Report

Reference Material

BAM-P201

Artificially Aged Polyethylene
(powder)

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Summary

This report describes preparation and analysis of the reference material BAM-P201.

The following particle sizes and uncertainties have been determined:

	Particle size[1] in µm	**Standard deviation s** in µm	**Rel. Standard deviation s** in %
D10	17.9	0.3	1.8
D50	61.2	1.4	2.3
D90	158.6	7.5	4.7

1 Mean values of 30 measurements with 10 randomly selected sample bottles of 10 mg, where each was tested 3 times with 3 mg aged PE by laser diffraction under dry dispersion (HELOS/BR+RODOS/L+ASPIROS, Sympatec, Germany)

2 The standard deviation (s) was calculated according to the following formula from three individual measurements each 3 mg. Formula: $s = \sqrt{\frac{\sum(x-\bar{x})^2}{(n-1)}}$

This report contains detailed information on the preparation of the reference material as well as on homogeneity and stability investigations and on the analytical methods used for accompanied analysis.
The values for particle size distribution analysis are based on the results of thirty measurements of the reference material.

Content

List of abbreviations
(if not explained elsewhere)

RM	reference material
PE	polyethylene
D10	The D10 value describes the particle diameter of the measured volume below which 10.3% of the particles fall below.
D50	The D50 value describes the particle diameter of the measured volume below which 50.3% of the particles fall below.
D90	The D90 value describes the particle diameter of the measured volume below which 90.3% of the particles fall below.
s	standard deviation
r.H.	relative humidity
ANOVA	one-way analysis of variance

1. Introduction

PE is the most abundant polymer in the environment. The material has a density of less than 1 g/cm^3, which causes it to float in water on the surface. PE in water can only be produced as a stable suspension by adding compatibilizers, which is not helpful for reference material, where the material shall be pure. In the environment, however, PE is mainly present in an aged state and thus changes its hydrophilicity. Afterwards, it is easier to suspend and shows a changed sinking behaviour in the water column. Furthermore, small non circular PE particles (< 500 µm) with sharp edges cannot be produced by cryogenic grinding due to the very low glass transition temperature of PE (~ -100 °C). Artificially aged PE has the advantage that the material becomes first brittle by aging and hence is easier to grind.

The idea is to offer reference material close to reality for the validation of sampling, sample preparation and detection of microplastics. At the same time, it can be used for the evaluation of effects in the field of ecotoxicology, human toxicology, pollutant transport and agglomeration behaviour related to microplastics. The particle size distribution shall be < 500 µm. The mass content in real environmental sample is very low so that the number of particles in a single reference bottle as reference material close to reality has to be very low too. Since an exact weighing of a few thousand particles is not possible, we produce reference samples with a weight of 10 mg, which corresponds to a number of about 1 Mio. particles larger than 9 µm regarding to our produced artificially aged PE.

2. Material

PE-foil was delivered by Lyondellbasell (Rotterdam, Netherlands). 70 g of the foil was irradiated at 75 °C under constant UV-A radiation and 6% r.H. for 100 h in a climate chamber. Afterwards the artificially aged PE foil was cryogenic ground in the cryomill with five stainless steel balls (diameter 12 mm each) in a 25 ml grinding vessel. The pre-cooling time was 15 min (5 Hz). Milling occurred by 6 cycles each 5 min (25 Hz). The time between the individual cycles was 2 min (5 Hz). The ground powder was homogenized in a tumbler mixer for 2 hours.

Subsequently 500 units with 10 mg PE powder each were bottled in amber glass bottles. The metal lids have seals consisting of silicone and Teflon.

3. Homogeneity

For testing the homogeneity, 10 individual units of BAM-P201 were randomly selected for particle size distribution measurements by laser diffraction with dry powder dispersion (HELOS/BR + RHODOS/L + ASPIROS, Sympatec, Deutschland). Three replicate measurements per bottle were carried out under repeatability conditions with approximately 3 mg each.

Table 1: Comparison of ANOVA results for D10, D50 and D90

	Source of Variation	Mean square sum (MS)	*Test value (F)*	*Critical F-value*
D10	Between Groups	0,2067	3,3286	2,3928
	Within Groups	0,0621		
D50	Between Groups	2,8240	1,7794	2,3928
	Within Groups	1,5871		
D90	Between Groups	75,4834	1,5728	2,3928
	Within Groups	47,9935		

At D50 and D90 the variation between the bottles is not significantly larger than within the bottles, which means that the samples are homogeneous.

