



The EU FP7 NanoDefine Project

Development of an integrated approach based on validated and standardized methods to support the implementation of the EC recommendation for a definition of nanomaterial

Review and practical evaluation of sampling guidelines

NanoDefine Technical Report D2.7

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The NanoDefine Consortium 2017

NanoDefine in a nutshell:

The EU FP7 NanoDefine project was launched in November 2013 and will run until October 2017. The project is dedicated to support the implementation of the EU Recommendation on the Definition of Nanomaterial by the provision of the required analytical tools and respective guidance. Main goal is to develop a novel tiered approach consisting of (i) rapid and cost-efficient screening methods and (ii) confirmatory measurement methods. The "NanoDefiner" eTool will guide potential end-users, such as concerned industries and regulatory bodies as well as enforcement and contract laboratories, to reliably classify if a material is nano, or not. To achieve this objective, a comprehensive inter-laboratory evaluation of the performance of current characterisation techniques, instruments and software is performed. Instruments, software and methods are further developed. Their capacity to reliably measure the size of particulates in the size range 1-100 nm and above (according to the EU definition) is validated. Technical reports on project results are published to reach out to relevant stakeholders, such as policy makers, regulators, industries and the wider scientific community, to present and discuss our goals and results, to ensure a continuous exchange of views, needs and experiences obtained from different fields of expertise and application, and to finally integrate the resulting feedback into our ongoing work on the size-related classification of nanomaterials.

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1 Abbreviations and acronyms

Please, include here specific abbreviations and acronyms used in this deliverable. For example:

CLS	Centrifugal Liquid Sedimentation
C_p	specific heat capacity [J / g*K]
DLS	Dynamic Light Scattering
M	weight water [g]
P_{ac}	acoustic energy [W]
Pdi	Polydispersity Index (a number calculated from a simple 2 parameter fit to the correlation data (the cumulants analysis) measured using DLS.
SHMP	Sodium HexaMetaPhosphate
T	temperature [°C]
t	time [seconds]
U	expanded measurement uncertainty (k = 2) [%]
VC	variation coefficient
WP	work package

2 Summary and Conclusions

There are not a lot of publications dealing with the sampling or sub-sampling of Nanomaterials. In general, the known procedures for coarser materials are applied. In this NanoDefine task it should be tested if there is an influence on the measurement uncertainty if the materials are sampled by powder, slurry or paste. Sampling by these methods is described in the ISO 14488:2007. Due to that the norm was selected as guideline for the practical evaluation.

Precise determination of particle size distribution depends on a reproducible sampling and sub-sampling of the powders. The increase in the total surface area of the powders at nanometer scale particle sizes may lead to improper characterization of the bulk if the sampling fails (El-Shall, Moudgil 2014). In this report the influence of four different sub-sampling procedures on the expanded measurement uncertainty ($k = 2$) was investigated. The tested procedures were slurry, paste and heap sampling as well as dividing by spinning riffler. For the investigations three materials were selected which are in line with the test materials from work package 1. Materials under investigation were coated titanium dioxide and two barium sulfate materials with different particle sizes. These materials are similar to the test materials IRMM_381, IRMM_387 and IRMM_388 provided by work package 1.

With the test materials IRMM_381, IRMM_387 and IRMM_388 the expanded measurement uncertainties ($k = 2$) for the steps dispersion and DLS measurement were estimated as reference values. These values were used to assess the influence of the sampling procedures to the total uncertainty.

The practical evaluation of the sub-sampling procedures started with approximately 1 kg of the materials in the laboratory. This is a typical starting point for service laboratories. The actual on-site sampling is often carried out by the laboratory customer himself. The laboratory then takes over for the sub-sampling down to the ready-to-measure sample.

For the barium sulfate fine-grade the results showed a tendency to a heterogeneous particle distribution in the heap between the inner and outer zones of the heap. In average, there were no significant differences between the z-average values in correlation to the sampling procedures. It could be observed that the expanded measurement uncertainties for the heap and the slurry sampling increased in comparison to the uncertainty calculated for the test material IRMM_381 as reference. Pdi results were in good correlation independent of the sub-sampling procedure. The expanded measurement uncertainties for the Pdi results showed no increase caused by the sampling procedure.

For the barium sulfate ultrafine grade the results showed no significant differences between the z-average values in correlation to the sampling procedures. It could be observed that the expanded measurement uncertainties increase in comparison to the uncertainty calculated for the reference IRMM_387. Heap sampling shows the highest effect and the spinning riffler the lowest. The expanded measurement uncertainties for the Pdi results showed no increase caused by the sampling procedures. But there is a difference in the average results for the Pdi between heap and slurry sampling. This indicates that the accuracy could be influenced by these sampling procedures.

For the coated titanium dioxide the results showed no significant differences between the z-average values in correlation to the sampling procedures. It could be observed that the expanded measurement uncertainties are nearly the same for the procedures spinning riffler, slurry and paste. Heap sampling shows the highest effect on the expanded measurement uncertainty. The expanded measurement uncertainty for the Pdi results showed no increase caused by the sampling procedures. But again the heap sampling shows the highest variance.

A final comparison of the expanded measurement uncertainties for all materials and sub-sampling procedures was made. It was observed that independent of the material the heap sampling leads to the highest variance. The sub-sampling methods paste and slurry show comparable influence on the measurement uncertainties. The spinning riffler seems to have the smallest effect. A comparison of the two barium sulfate materials indicated a tendency. The observation was that for the ultrafine grade for all sub-sampling procedures the expanded measurement uncertainties increased more than for the fine grade material. For further investigations on nanoparticle sampling scenarios, a combination of methods and more sophisticated methods should be used. Additionally the use of a material with a known particle distribution or with labeled particles of defined sizes should be considered in order to be able to better understand changes in the particle distribution.

3 Introduction

This deliverable document (D2.7) was prepared in the context of WP2 (Sample preparation, dispersion & sampling methods) of the NanoDefine Project. The task of this deliverable is to review standardised sampling guidelines for representative sub-sampling of substances. A selection of sampling procedures (powder, slurry, paste) should be applied to three industrial materials. The sub-samples should be tested by DLS to assess if the particle fractions are homogeneously distributed. During the data evaluation it will be estimated if the sampling procedure has a significant impact on the measurement results.

The NanoDefine project aims to the development of methods supporting the implementation of the commission's recommendation for a definition of a nanomaterial. An important part to all chemical or physical analysis is the sampling and sub-sampling. Thinking about an industrial application, sampling starts from a large amount of material. The primary challenge will be that the sample has to be indicative for the bulk from which it was taken. To find a suitable sampling technique for particle size testing is driven by different considerations. Some aspects are the amount of the sample, number concentration, particle size, size distribution and the chemical composition. In addition these factors are related to the test method used (Guidarelli et al. 1998; Fabries et al. 2000; Jaffari et al. 2013). When sampling powders, there are two types of general errors discussed: Errors due to segregation of the bulk powder and statistical errors resulting from random fluctuations. The first error can be influenced by suitable mixing and collecting the sample. The statistical error can be estimated beforehand and reduced by increasing the sample size. But it cannot be prevented. On the contrary the segregation error can be minimized by using an increased amount of the sample (Barbosa-Cánovas 2005). Deviations from statistical values occur due to the presence of particles of different sizes and shapes for each component in a powder obtained from a sampled mass of powder. Powders with particles at the nanometer scale may lead to improper characterization of the bulk if the sampling or sub-sampling technique fails to collect and represent them in the analyses (Basim, Khalili 2015). Therefore a description of material characteristics like size, size distribution and shape need a well-planned sampling approach to avoid a non-representative sampling.

For task 2.1 the sampling starts with approximately 1 kg batches of the materials in the laboratory. This corresponds to a usual procedure in analytical service laboratories: the customer takes a sample by his own procedure and sends it to a laboratory. Subsequently, the laboratory takes over for the offline sub-sampling down to the amount which is necessary for the measurement. It was planned to determine the particle size by DLS after the materials are dispersed following the protocols published in D 2.3. To obtain comparable conditions the portion of the sub-sampled material should finally meet the amounts mentioned in the dispersion protocols (D 2.3) to follow the methods developed in the NanoDefine project.

The task delivers a comparison of different sub-sampling procedures (heap sampling, spinning riffler, slurry sampling and paste sampling) for the three materials (i) Barium sulfate (fine grade), (ii) Barium sulfate (ultrafine grade) and (iii) Titanium dioxide.

The following points are being addressed and the results will be presented in the following chapters:

- Description of the sub-sampling procedures by reviewing standardized guidelines and literature
- Selection of the three materials which are suitable for the NanoDefine dispersion protocols (Deliverable 2.3) and DLS measurements
- Practical testing and data evaluation.

4 Review standardized guidelines and literature

Sampling a powder material is more difficult than it seems. The sampling can be done from a bulk sample of a few grams or from a production facility with tons of material. To ensure a representative sampling various conditions should be taken into account. What is the supposed particle size and size distribution? In what range varies the particle size and what particle shapes are to be expected. Is disintegration due to segregation possible? Is the bulk sample homogeneously mixed? The most important question is: Does every particle has the same probability of being sampled?

