Interlaboratory Study on Microplastics Analysis Development Exercise – DE 17

Round 1 (2019)

Final Report (version 2)

van Mourik, L.M., Crum ,S.J.H., van Bavel, B., Leslie, H.A., de Boer, J., Cofino, W.P.

9 December 2019

Overview of changes made with respect to the previous version of this report (15th November 2019)

This report is replacing the first version published on the 15th of November. Compared to the first version of this report the following aspects were changed:

- Table 2.3 is updated as the weights added polymers for tablets 7 and 11 were interchanged.
- Table 3-2 "Summary of the numbers of correct identification of the polymers in the pellets (position nos. 1-6)", has been changed as a small counting error was made for the grand total numbers for position 1
- New calculations were done for position 7 (all particles), as we made a mistake for one of the labs by summing the individual results for this tablet. A new assigned value was calculated and related figures (Fig 3-2 and appendix B) were corrected, as well as table A-14 presenting the z-scores for all particles.
- Figure 3-4 was changed, as the laboratories who reported "> than" values were not included in the Figure. As statistics cannot cope with results reported as being "> than", we removed the calculations of the z-scores for the total particles of position 9. The calculations in the former report were based only on numerical values, implying that the assigned value was underestimated and therefore less reliable.
- Table 3-5 was changed, as the weights op polymers added to the tablet were introduced in the table.
- On request of some participants a new figure (3-7) was added containing the results for all particles reported for tablet 12 (blank)
- A correction was made for calculations regarding the within and between laboratory variances on page 26
- Table A-14 presenting the z-scores for tablets 7-11 for the total number of particles has been removed. Only the z-core plots of the total number of particles were left in.

Table of Contents

1	**Introduction**	**8**
1.1	Confidentiality of results	8
2	**Materials and methods**	**9**
2.1	Study design	9
2.2	Material preparation	9
2.3	Analytes of interest	10
2.4	Methods applied	13
2.4.1	Preproduction pellets (position nos.1-6)	13
2.4.2	Tablets (position nos.7-12)	13
2.5	Data assessment	14
2.6	Z-score assessment	14
3	**Results**	**17**
3.1	Preproduction pellets (position no. 1-6)	17
3.2	Tablets (position no. 7-12)	19
3.3	Youden analysis	26
3.4	Z-scores	29
4	**Discussion**	**31**
5	**Conclusions**	**32**
6	**References**	**33**
Appendices		**34**

This report can be cited as: van Mourik, L.M., Crum ,S.J.H., van Bavel, B., Leslie, H.A., de Boer, J., Cofino, W.P. Interlaboratory Study on Microplastics Analysis, Quasimeme Development Exercise DE 17 Round 1.

List of Figures

Figure 2-1 Aluminium strip pellet and tablet number order (left) and image of tablets present in positions 7 through 12. The aluminium strip sent to participants had tablet positions numbered on the packaging. 10

Figure 2-2 Number of participant laboratories applying gravimetric, microscopic, attenuated total reflection- or µ-Fourier Transform Infrared spectroscopy (ATR-FTIR, µ-FTIR), pyrolysis gas chromatography-mass spectrometry (Py-GC-MS), Raman spectroscopy or other determination methods for the identification of polymers in preproduction pellets (position nos. 1-6). 13

Figure 2-3 Number of participant laboratories applying gravimetric, microscopic, attenuated total reflection- or µ-Fourier Transform Infrared spectroscopy (ATR-FTIR, µ-FTIR), pyrolysis gas chromatography-mass spectrometry (Py-GC-MS), Raman spectroscopy or other determination methods applied for tablets (position nos. 7-12). 14

Figure 2-4 Illustration of z-score zones in relation to the assigned value. 15

Figure 3-1 Flow diagram showing number of participants and number of submitted results 17

Figure 3-2 Number of particles reported per laboratory for tablet position no. 7 22

Figure 3-3 Number of particles reported per laboratory for tablet position no. 8 22

Figure 3-4 Number of particles reported per laboratory for tablet position no. 9 23

Figure 3-5 Number of particles reported per laboratory for tablet position no. 10 23

Figure 3-6 Number of particles reported per laboratory for tablet position no. 11 24

Figure 3-7 Number of particles reported per laboratory for tablet position no. 12 24

Figure 3-8 Relationship between sum of added polymer particles and total number of particles. 26

Figure 3-9 Biplot for polystyrene (PS) showing the relationship between the reported number of PS particles in tablets position nos. 10 and 11. 27

Figure 3-10 Biplot for Polyvinylchloride (PVC) showing the relationship between the reported number of PVC particles in tablets position nos. 10 and 8. 28

Figure 3-11 Biplot for Polyethylene terephthalate (PET) showing the relationship between the reported number of PET particles in tablets position nos. 10 and 7. 28

Figure 3-12 Biplot for ‘total particles’ showing the relationship between ‘total particles’ in tablet position no. 8 to 11. 29

List of Tables

Table 2-1. Overview of test samples participants received and the type of measured data that was reported. 11

Table 2-2. Characteristics of the preproduction pellets distributed in strip position numbers 1 to 6 11

Table 2-3. Characteristics of the tablets distributed in strip position numbers 7 to 12 12

Table 3-1. For preproduction pellet (strip position nos. 1-6): number of laboratories reporting data, average number of pellets, reported weights of pellets (minimum, maximum, average, standard deviation (SD) and relative standard deviation (RSD)); green highlights the added polymer type 18

Table 3-2. Summary of the numbers of correct identification of the polymers in the pellets (position nos. 1-6) 19

Table 3-3. For tablets (strip position nos. 7-11): number of laboratories reporting data, number of particles (average, standard deviation (SD) and relative standard deviation (RSD)) 20

Table 3-4. For tablets (strip position nos. 7-11): number of laboratories reporting data, total number of particles (average, standard deviation (SD) and relative standard deviation (RSD)) 21

Table 3-5 Overview reported weights of microplastics found in tablets 7 to 12 by pyrolysis GC-MS. 21

Table 3-6 Summary of degree to which the polymers added are identified 25

Table 3-7 Summary of the identification of polymer particles by laboratories in tablets position nos. 7-11. 25

Table 3-8. Summary of amounts of polymers added to tablets in position no. 7,8,10 and 11 26

Table 3-9 Youden statistics showing values for tablet position nos. 7,8 and 10 27

Table 3-10. Summary statistics for added polymers in tablets (position no. 7-11) for z-score assessment 29

Table 3-11. Summary statistics for total number of particles in tablets (position no. 7-11) for z-score assessment 30

Table A-1 Type, weight and number of plastic particles reported for position no. 1 35

Table A-2 Type, weight and number of plastic particles reported for position no. 2 36

Table A-3 Type, weight and number of plastic particles reported for position no. 3 37

Table A-4 Type, weight and number of plastic particles reported for position no. 4 38

Table A-5 Type, weight and number of plastic particles reported for position no. 5 39

Table A-6 Type, weight and number of plastic particles reported for position no. 6 40

Table A-7 Type and number of plastic particles reported for tablet in position no. 7 41

