Report

Reference Material

BAM-P206

Polyethylene terephthalate
(powder)

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Coordinator: Dr. Korinna Altmann
Bundesanstalt für Materialforschung und -prüfung (BAM)
Division 6.6
Unter den Eichen 87
12205 Berlin, Germany
Phone: +49 30 8104 4305
Fax: +49 30 8104 71619
E-mail: korinna.altmann@bam.de

Summary

This report describes the preparation and the analysis of the reference material BAM-P206.

The following equivalent particle diameter and standard deviations have been determined:

Particle size distribution	Equivalent particle diameter[2] in µm	Expanded uncertainty[3] $\boldsymbol{U}$ in µm
D10[1]	30.5	2.3
D50[1]	62.6	1.9
D90[1]	107	4

[1] Equivalent particle diameter D10/D50/D90 of the measured volume below which 10.3/50.3/90.3 % of the particles are.

[2] Mean values determined by laser diffraction under dry dispersion with 3 different devices measuring 4 units 3 times each. For further information see the characterization study for the property of interest (section 2.2).

[3] Estimated expanded uncertainty $U = k \cdot u_c$ with a coverage factor $k = 2$, corresponding to a level of confidence of approximately 95%, calculated according to ISO Guide 35. The combined uncertainty $\boldsymbol{u_c}$ includes the standard uncertainty due to characterization, the contribution of variation between bottles and the long-term stability contribution.

This report contains detailed information on the preparation of the reference material as well as on homogeneity and stability investigations of the property of interest, the equivalent particle diameter, and on the analytical methods to determine the additional properties. The values for particle size distribution are based on the results from laser diffraction measurements of 3 different devices with at least 3 replicate measurements of 4 randomly chosen units of the reference material P206.

Content

List of abbreviations

(If not explained elsewhere)

ANOVA	analysis of variance
BAM	Bundesanstalt für Materialforschung und -prüfung, Berlin, Germany
D10	D10 value describes the equivalent particle diameter of the measured volume below which 10.3 % of the particles are below
D50	D50 value describes the equivalent particle diameter of the measured volume below which 50.3 % of the particles are below
D90	D90 value describes the equivalent particle diameter of the measured volume below which 90.3 % of the particles are below
k	coverage factor for expanded uncertainty U (k = 2)
PET	polyethylene terephthalate
PSD	particle size distribution
RM	reference material
rel.	relative
RSD	relative standard deviation
s	standard deviation
s_r	standard deviation of repeatability within the bottles
s_x	standard deviation of all measurements of a study
Std. Dev.	standard deviation
U	expanded standard uncertainty of a property value
u_c	combined standard uncertainty of a property value
u_{char}	standard uncertainty due to characterization
u_{hom}	standard uncertainty due to (in)homogeneity
u_{lts}	standard uncertainty due to long-term (in)stability
x_{CRM}	property value of the RM
$\overline{x}$	mean property value of material within a study
y_{char}	value assigned to RM in characterization study

1. Introduction

Polyethylene terephthalate (PET) is one of the most abundant polymers used in industry and hence, relevant for microplastic analysis. Microplastics in the environment often originate from plastic products, which are aged by environmental weathering and fragmented into small particles with irregular shapes. Microplastic particles have a size of 1-1000 µm [1].
The idea is to offer a reference material close to reality for the validation of methods for sampling, sample preparation and detection of microplastics.

The evaluation of this new reference material (RM) has been carried out based on ISO 17034 [2] and relevant ISO Guides [3,4].

2. Material

PET-granulate in bottle grade quality (PET Lighter C 93) was kindly provided by Equipolymer, Netherlands. The granules were pre-cooled with liquid nitrogen for 3 min and transferred spoon by spoon to the grinding chamber of the centrifugal mill (ZM 200, Retsch, Haan, Germany). The mill is equipped with a stainless-steel ring sieve with trapezoidal hole of 120 µm. Subsequently, 370 units with 1 g PET powder each were filled in amber glass bottles. The metal lids have a seal consisting of silicone and polytetrafluorethylene.

2.1 Informative parameter for material characterization

The RM was characterised by imaging the particle shape by scanning electron microscopy (SEM) (Fig. 1), by Fourier-transform infrared (FTIR) spectroscopy (Fig. 2), and by determining the glass transition, and melting temperature by differential scanning calorimetry (DSC) (Fig. 3, Table 1).

PET particles were analysed by SEM (Zeiss Supra 40, Oberkochen, Germany) with a Schottky field emitter and equipped with a high-resolution In-lens SE (secondary electrons) detector with an acceleration voltage of 1.0 kV. An image of the PET particles is presented in Fig. 1.

Attenuated total reflection - Fourier transform infrared (ATR-FTIR) spectroscopy was performed on BAM-P206 powder with a Nicolet Nexus 6700 FTIR spectrometer equipped with SmartOrbit Diamond module and DTGS detector. The spectra were recorded from 4000 to 500 cm^{-1} averaging 32 scans with a resolution of 4 cm^{-1}. The obtained data were processed with ATR correction (Diamond, 45°, 1 reflection, n_r = 1.64 [5]), automated baseline correction with the OMNIC 9 software (Thermo Fischer Scientific, Karlsruhe, Germany). Characteristic functional groups/structure elements were identified by associated bands and additionally compared with the Hummel Polymer Sample Library from Thermo Scientific™. The results confirm that the material is composed of PET (Fig. 2).

