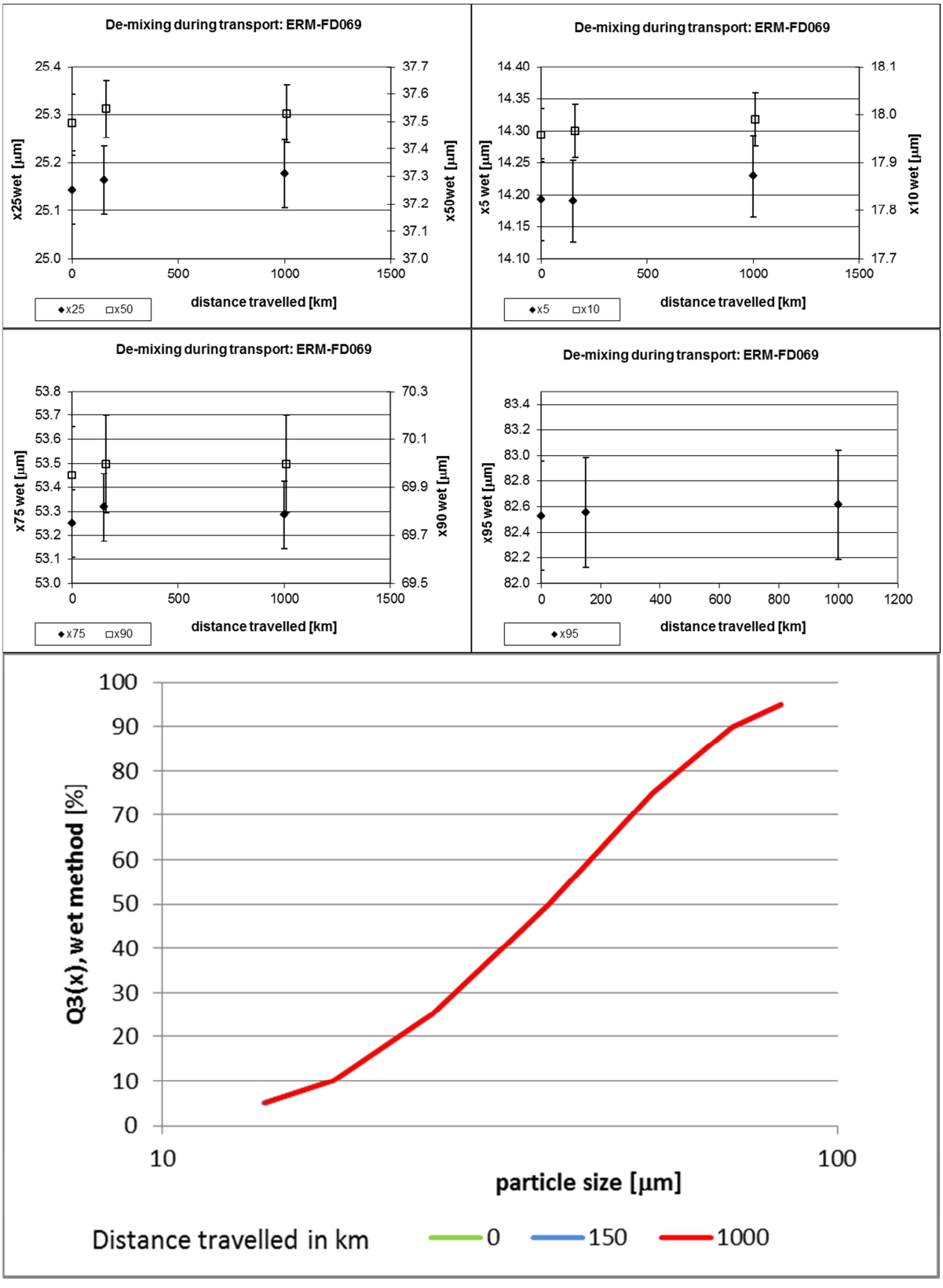

Homogeneity study ERM-FD069
x5, wet [µm]
x10, wet [µm]
x5, wet
x10, wet
Bottle number
Homogeneity study ERM-FD069
x25, wet [µm]
x50, wet [µm]
x25, wet
x50, wet
Bottle number
Homogeneity study ERM-FD069
x75, wet [µm]
x90, wet [µm]
x75, wet
x90, wet
Bottle number
Homogeneity study ERM-FD069
x95, wet [µm]
x95, wet
Bottle number
Q3(x), wet method [%]
particle size [µm]
Bottle number
13
188
266
747
493
575
602
722
870
970
1045
1119
1271
1320
1444

Annex B: Results of the short-term stability study

Shown are the average percentiles for each bottle. The error bars represent the 95 % confidence interval of the percentile for the mean for each travel conditions, based on the repeatability standard deviation over all results. Also given is one graph compiling all cumulative Q3(x) of all bottles (the individual lines overlap, giving the impression of a single line).






De-mixing during transport: ERM-FD069
x25wet [µm]
x50wet [µm]
distance travelled [km]
x25
x50
De-mixing during transport: ERM-FD069
x5 wet [µm]
x10 wet [µm]
distance travelled [km]
x5
x10
De-mixing during transport: ERM-FD069
x75 wet [µm]
x90 wet [µm]
distance travelled [km]
x75
x90
De-mixing during transport: ERM-FD069
x95 wet [µm]
distance travelled [km]
x95
Q3(x), wet method [%]
particle size [µm]
Distance travelled in km
0
150
1000

Annex C: Methods used by the participants

Annex C1: Method description for laser diffraction, Fraunhofer approximation

Laboratory Code	Sample preparation	Instrument	Verification	Evaluation
L1 wet	The samples were shaken thoroughly to ensure homogenisation. About 2 g sample was dispersed in isopropanol	Wet disperser QUIXEL HELOS H1933(Sympatec), lens R4 (measurement range 0.5-350 µm)		Laser: 632.8 nm Evaluation: Fraunhofer
L1 dry	Dispersion pressure: 1.0 bar Sample intake: 0.3 g	Dry dispersion system RODOS with Feeder VIBR/L (Sympatec) HELOS H1933(Sympatec)		Laser: 632.8 nm Measurement range 01. µm – 350 µm Evaluation: Fraunhofer
L2 wet	The sample was inverted several times; 0.5 mL 2 % Novachem was added to about 100 mg of powder. The suspension was shaken. Before measuring, the suspension was placed in an ultrasonic bath for 1 min.	Universal Liquid Module (Beckmann) Beckmann Coulter LS13 320	Regular maintenance and performance check; latest check 20 d before the measurements	Laser: 780 nm Measurement range: 0.4 µm – 2000 µm Evaluation: Fraunhofer
L2 dry	The sample was inverted several times; subsamples were taken at different depths of the bottle using a spatula Sample intake: 4 g	Tornado Dry Powder System Coulter LS13320	Regular maintenance and performance check; latest check 20 d before the measurements	Laser: 780 nm Measurement range: 0.4 µm – 2000 µm Evaluation: Fraunhofer

Laboratory Code	Sample preparation	Instrument	Verification	Evaluation
L7 wet	Sample dispersed in water The sample was sonicated for 30 sec and stirred while measured	Wet disperser QUIXEL HELOS H1933(Sympatec); lens R3 (0.5-175 µm)	Inhouse QCM used for every new analysis request. Sympatec OCM every 6 months	Laser: 632.8 nm Evaluation: Fraunhofer
L8 dry	Sample was gently inverted and rotated 10 times. Several sub-samples were taken from the top, middle and bottom of the bottle (total 1 g). Sample intake: 1 g Dispersion pressure: 1 bar	Sirocco 2000 dispersion unit Malvern Mastersizer 2000 LF	Performance check/calibration on the day of the measurement.	Laser: 632 nm and 466 nm Measurement range: 0.4 µm – 2000 µm Evaluation: Fraunhofer
L9 dry	Sample was taken with a spatula	Beckmann coulter dry powder system Beckmann-Coulter 133-20	One month before the tests	Laser: 750 nm Evaluation: Fraunhofer
L9 wet	Approximately 0.01 g was suspended in water of pH 9.5. A paste was produced by adding 4 % $Na4P_2O_7$ (5 µL). The sample was transferred to the measurement cell containing de-ionised water adjusted to pH 9.5.	Micro Liquid Module Beckmann Coulter LS13 320	Performance check 2 weeks before the measurements	Laser 750 nm Evaluation: Fraunhofer