Various sampling methods and guidelines that are published address this problem (Muzzio, F.J. et al. 2003; Muzzio, F. J. et al. 1997; Susana, L. et al. 2011; A. Boschetto 2012; PROSPECT 2010).

The guideline that summarise those documents and the most important methods is the ISO 14488 (ISO ISO 14488:2007(E)). The scope of this standard is to specify methods for obtaining samples from a bulk of particulate material that can be considered to be representative of the bulk.

The bulk sample consists normally of discrete particles. Sometimes the material is well mixed and there are only random variations in the properties that are of interest. For well mixed materials the sampling is easy and can be done at a random location. But for the most material some degree of segregation is to be expected. This results in a bias between the mean properties. It can occur due to free-flowing behavior of the material or to fluctuations in the production process. In this case the sampling has to be done at different locations or different production-times.

The amount of the sample can also be a crucial parameter and depends of the expected maximum size of the particles. In the case of nanomaterial this factor can be neglected because the small dimension of the particles results in very small minimum samples amounts to be taken. The ISO 14488 specifies about 1 µg for the sub-micrometer region.

The total error of the sampling process consists of two parts: the fundamental error, related to the different properties of the particles and the segregation error which is related to the degree of the segregation of the material. The segregation error can be assessed only by measuring samples taken at different locations. These measurements can provide an estimation of the segregation error.

The ISO 14488 does also provide some general advices for the sample handling. The sampling from a moving stream is to be preferred and it should always be sampled the whole stream. Furthermore when splitting the sample it should be uses the whole increment of the sample and the sample should be protected from any contamination by foreign particles.

4.1 Description of Sampling Methods

In the following section the sampling methods for powder sampling respectively sub-sampling are described. As outlined by Allen (Basim, Khalili 2015; Allen 2003; Muzzio, F. J. et al. 1997) the first choice of powder sampling should always be the sampling from a moving stream. A sample of the whole stream should be taken as often as necessary. These are the so called golden Rules of powder sampling.

When a sub-sample is to be taken from a bulk there is no longer a moving stream. A method that provides a “moving sampling” anyway is the spinning riffler. It divides the bulk sample while moving its vessels. This provides the most representative sub samples.

In this deliverable there are three more methods of sub sampling discussed: the slurry sampling, the paste sampling and the heap sampling.

The slurry and the paste sampling methods need a sample preparation prior the sampling. The possibility of producing a slurry or a paste in an adequate solvent is of course a requirement to perform this sampling.

4.1.1 Heap sampling

Coning/Quartering

Prior the coning and quartering procedure the sample should be mixed thoroughly in a mixing container. The sample should be poured on a nonporous hard surface in one single pass. For quartering a knife with four crossed blades shall be used and the height of the blades should be higher than the cone of the material. The knife is to be moved down from the center top of the cone right to the bottom. One quarter is randomly removed from the cone. All particles should be removed.

This method shall not be used for powders with a tendency to segregation due to large differences in particle size or density. The method is also not suitable for hazardous material.

Scoop sampling

For the scoop sampling it is necessary to have a fairly narrow size distribution. It should only be used for sticky powders that have been well mixed. The scoop sampling is in general subject to large errors. Several sample increments are to be taken with a scoop, spoon or spatula.

4.1.2 Spinning Riffler

For the sub sampling of free flowing powder a spinning riffler is the best choice ((Allen 2003), (Muzzio, F. J. et al. 1997)). It was first described 1934 (C. K. Wentworth 1934).

It is a rotary sample divider and a development from the chute riffler. In a chute riffler the sample is divided by a series of chutes feeding two trays on either side of the riffler. The chutes are static and the sample is poured into the chutes.

When using a spinning riffler the sample is divided by flowing into a series of circulating sampling vessels. Above the vessel a hopper is mounted and the powder is flowing in a constant flow into the vessel. Every time a vessel passes the stream, the whole stream is collected until the next vessel replaces the first vessel. This happens many times with one sample and in the result every vessel has gathered many times the whole stream. In this manner the whole bulk sample is divided in as many vessels are mounted at the riffler. Normally there are 6 or 8 places for vessels to be mounted.

Because the vessels are sampling a moving stream and are collecting every time the whole stream, the "golden rules of sampling" are met.

The spinning riffler can be made for different amounts of sample, from a few grams to some kilogram.

4.1.3 Slurry

When sampling a slurry the sampling in motion is again the best choice (Allen 2003). To get from a powder to a slurry an adequate solvent is needed and a particle concentration that provides a good viscosity. When material like TiO₂ or BaSO₄ is used, water is a suitable solvent. The concentration can vary in a range from 3.5 to 0.6 weight percent. In this range the viscosity is still near the viscosity of water at 20 °C.

For a homogenous slurry a stirrer or a ultra turrax is recommended. The stirrer or ultra turrax is setting the dispersion in motion and keeps it moving. Meanwhile the sample can be extracted with a pipette. The sample amount depends on the further sample preparation. It should be taken more than one sample. Assuming the slurry is homogenous the sample can be taken from everywhere in the beaker.

4.1.4 Paste

A paste is done in a comparable way as the slurry, but the ratio between particles and solvent are different. It is used much less solvent than in the slurry. The viscosity is much higher and therefore the sampling in motion in the laboratory is difficult.

The ratio between particles and solvent depends on the materials. The homogenization can be done with a glass rod with a rubber head. The powder is filed in a beaker and the solvent is added.

When preparing the paste in this manner it is not possible to extract a sample while the paste is in constant motion. When a stirrer is used in this step a sample can be taken while the paste is moving. The sample amount depends on the further sample preparation. It should be taken more than one sample.

Assuming the paste is homogenous the sample can be taken from everywhere in the beaker.

4.2 Practical evaluation of sampling procedures

4.2.1 Material

For the tests of the different sub-sampling methods the inorganic materials barium sulfate fine grade, barium sulfate ultrafine grade and titanium dioxide are used (Table 1. all of them are fine white powders and can be dispersed in a solution of sodium hexametaphosphate (SHMP) in water according to D2.3.

Table 1: Overview of the materials made available by the workpackage 1 partners

testmaterial from Work-package 1*	No.	Material for sampling procedures	Type
barium sulfate fine grade	IRMM_381	barium sulfate fine grade	HD80
barium sulfate ultrafine grade	IRMM_387	barium sulfate ultrafine grade	BFN40NC
titanium dioxide	IRMM_388	titanium dioxide	K2360

* These materials were used to estimate an expanded measurement uncertainties ($k = 2$) in 4.3.1 as reference values.

More detailed information about the test materials are to be found in D1.6.

4.2.2 Sub-sampling methods

For all of the sampling methods it is important to gather a representative sample. In the ISO 14488:2007 a minimum sampling amount is described, depending on the particle size. If the particle size is in sub-micrometer region it is defined that a minimum of 1 μg has to be sampled. If the density of the material is higher than 1000 kg/m^3 this amount has to be multiplied with the density. For the three materials under study this results in minimum amount of 4 to 5 μg .

Every tool or materials used in the sampling process are cleaned with MilliQ water and Isopropanol.

4.2.2.1 Heap sampling

For the sampling from a heap of material the powders were poured on to a glass plate. The form of the heap was conus. The samples were gathered with a spatula (bigger that 10 mm) at different zones at the outside of the cone. To collect also samples from the inside of the cone the cone was parted in the middle. In total there were gathered 10 samples from the cone (see Figure 1). The amount of the increments was between 10 and 15 mg.



Figure 1: Illustration for the sampling zones from the heap

4.2.2.2 Spinning riffler

The whole bulk sample (750 – 1300 g) was poured in a constant flow into the hopper of the spinning riffler. Meanwhile the eight sampling vessels (glass flasks) were rotating. After the last material had passed the hopper the riffler rotated additionally 20 seconds to make sure that every material was collected by the vessels.

The eight sub-samples were transferred into a glass beaker and sealed with parafilm. One of the eight sub-samples was another three times parted with the spinning riffler until there was no further parting possible. The resulting sample amount was 0.15 - 0.3 g. After every sampling the spinning riffler was cleaned with MilliQ-water and Isopropanol.

Because of the eight sampling vessels the result was eight sub-samples.

4.2.2.3 Slurry

The particle concentration of the slurry has an influence in the particle size measured by the DLS. Because of this the particle concentration of the slurry was adjusted to 21.75 mg/ml for barium sulfate fine grade and 6 mg/ml for barium sulfate ultrafine grade.

The slurry was made from one sub-sample of the first spinning riffler dividing. The powder was transferred in to a 5 L glass beaker and dispersed in 2 L SHMP (2%). To mix the dispersion a Ultra-Turrax was used.

After 5 minutes further SHMP (2%) was added to achieve the particle concentration mentioned above. The dispersion was further 10 min mixed.

Following T. Allen (Allen 1990) the sampling should be done from a moving stream. The Ultra-Turrax was set on the lowest speed and the sampling was done by extracting 0.72 ml (barium sulfate fine grade) and 1.2 ml (barium sulfate ultrafine grade) with an Eppendorf pipette. Because of not losing particles the tip of the pipette was flushed with SHMP. The samples were diluted in a 50 ml plastic vessel with SHMP to a particle concentration of 2.6 mg/L.