Differential scanning calorimetry (DSC) was carried out 3 times with a DSC 7020 (Seiko, THASS, Germany) from -30 to 300 °C at a constant heating rate of 10 K/min. Measurements revealed a glass transition temperature T_g of 78.5 °C and a melting temperature T_m of 247.87 °C (Fig. 3 and Table 1), which is in accordance with PET literature [6,7].

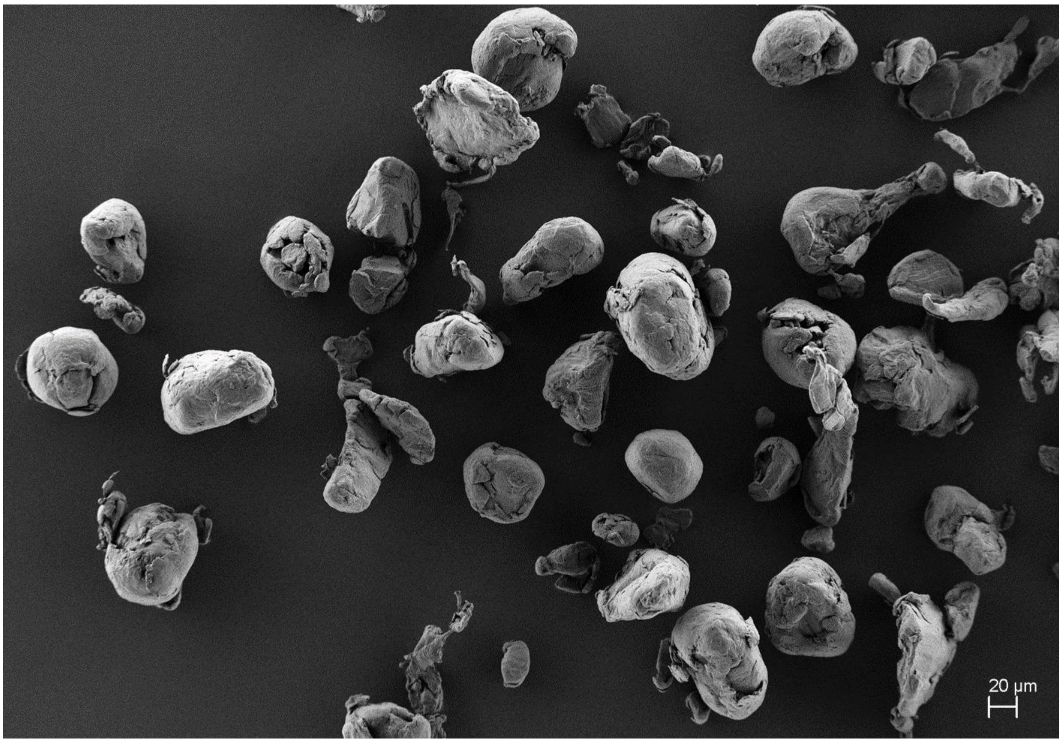

Fig. 1 SEM image of BAM-P206 particles.

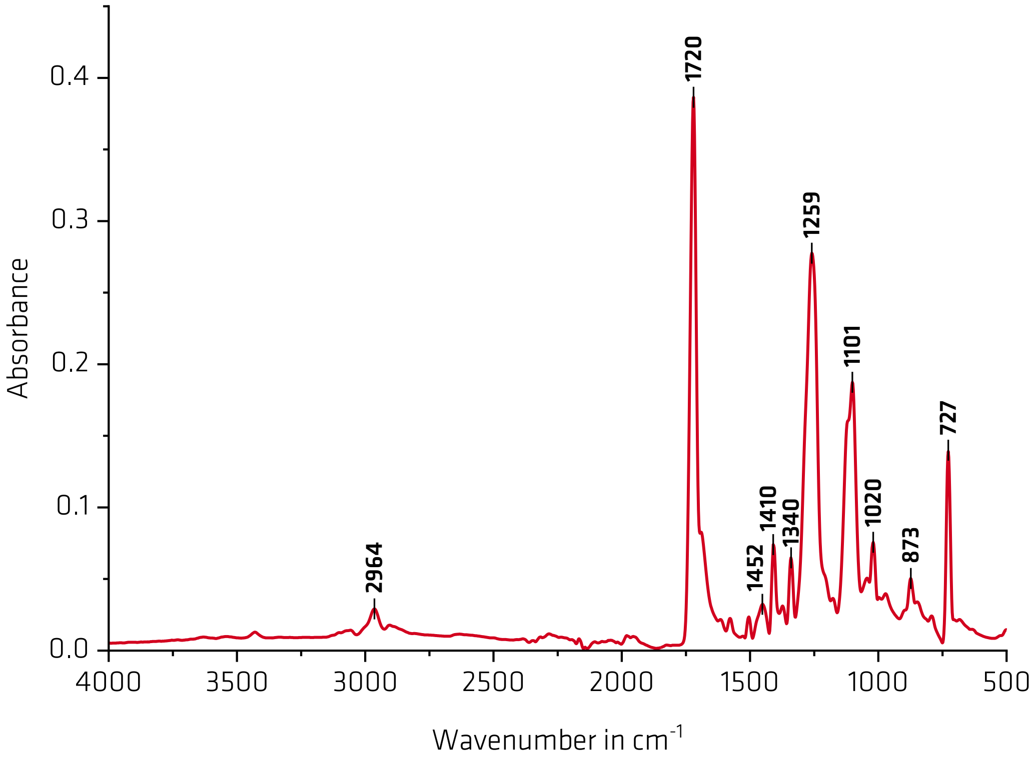

Fig. 2: ATR-FTIR spectrum of RM BAM-P206.