At D10 the variation between the bottles is significantly larger than within the bottles, which is probably due to the fact that the small, statically charged particles are difficult to separate in the measuring device and larger measurement uncertainties are caused.

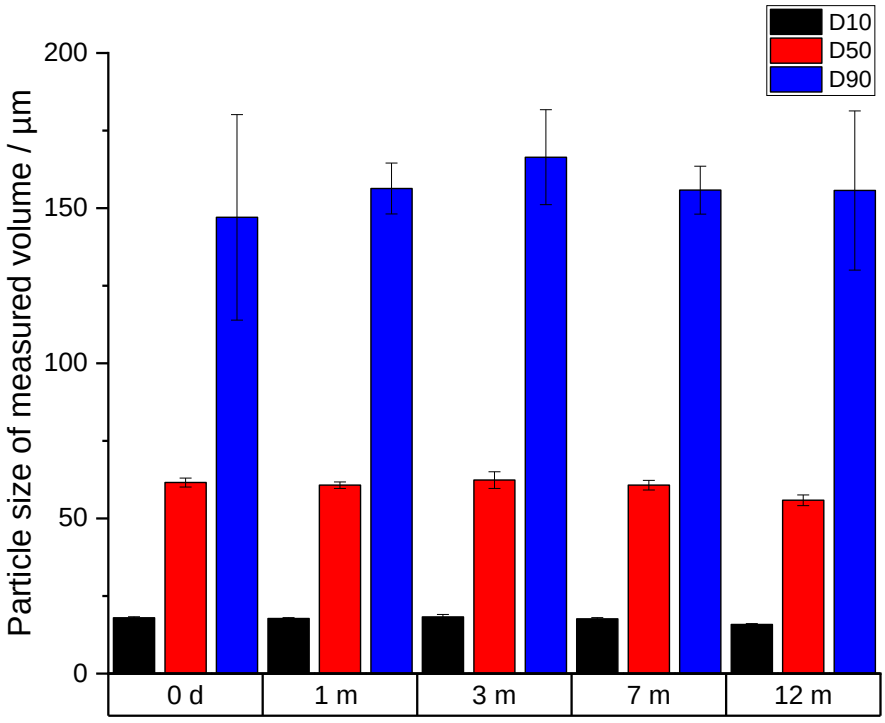
The successful participation in interlaboratory comparison (OE 5.5, Frau Kuchenbecker, 2019) shows the suitability of the measurement procedure.

4. Stability

Based on expert knowledge and literature in the field of polymers, it is very unlikely that BAM-P201 composition will change if the samples are stored and handled properly. Nevertheless, a stability check of the bottled material was performed.

Therefore, immediately after bottling selected units were stored at a temperature of 5 °C (the indicated temperature values imply a tolerance of ±3 °C). After a storage time of 0, 1, 3, 7 and 12 months, respectively, three bottles were tested in terms of particle size distribution. Three particle size distribution measurements with 3 mg each were carried out from each bottle. The results are presented in Table 2.

Table 2: Comparison of mean values of measured volumes in particle size distribution measurement of 0, 1, 3, 7 and 12 m



BAM-P201 is stable regarding particle size distribution over 12 months period.

5. Characterization

5.1 Analytical methods

The RM was characterised by measuring the particle size distribution by laser diffraction with dry powder dispersion, determining the carbonyl index by Fourier transform infrared spectroscopy and differential scanning calorimetry.

Particle size distribution:

- Device: HELOS/BR+RODOS/L+ASPIROS (Sympatec, Germany)
- Laser diffraction under dry dispersion, pressure: 2,5 bar, velocity of ASPIROS sleigh: 100 mm/s,
- Evaluation is carried out with Fraunhofer approximation
- Homogeneity test with 10 randomly selected sample bottles of 10 mg, where each was tested 3 times with 3 mg. Number of measurements in total 30.
- Stability tests with 3 randomly selected sample bottles of 10 mg, where each was tested 3 times with 3 mg. Number of measurements per single period in total 9.