Table A-8 Type and number of plastic particles reported for tablet in position no. 8 42

Table A-9 Type and number of plastic particles reported for tablet in position no. 9 43

Table A-10 Type and number of plastic particles reported for tablet in position no. 10 44

Table A-11 Type and number of plastic particles reported for tablet in position no. 11 45

Table A-12 Type and number of plastic particles reported for tablet in position no. 12 46

Table A-13. Z-scores for tablets position nos. 7-11 for the polymers added and for laboratories that report numerical results for these 55

Table A-14 Additional method information 58

Abbreviations and acronyms

ATR	Attenuated total reflection
AV	Assigned value
DE	Development exercise
EPS	Expanded polystyrene
FTIR	Fourier transform infrared spectroscopy
ILS	Interlaboratory study
LDPE	Low-density polyethylene
Max	Maximum
Min	Minimum
n	Number
NIAS	Non-intentionally added substances
NIVA	Norwegian Research Institute for Water Research
no.	Number
PC	Polycarbonate
PET	Polyethylene terephthalate
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinylchloride
Py-GC-MS	Pyrolysis gas chromatography-mass spectrometry
QAQC	Quality assurance and quality control
RSD	Relative standard deviation
SD	Standard deviation
VUA	Vrije Universiteit Amsterdam

Summary

The first round of this international interlaboratory study (ILS) on microplastic analysis consisted of twelve different tests: six tests on quantification and identification of preproduction pellets and six tests using tablets that were to be dissolved in water containing different polymer particles or fibres.

In total, 34 laboratories participated of which 30 submitted data. Participants analysed the test materials using in-house methods. Currently no standard or harmonised methods exist. Several instrumental and quantification methods (*n*=7) were used. Most commonly applied identification method for the pellets was method attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR, *n*=14), while the μFTIR was most commonly applied for the tablets (*n*=19). For quantification, gravimetric and microscopy were most commonly used for the pellets and tablets, respectively. Two laboratories used pyrolysis gas chromatography coupled to mass spectrometry (Py-GC-MS).

Although some polymer misidentifications occurred, in most cases the polymer type was correctly identified for both the larger preproduction pellets (2-4 mm) and the particles and fibres added to the tablets (150-300 μm). Also, the results of weight determination of the preproduction pellets were satisfactory. In an ILS, the relative standard deviations (RSD) in reported values is a measure of the agreement of the values submitted by the participating laboratories. The RSDs of the determination of the polymer type present in particles and fibres in the six tablet tests varied from 29% (for polyethylene terephthalate) to 99% (for polystyrene).

Overall, the results of this first round indicate that polymer identification and quantification of the number of plastic particles in a sample (especially in the smaller size fractions) is not simple or straightforward. The participating laboratories are to be commended, though further improvements to the quality control of microplastics analysis are desirable in this pioneering phase of measuring an emerging environmental contaminant. The quality control issues can be addressed in the successive exercises in this ILS initiative. As a follow-up, a second round exercise is being organised shortly after the finalization of this report, and will include samples with more complexity than the test samples in the first round.

1 Introduction

Microplastics are present in every environmental compartment and have gained recent interest as an environmental pollutant. 'Plastic' is not a well-defined analyte, but rather a set of materials that encompass a wide range of high molecular weight synthetic polymers such as thermoplastics and thermosets. 'Microplastics' are plastic particles spanning 6 orders of magnitude in particle size (low nanometre to 5 mm) and a large variety of chemical compositions: (co)polymers, chemical additives, residual monomers, fillers, catalysts, non-intentionally added substances (NIAS) etc.

The diversity of this analyte class gave rise to a search for a mix of methodologies to answer the burning questions in microplastic research and to support plastic pollution monitoring and mitigation policies under consideration by state and non-state actors. To date there are no validated standard methods available for the analysis of microplastic and various number of analytical protocols, methods and techniques are used. The analysis of microplastics is difficult due to the large number of different polymers, size fractions and shape. Furthermore, as there is still not consensus on the reporting format, microplastic are reported as number of particles, fibres or mass of different size fractions. There is an obvious need to validate and harmonize the different methods for the analysis of microplastics. Another challenge analytical scientists face with microplastics analysis is how to check and demonstrate analytical proficiency. There is currently a lack of open interlaboratory studies (ILSes) and a total absence of certified reference materials to investigate analytical proficiencies.

Participation in ILS studies increase confidence in the data produced, both for the analytical laboratories and the data users. For accreditation, proficiency testing will be required. ILS studies will also give a 'state of the art' of the analytical procedures used for polymer identification and quantification and are a useful tool for method development and further standardisation. Each participating laboratory confidentially receives a laboratory code in the beginning of the round as well as a study report presenting the overall results among all the anonymized participating laboratories at the end of the round. Participants benefit from follow-up workshops in which the study results of the testing rounds are discussed in light of analytical performance of different methods used.

The Vrije Universiteit Amsterdam (VUA), the Norwegian Research Institute for Water Research (NIVA) and WEPAL-QUASIMEME Laboratory Performance Studies (Wageningen Environmental Research) have taken the initiative to organise an interlaboratory study on microplastics. The study has been supported by the NORMAN workgroup nano-and micro scale particulate contaminants, which has recognized microplastics as an emerging issue. The four institutions have joined forces to set up a program to address the quality of microplastic analyses.

As a first step, a workshop on microplastics was organised in Amsterdam, the Netherlands, in November 2018. During this workshop (ca. 110 participants) it was generally agreed that an ILS on microplastics was needed, preferably designed in a step-wise way. The set-up of this ILS started with the analysis of 'standard' like test samples (i.e. the first round) and will be followed by a series of more samples and exercises with increasing complexity and difficulty. Because this ILS focuses on a new and difficult analysis, we term this study a 'Development Exercise' (DE).

This report describes the design and the results of this first ILS round, DE-17. The objective of this round was to assess the ability to determine the polymer type in pellets and plastic particles, as well as the number of plastic particles in test samples prepared specifically for this exercise.

1.1 Confidentiality of results

The confidentiality of the results is extremely important in the WEPAL-QUASIMEME programs. In the report only the laboratory codes are mentioned in the data reporting and therefore, no list of participants is included in this report. When an accreditation body or a regulatory authority requests the proficiency test results to be provided by WEPAL-QUASIMEME, the participants shall be notified and asked for permission first.
Participants may not use or report individual data from other laboratories. Assigned values, means and standard deviations of the interlaboratory studies published in this report may be used.

2 Materials and methods

2.1 Study design

This study was setup in agreement between WEPAL-QUASIMEME, VUA and NIVA. WEPAL-QUASIMEME is a leading expert in the organisation of interlaboratory studies with a focus on e.g. the marine environment. It is accredited for organizing proficiency tests for several determinands and matrices. WEPAL-QUASIMEME handled the logistics and analysed the data. VUA has an extensive experience in environmental analysis and in the organization of interlaboratory studies, many in collaboration with WEPAL-QUASIMEME, and is actively involved in the field of microplastics. VUA organised the preparatory workshop, coordinated the project and reporting, and gave input to the data interpretation. NIVA is Norway's leading institute concerning the aquatic environment. NIVA is involved in several quality assurance and quality control (QA/QC) studies and develops certified reference materials for different contaminants including microplastics. NIVA has prepared a number of microplastic standard and test materials. NIVA's standard materials were used for this ILS round.