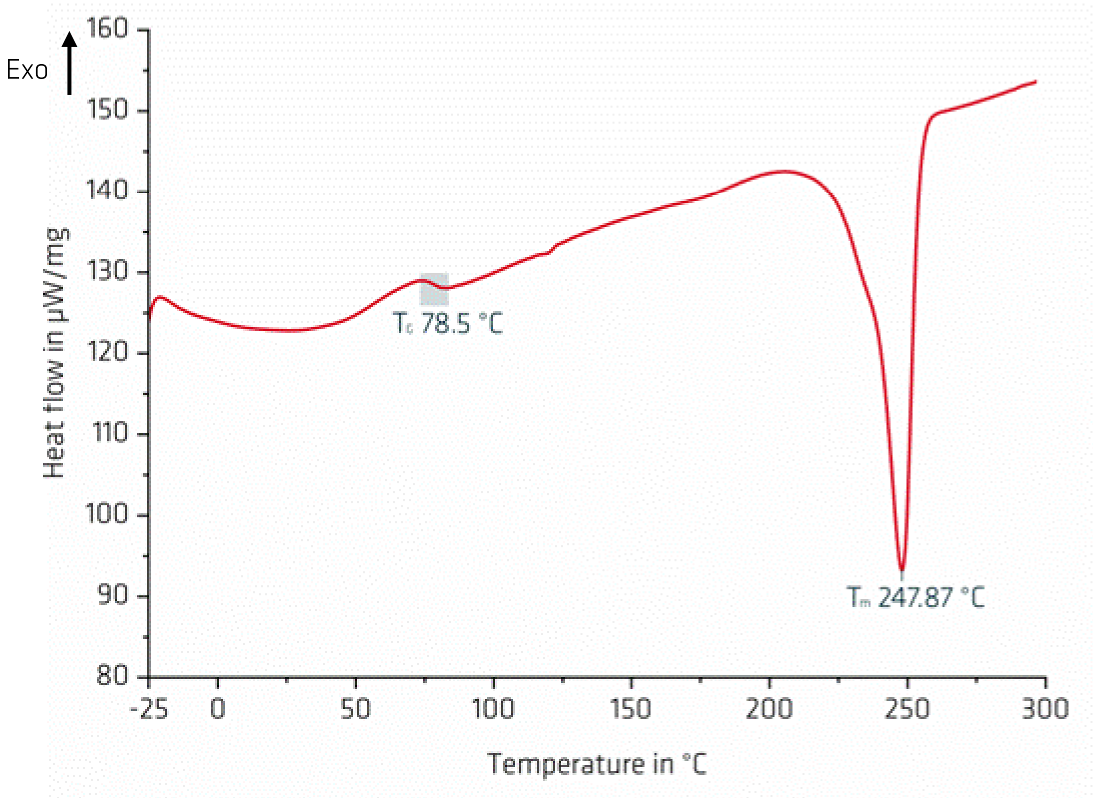

Fig. 3: DSC measurement of RM BAM-P206.

Table 1 Glass transition T_g and melting temperature T_m of BAM-P206 from DSC measurements. Mean value of 3 measurements.

Parameter	**Temperature** in °C	**Standard deviation *s*** in °C	**RSD** in %
Glass transition temperature T_g	78.5	0.5	0.7
Melting temperature T_m	247.87	0.03	0.01

2.2. Particle size distribution (property of interest)

The particle size of BAM-P206 has been characterized by laser diffraction in dry dispersion with 3 different devices.

1. HELOS/BR + RODOS/L + ASPIROS, (Sympatec, Germany, ISO 13320:2009 certified) at BAM as described in chapter 3 for the homogeneity study.
2. Mastersizer3000 + Aero S (Malvern Panalytical, Germany) at BAM (see Table S1.1)
3. Mastersizer3000 + Aero S (Malvern Panalytical, Germany) by Fraunhofer IKTS (Dresden, Germany) (see Table S1.2)

The measurements with the Mastersizer3000 were in both laboratories carried out under dry dispersion with 250 mg of material for each measurement at a pressure of 1.5 bar. Evaluation was executed applying Fraunhofer approximation. 4 randomly selected bottles were measured 3 times each.

For each device the average PSD values y_i have been obtained. The values are shown in Table 2.

Table 2 Average PSDs and standard deviation of all measurements obtained from laser diffraction in dry dispersion with different devices.

Device	**BAM HELOS/BR**	**BAM Mastersizer3000**	**IKTS Mastersizer3000**
D10 average y_i	28.58	31.52	31.35
D10 Std. Dev.	0.27	0.09	0.32
D50 average y_i	62.3	62.4	63.0
D50 Std. Dev.	0.4	0.2	0.3
D90 average y_i	107.2	106.0	107.4
D90 Std. Dev.	1.3	1.1	1.5

The assigned value y_{char} for the PSD was calculated from the average values y_i obtained from the measurements of each device and the number of device p = 3 (equation 1). u_{char} is then calculated according to equation (2) [3].

$$y_{char} = \frac{\sum y_i}{p} \qquad (1)$$

$$u_{char} = \frac{1}{\sqrt{p}} \sqrt{\frac{\sum (y_i - y_{char})^2}{p-1}} \qquad (2)$$

Table 3 Assigned values y_{char} and uncertainty u_{char} from the characterization study.