Fourier transform infrared spectroscopy:

- Device: Nicolet Nexus 6700 FTIR spectrometer (Thermo Scientific, USA)
- Aged PE embedded in KBr pill measured by Transmission – Fourier-transform infrared spectroscopy
- Integration limit: 1805 - 1679 cm^{-1} and 1390 – 1330 cm^{-1} (C=O / C-H)
- Number of measurements: 6

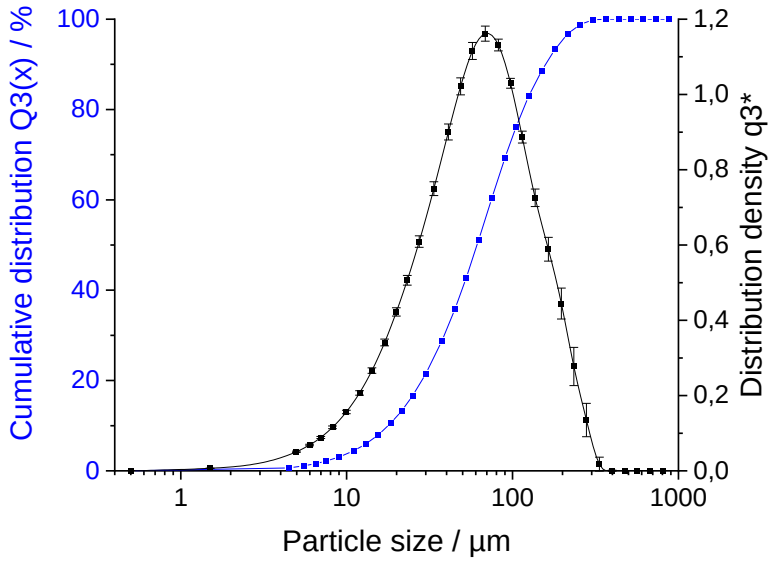
Differential scanning calorimetry:

- Device: DSC 7020 (Seiko, THASS, Germany)
- Integration limit: 75 – 136 °C
- Last calibration date: 26th of March 2019
- Number of measurements: 3

5.2 Analytical results and statistical evaluation

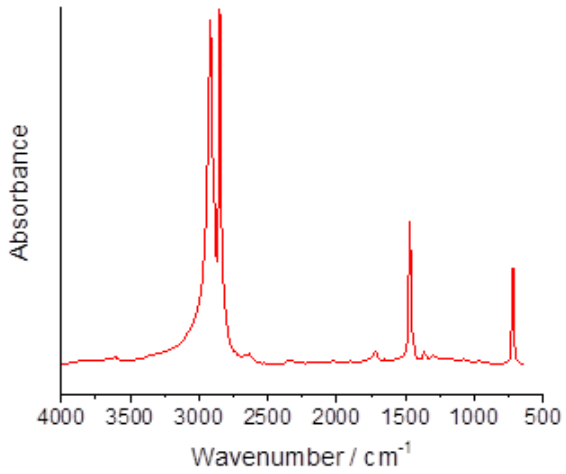
The analytical results are presented below.

Particle size distribution:



	Particle size[1] in µm	**Standard deviation s** in µm	**Rel. Standard deviation s** in %
D10	17.9	0.3	1.8
D50	61.2	1.4	2.3
D90	158.6	7.5	4.7

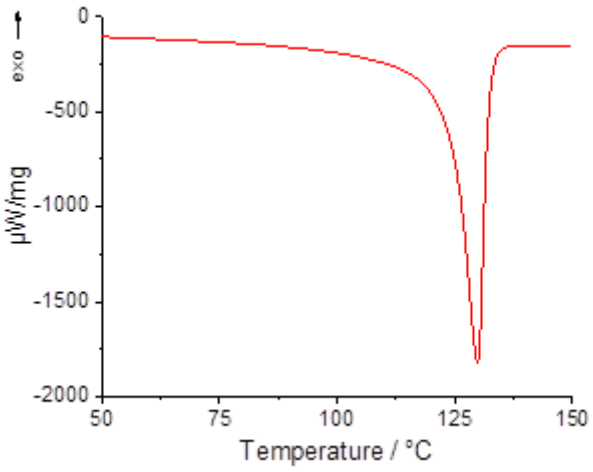
Fourier transform infrared spectroscopy:



The peak between 1600 and 1700 cm^{-1} represents the oxidised part within the artificially aged PE.

Carbonyl-Index*	Standard deviation s	Rel. Standard deviation s in %
1.86	0.12	6.69

Differential scanning calorimetry:



ΔH* in µW/mg	Standard deviation s in µW/mg	Rel. Standard deviation s in %
12359.97	1011.08	8.18

6. Information on the proper use of the reference material

6.1 Recommended use

The present material is a reference material close to reality for the validation of sampling, sample preparation and detection of microplastics. At the same time, it can be used for the evaluation of effects in the field of ecotoxicology, human toxicology, pollutant transport and agglomeration behaviour related to microplastics.