In total eight samples were collected from the slurry.

For the titanium dioxide the concentration for the DLS had to be smaller. Therefore the concentration in the 5 L beaker was set to 11.3 mg/ml and 2.13 ml were transferred into a 100 ml volumetric flask. The slurry was diluted with water and the flask was treated 10 minutes in an ultrasonic bath. 5 ml of the dispersion were transferred into a 50 ml plastic vessel.

4.2.2.4 Paste

The paste was also made from one sub-sample of the first spinning riffler dividing. 90 - 170 g of the powder was transferred into a glass beaker and SHMP (2%) was added until a homogeneous paste was achieved. The paste was mixed with a glass rod. About 20 mg were transferred into a 50 ml plastic vessel and diluted with SHMP (2%).

For titanium dioxide the sample preparation needs an additional dilution step because the particle concentration for the DLS has to be lower. About 40 mg of the paste was transferred into a 50 ml plastic vessel and diluted with 10 ml SHMP (2%). The dispersion needs ultrasonication for 10 minutes. 0.4 ml of the dispersion was transferred into a 50 ml plastic vessel and 4.6 ml MiliQ water was added.

4.2.3 Sample dispersion

The sample preparation is done as described in deliverable D 2.3.

4.3 Results and discussion

4.3.1 Pre-measurements

A) Calibration ultrasonicator

The calibration of the ultrasonicator (HD3100 (Bandelin, Germany)) follows the protocol from D2.3. For a given power output, the supplied acoustic energy (P_{ac}) was determined by means of the temperature rise over a defined period of time using the following equation (Taurozzi et al. 2012):

$$P_{ac} = \frac{\Delta T}{\Delta t} \cdot M \cdot C_p$$

P_{ac} = acoustic energy [W]

T = temperature [°C]

t = time [seconds]

M = weight water [g]

C_p = specific heat capacity [J / g*K]

The rise of temperature was measured over a period of 5 minutes. Temperature was measured every 30 seconds.

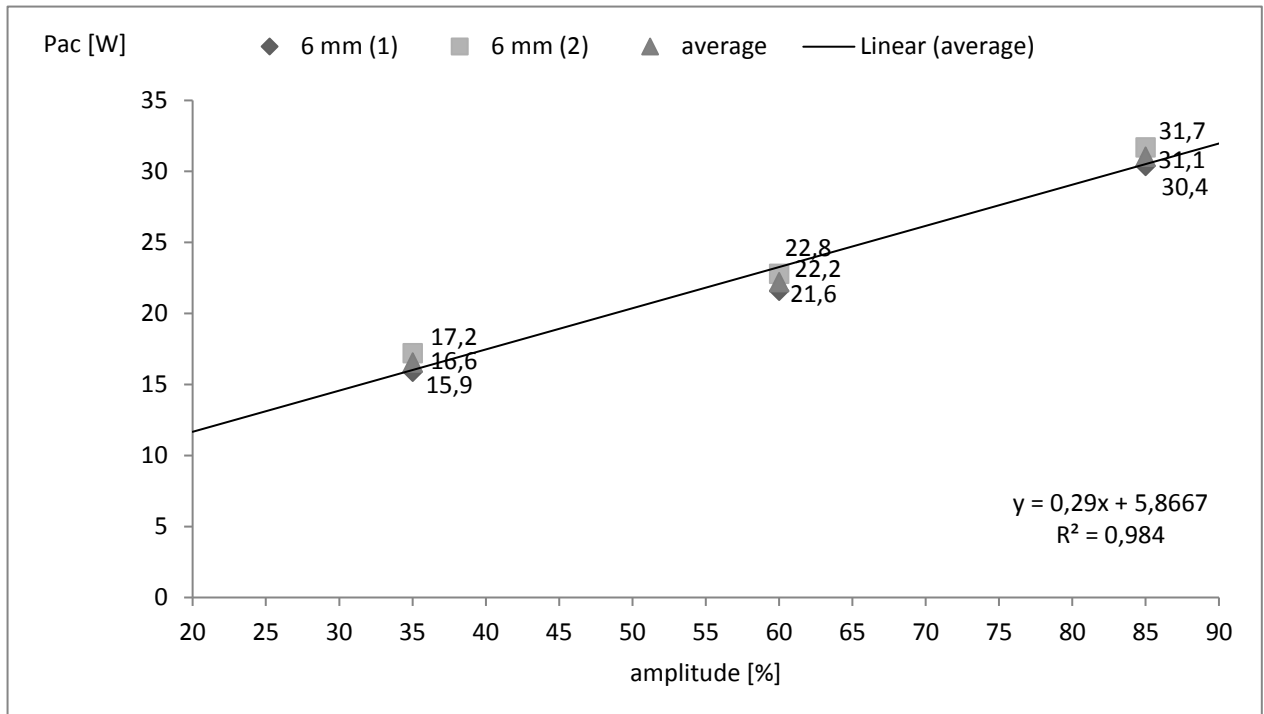


Figure 2: Results for the calibration of the tip ultrasonicator (6 mm)

Finally a KE76 (Bandelin, Germany) tip with a 6 mm diameter was used. To meet the recommended values of D 2.3 the following conditions were used for the dispersion of the materials (**Table 2**):

Table 2: Ultrasonication conditions used for the dispersion of the materials

Material	Amplitude [%]	Energy level [W]
Bariumsulfate (fine grade)	15	10.3
Bariumsulfate (ultrafine grade)	10	8.7
Titanium dioxide	29	7.8

B) Measurement uncertainty for the test materials:

To describe the measurement uncertainty the intermediate precision was determined. Following the “Guide to the Expression of Uncertainty in Measurement (GUM)” the uncertainty stated in this report is the expanded measurement uncertainty obtained by multiplying the standard measurement uncertainty by the coverage factor $k = 2$. The value of the measurand then normally lies, with a probability of 95 %, within the attributed coverage interval.”

The testing was carried out on different days. The test materials of WP 1 barium sulfate fine grade IRMM_381, barium sulfate ultrafine grade IRMM_387 and titanium dioxide IRMM_388 were dispersed following the protocols delivered in (D2.3).

The calculated expanded measurement uncertainties ($k = 2$) described in this section should only include the error for the steps dispersing and DLS measurement. Every sample was prepared 11 times for 33 measurements. The values serve later for a comparison to assess the influence of the sub-sampling procedures on the measurement uncertainties (“reference values”).

Table 3: Measurement results for the test materials (WP 1)

Material	Z-Average [d.nm]	s [d.nm]	CV [%]	u [%]	Pdi	s [d.nm]	CV [%]	u [%]
IRMM_381	364.78	3.98	1.09	2.18	0.203	0,020	9,86	19,72
IRMM_387	119,33	1.24	1.04	2.08	0.138	0.009	6.52	13.04
IRMM_388	310.27	5.76	1.86	3.71	0.151	0.025	16.56	33.11

The z-average results were in accordance with the values reported in deliverable D2.3 where the same ultrasonication conditions were used.

IRMM_381	377.4 ± 1.3 nm	(measured by DLS)
IRMM_387	124.3 ± 1.2 nm	(measured by DLS)
IRMM_388	316 nm	(measured by CLS)

4.3.2 Sub-sampling of BaSO₄ (fine grade)

The amount of the bulk sample was about ca. 750 g. After the first spinning riffler run, the fractions weight between 87 – 100 g.

Independent from the sampling procedure the values for the z-average of the barium sulfate fine grade differ from the z-average for the test material IRMM_381 of WP 1 (364.78 ± 3.98 nm, Table 3). This is probably caused by different batches of the material. The difference is not linked to the sub-sampling procedure as the sub-sampling procedures result at comparable values.

a) Heap sampling

For the heap sampling with a scoop a number of increments from different zone were analyzed to minimize the sampling error (Figure 1). The values H.1 to H.5 in **Table 4** represent the outer zones. For H.1 the top was sampled. Further sampling was along the flank of the heap down to the bottom (H.2 to H.5). Values H.6 to H.10 are the results of the inner zones.

Table 4: Measurement results for the heap sub-sampling of the BaSO₄ (fine grade)

	Z-Average [d.nm] NNLS	s [d.nm]	Pdi
381_H.1	415.00	1.41	0.193
381_H.2	406.10	4.10	0.150
381_H.3	404.90	7.92	0.169
381_H.4	401.00	2.69	0.138
381_H.5	399.77	4.26	0.169
381_H.6	408.67	2.75	0.194
381_H.7	424.15	4.74	0.202
381_H.8	403.83	7.69	0.180
381_H.9	423.50	2.55	0.195
381_H.10	408.00	8.20	0.169
average [d.nm]	409.49		0.176
s [d.nm]	8.66		0.021
VC [%]	2.12		11.87
u [%]	4.23		23.74

The results of the heap sub-sampling showed a tendency. The values for the inner zones showed slightly higher results than the outer zones (inner zones H.6-H.10: average 413.63 ± 9.49 d.nm; outer zones H.1 – H.5: average 405.35 ± 5.99 d.nm). Additionally the repetition measurements of the fractions for the inner zones showed a higher variance. The difference in z-average for the inner and outer zones could be an indicator for a heterogeneous particle distribution in the heap. The expanded measurement uncertainty ($k = 2$) for the test material was 2.18 % for the z-average and 19.72 % for the Pdi (Table 3). The results for the heap sub-sampled fractions showed a higher uncertainty for the z-average 4.23 % and a slightly higher uncertainty for the Pdi 23.74 %.

b) Spinning Riffler

The sub-sampling was performed four times unless the final amount of each fraction was around 0.15 g. This results in eight fractions. These were tested in double by DLS.