PSD	y_{char} in µm	u_{char} in µm	**Rel.** u_{char} in %
D10	30.5	1.0	3.1
D50	62.6	0.2	0.3
D90	106.9	0.5	0.5

3. Homogeneity

For testing the homogeneity, 10 individual bottles of BAM-P206 were randomly selected for particle size distribution measurements by laser diffraction with dry powder dispersion (HELOS/BR + RODOS/L + ASPIROS, Sympatec, Deutschland, ISO 13320:2009 certified). 3 replicate measurements per bottle were carried out under repeatability conditions with approximately 100 mg each to detect the standard deviation between and within the bottles (see Appendix Table S2).

The results are shown as cumulative and density distribution curves in Figure 4 and are summarized as mean values and corresponding standard deviations in Table 4.

Table 4 Mean values of PSD and respective standard deviations of the 30 measurements from the homogeneity test of RM BAM-P206.

PSD	**Equivalent particle diameter** in µm	**Standard deviation s_x** in µm	**RSD** in %
D10	28.58	0.27	0.94
D50	62.3	0.4	0.6
D90	107.1	1.3	1.2

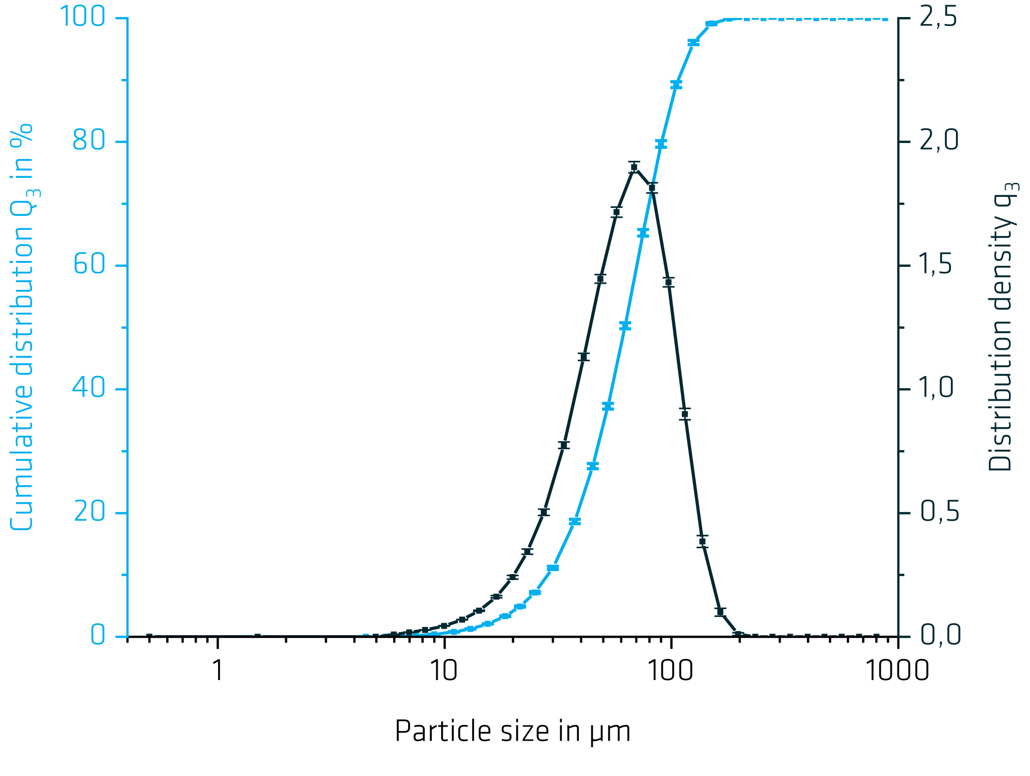

Fig. 4 Equivalent particle diameter with standard deviation of all 30 measurements of RM BAM-P206. The blue curve represents the cumulative distribution $Q_3(x)$ and shows the volume fraction of particles smaller than x in relation to the total volume. The black curve represents the distribution density $q_3(x)$ (1^{st} derivate of Q_3) and displays the probability of finding a particle with an equivalent particle diameter x in the population. 10 individual bottles of BAM-P206 were randomly selected and measure 3 times each. Table S2 shows the corresponding measured values.

The contribution of inhomogeneities to the total measurement uncertainty was calculated using a 1-way-ANOVA (Table 5 and Appendix Table S4).

Table 5 Analysis of variances calculated for PSD analysis of RM BAM-P206.

PSD	Source of variation	Mean sum of squares (MS)	Test value (F)	Critical F-value 95%
D10	Between Groups	0.182	7.593	2.393
	Within Groups	0.024		
D50	Between Groups	0.370	6.218	2.393
	Within Groups	0.060		
D90	Between Groups	1.654	0.911	2.393
	Within Groups	1.815		

ANOVA results depict a homogenous distribution regarding D90 because the test value F is below the critical F-value. For the smaller particle fractions D10 and D50 the test F-value is bigger than the critical F-value, which indicates an inhomogeneous bottling. The inhomogeneities will be regarded in the calculation of the uncertainty for homogeneity study u_{hom}.