The material is produced as "one shot" reference material and intended for single use. The glass bottle must be carefully rinsed with a liquid to fully use the 10 mg.

6.2 Transport, storage and handling

RM BAM-P201 should be stored dark and dry at temperatures of 5 ± 3 °C in its original tightly closed bottle. The material is produced as "one shot" reference material and intended for single use. The glass bottle must be carefully rinsed with a liquid to fully use the 10 mg.

6.3 Shelf life

The initial stability study after storage for 3 months of selected units at temperatures of 5 ± 3 °C did not reveal any statistically significant deterioration of the particle size distribution. However, starting with dispatch of the material from BAM the validity of the material expires after 24 months. Post-

certification measurements will be conducted in appropriate periods to keep this information up to date.

6.4 Safety information

The usual laboratory safety precautions must be applied. No hazardous effects are to be expected when the material is used under conditions commonly adopted for the analysis of environmental samples.

6.5 Legal notice

Neither BAM, its contractors nor any person acting on their behalf:

(a) make any warranty or representation, express or implied, that the use of any information, material, apparatus, method or process disclosed in this document does not infringe any privately owned intellectual property rights; or

(b) assume any liability with respect to, or for damages resulting from, the use of any information, material, apparatus, method or process disclosed in this document.

7. Information on purchase of the reference material

Reference material BAM-P201 is supplied by

Bundesanstalt für Materialforschung und -prüfung (BAM)
Richard-Willstätter-Str. 11, D-12489 Berlin, Germany
Phone +49 (0)30 - 8104 2061
Fax: +49 (0)30 – 8104 72061
E-Mail: sales.crm@bam.de

Each bottle of BAM-P201 will be distributed together with an accompanying document containing the mean values and standard deviations of all accepted data sets and information on the analytical methods used.

https://www.bam.de.
www.webshop.bam.de

Appendix

Table 3: Results of homogeneity testing of 10 randomly selected units and their replicate measurements within the units for particle size D10

Bottle	Replicate measurement	Particle size in µm (D10)	Average Particle size of three replicate measurements per bottle with standard deviations s * in µm (D10)
ID256	1 2 3	18.02 17.94 17.71	17.89+/-0.16 (0.92 %)
ID370	1 2 3	17.87 17.28 18.27	17.81+/-0.50 (2.79 %)
ID317	1 2 3	17.81 17.43 17.23	17.49+/-0.29 (1.68 %)
ID017	1 2 3	17.84 17.73 17.65	17.74+/-0.10 (0.55 %)
ID333	1 2 3	17.93 18.04 17.93	17.97+/-0.06 (0.35 %)
ID045	1 2 3	17.58 17.44 17.70	17.57+/-0.13 (0.74 %)
ID338	1 2 3	18.05 17.71 17.59	17.78+/-0.24 (1.36 %)
ID464	1 2 3	18.01 17.61 17.57	17.73+/-0.25 (1.38 %)
ID127	1 2 3	18.05 17.96 18.40	18.14+/-0.23 (1.27 %)
ID046	1 2 3	18.63 18.17 18.35	18.38+/-0.23 (1.24 %)

Table 4: Results of homogeneity testing of 10 randomly selected units and their replicate measurements within the units for particle size D50

Bottle	Replicate measurement	Particle size in µm (D50)	Average Particle size of three replicate measurements per bottle with standard deviations s * in µm (D50)
ID256	1 2 3	60.13 61.12 61.74	61.00+/-0.8 (1.34 %)
ID370	1 2 3	63.22 58.10 61.61	60.97+/-2.62 (4.29 %)
ID317	1 2 3	58.04 59.24 61.66	59.65+/-1.84 (3.09 %)
ID017	1 2 3	60.26 60.50 61.21	60.66+/-0.49 (0.81 %)
ID333	1 2 3	61.29 61.60 61.81	61.57+/-0.26 (0.43 %)
ID045	1 2 3	60.81 60.09 60.25	60.38+/-0.38 (0.63 %)
ID338	1 2 3	60.20 61.16 62.43	61.26+/-1.12 (1.82 %)
ID464	1 2 3	59.91 60.09 62.45	60.82+/-1.42 (2.33 %)
ID127	1 2 3	63.30 62.14 61.92	62.46+/-0.74 (1.19 %)
ID046	1 2 3	62.66 62.35 63.92	62.98+/-0.83 (1.32 %)