Similar to the approach for other emerging contaminants, the ILS was designed in a step-wise manner, consisting of a number of rounds of sending out samples for analysis to participants, collecting the participants' data, and then analysing and reporting the data back to participants. The first step (i.e. the first round), started with the analysis of 'standard' like test samples. This creates a basis for laboratories to check their performance in both identifying and quantifying polymers in samples in the absence of a (complex) matrix. This round will be followed by exercises with increasing complexity and difficulty of samples. After several ILS rounds, the analytical methodologies for microplastics are expected to be better comparable and will be included in the routine proficiency testing scheme of WEPAL-QUASIMEME.

National reference, governmental, research, academic and commercial laboratories as well as other research facilities from all over the world were invited to participate. The analytical work of ILS DE-17 was performed between May 2019 and August 2019. Participants were asked to identify and quantify, i.e. count particles (integer) and/or determine the mass of particles (mg or µg) and polymer types in six preproduction pellets and six tablets, using their own method of choice. In addition to the results, information was requested about the participants' analysis methods for a more in-depth analysis of the submitted data as well as performance characteristics. All the requested data was filled in and submitted by Excel report forms. The laboratory code of the participating laboratories is kept confidential and will not be revealed to other participants.

This ILS was designed as a development exercise. The study aims to identify strengths and weaknesses of different methodologies and to assist laboratories in improving their methods and the implementation thereof. The ILS does explicitly not have the intention to judge the performance of laboratories, but rather to provide an objective assessment and feedback of the analytical data, with comparative information on the methods/instruments of choice. These types of information may potentially be used to improve the analytical quality and aspects of the technical work. The z-scores calculated should therefore not be used for laboratory performance assessment nor accreditation.

2.2 Material preparation

The 12 test samples were prepared at the NIVA. The test samples were prepared to enable the analysis by a broad variety of analytical methods and techniques (visual, hyperspectral imaging, Fourier transform infrared spectroscopy (FTIR), Raman and mass spectrometry) and consisted of six preproduction pellets, five tablets containing microplastic fragments or fibres and one blank tablet. The preproduction pellets were added to the aluminium strip as they were received. The tablets consisted of a mixture of sodium hydrogen carbonate ($NaHCO_3$) and citric acid ($C_6H_8O_7$), and a binder (lactose) which were not expected to interfere during the analysis as the tablets completely dissolve in water. All tablets were made by hand by combining the ingredients and the different polymers into a mixture and apply the mixture to a metal form in which the tablets were moulded by applying pressure. Blank tablet consisted only of the ingredients without the addition of polymers. No lubricants were used as most lubricants are not

completely soluble in water. Both the preproduction pellets and the tablet were sealed in aluminium strip before shipment.

The different fragments were obtained after filtration of polyethylene terephthalate (PET), polyvinylchloride (PVC) and polystyrene (PS) powder. Fractions of 150-250 um, 250 – 300 µm and 250-350 respectively were added to the tablets. The microplastic fibres were created by washing polyester blankets in a typical domestic washing machine. The blankets ('Skogsklocka', IKEA, Norway) were washed in a clean washing machine system on a 15-minute cycle at 40°C and 1200 rpm. No detergents or softeners were added. The effluent was collected in a stainless-steel pressure vessel and vacuum filtered through a 10 µm nylon membrane. This method yields fibres 101-2194 µm in length and 28.9 µm wide. The fraction of 300-400 µm was used for tablet 9.

Homogeneity of the tablets samples was verified by analysing 10 tablets from each batch. The variation of the test material was between 10 and 21%, depending on the polymer and the number of particles added. This was considered sufficient in relation to the expected variation between the laboratories. All samples were tested for particles present in the materials to make the tablets or during production. Although extreme care had been taken during production, particles of polymers and fibres, not added to the tablets were found. The number of these other polymers are given in Table 2-3 and defined as background. Detailed analysis of the tablets showed a relatively large amount of small particles (i.e. < 20 µm) using a Coulter counter (3-18 um) for the fibre sample (Tablet 9) and PCSS fluid lite particle counter (0.8 – 400 um), especially in the samples where PET fragments were added (Tablet 7 and 10).

The aluminium strip was coded as shown in Figure 2.1. Positions 1-6 contained the preproduction pellets, position 7-11 the tablets with the plastic particles and position 12 the blank tablet.

Figure 2-1 *Aluminium strip pellet and tablet number order (left) and image of tablets present in positions 7 through 12. The aluminium strip sent to participants had tablet positions numbered on the packaging.*

2.3 Analytes of interest

Table 2-1 shows an overview of the test samples and the type of data that was requested and reported. For the preproduction pellets, which were positioned on number 1 to 6 (Table 2-2), the results on the *number*, *polymer type* and *weight* of the pellets had to be reported. For the tablets, which were positioned in number 7 to 11, the results on the *polymer type of plastic particles present*, and the *number of plastic particles* and/or the *mass* of the plastic particles had to be reported.

Table 2-1. Overview of test samples participants received and the type of measured data that was reported.

Round	Analysis Group Code	Test sample	Type of data reported
1	DE-17	Preproduction pellets (*n*=6) Pellet position nos. 1 -6	polymer type(s) in each pellet; weight of plastic pellets; all analytical methods
1	DE-17	Tablets containing plastic particles (*n*=5) Tablet position nos. 7-11	polymer type(s) in each tablet; number of polymer particles in each tablet (and corresponding polymer types); and/or mass of polymer particles in each tablet (and corresponding polymer types); all analytical methods
1	DE-17	Blank tablet (no plastic added) as a control sample for background contamination. (n=1) Tablet position no. 12	polymer type(s) detected in the blank tablet; number of plastic particles detected in the blank tablet, categorized per polymer type and/or mass of plastic particle present in each tablet, categorized per polymer type; all analytical methods

Tablet 12 was a blank tablet with no added plastic particles and was to be analysed and reported with the same procedural steps as for tablets 7-11. This sample was used as a quality control sample only and was not validated statistically in terms of standard deviation or z-scores.

Tables 2-2 and 2-3 show the characteristics of the preproduction pellets and the tablets, of which the data have been obtained in the homogeneity studies carried out by NIVA. For the tablets, the number of the added polymers particles for each batch are given, as well as the number of other particles detected in the tablets, which are given as background.