The estimation of inhomogeneity contribution u_{hom} to be included into the total uncertainty budget was calculated from the maximum uncertainty using Equation (3) to (6) according to ISO Guide 35 [3], with $M_{between}$ mean of squared deviations between bottles, M_{within} mean of squared deviations within one bottle, n number of replicate measurements per bottle and N number of bottles selected for homogeneity study. Test results to determine the maximum (in)homogeneity contribution to the total uncertainty are summarized in Table 6.

Standard deviation of repeatability within bottles

$$s_r = \sqrt{M_{within}} \qquad (3)$$

Standard uncertainty due to between-bottle variation

$$s_{\mathrm{bb}} = \sqrt{\max\left(\frac{M_{between} - M_{within}}{n}, 0\right)} \qquad (4)$$

Maximum between bottle variation that could be masked by within bottle variation

$$u'_{bb} = \sqrt{\frac{M_{within}}{n}} \sqrt[4]{\frac{2}{N(n-1)}} \qquad (5)$$

Standard uncertainty of homogeneity study

$$u_{\mathrm{hom}} = \sqrt{s_r^2 + \max\left(s_{\mathrm{bb}}, u'_{\mathrm{bb}}\right)^2} \qquad (6)$$

Table 6 Results to determine the maximum inhomogeneity contribution u_{hom} of BAM-P206.

PSD	D10	D50	D90
$\bar{x}_{hom}$ in µm	28.58	62.3	107.1
$M_{between}$	0.18	0.4	1.7
M_{within}	0.02	0.1	1.8
s_r in µm	0.15	0.2	1.3
s_{bb} in µm	0.23	0.3	0.0
s_{bb} rel. in %	0.80	0.5	0.0
u'_{bb} in µm	0.05	0.08	0.4
u'_{bb} rel. in %	0.18	0.13	0.4
u_{hom}	0.28	0.4	1.4
u_{hom} rel. in %	0.97	0.7	1.3

4. Stability

Based on expert knowledge and literature in the field of polymers, it is very unlikely that BAM-P206 composition and particle size will change, provided that 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 period of 0, 1, 3, 6 and 12 months, 3 randomly selected bottles, each with 1 g PET per bottle, were tested in terms of particle size distribution. 3 measurements (100 mg each) per bottle were carried out (see Appendix Table S3). The results are summarized in Table 7 and presented in Figure 5.

Table 7 Average values of stability test for RM BAM-P206.

Storage period	Particle size distribution	Equivalent particle diameter in µm	Standard deviation of measurements s_x in µm	RSD in %
0 months	D10	28.58	0.27	0.94
	D50	62.3	0.4	0.6
	D90	107.1	1.3	1.2
1 months	D10	28.85	0.10	0.4
	D50	62.5	0.3	0.4
	D90	107.2	1.5	1.4
3 months	D10	28.35	0.11	0.40
	D50	61.8	0.4	0.6
	D90	106.3	1.7	1.6
6 months	D10	28.77	0.24	0.84
	D50	62.4	0.1	0.2
	D90	107.6	0.6	0.5
12 months	D10	28.59	0.08	0.27
	D50	62.5	0.4	0.6
	D90	107.7	0.9	0.8

The stability was assessed according to ISO Guide 35 [3], using linear regression (Fig. 5) followed by testing for statistically significant slopes different from zero. The t-test statistics for slopes were calculated using Equation (7) and compared with the critical values at the 95% level of confidence.

$$t\text{-statistic for slope b significance} \quad t_b = \frac{|b|}{s(b)} \tag{7}$$

Results of linear regression are presented in Figure 5 and values of t-statistics in Table 8. For all particle size distributions, the slopes are not significantly different from zero, and thus, no significant instability is detected.