Table 5 Measurement results for the spinning riffler sub-sampling of the BaSO₄ (fine grade)

	Z-Average [d.nm] NNLS	s [d.nm]	Pdi
381_SR4.1	407.05	2.83	0.144
381_SR4.2	405.62	5.49	0.133
381_SR4.3	410.35	1.91	0.178
381_SR4.4	410.15	3.53	0.138
381_SR4.5	405.13	0.67	0.135
381_SR4.6	402.15	4.88	0.162
381_SR4.7	396.95	4.74	0.155
381_SR4.8	404.68	4.77	0.152
average [d.nm]	405.26		0.149
s [d.nm]	4.35		0.016
VC [%]	1.07		10.47
u [%]	2.15		20.93

The expanded measurement uncertainty ($k = 2$) for the test material was 2.18 % for the z-average and 19.72 % for the Pdi (Table 3). The results for the sub-sampled fractions showed nearly the same uncertainty for the z-average 2.15 % and a negligible higher uncertainty for the Pdi 20.93 % (Table 5).

c) Slurry sampling

A complete fraction of the first spinning riffler run was used to prepare a slurry with SHMP (2%). Eight samples were taken from the moving slurry.

Table 6 Measurement results for the slurry sub-sampling of the BaSO₄ (fine grade)

	Z-Average [d.nm] NNLS	s [d.nm]	Pdi
381_SL1	414.60	11.31	0.151
381_SL2	418.00	8.49	0.163
381_SL3	399.35	7.57	0.157
381_SL4	405.40	15.79	0.165
381_SL5	410.45	9.07	0.184
381_SL6	414.00	11.17	0.176
381_SL7	405.25	11.24	0.127
381_SL8	402.50	2.69	0.136
average [d.nm]	408.69		0.157
s [d.nm]	6.56		0.019
VC [%]	1.60		12.26
U [%]	3.21		24.51

No significant differences in the values (z-average and Pdi) were observed between the tested increments. This indicates that the particles are distributed homogeneously in the slurry. The results of the slurry sub-sampling showed an increased expanded measurement uncertainty ($k = 2$) compared to the reference values. The measurement uncertainty for the test material was 2.18 % for the z-average and 19.72 % for the Pdi (Table 3). The results for the slurry sub-sampled fractions showed a higher uncertainty for the z-average

3.21 % and a higher uncertainty for the Pdi 24.51 % (Table 6).

d) Paste

A complete fraction of the first spinning riffler run was used to prepare a paste with SHMP (2%).

Table 7 Measurement results for the paste sub-sampling of the BaSO₄ (fine grade)

	Z-Average [d.nm] NNLS	s [d.nm]	Pdi
381_P1	396.80	1.98	0.166
381_P2	398.85	0.64	0.154
381_P3	395.05	11.67	0.150
381_P4	402.95	9.69	0.176
381_P5	395.85	10.39	0.139
381_P6	394.10	7.50	0.185
381_P7	393.95	5.87	0.182
381_P8	397.50	2.69	0.151
average [d.nm]	396.88		0.163
s [d.nm]	2.97		0.017
VC [%]	0.75		10.35
u [%]	1.50		20.69

No significant differences in the values (z-average and Pdi) were observed between the tested increments. This indicates that the particles are distributed homogeneously in the paste. The results of the paste sub-sampling showed a lower expanded measurement uncertainty ($k = 2$) for the z-average compared to the reference values. The measurement uncertainty for the test material was 2.18 % for the z-average and 19.72 % for the Pdi (Table 3). The results for the paste sub-sampled fractions showed an uncertainty for the z-average of 1.50 % and a comparable uncertainty for the Pdi 20.69 %. Therefore the sampling doesn't affect the particle size distribution in a measurable manner.

4.3.2.1 Comparison of the different sub-sampling procedures for the BaSO₄ (fine grade)

Figure 3 shows a comparison of the different z-average values. Additionally the figure shows a comparison of the expanded measurement uncertainties ($k = 2$, error bars) calculated for the different sampling procedures and the test material IRMM_381 (see Table 3). The reference value should reflect the error which corresponds to the dispersion and the DLS measurement steps. The additional amount to the uncertainty is caused by the sampling procedure.

As mentioned above, the values for the z-average of the test material of WP 1 differ from the results for the barium sulfate fine grade which was used for the testing. A comparison of the results for the sampled material leads to the conclusion that the accuracy of the z-average is not significantly affected by the sampling procedure. Next the influence on the measurement uncertainty should be estimated. The sub-sampling by paste and the spinning riffler didn't affect the expanded measurement uncertainty compared to the uncertainty calculated for the test material. For the other two procedures (heap and slurry) an increase is observed.

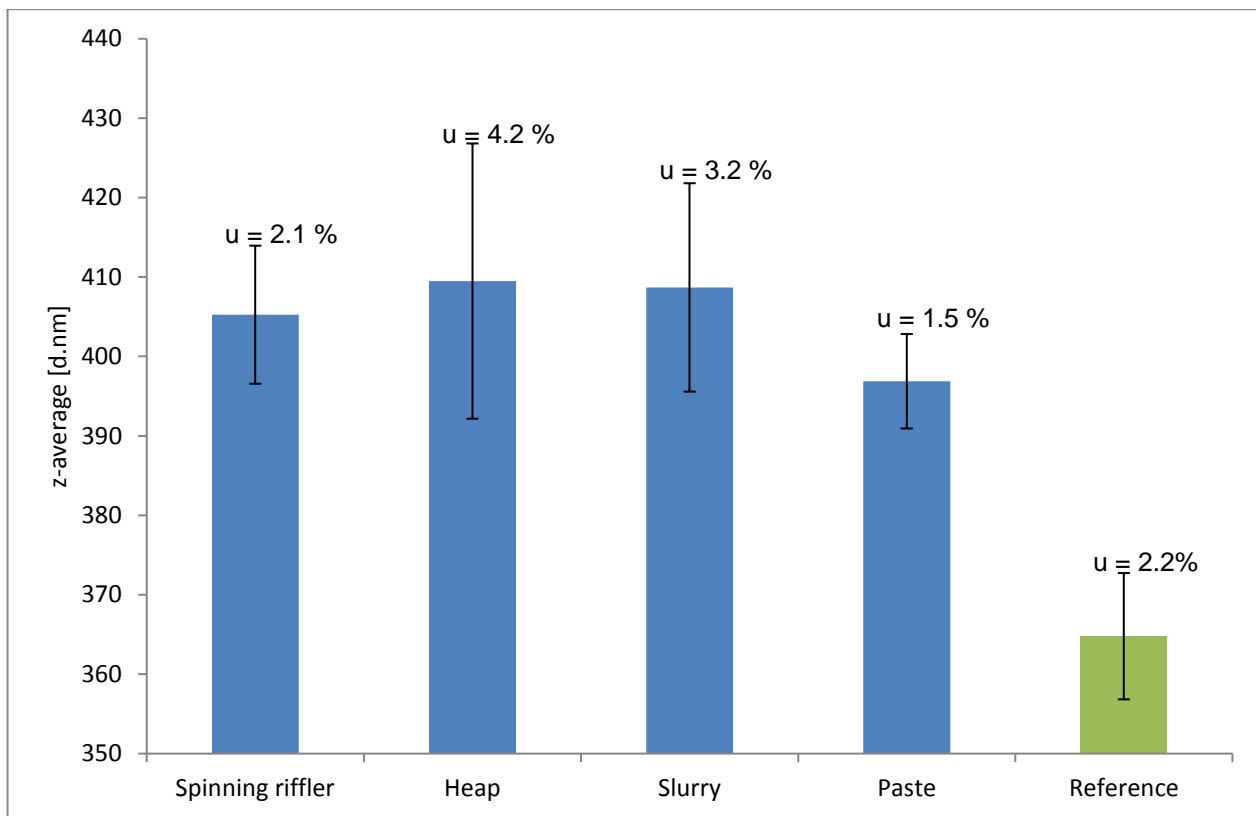


Figure 3 BaSO_4 (fine grade): Comparison of z-average [d.nm] values resulting after the different sampling procedures. Error indicators consider the expanded measurement uncertainties u ($k = 2$).

Figure 4 shows a comparison of the different Pdi values. Additionally the figure shows a comparison of the expanded measurement uncertainties ($k = 2$, error bars) calculated for the different sampling procedures and the test material IRMM_381 (see Table 3). The reference value should reflect the error which corresponds to the dispersion and the DLS measurement steps. The additional amount to the uncertainty is caused by the sampling procedure.