Table 2-2. Characteristics of the preproduction pellets distributed in strip position numbers 1 to 6

Pellet	Polymer	Average weight per pellet (mg)[a]	Total weight (*n* = 3)	Average size (mm)[a]
1	Polycarbonate (PC)	15.4	46.2	2.40 x 1.94 x 3.33
2	Polystyrene (PS)	21.6	64.8	2.27 x 3.08 x 3.58
3	Polypropylene (PP)	29.4	88.2	4.31 x 4.67 x 2.43
4	Polyethylene terephthalate (PET)	18.6	55.8	3.33 x 2.18 x 2.44
5	Low-density polyethylene (LDPE)	26.2	78.6	2.83 x 4.00 x 4.19
6	Expanded polystyrene (EPS)	0.6	1.8	NA[b]

[a] Unknown to participants

[b] Not analysed

Table 2-3. Characteristics of the tablets distributed in strip position numbers 7 to 12

Tablet 7		Polyethylene terephthalate (PET)			Background
	Pill weight (g)	mg added to tablet	(*n* particles)	PET particle size (µm)	(*n* particles)
		0.556		250-300	
Mean	0.50		50		3.3
SD	0.003		7.7		1.3
RSD	0.66 %		15 %		38 %
Tablet 8		**Polyvinylchloride (PVC)**			**Background**
	Pill weight (g)	**mg added to tablet**	**(*n* particles)**	**PVC particle size (µm)**	**(*n* particles)**
		0.0556		150-250	
Mean	0.49		27		2.0
SD	0.005		3.8		1.2
RSD	0.93 %		14 %		52 %
Tablet 9		**Polyethylene terephthalate (PET) fibres**			**Background**
	Pill weight (g)	**mg added to tablet**	**(*n* particles)**	**PET fibre size (µm)**	**(*n* particles)**
		-[b]		250-300	
Mean			22		19
SD			4.6		4.1
RSD			21 %		22 %

Tablet 10		Polyethylene terephthalate (PET)		Polystyrene (PS)		Polyvinylchloride (PVC)		Background
	Pill weight (g)	mg added to tablet	(*n* particles)	mg added to tablet	(*n* particles)	mg added to tablet	(*n* particles)	(*n* particles)
		0.0900		0.0900		0.0900		
Mean	0.50		8		25		27	5.0
SD	0.02		3.0		4.0		6.8	1.8
RSD	4.0 %		38 %		16 %		25 %	37 %

Tablet 11		Polystyrene (PS)			Background
	Pill weight (g)	mg added to tablet	(*n* particles)	PS particle size (µm)	(*n* particles)
		0.0738		250-300	
Mean	0.50		24		3.4
SD	0.002		2.5		1.6
RSD	0.39 %		10.8 %		48 %
Tablet 12		**Blanks**			**Background**
	Pill weight (g)				**(*n* particles)**
Mean	0.50				3.0
SD	0.007				1.4
RSD	1.3 %				53 %

[a] Unknown to participants

[b] Fibres were added individually by hand to each tablet

2.4 Methods applied

Details on the methods used by participants are found in Appendix C. Participants were informed that samples could be stored at room temperature and that samples were to be kept dry in order not to compromise the tablets. Instructions were given on how to open the strip with a tweezer in order not to damage the tablets and to not push the tablets through the aluminium strip because this could potentially damage the tablets. Instructions were also given on how to dissolve the tablets in analytical grade water. Participants were asked to take every effort to control background contamination and to correct results for procedural or laboratory blanks.

2.4.1 Preproduction pellets (position nos.1-6)

Most participants (*n*=20) did not use any sample pre-treatment (i.e. extraction, clean-up, purification and/or modification of the sample prior analysis) for the pellets (position no.1-6), while six participants did not report whether they used sample pre-treatment. Four participants reported filtration as sample pre-treatment. Of those four, one also reported staining using Nile Red, while another reported washing with MilliQ analytical grade water as additional sample pre-treatment steps.

Number of applied identification methods are summarized in Figure 2.2. In short, many different methods were (*n*=6) used. ATR-FTIR was most commonly applied to identify polymer types. Of the laboratories that applied Raman, one reported to have used µRaman.

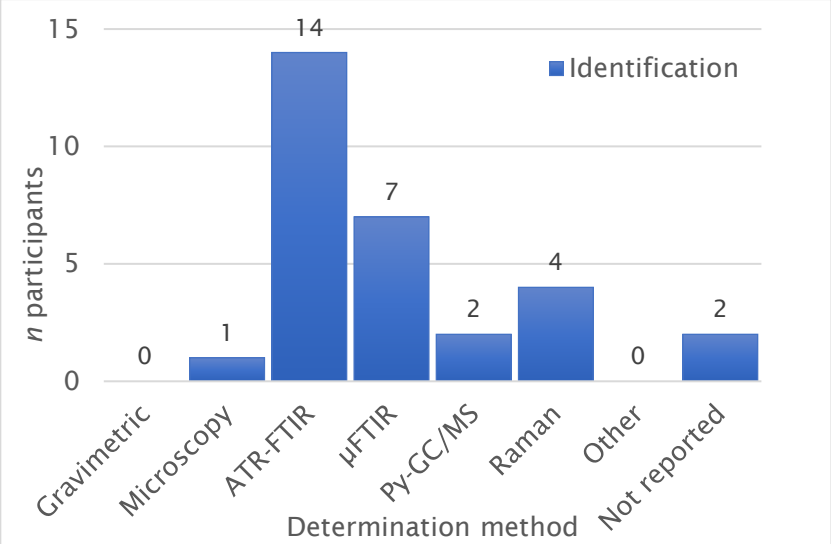


Figure 2-2 *Number of participant laboratories applying gravimetric, microscopic, attenuated total reflection- or µ-Fourier Transform Infrared spectroscopy (ATR-FTIR, µ-FTIR), pyrolysis gas chromatography-mass spectrometry (Py-GC-MS), Raman spectroscopy or other determination methods for the identification of polymers in preproduction pellets (position nos. 1-6).*

2.4.2 Tablets (position nos.7-12)

For the tablets 7-12, 26 laboratories reported to have used sample pre-treatment, of which 25 reported filtration. After filtration, five laboratories reported additional pre-treatment steps. Two reported staining using Nile Red, one reported hydrogen peroxide treatment of filter and then rinsing with MilliQ water of filter, one washing with MilliQ water, and one oven drying. One laboratory used first organic digestion with hydrogen peroxide and KOH for destroying the organic content, then density separation with potassium formate and pressure filtration of the remaining liquid on a filter.

Number of applied identification and quantification methods are summarized in Figure 2.3. Again, many different methods (*n*=7) were applied to identify and quantify the polymer particles. Two laboratories reported as other quantification method using Nile Red staining, while one laboratory reported using

binocular magnifying. Of the laboratories that applied Raman, one reported to have used µRaman. The most commonly applied method for identification was µFTIR, while microscopy was the most commonly applied method for quantification.