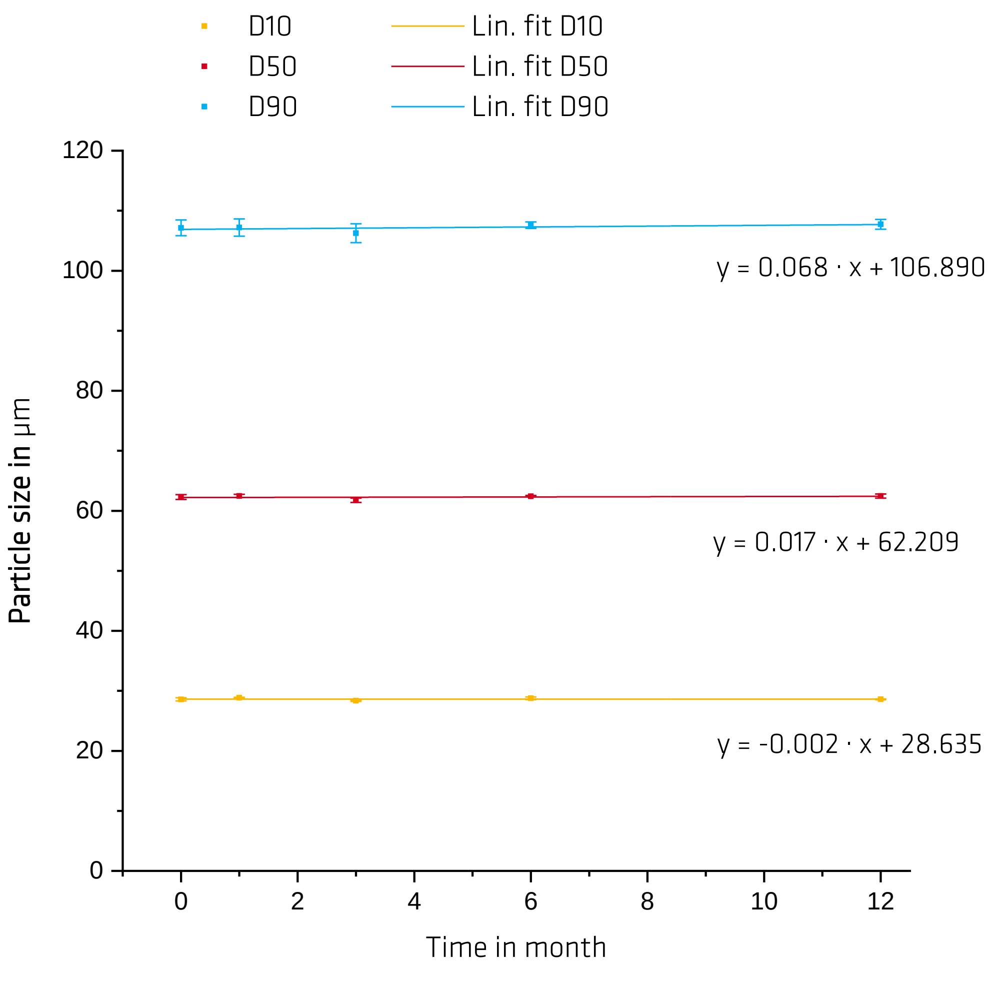

Fig. 5: Stability monitoring of PSD by laser diffraction and linear regression analysis for statistical evaluation of stability of BAM-P206.

Table 8 Testing for significant instability. Values of slope from linear regression of stability data, calculated t-statistic, and critical value at the 95% level of confidence.

PSD	Slope b	s (b)	Intercept in µm	t-statistic (b)	Critical value at 95 %
D10	-0.002	0.023	28.63	-0.079	0.073
D50	0.017	0.035	62.2	0.494	0.129
D90	0.068	0.058	106.9	1.185	0.252

Altogether, results of the statistical evaluation of the stability data indicate that there is no instability and that RM BAM-P206 is stable regarding particle size distribution over a 12-month period at least (see Figure 5, and Table 7, 8 and 9). However, the contribution of uncertainty of the long-term stability u_{lts} was calculated according to Equation (8), as in ISO Guide 35 [3], with *s(b)* as standard error for estimated slope, t_m time interval between value assignment (12 month) and initial stability monitoring point, and t_{cert} period of validity issued (12 month) during that time. Results of uncertainty of the long-term stability are summarized in Table 9.

Contribution of standard uncertainty of long-term stability $u_{lts} = s(b)(t_m + t_{cert})$ (8)

Table 9 Results of stability data evaluation of BAM-P206 according to ISO Guide 35 [3].

PSD	$\overline{x}_{stab}$ in µm	$s_{x,stab}$ in µm	Intercept in µm	Slope b	s (b)	u_{lts}(x) in µm	Rel. u_{lts}(x) in %
D10	28.63	0.19	28.63	-0.002	0.023	0.56	1.96
D50	62.3	0.3	62.2	0.017	0.035	0.8	1.4
D90	107.2	0.6	106.9	0.068	0.058	1.4	1.3

5. Calculation of combined uncertainty

The combined uncertainty u_c was calculated according to Equation (9), using the numerical values summarized in Table 10. This equation is a combination of the standard uncertainty due to characterization, the contribution of the variation between the bottles and the long-term stability contribution. Furthermore, the certified value x_{CRM} can be assigned as y_{char} since no between-unit variation or stability effects need to be regarded (Equation 10).

Combined uncertainty $u_c^2 = u_{\text{char}}^2 + u_{\text{hom}}^2 + u_{\text{lts}}^2$ (9)

Certified value for RM $x_{CRM} = y_{char}$ (10)

Table 10 Values of the uncertainty components for the PSD of RM BAM-P206.

PSD	x_{CRM} in µm	u_{hom} in µm	u_{lts} in µm	u_{char} in µm	u_{c} in µm	U in µm
D10	30.5	0.3	0.6	1.0	1.1	2.3
D50	62.6	0.6	0.8	0.2	1.0	1.9
D90	106.9	1.8	1.4	0.5	2.0	4

The final attested values of the particle size distribution with a reasonable number of digits (rounded according to DIN 1333 [8]) and the respective expanded uncertainties U ($U = k \cdot u_c$ with $k = 2$) are summarized in Table 11.

Table 11 Final attested values for PSD of RM BAM-P206.

PSD	**Equivalent particle diameter** $D = x_{CRM}$ in µm	**Expanded uncertainty** U in µm
D10	30.5	2.3
D50	62.6	1.9
D90	107	4

6. Information on the proper use of the reference material

6.1 Recommended use

The present material is a top-down produced reference material for the validation of sampling, sample preparation and detection of microplastics.

6.2 Transport, storage, and handling

RM BAM-P206 can be shipped at ambient temperature. It should be stored under dark and dry conditions at a temperature of 5 ± 3 °C in its original tightly closed bottle. BAM cannot be held responsible for changes that happen during storage of the material at the customer's premises, especially of opened bottles. In case of further transport, the packaging should be free of plastic to avoid contamination.