As expected all sub-sampling procedures lead to higher expanded measurement uncertainties ($k = 2$). Slurry and paste sampling showed a minor influence on the expanded measurement uncertainty. The heap and the slurry sub-sampling showed the highest increase.

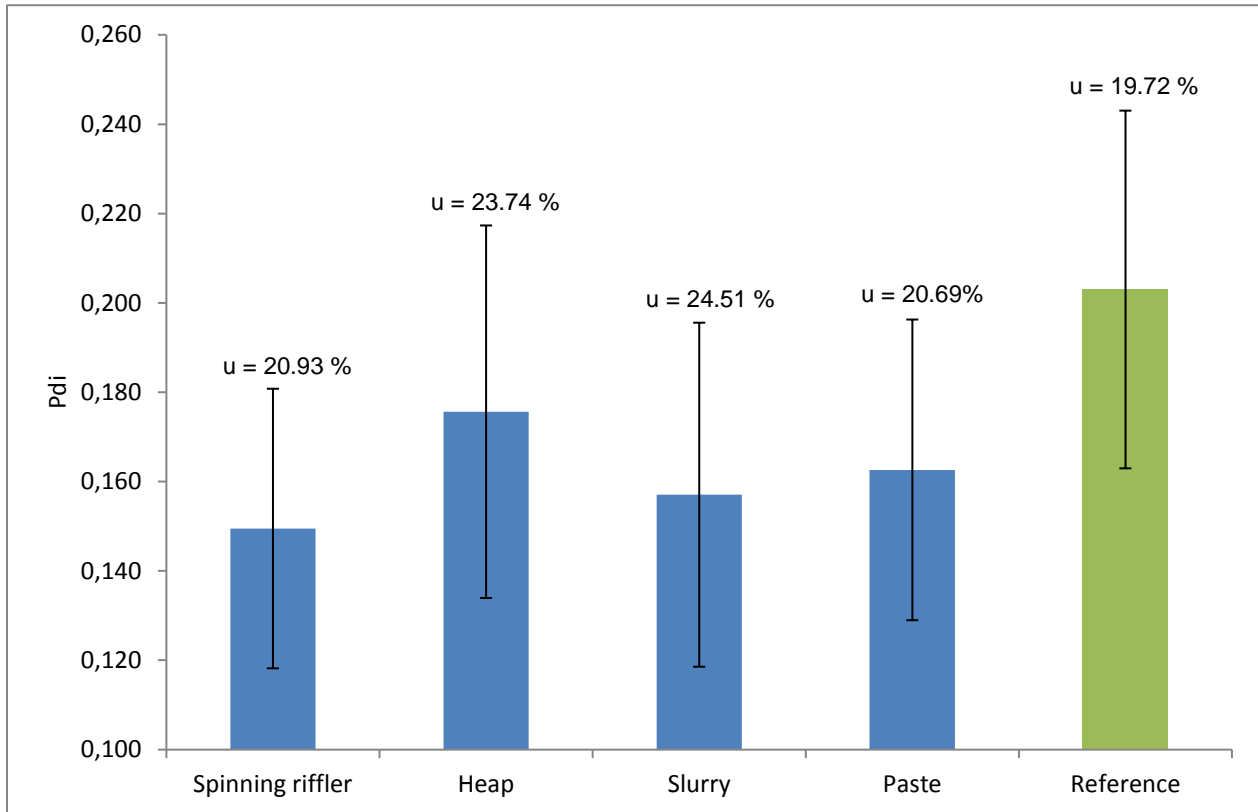


Figure 4 BaSO_4 (fine grade): Comparison of the Pdi results after the different sampling procedures. Error indicators consider the expanded measurement uncertainties ($k = 2$).

4.3.3 BaSO₄ (ultrafine grade)

The amount of the bulk sample was about ca. 960 g. After the first spinning riffler run the fractions weight about 120 g.

a) Heap

Table 8: Measurement results for the heap sub-sampling of the BaSO₄ (ultrafine grade)

	Z-Average [d.nm] NNLS	s [d.nm]	Pdi
387_Z.1	117.37	2.93	0.251
387_Z.2	123.23	1.53	0.285
387_Z.3	124.93	1.86	0.282
387_Z.4	124.27	2.51	0.301
387_Z.5	122.13	2.80	0.294
387_Z.6	125.67	2.29	0.315
387_Z.7	128.47	0.30	0.308
387_Z.8	126.87	1.70	0.301
387_Z.9	130.47	0.90	0.304
387_Z.10	127.60	0.40	0.293
average [d.nm]	125.10		0.293
s [d.nm]	3.69		0.019
VC [%]	2.95		6.50
u [%]	5.90		13.01

The measured z-average 125.10 ± 3.69 nm is higher than the z-average for the test material 119.33 ± 1.24 nm. The Pdi values show a difference with 0.293 for the sampled fractions and 0.138 for the reference. The measurement uncertainty for the test material was 2.08 % for the z-average and 13.04 % for the Pdi (Table 3). The results for the sub-sampled fractions showed a slightly higher uncertainty for the z-average 5.90 % and comparable uncertainty for the Pdi 13.01 % (Table 8).

b) Spinning Riffler

Table 9: Measurement results for the spinning riffler sub-sampling of the BaSO₄ (ultrafine grade)

	Z-Average [d.nm] NNLS	s [d.nm]	Pdi
387_SR4.1	120.15	2.28	0.253
387_SR4.2	123.03	1.76	0.262
387_SR4.3	119.28	4.46	0.244
387_SR4.4	116.37	2.01	0.247
387_SR4.5	119.00	1.58	0.265
387_SR4.6	120.30	2.21	0.270
387_SR4.7	120.87	1.96	0.269
387_SR4.8	119.28	0.64	0.222
average [d.nm]	119.79		0.254
s [d.nm]	1.89		0.016
VC [%]	1.58		6.46
u [%]	3.15		12.92

The measured z-average 119.79 ± 1.89 nm meet the z-average for the test material 119.33 ± 1.24 nm. The Pdi values show a difference with 0.254 for the sampled fractions and 0.138 for the reference. The expanded measurement uncertainty for the test material was 2.08 % for the z-average and 13.04 % for the Pdi (Table 3). The results for the sub-sampled fractions showed a higher uncertainty for the z-average 3.15 % and a lower uncertainty for the Pdi 12.92 % (Table 9).

c) Slurry

Table 10: Measurement results for the slurry sub-sampling of the BaSO₄ (ultrafine grade)

	Z-Average [d.nm] NNLS	s [d.nm]	Pdi
387_SL2 1	114.00	0.90	0.197
387_SL2 2	116.60	0.66	0.219
387_SL2 3	119.87	0.96	0.221
387_SL2 4	112.33	0.90	0.187
387_SL2 5	120.53	1.22	0.214
387_SL2 6	117.97	1.00	0.198
387_SL2 7	117.10	1.80	0.197
387_SL2 8	117.13	1.02	0.203
average [d.nm]	116.94		0.204
s [d.nm]	2.74		0.012
VC [%]	2.34		5.85
u [%]	4.69		11.69

The measured z-average 116.94 ± 2.74 nm is comparable with the z-average for the test material 119.33 ± 1.24 nm. The Pdi values show a difference with 0.204 ± 0.012 for the sampled fractions and 0.138 ± 0.009 for the reference. The measurement uncertainty for the test material was 2.08 % for the z-

average and 13.04 % for the Pdi (Table 3). The results for the sub-sampled fractions showed a higher uncertainty for the z-average 4.69 % and comparable uncertainty for the Pdi 11.69 % (Table 10).

d) Paste

Table 11: Measurement results for the paste sub-sampling of the BaSO₄ (ultrafine grade)

	Z-Average [d.nm] NNLS	s [d.nm]	Pdi
387_P1	119.53	2.00	0.247
387_P2	116.07	0.61	0.233
387_P3	118.57	1.55	0.255
387_P4	115.63	1.81	0.243
387_P5	112.27	1.63	0.218
387_P6	113.53	2.80	0.238
387_P7	116.63	1.72	0.235
387_P8	114.27	1.18	0.231
387_P9	111.77	1.36	0.204
average [d.nm]	115.36		0.234
s [d.nm]	2.67		0.015
VC [%]	2.31		6.60
u [%]	4.62		13.20

The measured z-average 115.36 ± 2.67 nm is slightly lower as the z-average for the test material 119.33 ± 1.24 nm. The Pdi values show a difference with 0.234 ± 0.015 for the sampled fractions and 0.138 ± 0.009 nm for the reference. The measurement uncertainty for the test material was 2.08 % for the z-average and 13.04 % for the Pdi (Table 3). The results for the sub-sampled fractions showed a higher uncertainty for the z-average 4.62 % and comparable uncertainty for the Pdi 13.20 % (Table 11).