Laboratory Code	Sample preparation	Instrument	Verification	Evaluation
L13 wet	The bottle was turned 10 times. The sample is split on a rotary divider into subsamples of a few g and then split by cone and quartering technique to about 100 mg. Approx. 200 mg sample are turned into a paste by adding 2 drops of 0.1 mol/L $Na_4P_2O_7$. The whole sample is added to the dispersion unit and subjected to sonication,	Hydro 2000S sample system Malvern Mastersizer 2000	Performance check one week before the measurements	Laser: 632 nm and 466 nm Evaluation: Fraunhofer
L14 dry	Dispersion pressure: 1.05 bar	Dry dispersion system RODOS with Feeder VIBR/L (Sympatec) HELOS (Sympatec)	PSL standards, ThermoScientific (3800A, 5205A, DC-05) and SiC P600 (x75=27 µm)	Laser: 632.8 nm Measurement range: 0.1 µm – 40 µm Evaluation: Fraunhofer

Annex C2: Method description for laser-diffraction, Mie theory

Laboratory Code	Sample preparation	Instrument	Verification	Evaluation
L3 wet	Each bottle was split into 8 fractions using a micro riffler (Quantachrome). Three of these fractions were measured as independent subsample. The fraction was dispersed in 40 mL isopropanol and placed in an ultrasonic bath for 3 minutes. Of this dispersion, approximately 5 mL were transferred into the small volume dispersion unit filled with isopropanol.	Small volume dispersion unit DIF2022 Malvern Mastersizer APA 2000	In-house QCM used monthly	Laser: 632 nm and 466 nm Evaluation: Mie theory
L3 dry	Each bottle was split into 8 fractions using a micro riffler (Quantachrome). Three of these fractions were measured as independent subsample. Sample intake: 5 g Dispersion pressure: 1 bar.	Sirocco 2000 dispersion unit Malvern Mastersizer APA 2000	In-house QCM used monthly	Laser: 632 nm and 466 nm Evaluation: Mie theory

Laboratory Code	Sample preparation	Instrument	Verification	Evaluation
L6 wet	Samples were gently inverted before putting them into a micro spinning riffler (Microscal SR1AB) with 20 segments. One segment (0.6-1.0 g) formed one subsample. The sample was dispersed in 20 mL de-ionised water and ultrasonicated for 1 min (3 replicates) or stirred manually (the other 3 replicates). 15-20 drops of the sample were added to the dispersion cell	Hydro MV dispersion cell Malvern Mastersizer 3000	Performance check before the measurements	Laser: 632.8 nm Evaluation: Mie theory
L6 dry	Dispersion pressure: 1 bar	Mastersizer 3000 Aero S Malvern Mastersizer 3000	Performance check before the measurements	Laser: 632.8 nm Evaluation: Mie theory
L10 wet	The bottle was several times inverted. Sub-samples of the material were taken from the top, middle and bottom of the bottle (1 g each). The sample was dispersed in 30 mL ultrapure water containing 0.1 mol/L $Na_4P_2O_7$ and sonicated for 30 min.	Malvern Mastersizer 2000	PSL CRMs from Thermo; diameter = 3 μm	Laser: 632 nm and 466 nm Evaluation: Mie theory
L11 wet	About 0.2 g of sample was take from different depths and were dispersed in 0.1 mol/L $Na_4P_2O_7$ solution until a laser obscuration of 6 % was obtained. The sample was sonicate for 1 min and stirred with a maximum speed of 3500 rpm	Hydro 2000S dispersing device (Malvern) Malvern Mastersizer 2000	Performance check 4 months before the measurements	Laser: 632 nm and 466 nm Evaluation: Mie theory

Laboratory Code	Sample preparation	Instrument	Verification	Evaluation
L12 wet	The sample was divided into 8 samples of 5.3 g using a cross-riffler. 1 Sample was selected and divided again, to yield 8 samples of 0.6 g. Concentrated suspensions were prepared by mixing the sample with 40 mL 3 mmol $Na_4P_2O_7$. The concentrated suspension was added to 950 mL 3 mmol $Na_4P_2O_7$ and a further 10 mL were4 used to rinse the glass bottle. The sample was ultrasonicated for 10 s before measurement	Mastersizer 3000 Hydro EV Malvern Mastersizer 3000	not given	Laser: 632.9 and 470 Evaluation: Mie

Annex C3: Method description for optical microscopy measurements

Laboratory Code	Sample preparation	Instrument	Calibration	Evaluation
L3	Samples are tumbled 10 times and aliquots are taken with a special spatula. Sample intake: 0.3 mm^3	Malvern Morphologi G3Se	4 gratings traceable to NIST and NPL CRMs	Magnification: 494 x 15000-48000 particles counted Software: Malvern Morphologi G3Se

Laboratory Code	Sample preparation	Instrument	Calibration	Evaluation
L4	The bottle was inverted and rolled several times. Subsamples from top, middle and bottom were transferred to a glass vial and mixed. A representative subsample was placed on a freshly cleaned microscope slide, mounted in glycerol and gently dispersed with a tungsten needle.	Olympus BHSP polarized light microscope with Jenoptik ProRes C3 digital camera	Micrometer scale traceable to NIST CRMs	Magnification: 40 x 5103-5412 particles counted Software: ImageJ
L5	Three subsamples at different depths (top, middle and bottom of the bottle) were taken, mixed and a dispersion liquid was added to prepare a paste according to ISO 14887. The paste was diluted andand a drop was placed on an ethanol-cleaned glass slide. The particles were allowed to settle for 1 hour, then the drop was covered with ethanol-cleaned cover glass for imaging.	Mitutoyo reflection optical microscope with Pixelink camera	NIST SRM 2800 (microscope magnification standard)	Magnification: 5 x 5036-5658 particles measured Software: ImageJ 1.48
L8	7-8 mg powder was prepared in an Eppendorf tube and dispersion liquid was added. The suspensions were gently agitated and one drop (approximately 0.2 mL) was spread as a monolayer on a microscope slide and covered with a cover glass.	Leica DM6000 with ProgRes CFscan CCD camera In bright field mode	Calibration plate with fixed diameters (200-1000 μm)	Magnification: 5 x 5017-5706 particles counted Software: Imagic V14
L9	The sample was homogenised by shaking and inverting the bottle several times. Subsamples at different depths (top, middle and bottom of the bottle) were transferred into a clean vial. 11 mm^3 were taken with a special spatula and transferred to the dispenser of the Malvern Morphology G3 particle analyser system. Using pressurised air, the sample was dispersed.	Microscope Keyence VHX 700 F, zoom lens VH-Y100 In brightfield mode	Object micrometre OP-87657	Magnification: 300 5002-5107 particles counted Software: Olympus iTEM 5.2

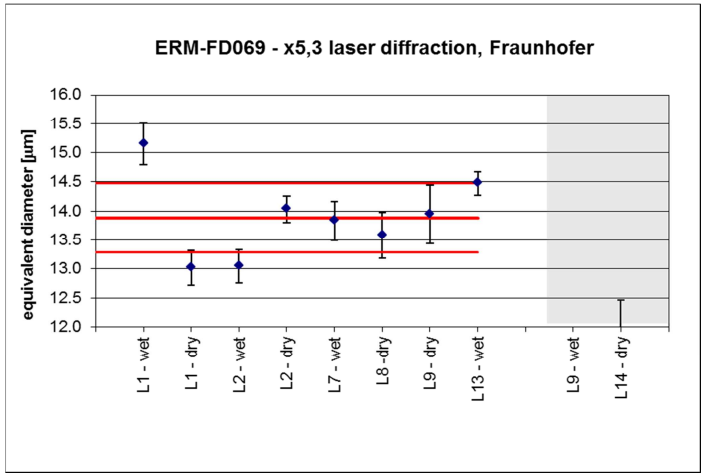
Laboratory Code	Sample preparation	Instrument	Calibration	Evaluation
L10	Samples were inverted several times before taking subsamples. 3 subsamples (approx. 1 g each) were taken from top, middle and bottom of the bottle and mixed. 100 µL non-drying immersion oil was put on a slide and 0.1 g of the sample was put onto the droplet of immersion oil.	Olympus BC51 With Canon EOS 600D camera	Certified micrometre (400 µm)	Magnification: 10 x 5032-5169 particles counted Software: ImageJ

Annex D: Individual results of the characterisation study

Uncertainties in the graphs are expanded uncertainties as reported by the laboratories. Frau: evaluation by the Fraunhofer approximation; Mie: Evaluation by Mie theory.