6.3 Shelf life

The stability study after storage for 12 months of selected bottles 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 data sheet 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-P206 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 https://www.bam.de
E-Mail: sales.crm@bam.de www.webshop.bam.de

Each bottle of RM BAM-P206 will be distributed together with a data sheet containing the mean values, standard deviations and uncertainties of all data sets and information on the analytical methods used.

8. References

[1] ISO/TR 21960, Plastics Environmental aspects - State of knowledge and methodologies. International Organization for Standardization, Geneva 2020.

[2] ISO 17034, General requirements for the competence of reference material producers. International Organization for Standardization, Geneva 2016.

[3] ISO Guide 35, Reference materials - Guidance for characterization and assessment of homogeneity and stability.
International Organization for Standardization, Geneva 2017.

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International Organization for Standardization, Geneva 2015.

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9. Appendix

Table S1.1 Results of characterization study in 2.2 4 randomly selected samples with 3 replicate measurements (Rep. Meas.) from a single bottle measured with Mastersizer3000 at BAM.

Bottle ID	Rep. Meas.	D10 in µm	D10 average per bottle in µm, Std. Dev. RSD	D50 in µm	D50 average per bottle in µm, Std. Dev. RSD	D90 in µm	D90 average per bottle in µm, Std. Dev. RSD
71	1	31.62	31.56	62.5	62.3	104.8	104.7
	2	31.56	0.06	62.2	0.1	104.2	0.4
	3	31.50	0.19%	62.3	0.2%	105.0	0.4%
120	1	31.62	31.55	62.8	62.4	107.4	106.5
	2	31.59	0.09	62.4	0.3	105.2	1.2
	3	31.45	0.28%	62.2	0.5%	106.9	1.1%
167	1	31.38	31.39	62.5	62.5	106.2	106.9
	2	31.45	0.05	62.6	0.2	107.7	0.8
	3	31.35	0.16%	62.2	0.3%	106.9	0.71%
304	1	31.57	31.56	62.5	62.5	105.5	105.9
	2	31.60	0.06	62.5	0.1	105.4	0.8
	3	31.50	0.18%	62.5	0.1%	106.9	0.8%

Table S1.2 Results of characterization study in 2.2 4 randomly selected samples with 3 replicate measurements (Rep. Meas.) from a single bottle measured with Mastersizer3000 at Fraunhofer IKTS.

Bottle ID	Rep. Meas.	D10 in µm	D10 average per bottle in µm, Std. Dev. RSD	D50 in µm	D50 average per bottle in µm, Std. Dev. RSD	D90 in µm	D90 average per bottle in µm, Std. Dev. RSD
8	1	31.60	31.27	63.3	63.0	106.0	107.0
	2	30.70	0.49	62.7	0.3	108.0	1.0
	3	31.50	1.58%	63.1	0.5%	107.0	0.9%
94	1	31.60	31.67	63.5	63.2	109.0	108.7
	2	31.80	0.12	63.0	0.3	108.0	0.6
	3	31.60	0.36%	63.0	0.5%	109.0	0.5%
277	1	31.20	31.27	62.9	62.9	107.0	108.3
	2	31.20	0.12	62.9	0.1	109.0	1.2
	3	31.40	0.37%	63.0	0.1%	109.0	1.1%
324	1	31.50	31.20	63.1	62.7	105.0	105.7
	2	30.90	0.30	62.5	0.4	105.0	1.2
	3	31.20	0.96%	62.4	0.6%	107.0	1.1%

Table S2 Results of homogeneity test of 10 randomly selected samples with 3 replicate measurements (Rep. Meas.) from a single bottle.

Bottle ID	Rep. Meas.	D10 in µm	D10 average per bottle in µm, Std. Dev. RSD	D50 in µm	D50 average per bottle in µm, Std. Dev. RSD	D90 in µm	D90 average per bottle in µm, Std. Dev. RSD
61	1	28,69	28,70	62,2	62,0	107,6	106,2
	2	28,67	0,04	61,8	0,2	104,7	1,4
	3	28,74	0,13%	62,1	0,4%	106,2	1,3%
75	1	28,72	28,76	62,1	62,3	106,2	107,5
	2	28,73	0,06	62,3	0,3	107,8	1,2
	3	28,82	0,19%	62,6	0,4%	108,5	1,1%
97	1	28,59	28,61	62,4	62,4	108,3	107,3
	2	28,66	0,04	62,5	0,2	108,0	1,5
	3	28,59	0,14%	62,2	0,0	105,6	0,0
161	1	28,53	28,34	62,2	61,8	107,9	106,5
	2	28,10	0,22	61,6	0,3	106,9	1,6
	3	28,38	0,77%	61,6	0,5%	104,8	1,5%
258	1	28,57	28,49	62,6	62,6	107,6	108,2
	2	28,45	0,07	62,6	0,1	108,0	0,7
	3	28,45	0,24%	62,7	0,1%	109,0	0,7%
280	1	28,71	28,68	62,0	62,3	105,4	106,8
	2	28,54	0,13	62,2	0,4	107,1	1,3
	3	28,79	0,45%	62,7	0,6%	108,0	1,3%
288	1	28,79	28,77	62,0	62,2	104,8	106,1
	2	28,76	0,02	62,4	0,2	107,0	1,1
	3	28,77	0,05%	62,4	0,3%	106,6	1,1%
313	1	28,74	28,80	63,2	63,0	109,4	108,2
	2	28,84	0,06	62,7	0,2	106,4	1,6
	3	28,83	0,19%	63,0	0,3%	108,8	1,5%
317	1	28,80	28,61	62,2	62,4	105,3	107,4
	2	28,57	0,17	62,6	0,2	108,3	1,8
	3	28,46	0,61%	62,4	0,3%	108,6	1,7%
366	1	28,30	28,00	62,1	61,8	107,8	107,4
	2	28,11	0,36	61,8	0,2	106,5	0,8
	3	27,60	1,29%	61,6	0,4%	107,8	0,7%

Table S3 Results of the stability test after storage times of 1, 3, 6, 12 and 18 months with 3 replicate measurements (Rep. Meas.) from a single bottle.