4.3.3.1 Comparison of the different sub-sampling procedures for the BaSO₄ (ultrafine grade)

Figure 5 represents a comparison of the different z-average values. Additionally the figure shows a comparison of the expanded measurement uncertainties ($k = 2$, error bars) calculated for the different sampling procedures and the test material IRMM_387 (see Table 3) as reference. The reference value should reflect the error which corresponds to the dispersion and the DLS measurement steps. The additional amount to the uncertainty is caused by the sampling procedure.

A comparison of the results for the z-average leads to the conclusion that the accuracy is not effected by the sampling procedures as the values are in good accordance to the values published for the test materials within the NanoDefine reports. Next the influence of the sampling procedure on the expanded measurement should be estimated. All the sub-sampling procedures result in a higher variance compared to the uncertainty calculated for the test material. This is in line with the expectation from theory as there are more error steps included. The heap sampling shows the highest effect on the expanded measurement uncertainty and the spinning riffler the lowest. This corresponds to the observations from other publications where coarser materials were investigated (Basim, Khalili 2015). Slurry and paste sampling showed a comparable impact on the measurement uncertainty.

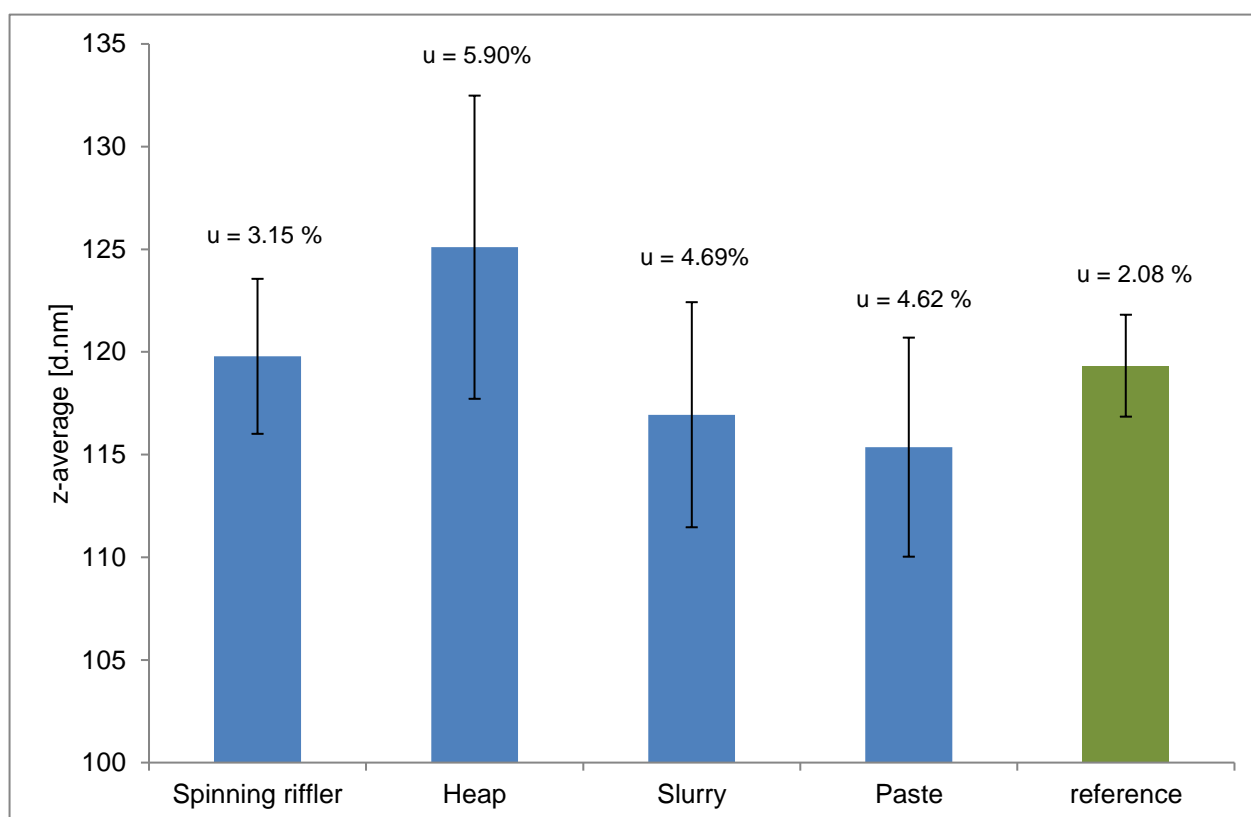


Figure 5: BaSO₄ (ultrafine grade): Comparison of z-average [d.nm] values resulting after the different sampling procedures. Error indicators consider the measurement uncertainties ($k = 2$).

Figure 6 shows a comparison of the different Pdi values. Additionally the figure shows a comparison of the expanded measurement uncertainties ($k = 2$) calculated for the different sampling procedures and the test material IRMM_387 (see Table 3). The reference value should reflect the variance which corresponds to the dispersion and the DLS measurement steps. The additional amount to the uncertainty is caused by the sampling procedure.

The expanded measurement uncertainties for the Pdi were not affected by the sampling procedures and have nearly the same amounts. Even when the measurement uncertainties are taken into account, a difference occurs between the Pdi values for the heap sampling and the slurry. Additionally the Pdi values are rising after all sampling procedures resulting in values above 0.200. The Pdi for the test material IRMM_387 indicated a narrow particle distribution (Pdi = 0.138). Probably there is an influence on the particle size distributions caused by the sampling procedures. Another reason for the deviations may be that there are production fluctuations. Probably the investigated material doesn't show the same distribution like the test material IRMM_387 of work package 1.

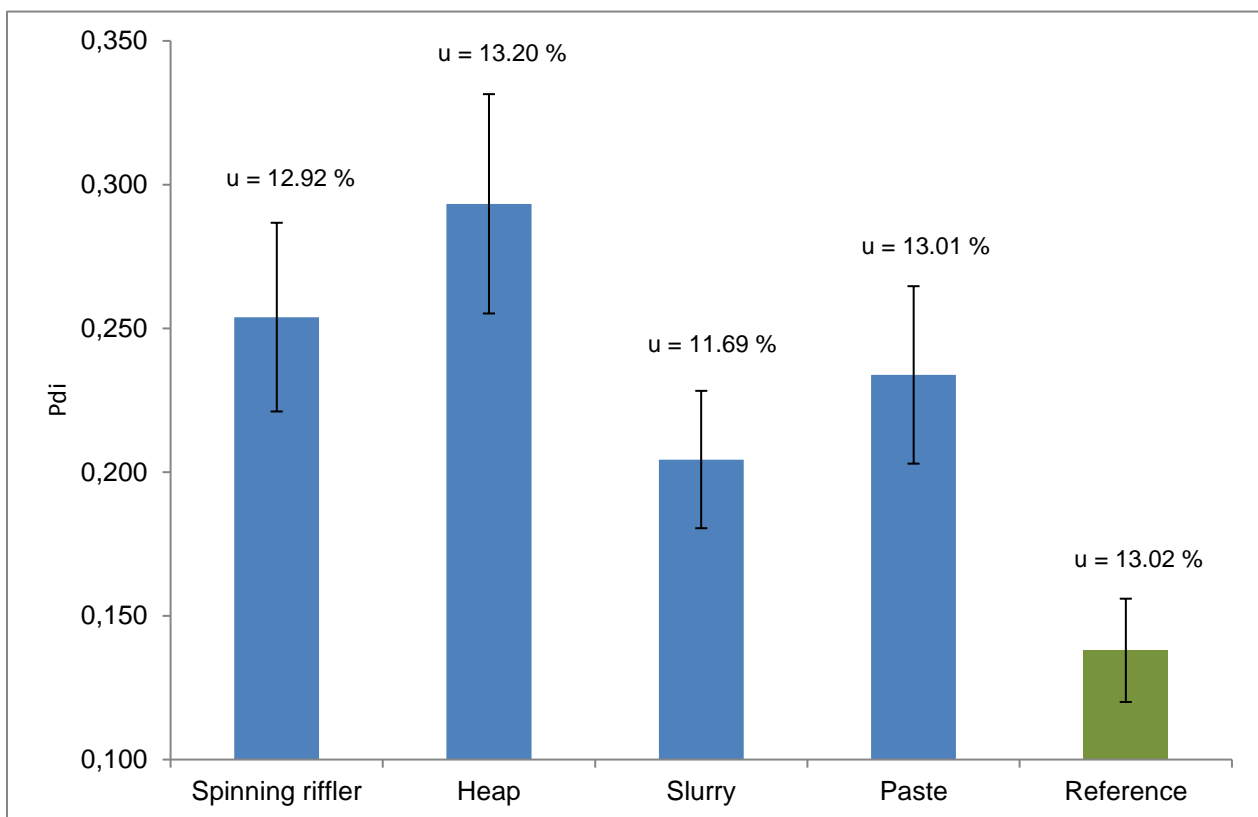


Figure 6: BaSO₄ (ultrafine grade): Comparison of the Pdi results after the different sampling procedures. Error indicators consider the expanded measurement uncertainties u ($k = 2$).

4.3.4 TiO₂

The amount of the bulk sample was about ca. 1300 g. After the first spinning riffler run, the fractions weight between 168-172 g.