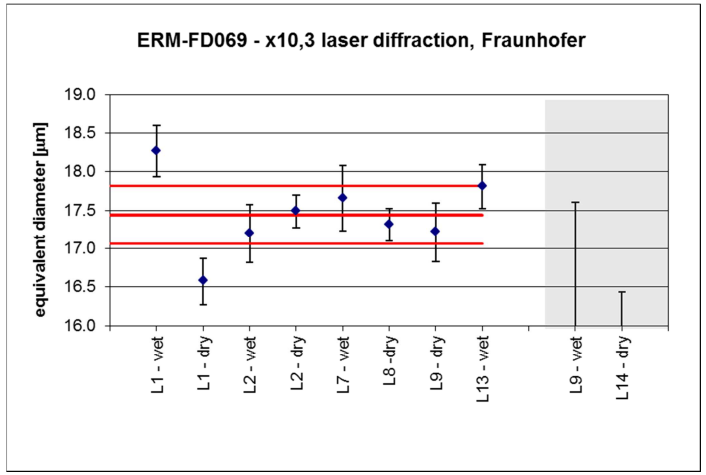
Laser diffraction Fraunhofer approximation $x_{5,3}$

Laboratory code -model	rep. 1 [µm]	rep. 2 [µm]	rep. 3 [µm]	rep. 4 [µm]	rep. 5 [µm]	rep. 6 [µm]	mean [µm]	U [%]
L1 - wet	14.62	15.13	15.03	15.47	15.31	15.34	15.15	2.4
L1 - dry	13.17	12.88	12.84	13.16	13.11	12.96	13.02	2.4
L2 - wet	13.08	12.98	13.11	12.78	13.04	13.26	13.04	2.2
L2 - dry	12.10	14.23	14.61	14.38	14.53	14.34	14.03	1.6
L7 - wet	13.92	13.68	13.93	13.75	13.89	13.82	13.83	2.4
L8 -dry	13.93	14.03	13.98	12.82	13.26	13.46	13.58	2.9
L9 - dry	14.02	14.01	13.88	13.89	14.04	13.85	13.94	3.6
L13 - wet	14.65	14.66	14.58	13.49	14.33	15.13	14.47	1.4
Data not used for value assignment (grey area in graph)								
L9 - wet	9.72	11.23	11.20	4.56	6.33	10.51	8.93	8.6
L14 - dry	12.10	11.80	12.10	11.65	11.58	11.85	11.85	5.2



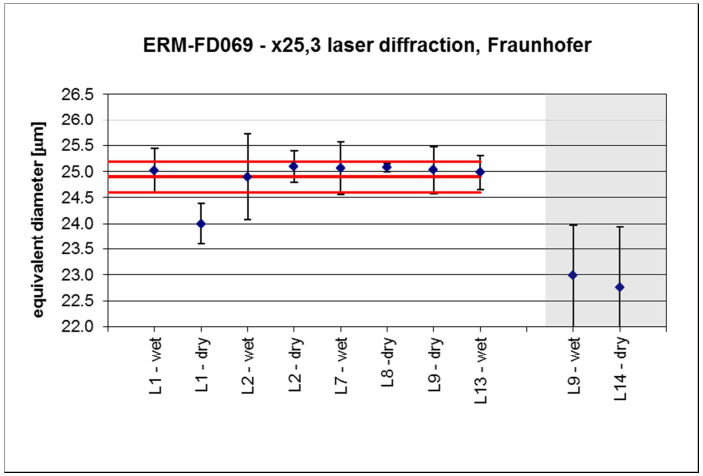
Laser diffraction Fraunhofer approximation: $x_{10,3}$

Laboratory code -model	rep. 1 [µm]	rep. 2 [µm]	rep. 3 [µm]	rep. 4 [µm]	rep. 5 [µm]	rep. 6 [µm]	mean [µm]	U [%]
L1 - wet	17.94	18.24	18.11	18.51	18.37	18.41	18.26	1.8
L1 - dry	16.78	16.40	16.33	16.74	16.70	16.50	16.58	1.8
L2 - wet	17.18	17.04	17.19	16.98	17.25	17.55	17.20	2.2
L2 - dry	16.22	17.44	17.99	17.73	17.87	17.65	17.48	1.2
L7 - wet	17.74	17.50	17.74	17.57	17.72	17.66	17.66	2.4
L8 -dry	17.47	17.57	17.52	16.91	17.14	17.25	17.31	1.2
L9 - dry	17.55	17.54	17.37	17.39	17.56	15.88	17.21	2.2
L13 - wet	18.01	18.05	17.95	17.04	17.63	18.17	17.81	1.6
Data not used for value assignment (grey area in graph)								
L9 - wet	15.50	16.44	16.20	13.89	14.55	16.06	15.44	14.0
L14 - dry	15.71	15.54	15.88	15.50	15.38	15.76	15.63	5.2



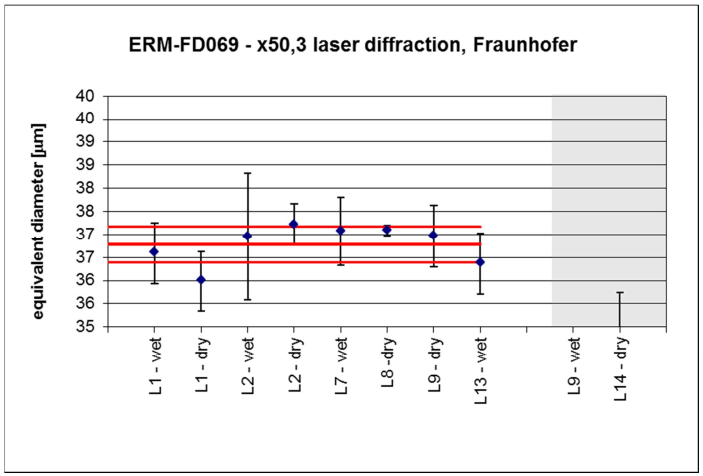
Laser diffraction Fraunhofer approximation: $x_{25,3}$

Laboratory code -model	rep. 1 [µm]	rep. 2 [µm]	rep. 3 [µm]	rep. 4 [µm]	rep. 5 [µm]	rep. 6 [µm]	mean [µm]	U [%]
L1 - wet	24.79	25.07	24.81	25.25	25.10	25.13	25.03	1.7
L1 - dry	24.37	23.78	23.63	24.19	24.13	23.86	23.99	1.7
L2 - wet	24.84	24.58	24.84	24.58	24.94	25.63	24.90	3.3
L2 - dry	24.21	24.75	25.66	25.37	25.46	25.15	25.10	1.2
L7 - wet	25.14	24.87	25.15	24.98	25.13	25.12	25.07	2.0
L8 -dry	25.07	25.20	25.13	24.95	25.02	25.07	25.07	0.3
L9 - dry	24.93	25.23	24.85	24.99	25.21	25.01	25.03	1.8
L13 - wet	25.31	25.37	25.23	24.19	24.71	25.07	24.98	1.3
Data not used for value assignment (grey area in graph)								
L9 - wet	22.46	24.07	23.42	22.16	22.12	23.67	22.98	4.3
L14 - dry	22.73	22.59	23.07	22.64	22.60	22.90	22.76	5.2



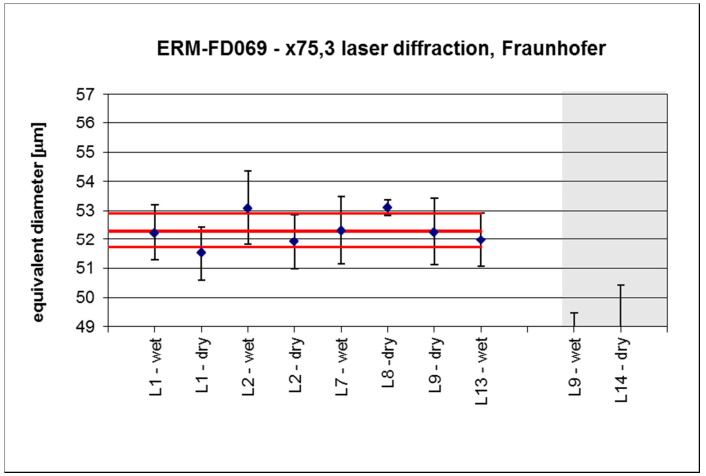
Laser diffraction Fraunhofer approximation: $x_{50,3}$

Laboratory code -model	rep. 1 [µm]	rep. 2 [µm]	rep. 3 [µm]	rep. 4 [µm]	rep. 5 [µm]	rep. 6 [µm]	mean [µm]	U [%]
L1 - wet	36.45	36.77	36.30	36.79	36.62	36.64	36.59	1.8
L1 - dry	36.65	35.73	35.50	36.22	36.07	35.74	35.99	1.8
L2 - wet	36.84	36.35	36.77	36.37	37.21	38.18	36.95	3.7
L2 - dry	36.74	36.50	37.86	37.56	37.51	37.10	37.21	1.2
L7 - wet	37.16	36.75	37.14	36.95	37.16	37.24	37.07	2.0
L8 -dry	36.89	37.09	37.00	37.18	37.16	37.18	37.08	0.3
L9 - dry	37.06	37.19	36.69	36.86	37.13	36.83	36.96	1.8
L13 - wet	36.93	37.02	36.84	35.30	35.91	36.21	36.37	1.8
Data not used for value assignment (grey area in graph)								
L9 - wet	32.29	35.47	34.08	33.17	32.25	34.71	33.66	2.4
L14 - dry	33.35	33.74	34.00	33.95	34.40	34.40	33.97	5.2