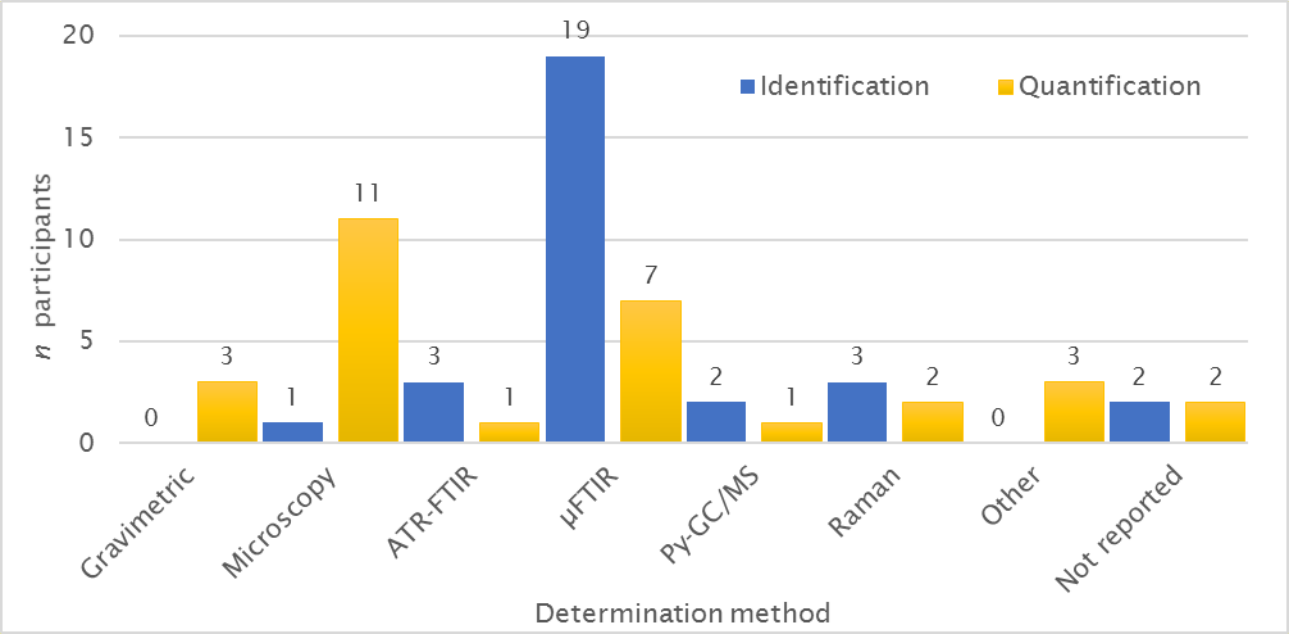


Figure 2-3 *Number of participant laboratories applying gravimetric, microscopic, attenuated total reflection- or µ-Fourier Transform Infrared spectroscopy (ATR-FTIR, µ-FTIR), pyrolysis gas chromatography-mass spectrometry (Py-GC-MS), Raman spectroscopy or other* determination methods applied for tablets (position nos. 7-12).

2.5 Data assessment

The evaluation of the data reported for the pellets (position nos. 1-6) focused on the identification of the polymers. No quantitative analysis of the masses reported was conducted because the main objective for the pellets was the identification of the polymer types. The weight of the pellets was asked to be reported as a common check of the content per position (see Appendix A for more details of the masses reported).

The data assessment was carried out according to the principles of data assessment employed by the WEPAL-QUASIMEME proficiency testing organisation (www.WEPAL-QUASIMEME.org). All data received from the participants were entered into an excel database and assessed using a robust method (NDA statistics, Molenaar et al. 2018) enabling direct comparison between participants. See appendix D for further details.

2.6 Z-score assessment

In this report, z-scores are presented for the polymers that were added to tablets 7,8,9,10 and 11. Please be aware that these z-scores are given to enhance the insights deduced from the ILS and as a support to improvements of methodology. The z-scores are in this case not intended to be used in evaluating the performance of laboratories.

Z-scores are calculated as

$$z_i = \frac{(\bar{x} - x_{pt})}{\sigma_{pt}}$$

In this formula, z_i is the z-score of laboratory i, x_{pt} is the assigned value (AV, i.e. consensus value of the dataset), and σ_{pt} is the standard deviation for proficiency assessment. The z-score z_i represents how far the result of laboratory i is from the assigned value in terms of the standard deviation σ_{pt}.

In this study, σ_{pt} is set to be 12.5% of the assigned value. This approach differentiates the dataset in three zones:

- Zone I: results that are within 25% of the assigned value, in proficiency tests denoted as 'satisfactory results';
- Zone II: results with 2<|z|<3, thus that differ in absolute sense between 25% and 37% from the assigned value, in proficiency tests referred to as 'questionable results';
- Zone III: results that differ 37.5% or more from the assigned value, indicated in proficiency tests as 'unsatisfactory results'.

The three zones of z-scores are illustrated in Figure 2.4.

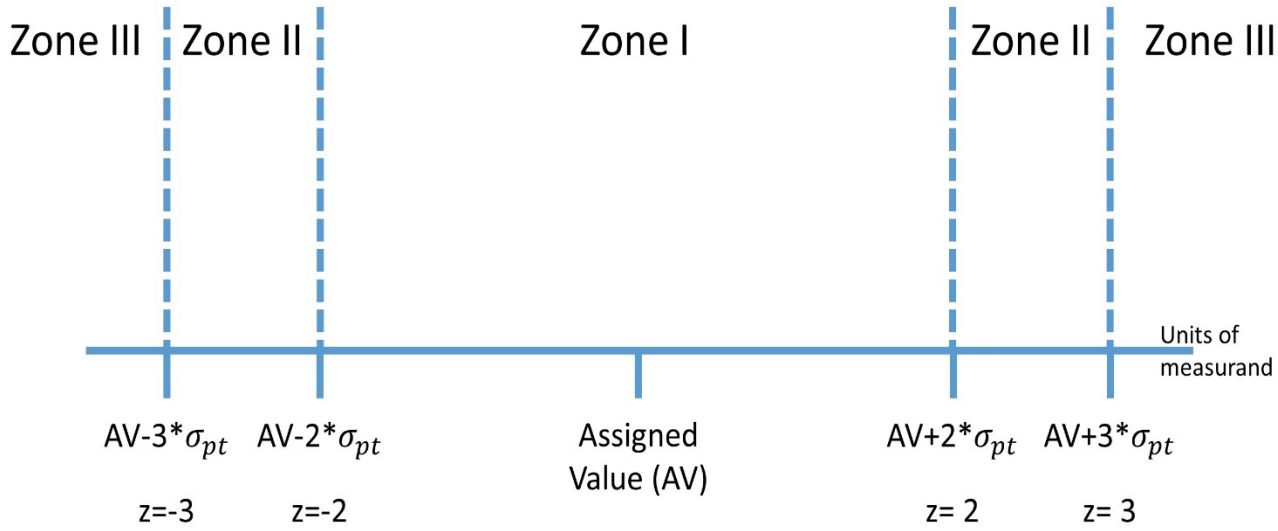


Figure 2-4 Illustration of z-score zones in relation to the assigned value.

The data have been analysed with a robust method described by Cofino *et al* (2000). The mathematical basis of the method has been strengthened in Molenaar et al. (2018).

The robust mean of the datasets is used as the assigned value x_{pt}. In proficiency tests, the standard uncertainty $u(x_{pt})$ of the assigned value is incorporated in the calculation of the z-score (giving rise to the z'- score, ISO 13528 (2016)). The term $u(x_{pt})$ is given by

$$u(x_{pt}) = 1{,}25 * \frac{s^*}{\sqrt{p}}$$

where s^* is the robust standard deviation of the exercise and p the number of data analysed.