A) Heap

Table 12: Measurement results for the heap sub-sampling of the TiO₂

	Z-Average [d.nm] NNLS	s [d.nm]	Pdi
388_Z.1	319.07	3.61	0.185
388_Z.2	320.47	4.82	0.166
388_Z.3	312.40	6.40	0.141
388_Z.4	313.00	2.26	0.130
388_Z.5	338.70	8.11	0.218
388_Z.6	311.87	4.90	0.154
388_Z.7	316.07	1.08	0.168
388_Z.8	310.40	2.63	0.167
388_Z.9	334.10	1.77	0.191
388_Z.10	311.17	1.27	0.132
average [d.nm]	318.72		0.165
s [d.nm]	9.95		0.027
VC [%]	3.12		16.13
u [%]	6.25		32.26

The measured z-average 318.72 ± 9.95 nm is a little higher than the z-average for the test material 310.27 ± 5.76 nm but under consideration of the variance the results are comparable. The Pdi values show a difference with 0.165 for the sampled fractions and 0.151 for the reference. The expanded measurement uncertainty ($k = 2$) for the test material was 3.71 % for the z-average and 33.11 % for the Pdi (Table 3). The results for the sub-sampled fractions showed a slightly higher uncertainty for the z-average 6.25 % and a comparable uncertainty for the Pdi 32.26 % (Table 12).

B) Spinning Riffler

Table 13: Measurement results for the spinning riffler sub-sampling of the TiO₂

	Z-Average [d.nm] NNLS	s [d.nm]	Pdi
388_SR4.1	312.22	5.49	0.148
388_SR4.2	312.75	2.12	0.145
388_SR4.3	316.27	3.48	0.167
388_SR4.4	316.05	2.71	0.168
388_SR4.5	311.10	5.18	0.126
388_SR4.6	311.53	3.98	0.174
388_SR4.7	314.98	5.76	0.159
388_SR4.8	312.03	3.64	0.149
average [d.nm]	313.37		0.154
s [d.nm]	2.08		0.016
VC [%]	0.66		10.10
u [%]	1.33		20.21

The measured z-average 313.37 ± 2.08 nm is a little higher than the z-average for the test material 310.27 ± 5.76 nm. The Pdi values show only a minor difference with 0.154 for the sampled fractions and 0.151 for the reference. The expanded measurement uncertainty ($k = 2$) for the test material IRMM_388 was 3.71 % for the z-average and 33.11 % for the Pdi (Table 3). The results for the sub-sampled fractions showed a minor uncertainty for the z-average 1.33 %. Also the uncertainty for the Pdi is lower with 20.21 % (Table 13).

C) Slurry

Table 14: Measurement results for the slurry sub-sampling of the TiO₂

	Z-Average [d.nm] NNLS	s [d.nm]	Pdi
388_SL1	311.13	4.22	0.145
388_SL2	309.13	2.87	0.143
388_SL3	316.63	8.64	0.168
388_SL4	317.60	3.22	0.164
388_SL5	309.13	5.71	0.142
388_SL6	317.23	4.15	0.173
388_SL7	316.53	7.05	0.178
388_SL8	308.57	3.55	0.161
average [d.nm]	313.25		0.159
s [d.nm]	4.09		0.014
VC [%]	1.31		8.94
u [%]	2.61		17.88

The measured z-average 313.25 ± 4.09 nm is a little higher than the z-average for the test material 310.27 ± 5.76 nm. The Pdi values show a slightly difference with 0.159 for the sampled fractions and 0.151 for the reference. The measurement uncertainty for the test material IRMM_388 was 3.71 % for the z-average and 33.11 % for the Pdi (Table 3). The results for the sub-sampled fractions showed a lower uncer-

tainty for the z-average 2.61 % and a lower uncertainty for the Pdi 17.88 % (Table 14).

D) Paste

Table 15: Measurement results for the paste sub-sampling TiO₂

	Z-Average [d.nm] NNLS	s [d.nm]	Pdi
388_P1	310.63	4.84	0.157
388_P2	310.90	8.45	0.161
388_P3	311.77	1.76	0.142
388_P4	311.37	4.75	0.136
388_P5	318.97	1.44	0.158
388_P6	311.70	5.91	0.158
388_P7	312.17	2.51	0.171
388_P8	306.20	6.32	0.141
average [d.nm]	311.71		0.153
s [d.nm]	3.49		0.012
VC [%]	1.12		7.82
u [%]	2.24		15.64

The measured z-average 311.71 ± 3.49 nm is a little higher than the z-average for the test material 310.27 ± 5.76 nm. The Pdi values show a minor difference with 0.153 for the sampled fractions and 0.151 for the reference. The expanded measurement uncertainty ($k=2$) for the test material IRMM_388 was 3.71 % for the z-average and 33.11 % for the Pdi (Table 3). The results for the sub-sampled fractions showed a lower uncertainty for the z-average 2.24 % and a lower uncertainty for the Pdi 15.64 % (Table 15).

4.3.4.1 Comparison of the different sub-sampling procedures for the TiO₂

Figure 7 shows a comparison of the different z-average values. Additionally the figure shows a comparison of the expanded measurement uncertainties ($k = 2$, error bars) calculated for the different sampling procedures and the test material IRMM_388 (see Table 3). The reference value should reflect the variance which corresponds to the dispersion and the DLS measurement steps. The additional amount to the uncertainty is caused by the sampling procedure.

A comparison of the results for the z-average leads to the conclusion that the accuracy is not effected by the sampling procedures as the values are in good accordance to the values published for the test material IRMM_388. Next the influence of the sampling procedure on the expanded measurement should be estimated. With the exception of the heap sampling procedure the sub-sampling has no effect to the expanded measurement uncertainty. For the heap sampling the expanded measurement uncertainty was nearly doubled compared to the other procedures.

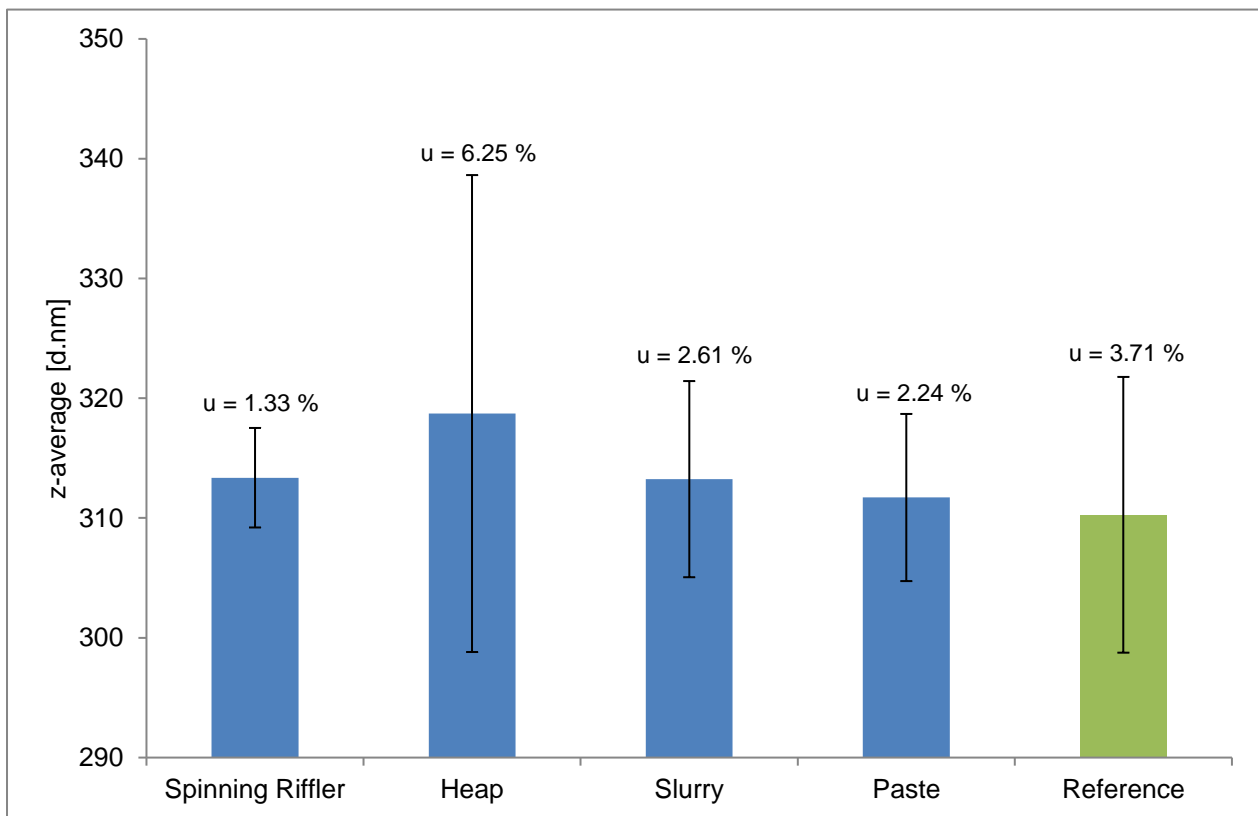


Figure 7: TiO₂: Comparison of z-average [d.nm] values resulting after the different sampling procedures. Error indicators consider the measurement uncertainties ($k = 2$).