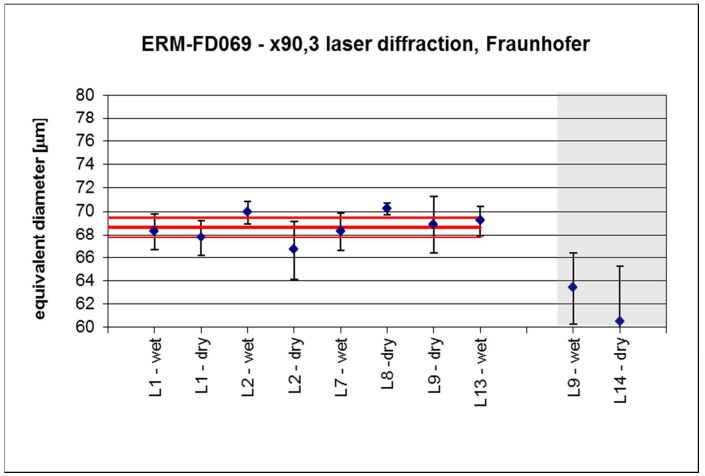
Laser diffraction Fraunhofer approximation: $x_{75,3}$

Laboratory code -model	rep. 1 [µm]	rep. 2 [µm]	rep. 3 [µm]	rep. 4 [µm]	rep. 5 [µm]	rep. 6 [µm]	mean [µm]	U [%]
L1 - wet	52.45	52.66	51.93	52.24	52.13	52.07	52.25	1.8
L1 - dry	52.43	51.27	50.99	51.79	51.51	51.14	51.52	1.8
L2 - wet	53.09	52.47	52.78	52.60	53.38	54.22	53.09	2.4
L2 - dry	51.95	50.65	52.73	52.26	52.15	51.82	51.93	1.8
L7 - wet	52.39	51.82	52.35	52.22	52.38	52.76	52.32	2.2
L8 -dry	52.64	52.95	52.84	53.45	53.35	53.36	53.10	0.5
L9 - dry	52.28	52.62	51.89	52.31	52.51	52.00	52.27	2.2
L13 - wet	52.89	52.99	52.77	50.48	51.27	51.58	52.00	1.8
Data not used for value assignment (grey area in graph)								
L9 - wet	46.28	50.90	48.47	48.32	46.20	49.78	48.33	2.4
L14 - dry	46.10	47.53	47.22	47.90	49.00	47.70	47.58	6.0



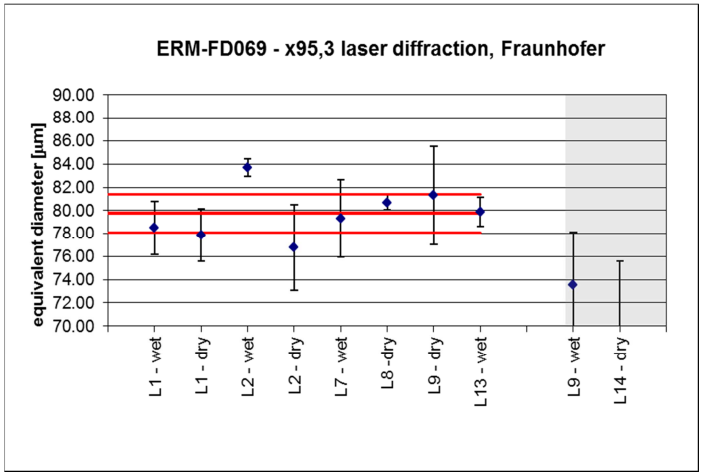
Laser diffraction Fraunhofer approximation: $x_{90,3}$

Laboratory code -model	rep. 1 [µm]	rep. 2 [µm]	rep. 3 [µm]	rep. 4 [µm]	rep. 5 [µm]	rep. 6 [µm]	mean [µm]	U [%]
L1 - wet	69.12	69.10	67.96	67.78	67.83	67.65	68.24	2.3
L1 - dry	68.41	67.61	67.41	67.85	67.55	67.42	67.71	2.3
L2 - wet	69.54	69.62	69.44	70.04	70.01	70.77	69.90	1.4
L2 - dry	67.80	63.46	67.96	67.11	66.83	66.61	66.63	3.8
L7 - wet	68.21	67.55	68.23	68.38	68.09	69.05	68.25	2.4
L8 -dry	69.42	69.87	69.73	70.85	70.70	70.70	70.21	0.7
L9 - dry	68.41	69.78	68.08	68.92	69.48	68.33	68.83	3.6
L13 - wet	70.32	70.43	70.20	67.21	68.25	68.72	69.19	1.8
Data not used for value assignment (grey area in graph)								
L9 - wet	60.55	67.11	63.50	63.26	60.11	65.42	63.33	4.8
L14 - dry	60.00	60.08	59.99	61.10	61.00	60.30	60.41	8.0

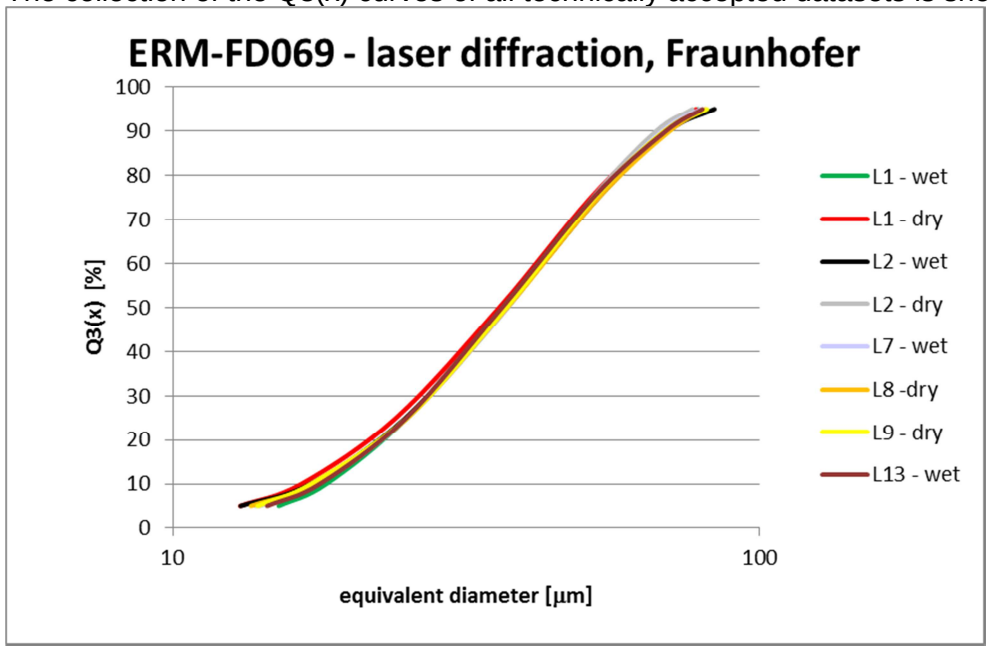


Laser diffraction Fraunhofer approximation: $x_{95,3}$

Laboratory code -model	rep. 1 [µm]	rep. 2 [µm]	rep. 3 [µm]	rep. 4 [µm]	rep. 5 [µm]	rep. 6 [µm]	mean [µm]	U [%]
L1 - wet	80.32	80.16	78.08	77.50	77.64	77.26	78.49	2.9
L1 - dry	78.52	77.93	77.71	77.86	77.46	77.65	77.86	2.9
L2 - wet	83.38	83.84	83.35	84.04	83.39	84.21	83.70	0.9
L2 - dry	81.03	71.18	78.89	77.11	76.29	76.20	76.78	4.8
L7 - wet	79.14	77.76	79.26	80.00	78.47	81.11	79.29	4.2
L8 -dry	79.67	80.22	80.06	81.51	81.32	81.31	80.68	0.8
L9 - dry	80.22	83.35	80.50	81.36	82.23	80.14	81.30	5.2
L13 - wet	81.04	81.15	80.92	77.63	78.84	79.65	79.87	1.6
Data not used for value assignment (grey area in graph)								
L9 - wet	69.66	79.89	75.75	72.41	67.89	75.82	73.57	6.2
L14 - dry	67.80	68.42	69.22	70.00	68.70	68.83	68.83	9.8

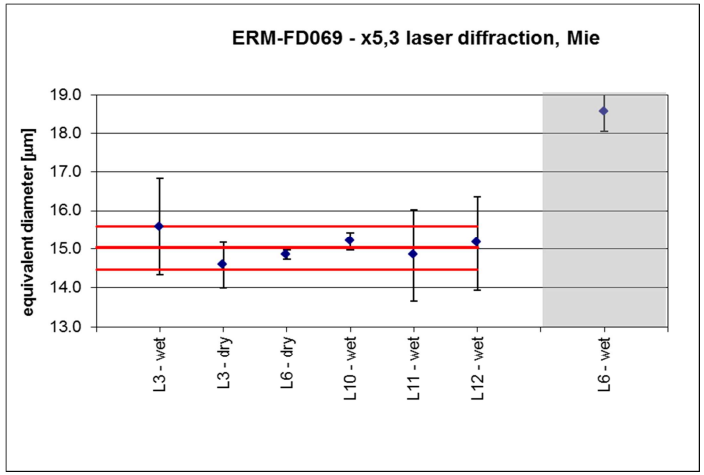


The collection of the Q3(x) curves of all technically accepted datasets is shown below.