In the calculations presented, the uncertainty in the assigned value is not taken into consideration as it hampers a consistent interpretation of the z-scores for the purpose of this study. The standard uncertainty of the assigned value is, however, given to illustrate its magnitude.

Z-scores have been calculated for the individual polymers that were added to tablets 7-11 and for the total number of particles in these tablets. This approach has been taken as some guidelines for monitoring, for instance the preliminary protocol for the monitoring of plastic in fish stomachs in the OSPAR maritime area provided by ICES to OSPAR, call for the determination of the number of plastic particles, if possible along with the identification of the type of plastic (ICES PLAST advice1). The total number of plastic particles includes particles present in the sample as "background" in the materials used, particles introduced at the laboratories following contamination, and particles that have been incorrectly identified by the laboratories as plastic (false positives). Given the method for preparation of the samples,

[1] https://www.ices.dk/sites/pub/Publication%20Reports/Advice/2015/Special_Requests/OSPAR_PLAST_advice.pdf

a close correspondence between the total number of individual polymer particles added and the total number of plastics reported by laboratories is expected. A complication arose, however, in tablet 9 (vide infra) owing to the mode of preparation of the sample and the contribution of laboratories that can identify particles with a very small size, i.e. <10 μm.

The assigned values, the robust standard deviations, the standard uncertainties and the standard deviation used to assess the data is given in Table 3-10 and Table 3-11. These tables show that the standard deviation used to assess the data are relatively high and illustrate that *z*-scores in this study should not be used to judge the performance of laboratories.
Tablet 10 is made up by adding the three polymers PS, PET and PVC to the substrate. Tablets 7, 8 and 11 contain respectively the individual PET, PVC and PS polymers in different amounts. Therefore, these samples enable a Youden type of analysis. This analysis is given in Section 3.3.

3 Results

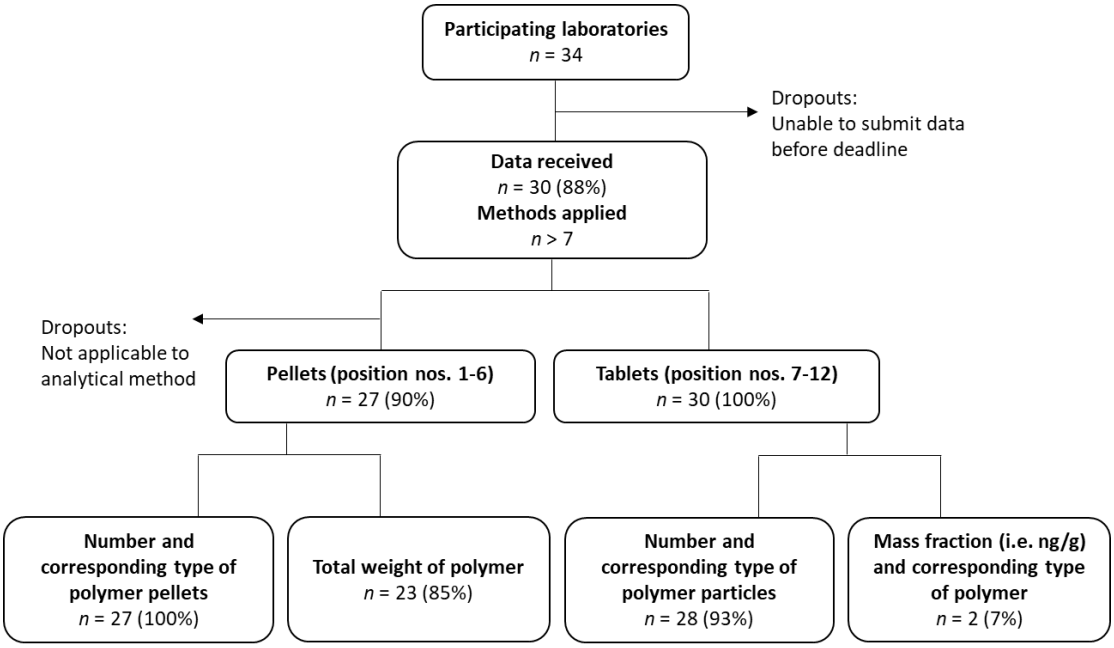


Figure 3-1 *Flow diagram showing number of participants and number of submitted results.*

In total, 34 laboratories participated of which 30 laboratories were able to submit the results before the deadline. Of the 30, 27 laboratories submitted data for the preproduction pellets, while 30 laboratories did so for the tablets. Of the laboratories that submitted data for the preproduction pellets, all laboratories submitted data for the number and corresponding type of polymer pellets, while 23 reported the total weight of the polymer pellets. Two laboratories reported the type of polymer and mass of plastic (i.e. ng/g by of pyrolysis gas chromatography-mass spectrometry, Py-GC-MS). The other 28 participants reported the number and corresponding type of polymer particles.

3.1 Preproduction pellets (position no. 1-6)

Table 2-2 provides the characteristics of the pellets. Table 3-1 presents the results obtained for the pellets, while Table 3-2 shows a summary of the number or correct polymer identification. Appendix A provides an overview of reported types and number of plastic particles per laboratory.

In general, the majority of laboratories (*n*=15 to 27 out of the 27) reported the correct type of polymer in all pellets (141 out of the 162). All laboratories correctly identified the polystyrene pellets given in position 6. Three laboratories correctly identified the polymers in four out of six pellets, 15 laboratories in five out of six pellets and nine laboratories identified the polymers in all pellets correctly.

One laboratory reported for position 4 two particles of PET and one particle PS, which resulted in a non-integer score. The low-density polyethylene (LDPE) preproduction pellets in position 5 exhibited the largest scatter in results, which is attributed to difficulties in making a distinction between low- and high-density polyethylene.

Reported weights of the pellets in position 1-5 agreed well among laboratories, with relative standard deviations (RSDs) between 6 and 16%. For position 6, a relatively higher RSD of 33% was found for weight determination compared to the other pellets, probably due to the low density of the expanded polystyrene pellets.

The reported total weights (Table 3-1) correspond well with those obtained by NIVA in the homogeneity study (Table 2-2), with relative errors <17%.