Figure 8 shows a comparison of the different Pdi values. Additionally the figure shows a comparison of the expanded measurement uncertainties ($k = 2$) calculated for results after the different sampling procedures and the test material IRMM_387 (see Table 3). The reference value should reflect the variance which corresponds to the dispersion and the DLS measurement steps. The additional amount to the uncertainty is caused by the sampling procedure.

The absolute values for the Pdi are nearly identical. The expanded measurement uncertainties for the Pdi are not affected by the sampling procedures compared to the calculated values for the test material IRMM_388. But it is obvious that the heap sampling lead to a higher variance. The spinning riffler procedure and the sub-sampling procedures (slurry and paste) showed a comparable effect to the expanded measurement uncertainty.

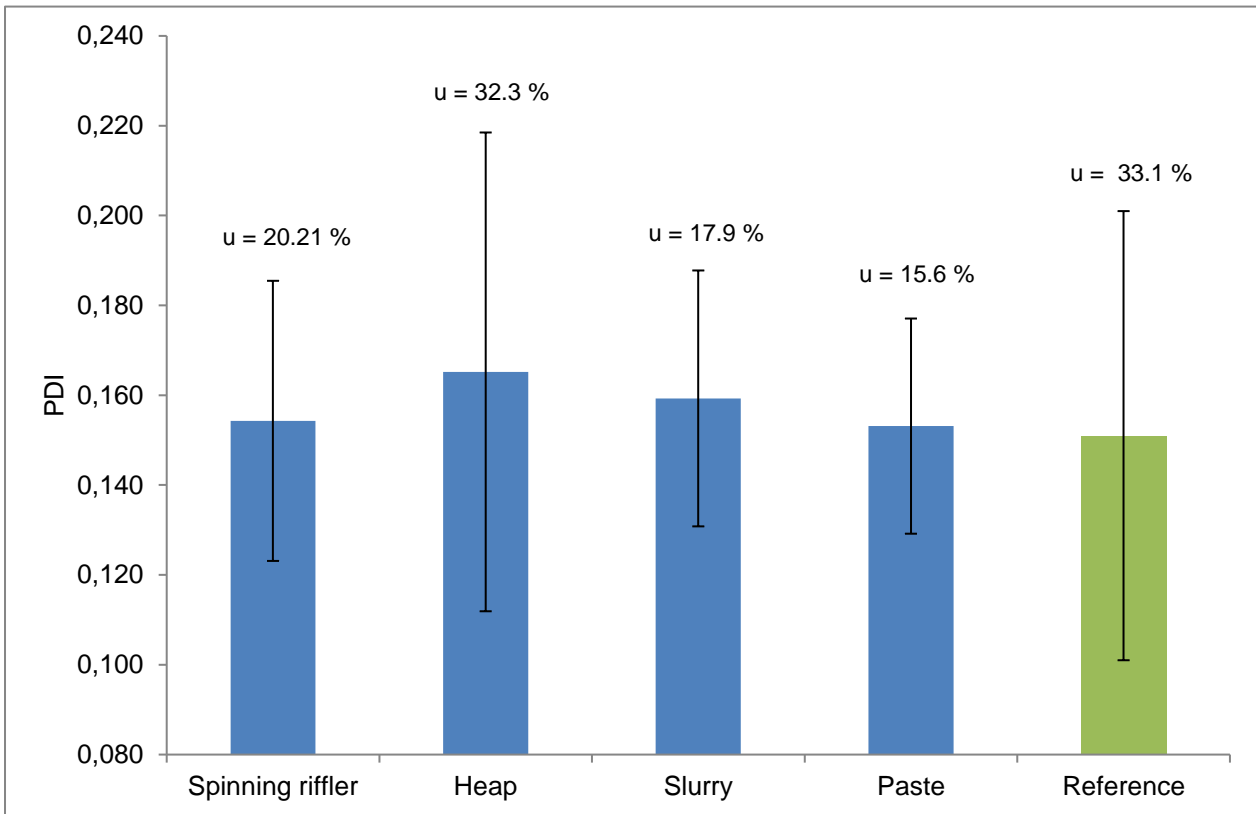


Figure 8: TiO₂: Comparison of the Pdi results after the different sampling procedures. Error indicators consider the expanded measurement uncertainties ($k = 2$).

4.3.5 Comparison of the different sub-sampling procedures

In order to assess which method is most suitable for routine applications, the practical implementation in the lab has been assessed. As heap sampling showed problems for the homogeneity of the fraction, the slurry sampling was the most practical method. The spinning riffler method included time consuming cleaning steps between the four runs. To prepare a homogenous paste was also a complex task.

To make a general estimation about the influence on the measurement uncertainties caused by the sub-sampling procedures the expanded measurement uncertainties ($k = 2$) are compared in Figure 9.

A material independent observation is that the heap sampling corresponds to highest measurement uncertainties. This is in line with other publications on coarser materials (ISO ISO 14488:2007(E); Basim, Khalili 2015) . There are no obvious differences between the slurry and paste sampling procedures. The flowing powder sub-sampling with the spinning riffler showed in all cases no or only a minimal effect on the expanded measurement uncertainty.

Comparing the two barium sulfate materials fine and ultrafine grade, which differ in their size, it is an observation that the ultrafine material tends to show higher expanded measurement uncertainties after the sub-sampling procedures.

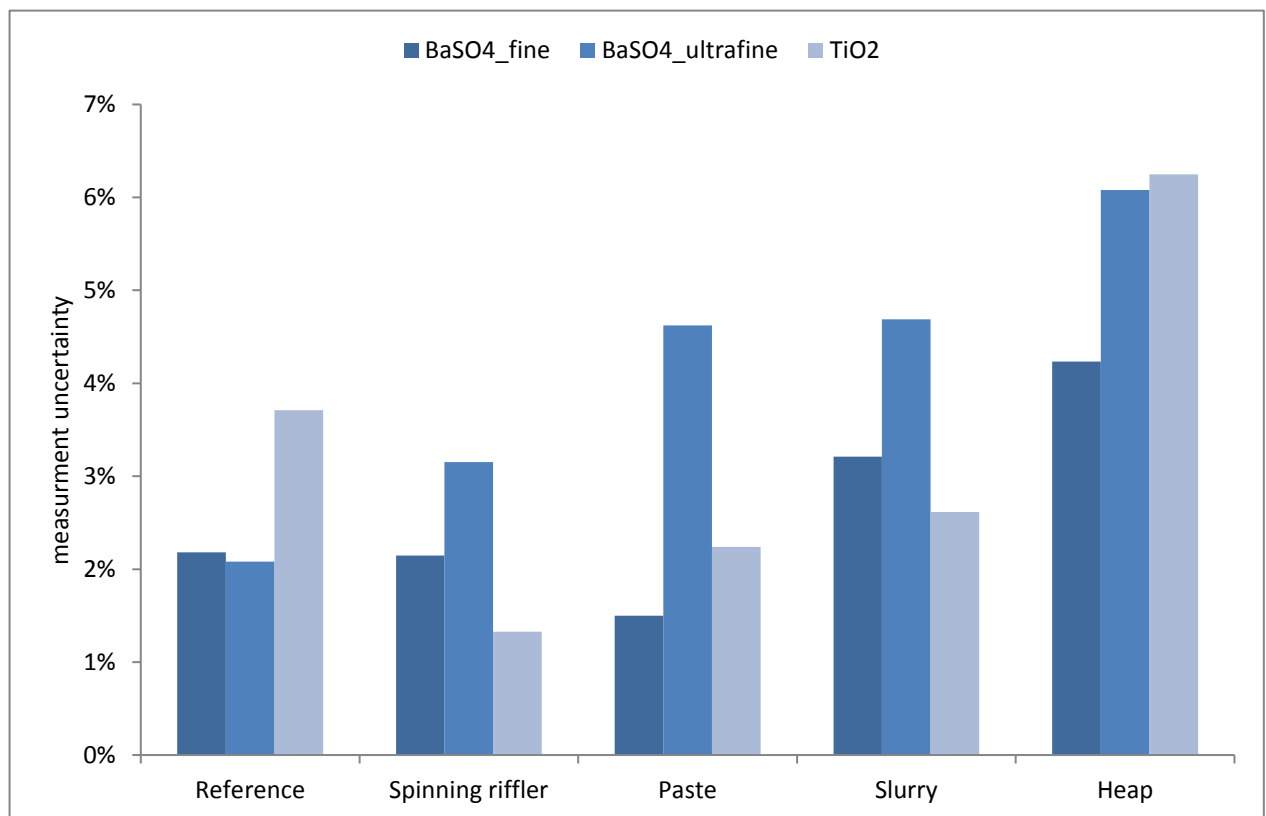


Figure 9: Comparison of the expanded measurement uncertainties ($k = 2$) for the z-average results. Compared are all investigated materials and sub-sampling procedures.

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