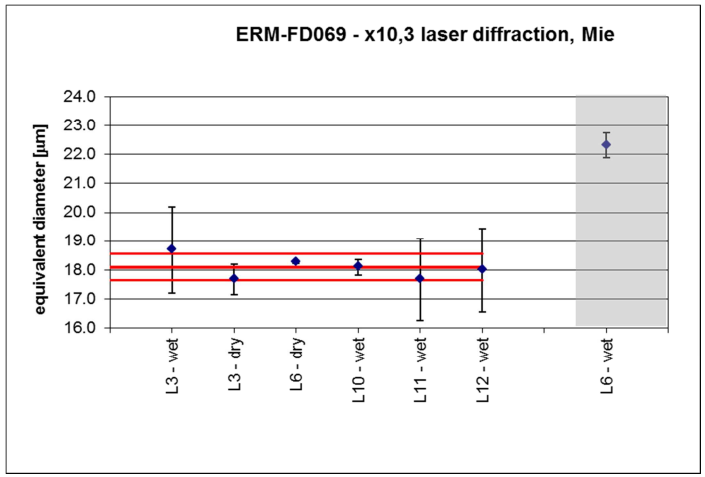
Laser diffraction Mie theory: $x_{5,}$

Laboratory code -model	rep. 1 [µm]	rep. 2 [µm]	rep. 3 [µm]	rep. 4 [µm]	rep. 5 [µm]	rep. 6 [µm]	mean [µm]	U [%]
L3 - wet	15.40	15.30	15.50	15.80	15.80	15.70	15.58	8.0
L3 - dry	14.50	14.40	14.60	14.80	14.60	14.60	14.58	4.0
L6 - dry	14.94	14.77	14.86	14.93	14.84	14.73	14.85	0.8
L10 - wet	15.31	15.21	15.20	15.19	15.14	15.08	15.19	1.5
L11 - wet	14.81	14.86	14.85	14.79	14.88	14.85	14.84	8.0
L12 - wet	15.13	15.18	15.12	15.11	15.25	15.11	15.15	8.0
Data not used for value assignment (grey area in graph)								
L6 - wet	19.48	20.44	19.81	16.64	17.85	17.17	18.57	2.8



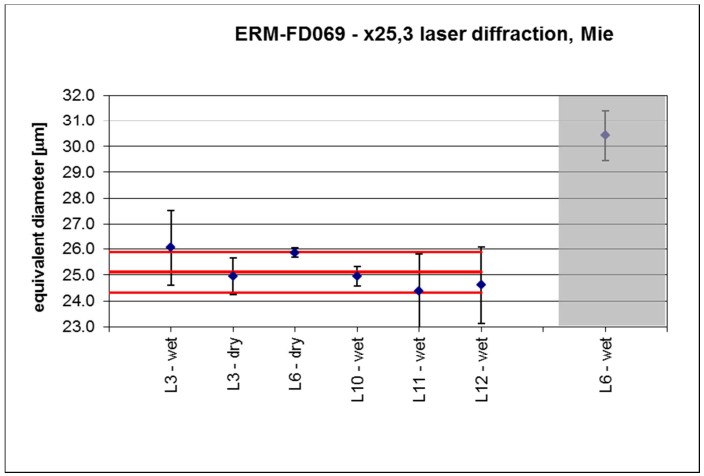
Laser diffraction Mie theory: $x_{10,3}$

Laboratory code -model	rep. 1 [µm]	rep. 2 [µm]	rep. 3 [µm]	rep. 4 [µm]	rep. 5 [µm]	rep. 6 [µm]	mean [µm]	U [%]
L3 - wet	18.50	18.30	18.60	19.00	19.00	18.80	18.70	8.0
L3 - dry	17.60	17.50	17.60	17.90	17.70	17.70	17.67	3.0
L6 - dry	18.28	18.17	18.33	18.31	18.30	18.13	18.25	0.2
L10 - wet	18.23	18.11	18.10	18.10	18.04	17.96	18.09	1.5
L11 - wet	17.63	17.69	17.67	17.60	17.73	17.68	17.67	8.0
L12 - wet	17.96	18.06	17.93	17.94	18.08	17.94	17.99	8.0
Data not used for value assignment (grey area in graph)								
L6 - wet	23.60	24.61	23.59	19.90	21.46	20.67	22.30	1.9



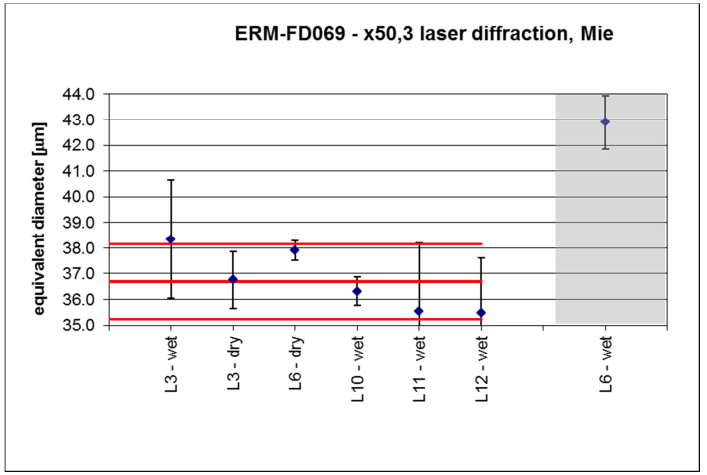
Laser diffraction Mie theory: $x_{25,3}$

Laboratory code -model	rep. 1 [µm]	rep. 2 [µm]	rep. 3 [µm]	rep. 4 [µm]	rep. 5 [µm]	rep. 6 [µm]	mean [µm]	U [%]
L3 - wet	25.70	25.40	25.90	26.50	26.50	26.30	26.05	5.6
L3 - dry	24.80	24.80	24.90	25.20	25.00	25.00	24.95	2.8
L6 - dry	25.79	25.78	25.98	25.87	25.99	25.77	25.86	0.7
L10 - wet	25.14	24.95	24.96	24.99	24.88	24.77	24.95	1.5
L11 - wet	24.33	24.40	24.39	24.30	24.50	24.41	24.39	5.8
L12 - wet	24.60	24.76	24.50	24.58	24.60	24.58	24.60	6.0
Data not used for value assignment (grey area in graph)								
L6 - wet	32.18	33.24	31.78	27.45	29.40	28.51	30.42	3.2



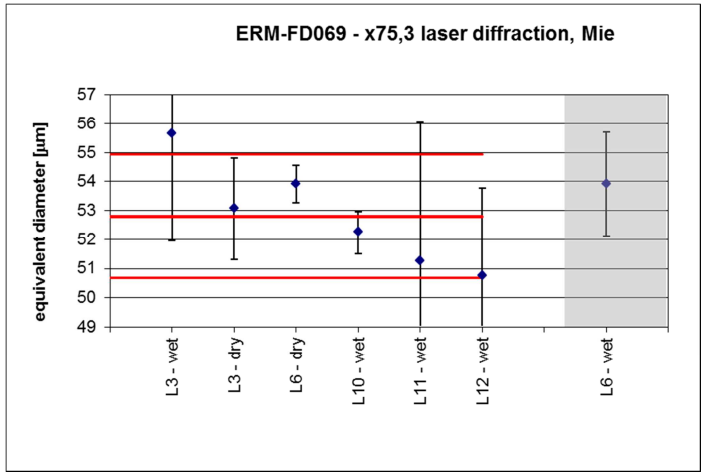
Laser diffraction Mie theory: $x_{50,3}$