Table 3-1. For preproduction pellet (strip position nos. 1-6): number of laboratories reporting data, average number of pellets, reported weights of pellets (minimum, maximum, average, standard deviation (SD) and relative standard deviation (RSD)); green highlights the added polymer type

Pellet and reported polymer type	N labs reporting number of pellets	Average reported number of pellets	N labs reporting weight of pellets	Min reported weight (mg)	Max reported weight (mg)	Average reported weight (mg)	SD of weight	RSD of weight
Position no. 1								
Polycarbonate	25	3.00	21	42.3	54.0	47.5	3.3	7%
poly (methyl methacrylate)/ polyvinylchloride blend	1	3.00	1	45.3	45.3	45.3		
Polyimide	1	3.00	1	47.0	47.0	47.0		
Position no. 2								
Polystyrene	24	3.00	20	60.3	78.4	65.5	3.8	6%
acrylonitrile butadiene styrene	2	3.00	2	63.1	65.9	64.5	2.0	
poly (methyl methacrylate)	1	3.00	1	66.9	66.9	66.9		
Position no. 3								
Polypropylene	26	3.00	22	72.1	124.4	96.9	14.6	15%
Unknown	1	3.00	1	78.5	78.5	78.5		
Position no. 4								
polyethylene terephthalate	24	2.96	20	37.4	63.9	57.5	5.8	10%
Polyester	3	3.00	3	57.2	67.3	60.6	5.8	
Polystyrene	1	1.00	1	0.5	0.5	0.5		
Position no. 5								
Low density polyethylene	15	3.00	13	66.9	116.9	79.5	12.5	16%
High density polyethylene	8	3.00	7	68.0	88.5	77.6	6.1	
polyethylene	4	3.00	3	66.0	79.2	74.8	7.6	
Position no. 6								
Polystyrene	27	3.26	23	0.9	3.3	2.1	0.7	33%

Table 3-2. Summary of the numbers of correct identification of the polymers in the pellets (position nos. 1-6)

Laboratory code	Pos1	Pos2	Pos3	Pos4	Pos5	Pos6	Total correctly identified
H221	1	1	1	0	1	1	5
Q104	1	1	1	0.67	1	1	5.67
Q110	1	1	1	1	1	1	6
Q114	1	1	1	1	0	1	5
Q134	1	1	1	1	1	1	6
Q152	1	0	1	1	1	1	5
Q153	1	1	1	1	1	1	6
Q3231	1	1	1	1	0	1	5
Q3239	1	1	1	1	0	1	5
Q3872	1	1	1	1	1	1	6
Q3873	1	1	1	0	1	1	5
Q3876	1	0	1	1	1	1	5
Q3877	0	0	1	1	1	1	4
Q3878	1	1	1	0	0	1	4
Q3879	1	1	1	1	0	1	5
Q3882	1	1	1	1	0	1	5
Q3883	1	1	1	1	1	1	6
Q3884	1	1	1	1	1	1	6
Q3885	1	1	1	1	0	1	5
Q3887	1	1	1	1	0	1	5
Q3888	1	1	1	1	1	1	6
Q3889	0	1	0	1	1	1	4
Q3890	1	1	1	1	1	1	6
Q3891	1	1	1	1	0	1	5
Q3892	1	1	1	1	0	1	5
Q3894	1	1	1	1	0	1	5
Q871	1	1	1	1	0	1	5
Grand Total	**25**	**24**	**26**	**24**	**15**	**27**	**141**

NB. For position 5, quite some laboratories (4) reported polyethylene without differentiating between high density polyethylene and low density polyethylene. As position 5 contained low density polyethylene pellets, we decided to assess only low density polyethylene as being correct.

3.2 Tablets (position no. 7-12)

Table 3-3 summarizes the results obtained for the five tablets (position nos. 7-11), while Figure 3-2 to 3-6 show the number of particles reported per laboratory. Appendix A provides full details of reported types and number of plastic particles per laboratory while Appendix B presents the z-score plots. The agreement in the reported number of particles in the tablets among laboratories varied greatly (RSD 29-99%), both of the added polymer as well as all the total of all polymer types (i.e. total (including other) particles, Table 3-4). Table 3-5 shows the results (in mass) obtained by pyrolysis GC-MS (Py-GC-MS).

The added polymer(s) were the most abundant reported polymers in the tablet. In case of tablet 9, one other polymer type other than the added polymer was reported in a high abundance, i.e. polystyrene.

For tablet 7, four laboratories reported non-numerical data (i.e. less than or more than values). Of the laboratories that submitted numerical data (*n*=26), most laboratories (*n*=20) reported a numerical value for PET. The average number of particles (41.7) is lower than was found in the homogeneity study, but still close (16% relative error, RE). Polypropylene (PP) and PS were reported by five and eight laboratories, respectively. The 20 laboratories that correctly identified PET, reported on average that 97.4% of the particles were PET and that 2.5% of the particles were different polymer types or classified as unknown. These percentages correspond well with those obtained by NIVA in the homogeneity study (respectively 93.8% and 6.2%).

For tablet 8, three laboratories submitted non-numerical data, while 27 submitted numerical data. The 21 laboratories that correctly identified PVC, reported on average that 95.6% of the particles were PVC, while 4.4% of the particles were attributed to a different plastic type or classified as unknown. These percentages correspond also well with those obtained by NIVA in the homogeneity study (respectively 93.1% and 6.9%).

Seven laboratories reported non-numerical data for tablet 9, while 23 reported numerical data. The data on the composition of the tablet show that the number of background particles (Section 2.3) is similar to the number of PET fibres added to the sample. The data submitted by the participants reflect this situation. Ten laboratories reported on average 13.4 PET fibres. The presence of PS is also reported by ten laboratories with an average of 40.5 particles. Polyester particles and "red/orange fibres" were each reported by four laboratories with averages of 25.2 and 13.9 particles, respectively. The ten laboratories that identified PET fibres, reported on average that 40% of the particles was PET and that 60% of the particles was a different plastic type or classified as unknown.

Only one laboratory reported non-numerical data for tablet 10. The number of particles for PVC, PS and PET given in Table 3-3 correspond reasonably well with the composition reported by NIVA (Table 2-3). The laboratories reported on average the sum of PVC, PET and PS as 91.4% of the particles, the percentage of background particles being 8.6%.

Similar to tablet 10, only one laboratory reported non-numerical data for tablet 11. Twenty-two out of 28 laboratories reported PS with an average number of 17.1. These 22 laboratories reported that on average 70.6% of the particles is PS, the remaining 29.4% being "background" (i.e. the other sum of the other particles that are reported). The composition given by NIVA entails that 87.5% of the particles were made of PS and that the remaining part being 12.5%.

Table 3-3. For tablets (strip position nos. 7-11): number of laboratories reporting data, number of particles (average, standard deviation (SD) and relative standard deviation (RSD))

Tablet	N labs reporting particles	Average number of particles	SD of number of particles	RSD of number of particles (%)
Position no. 7				
Polyethylene terephthalate	20	42	12	29
Position no. 8				
Polyvinylchloride	21	14	9.1	66
Position no. 9				
Polyethylene terephthalate fibres	10	13	6.1	46
Position no. 10				
Polyethylene terephthalate	15	5.5	4.0	73
Polystyrene	20	17	13.3	78
Polyvinylchloride	16	20	9.3	46
Position no. 11				
Polystyrene	22	12	9.1	75

Table 3-4. For tablets (strip position nos. 7-11): number of laboratories reporting data, total number of particles (average, standard deviation (SD) and relative standard deviation (RSD))

Tablet	N labs reporting particles	Average number of total particles	SD of number of total particles	RSD of number of total particles (%)
Position no. 7				
Total (incl other) particles	26	36.9	21.0	57
Position no. 8				
Total (incl other) particles	27	18.7	14.6	78
Position no. 9				
Total (incl other) particles	23	20.2	18.3	91
Position no. 10				
Total (incl other) particles	27	42	24.3	58
Position no. 11				
Total (incl other) particles	28	15.8	12.8	81
Position no. 12				
Total (incl other) particles	19	3.2	3.9	122

The 'blank' tablet in position 12 contained an average of 3 particles during production. The average of the analysis of the 19 reporting laboratories was 3.2 particles, but with a large variation (RSD 122%).