Table 5: Results of homogeneity testing of 10 randomly selected units and their replicate measurements within the units for particle size D90

Bottle	Replicate measurement	Particle size in µm (D90)	Average Particle size of three replicate measurements per bottle with standard deviations s * in µm (D90)
ID256	1	157.46	154.29+/-2.91 (1.89 %)
	2	153.66	
	3	151.74	
ID370	1	159.24	157.06+/-11.66 (7.42 %)
	2	144.47	
	3	167.47	
ID317	1	166.85	152.43+/-12.98 (8.82 %)
	2	148.77	
	3	141.66	
ID017	1	155.80	155.16+/-1.79 (1.16 %)
	2	153.13	
	3	156.53	
ID333	1	164.50	161.72+/-2.63 (1.63 %)
	2	161.39	
	3	159.27	
ID045	1	157.14	156.52+/-5.25 (3.35 %)
	2	161.43	
	3	150.98	
ID338	1	171.30	161.82+/-8.71 (5.38 %)
	2	160.02	
	3	154.15	
ID464	1	161.86	154.81+/-6.22 (4.02 %)
	2	150.11	
	3	152.45	
ID127	1	165.57	164.31+/-3.23 (1.97 %)
	2	166.72	
	3	160.64	
ID046	1	167.07	167.77+/-2.05 (1.22 %)
	2	166.16	
	3	170.07	

Table 6: Results of the stability test after storage times of 0, 1, 3, 7 and 12 months and their replicate measurements within the units for particle size D10

Storage time	Bottle	Replicate measurement	Particle size in µm (D10)	Average Particle size of three replicate measurements per bottle with standard deviations s in µm (D10)
0 d	ID185	1 2 3	17.85 17.59 18.49	17.98+/-0.46 (2,57 %)
	ID249	1 2 3	17.65 18.00 18.24	17.96+/-0.30 (1.66 %)
	ID349	1 2 3	17.80 17.82 18.37	17.99+/-0.32 (1.80 %)
1 m	ID 227	1 2 3	17.77 18.06 17.36	17.73+/-0.35 (2.00 %)
	ID 242	1 2 3	17.97 17.71 17.90	17.86+/-0.13 (0.74 %)
	ID 452	1 2 3	17.84 17.47 17.96	17.76+/-0.26 (1.44 %)
3 m	ID 234	1 2 3	18.39 17.41 17.91	17.90+/-0.49 (2.73 %)
	ID 111	1 2 3	18.20 17.14 17.86	17.73+/-0.54 (3.03 %)
	ID 103	1 2 3	19.14 19.31 19.07	19.17+/-0.12 (0-63 %)
7 m	ID 142	1 2 3	18.07 18.09 17.35	17.84 +/- 0.42 (2.36 %)
	ID390	1 2 3	17.06 17.58 17.91	17.51 +/- 0.43 (2.47 %)
	ID410	1 2 3	17.43 18.03 17.31	17.59 +/- 0.39 (2.20 %)
12 m	ID 070	1 2 3	15,88 16,44 15,67	15,99 ± 0,40 µm (2,49 %)
	ID360	1 2 3	15,56 15,70 16,03	15,76 ± 0,24 µm (1,53 %)
	ID385	1 2 3	16,01 15,66 15,70	15,79 ± 0,19 µm (1,21 %)

Table 7: Results of the stability test after storage times of 0, 1, 3,7 and 12 months and their replicate measurements within the units for particle size D50