Laboratory code -model	rep. 1 [µm]	rep. 2 [µm]	rep. 3 [µm]	rep. 4 [µm]	rep. 5 [µm]	rep. 6 [µm]	mean [µm]	U [%]
L3 - wet	38.00	37.50	38.10	38.90	39.00	38.60	38.35	6.0
L3 - dry	36.60	36.60	36.70	37.10	36.80	36.80	36.77	3.0
L6 - dry	37.74	37.79	38.04	37.84	38.12	37.85	37.90	1.0
L10 - wet	36.59	36.29	36.32	36.42	36.23	36.08	36.32	1.5
L11 - wet	35.47	35.54	35.55	35.44	35.76	35.58	35.56	7.4
L12 - wet	35.55	35.81	35.30	35.53	35.19	35.51	35.48	6.0
Data not used for value assignment (grey area in graph)								
L6 - wet	42.91	2.4	45.00	46.14	44.23	39.23	41.92	40.92



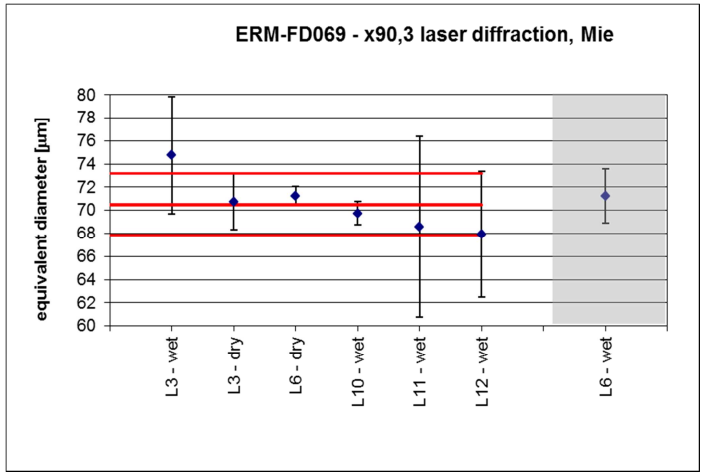
Laser diffraction Mie theory: $x_{75,3}$

Laboratory code -model	rep. 1 [µm]	rep. 2 [µm]	rep. 3 [µm]	rep. 4 [µm]	rep. 5 [µm]	rep. 6 [µm]	mean [µm]	U [%]
L3 - wet	55.30	54.50	55.20	56.40	56.40	56.00	55.63	6.6
L3 - dry	52.90	52.90	53.00	53.40	53.10	53.00	53.05	3.3
L6 - dry	53.65	53.81	54.03	53.77	54.23	53.96	53.91	1.2
L10 - wet	52.60	52.16	52.25	52.41	52.12	51.92	52.24	1.4
L11 - wet	51.10	51.16	51.21	51.10	51.53	51.26	51.23	9.4
L12 - wet	51.02	51.24	50.52	50.98	49.78	50.89	50.74	6.0
Data not used for value assignment (grey area in graph)								
L6 - wet	53.65	53.81	54.03	53.77	54.23	53.96	53.91	3.3



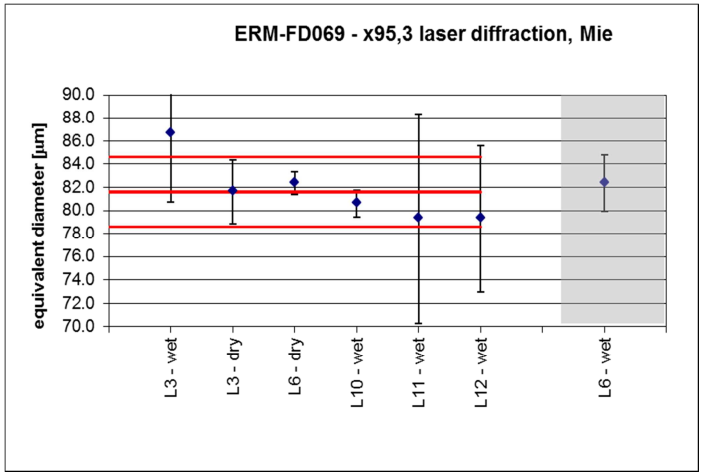
Laser diffraction Mie theory: $x_{90,3}$

Laboratory code -model	rep. 1 [µm]	rep. 2 [µm]	rep. 3 [µm]	rep. 4 [µm]	rep. 5 [µm]	rep. 6 [µm]	mean [µm]	U [%]
L3 - wet	74.5	73.5	74.1	75.7	75.7	75.1	74.77	6.8
L3 - dry	70.6	70.6	70.7	71.0	70.8	70.7	70.73	3.4
L6 - dry	70.9	71.2	71.3	71.0	71.6	71.5	71.24	1.2
L10 - wet	70.2	69.6	69.8	70.0	69.6	69.4	69.76	1.4
L11 - wet	68.4	68.4	68.5	68.4	69.0	68.6	68.56	11.4
L12 - wet	68.7	68.6	67.7	68.6	65.7	68.3	67.94	8.0
Data not used for value assignment (grey area in graph)								
L6 - wet	70.9	71.2	71.3	71.0	71.6	71.5	71.24	3.3

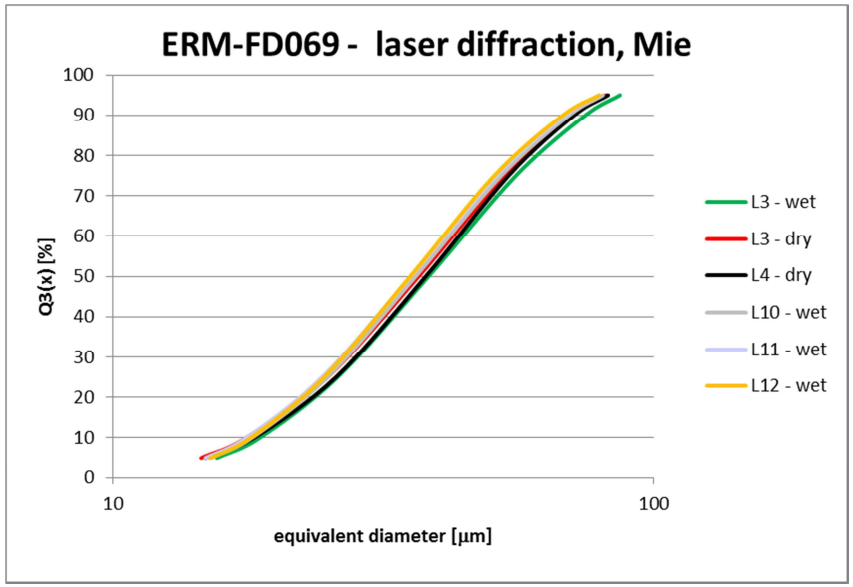


Laser diffraction Mie theory: $x_{95,3}$

Laboratory code -model	rep. 1 [µm]	rep. 2 [µm]	rep. 3 [µm]	rep. 4 [µm]	rep. 5 [µm]	rep. 6 [µm]	mean [µm]	U [%]
L3 - wet	86.50	85.30	85.90	87.60	87.50	86.90	86.62	6.8
L3 - dry	81.40	81.50	81.60	81.90	81.70	81.50	81.60	3.4
L6 - dry	81.91	82.40	82.38	82.05	82.74	82.68	82.36	1.2
L10 - wet	81.04	80.41	80.64	80.84	80.44	80.13	80.58	1.4
L11 - wet	79.11	79.14	79.27	79.17	79.78	79.31	79.30	11.4
L12 - wet	80.50	80.05	79.32	80.28	75.57	79.94	79.28	8.0
Data not used for value assignment (grey area in graph)								
L6 - wet	81.91	82.40	82.38	82.05	82.74	82.68	82.36	3.0

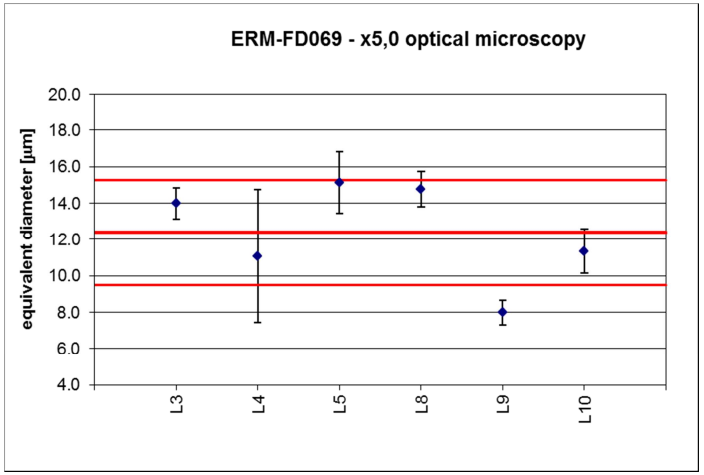


The collection of the Q3 curves of all technically accepted datasets is shown below.