Storage Time	Bottle ID	Rep. Meas.	D10 in µm	D10 average per bottle in µm, Std. Dev. RSD	D50 in µm	D50 average per bottle in µm, Std. Dev. RSD	D90 in µm	D90 average per bottle in µm, Std. Dev. RSD
1	282	1	28,81	28,87	62,7	62,6	108,8	108,5
		2	28,91	0,05	62,7	0,2	108,8	0,5
		3	28,88	0,18%	62,5	0,2%	108,0	0,5%
1	325	1	28,91	28,76	62,3	62,3	106,6	106,9
		2	28,70	0,13	62,2	0,1	106,3	0,9
		3	28,68	0,44%	62,5	0,2%	107,9	0,8%
1	326	1	28,85	28,91	62,7	62,5	107,1	106,1
		2	29,00	0,08	62,8	0,5	107,3	1,9
		3	28,88	0,27%	61,9	0,7%	103,9	1,8%
3	64	1	28,40	28,35	62,0	61,9	107,4	107,1
		2	28,18	0,15	61,6	0,2	106,8	0,3
		3	28,46	0,52%	62,0	0,4%	107,1	0,3%
3	231	1	28,28	28,30	62,1	61,6	107,9	105,9
		2	28,36	0,05	61,6	0,4	106,1	2,1
		3	28,27	0,17%	61,2	0,7%	103,7	2,0%
3	285	1	28,28	28,40	61,8	61,8	106,5	105,8
		2	28,36	0,14	61,4	0,5	103,3	2,2
		3	28,56	0,51%	62,4	0,8%	107,5	2,1%
6	134	1	28,75	28,79	62,7	62,6	108,2	108,0
		2	28,70	0,12	62,5	0,1	108,2	0,4
		3	28,92	0,40%	62,5	0,2%	107,6	0,4%
6	275	1	29,35	28,88	62,4	62,4	106,9	107,4
		2	28,60	0,41	62,3	0,1	107,7	0,5
		3	28,70	1,41%	62,5	0,1%	107,7	0,5%
6	286	1	28,60	28,62	62,3	62,3	106,5	107,3
		2	28,60	0,04	62,3	0,0	107,9	0,7
		3	28,67	0,14%	62,3	0,1%	107,6	0,7%

Table S3 continued.

Storage Time	Bottle ID	Rep. Meas.	D10 in µm	D10 average per bottle in µm, Std. Dev. Rel. error	D50 in µm	D50 average per bottle in µm, Std. Dev. Rel. error	D90 in µm	D90 average per bottle in µm, Std. Dev. Rel. error
12	50	1	28,41	28,53	62,1	62,2	107,6	107,1
		2	28,62	0,11	62,4	0,2	107,4	0,7
		3	28,57	0,38%	62,0	0,3%	106,4	0,6%
12	130	1	28,64	28,65	62,8	62,9	108,9	108,7
		2	28,66	0,01	63,0	0,1	108,8	0,3
		3	28,65	0,03%	62,8	0,1%	108,3	0,3%
12	276	1	28,64	28,60	62,3	62,3	107,1	107,4
		2	28,56	0,04	62,2	0,1	107,0	0,7
		3	28,60	0,14%	62,5	0,2%	108,2	0,6%
18	22	1	28,86	28,75	62,7	62,6	108,3	107,8
		2	28,78	0,12	62,7	0,2	108,3	0,9
		3	28,62	0,43%	62,3	0,4%	106,8	0,8%
18	24	1	28,66	28,68	62,3	62,5	107,5	107,5
		2	28,65	0,05	62,4	0,2	106,6	1,0
		3	28,74	0,17%	62,7	0,3%	108,5	0,9%
18	190	1	28,26	28,36	61,9	61,9	106,7	106,2
		2	28,50	0,12	61,6	0,2	104,5	1,5
		3	28,32	0,44%	62,1	0,4%	107,4	1,4%

Table S4 ANOVA results of homogeneity testing of 10 randomly selected bottles and their replicate measurements within the bottles.

	Source of Variation	Square sum (SS)	Degree of freedom (df)	Mean square sum (MS)	Test value (F)	p-Value	Critical F-Value
D10	Between groups	1.634	9	0.182	7.593	8.667E-05	2.393
	Within groups	0.478	20	0.024			
	Total	2.112	29				
D50	Between groups	3.331	9	0.370	6.218	3.374E-04	2.393
	Within groups	1.191	20	0.060			
	Total	4.522	29				
D90	Between groups	14.885	9	1.654	0.911	5.350E-01	2.393
	Within groups	36.308	20	1.815			
	Total	51.193	29				