Storage time	Bottle	Replicate measurement	Particle size in µm (D50)	Average Particle size of three replicate measurements per bottle with standard deviations s in µm (D50)
0 d	ID185	1 2 3	60.32 60.39 64.10	61.60+/-2.16 (3.51 %)
	ID249	1 2 3	59.93 61.47 62.95	61.45+/-1.51 (2.46 %)
	ID349	1 2 3	60.81 61.11 63.03	61.65+/-1.20 (1.95 %)
1 m	ID 227	1 2 3	60.76 61.35 58.73	60.28+/-1.38 (2.28 %)
	ID 242	1 2 3	60.68 60.13 60.95	60.59+/-0.42 (0.69 %)
	ID 452	1 2 3	62.39 60.03 61.51	61.31+/-1.19 (1.95 %)
3 m	ID 234	1 2 3	63.16 60.19 61.22	61.52+/-1.51 (2.45 %)
	ID 111	1 2 3	60.29 57.90 62.50	60.23+/-2.30 (3.82 %)
	ID 103	1 2 3	64.37 65.93 65.70	65.33+/-0.84 (1.29 %)
7 m	ID 142	1 2 3	61.64 62.68 59.36	61.23 +/- 1.70 (2.77 %)
	ID 390	1 2 3	58.95 61.00 60.83	60.26 +/- 1.13 (1.88 %)
	ID 410	1 2 3	59.62 63.15 59.25	60.67 +/- 2.15 (3.55 %)
12 m	ID070	1 2 3	55.96 59.69 55.25	56.97 ± 2,39 µm (4.19 %)
	ID360	1 2 3	54,51 55.02 57.50	55.68 ± 1.60 µm (2.87 %)
	ID385	1 2 3	55.50 54.62 54.69	54.94 ± 0.49 µm (0.89 %)

Table 8: Results of the stability test after storage times of 0, 1, 3, 7 and 12 months and their replicate measurements within the units for particle size D90

Storage time	Bottle	Replicate measurement	Particle size in µm (D90)	Average Particle size of three replicate measurements per bottle with standard deviations s in µm (D90)
0 d	ID185	1	151.39	158.90+/-8.53 (5.37 %)
		2	157.13	
		3	168.17	
	ID249	1	59.93	158.68+/-7.25 (4.57 %)
		2	158.03	
		3	151.78	
	ID349	1	153.81	158.98+/-5.17 (3.25 %)
		2	164.15	
		3	158.98	
1 m	ID 227	1	158.34	153.77+/-9.12 (5.93 %)
		2	159.70	
		3	143.26	
	ID 242	1	154.49	152.23+/-2.88 (1.89 %)
		2	148.98	
		3	153.21	
	ID 452	1	171.33	162.99+/-8.77 (5.38 %)
		2	153.85	
		3	163.79	
3 m	ID 234	1	169.89	162.16+/-7.41 (4.57 %)
		2	161.50	
		3	155.11	
	ID 111	1	151.74	154.93+/-13.02 (8.40 %)
		2	143.79	
		3	169.24	
	ID 103	1	171.97	182.17+/-10.58 (5.81 %)
		2	193.10	
		3	181.45	
7 m	ID 142	1	156.60	159.18+/-8.83 (5.55 %)
		2	169.00	
		3	151.92	
	ID 390	1	153.65	153.23+/-4.35 (2.84 %)
		2	157.36	
		3	148.69	
	ID 410	1	149.88	155.02+/-10.69 (6.90 %)
		2	167.31	
		3	147.86	
12 m	ID070	1	158.06	173.77 ± 40.17 µm (23.12 %)
		2	219.42	
		3	143.83	
	ID360	1	141.10	150.21 ± 15.13 µm (10.07 %)
		2	141.85	
		3	167.67	
	ID385	1	148.08	143.08 ± 4.42 µm (3.09 %)
		2	141.51	
		3	139.66	

Table 9: ANOVA results of homogeneity testing of 10 randomly selected units and their replicate measurements within the units for particle size D10

Source of variation	*Square sum (SS)*	*Degree of freedom (df)*	*Mean Square sum (MS)*	*Test value (F)*	*P-Value*	*Critical F-value*
Between Groups	1.8599	9	0.2067	3.3286	0.0120	2.3928
Within Groups	1.2417	20	0.0621			
Total	3.1015	29				

Table 10: ANOVA results of homogeneity testing of 10 randomly selected units and their replicate measurements within the units for particle size D50

Source of variation	*Square sum (SS)*	*Degree of freedom (df)*	*Mean Square sum (MS)*	*Test value (F)*	*P-Value*	*Critical F-value*
Between Groups	25.4162	9	2.8240	1.7794	0.1357	2.3928
Within Groups	31.7415	20	1.5871			
Total	57.1577	29				

Table 11: ANOVA results of homogeneity testing of 10 randomly selected units and their replicate measurements within the units for particle size D90

Source of variation	*Square sum (SS)*	*Degree of freedom (df)*	*Mean Square sum (MS)*	*Test value (F)*	*P-Value*	*Critical F-value*
Between Groups	679.3504	9	75.4834	1.5728	0.1907	2.3928
Within Groups	959.8709	20	47.9935			
Total	1639.2212	29				