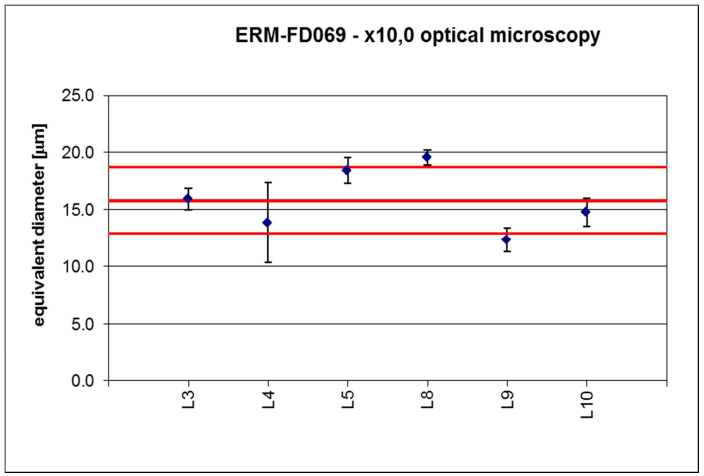
Optical microscopy: $x_{5,0}$

Laboratory code	rep. 1 [µm]	rep. 2 [µm]	rep. 3 [µm]	rep. 4 [µm]	rep. 5 [µm]	rep. 6 [µm]	mean [µm]	U [%]
L3	14.0	13.93	13.73	13.78	14.54	13.89	13.98	6.0
L4	8.8	10.8	13.6	9.5	11.6	12.2	11.08	26.0
L5	14.7	15.7	16.1	15.1	15.2	14	15.13	20.4
L8	15.3	14.8	15.8	13.1	14.2	15.3	14.75	6.0
L9	6.3	9.1	10.5	5.9	7.8	8.3	7.98	8.6
L10	10.956	11.366	10.631	11.731	11.869	11.522	11.35	9.0



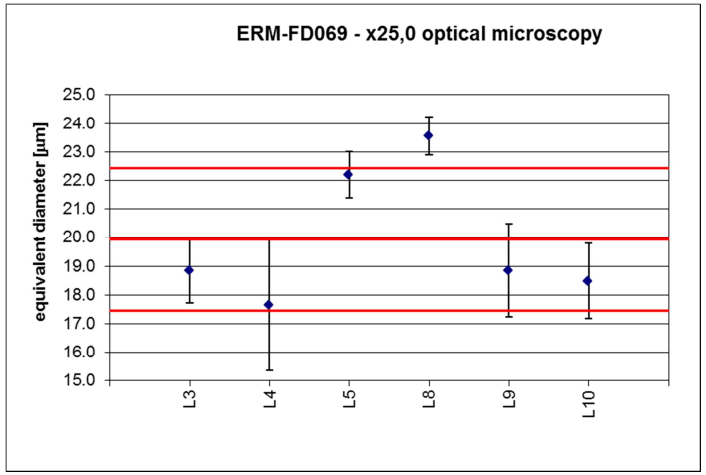
Optical microscopy: $x_{10,0}$

Laboratory code	rep. 1 [µm]	rep. 2 [µm]	rep. 3 [µm]	rep. 4 [µm]	rep. 5 [µm]	rep. 6 [µm]	mean [µm]	U [%]
L3	15.95	15.85	15.76	15.82	16.32	15.98	15.95	6.0
L4	10.8	14.1	16.2	13.6	14.1	14.4	13.87	24.2
L5	18.5	18.8	18.8	18.7	18.3	17.6	18.45	20.4
L8	20.3	19.6	19.6	19.1	18.8	20	19.57	3.6
L9	9.6	13.9	14.8	9.9	12.7	13.1	12.33	8.6
L10	14.225	15.21	14.302	14.967	15.126	14.97	14.80	5.8



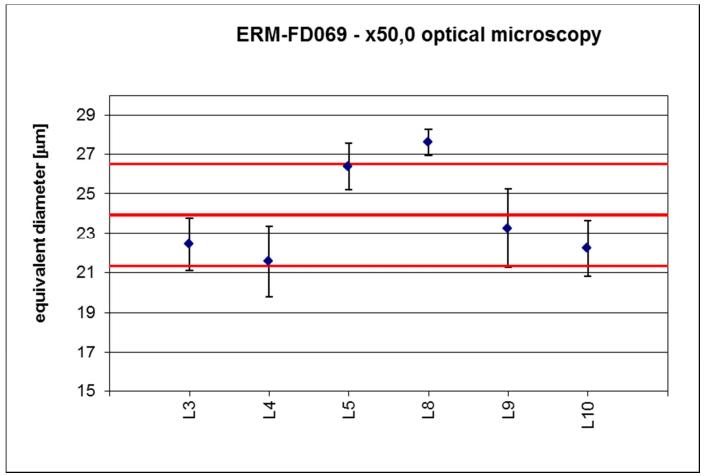
Optical microscopy: $x_{25,0}$

Laboratory code	rep. 1 [µm]	rep. 2 [µm]	rep. 3 [µm]	rep. 4 [µm]	rep. 5 [µm]	rep. 6 [µm]	mean [µm]	U [%]
L3	18.73	18.67	18.86	18.82	18.97	19.03	18.85	6.0
L4	15.9	18.2	19.2	18.1	17.1	17.4	17.65	13.2
L5	22.1	22.6	22.5	22.3	22.1	21.6	22.20	9.0
L8	24.2	23.7	23.2	23.2	23	24.1	23.57	3.0
L9	18.6	19.6	19.4	18.1	18.9	18.5	18.85	8.6
L10	19.001	18.532	18.065	18.426	18.506	18.395	18.49	3.4



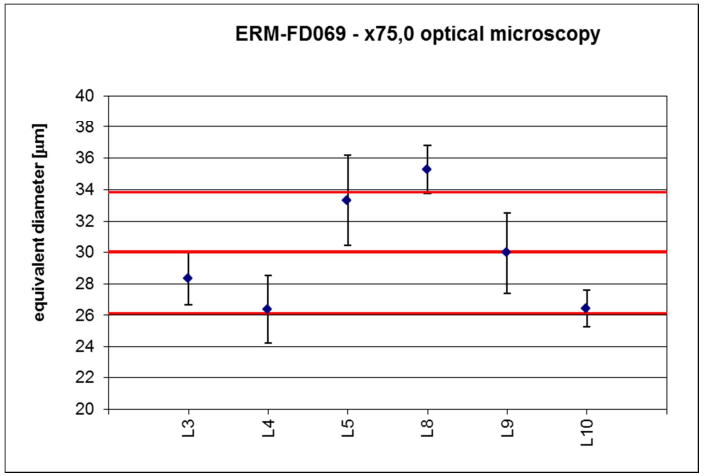
Optical microscopy: $x_{50,0}$

Laboratory code	rep. 1 [µm]	rep. 2 [µm]	rep. 3 [µm]	rep. 4 [µm]	rep. 5 [µm]	rep. 6 [µm]	mean [µm]	U [%]
L3	22.16	22.03	22.55	22.47	22.51	22.83	22.43	6.0
L4	21.5	22	22.9	21.9	20.5	20.6	21.57	8.4
L5	26.4	26.4	27	26.8	26	25.6	26.37	5.6
L8	27.9	27.8	27.1	27.4	27.1	28.3	27.60	2.4
L9	23.5	23.8	23.6	22.7	23.4	22.5	23.25	8.6
L10	22.627	22.101	22.213	22.139	22.23	22.12	22.24	1.8



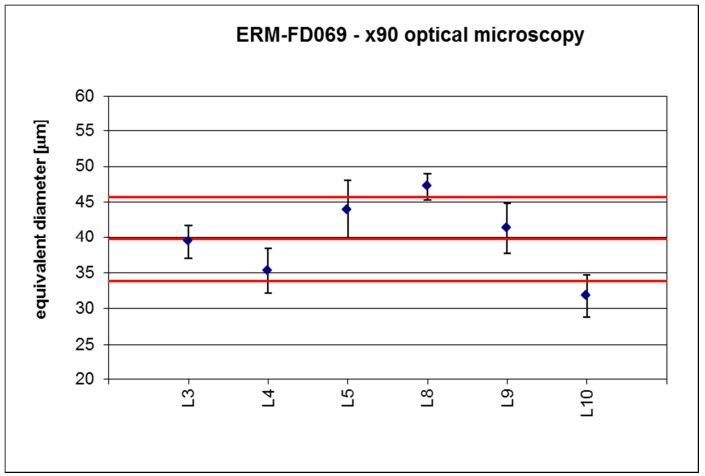
Optical microscopy: $x_{75,0}$

Laboratory code	rep. 1 [µm]	rep. 2 [µm]	rep. 3 [µm]	rep. 4 [µm]	rep. 5 [µm]	rep. 6 [µm]	mean [µm]	U [%]
L3	27.23	27.5	28.75	28.16	28.79	29.69	28.35	6.0
L4	26.6	26.9	28	26.3	25.1	25.4	26.38	8.4
L5	34.4	32.3	34	34.9	32.7	31.6	33.32	6.2
L8	35.6	36.2	34.4	35.3	33.5	36.8	35.30	4.0
L9	29.7	31.3	30.1	29.5	31.3	28	29.98	8.6
L10	26.657	26.406	26.542	26.375	26.197	26.327	26.42	1.4



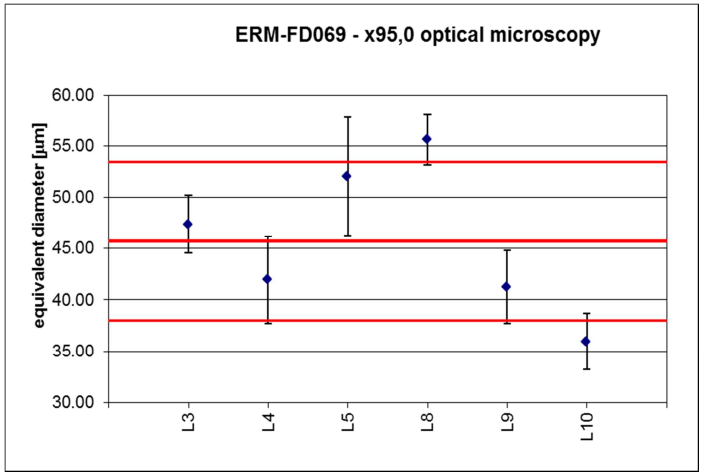
Optical microscopy: $x_{90,0}$

Laboratory code	rep. 1 [µm]	rep. 2 [µm]	rep. 3 [µm]	rep. 4 [µm]	rep. 5 [µm]	rep. 6 [µm]	mean [µm]	U [%]
L3	37.07	39.12	40.48	38.4	40.69	40.54	39.38	6.0
L4	35.4	35.7	38.1	33.7	34.3	34.4	35.27	9.0
L5	44.7	42	44.8	46.7	43.6	41.6	43.90	7.5
L8	47.5	47.9	46.1	47	45	49.3	47.13	4.0
L9	41.1	42.7	40.8	41.3	43.3	38.5	41.28	8.6
L10	32.202	30.026	32.584	32.063	32.069	31.628	31.76	5.8

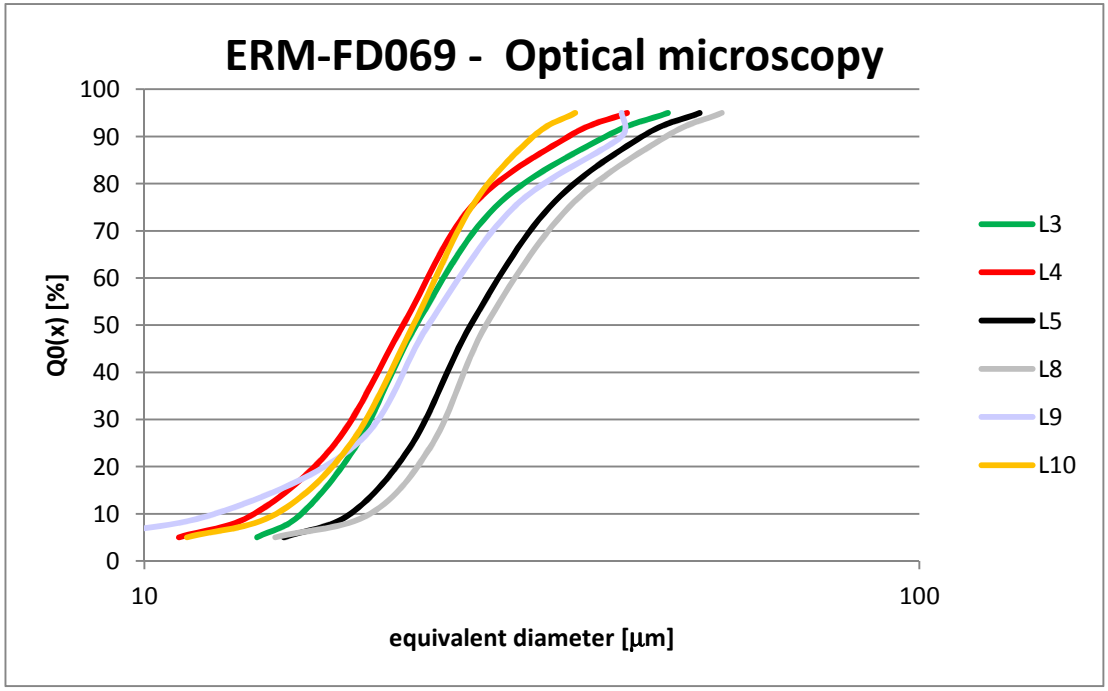


Optical microscopy: $x_{95,0}$

Laboratory code	rep. 1 [µm]	rep. 2 [µm]	rep. 3 [µm]	rep. 4 [µm]	rep. 5 [µm]	rep. 6 [µm]	mean [µm]	U [%]
L3	44.25	49.21	48.54	44.97	49.3	48	47.38	6.0
L4	42.6	42.6	45.2	39	40.3	42.1	41.97	10.0
L5	52.5	49.7	54.4	55.2	52.1	48.5	52.07	8.0
L8	57.3	56.1	53.8	55.1	53.2	58.2	55.62	4.6
L9	41.1	42.7	40.8	41.3	43.3	38.5	41.28	8.6
L10	36.946	33.96	37.691	35.697	35.79	35.776	35.98	7.6



The collection of the Q3 curves of all technically accepted datasets is shown below.



Annex E: Individual results for number-based distribution, dynamic image analysis and the volume-based mean diameter

*Results for number-weighted distributions by laser diffraction. Fraun: Fraunhofer approximation. * excluded from the characterisation of Q3 for technical grounds. Each result is the average of six measurements*

	Laser diffraction,dry				Laser diffraction,wet						
	L2	L9	L14	L6	L2	L9*	L13	L6*	L10	L11	L12
Model	Fraun	Fraun	Fraun	Mie	Fraun	Fraun	Fraun	Mie	Mie	Mie	Mie
$x_{5,0}$ [µm]	7.2	5.9	0.53	2.0	0.40	0.40	0.51	3.3	10.2	10.1	10.1
$x_{5,0}$ [µm]	8.1	6.8	0.55	2.1	0.42	0.42	0.53	3.4	11.1	10.9	11.1
$x_{10,0}$ [µm]	10.4	8.8	0.63	2.3	0.48	0.47	0.58	4.2	13.2	12.9	13.3
$x_{25,0}$ [µm]	14.6	12.9	0.76	2.8	0.58	0.56	0.67	9.8	17.0	16.6	17.3
$x_{50,0}$ [µm]	21.1	19.6	0.90	6.4	0.74	0.70	0.82	21.0	23.2	22.7	23.4
$x_{75,0}$ [µm]	30.1	28.3	1.27	17.8	0.96	0.89	1.00	31.5	31.7	30.9	31.8
$x_{90,0}$ [µm]	37.5	35.3	1.69	24.6	1.15	1.04	1.14	39.4	38.5	37.6	38.5

Results obtained by dynamic image analysis. The results are averages of two measurements

	$x_{5,3}$ [µm]	$x_{10,3}$ [µm]	$x_{25,3}$ [µm]	$x_{50,3}$ [µm]	$x_{75,3}$ [µm]	$x_{90,3}$ [µm]	$x_{95,3}$ [µm]
Occhio Morpho 3D	12.9	15.2	19.1	26.6	39.1	49.8	56.4
Sympatec QICPIC	11.8	15.7	22.7	33.8	47.9	61.6	70.8

Results for the volume-weighted mean diameter ($\bar{x}_{1,3}$.or $\bar{D}_{4,3}$).The results are averages of six measurements

Mie-theory		Fraunhofer approximation	
	$\bar{x}_{1,3}$. [mm]		$\bar{x}_{1,3}$. [mm]
L3w	43.0	L1w	40.3
L3d	40.9	L1d	39.4
L6d	41.7	L2w	40.7
L11w	39.8	L2d	40.6
		L7w	40.7
		L8d	40.7
		L9d	41.3
		L13w	40.2
		L7w	40.3

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