The results for the mass-based analysis is given in Table 3-5. Only two participants were using py-GC-MS for the analysis of the tablets, one lab determined the mass of the polymers in the tablet gravimetrically. Therefore, a separate statistical evaluation was not possible. Theoretical amounts are given in the Table 3-5 as "Added". The fibres in tablet 9 were added by hand and were not weighted during the making.

Table 3-5 Overview reported weights of microplastics found in tablets 7 to 12 by pyrolysis GC-MS.

	Labcode	Weight (µg) polyester	Weight (µg) polystyrene	Weight (µg) rubber	Weight (µg) polyethylene terepinthalate	Weight (µg) polyvinylchloride	Weight (µg) polyethylene	Weight (µg) polyamide	Weight (µg) ethylene-vinylacetate	Weight (µg) polypropylene	Weight (µg) acrylates	Weight (µg) unknown	Total Weight (µg)
Position 7	Q3231	5.27	0.03	1.5									
	Q3889				< 10								
	Q3894				50	39							
	Added				556								
Position 8	Q3231		0.08			1.1	0.02						
	Q3889												710
	Q3894					79							
	Added					55.6							
Position 9	Q3231		25										
	Q3889												640
	Q3894		50			55							
Position 10	Q3231	15	23									53	
	Q3889												810
	Q3894		73		12	131							
	Added		90		90	90							
Position 11	Q3231		2					10	1.9				
	Q3889												900
	Q3894		103			58							
	Added		73.8										
Position 12	Q3231		4.5	0.003				0.05	1.9	0.01	0.01		
	Q3889												410
	Q3894					15							

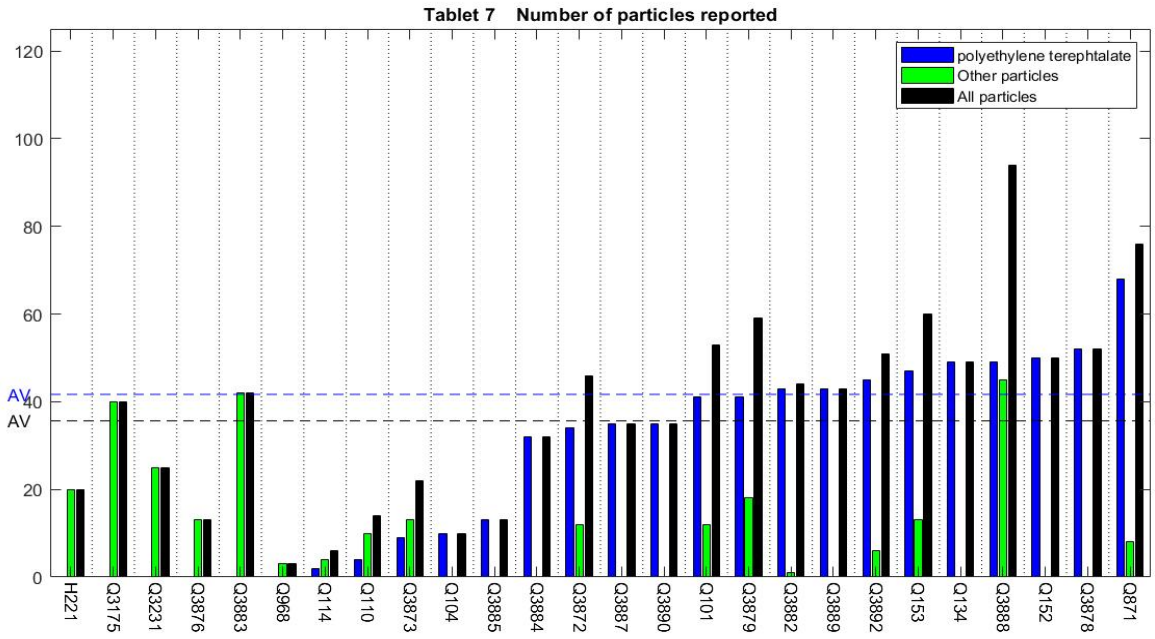


Figure 3-2 *Number of particles reported per laboratory for tablet position no. 7*

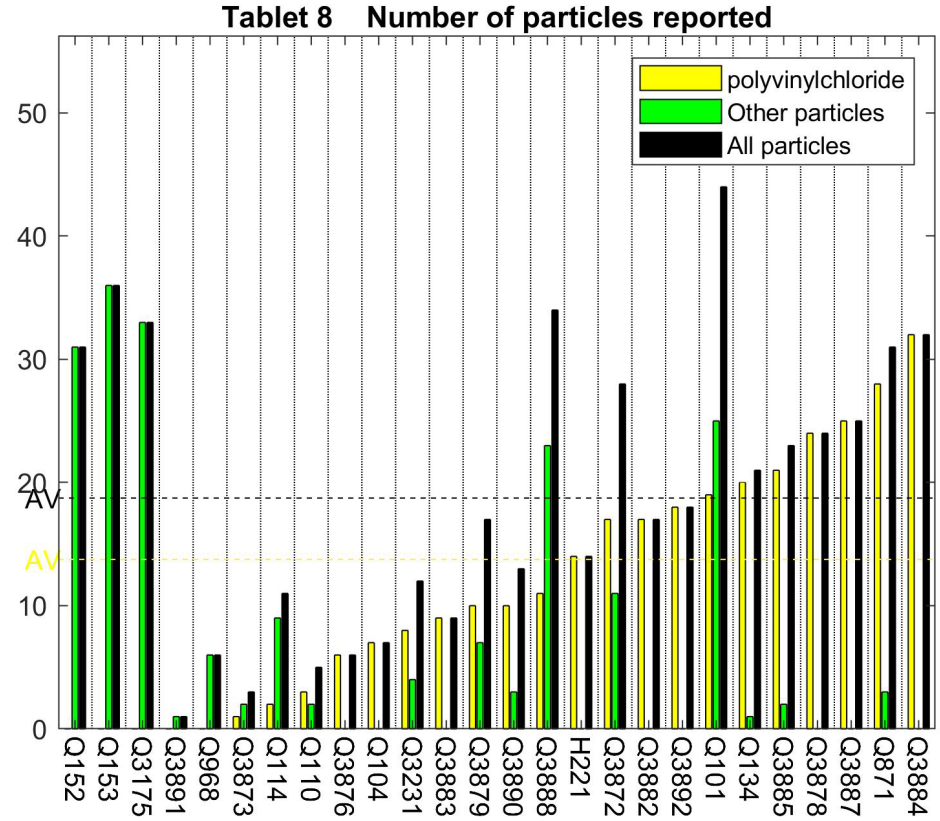


Figure 3-3 *Number of particles reported per laboratory for tablet position no. 8*

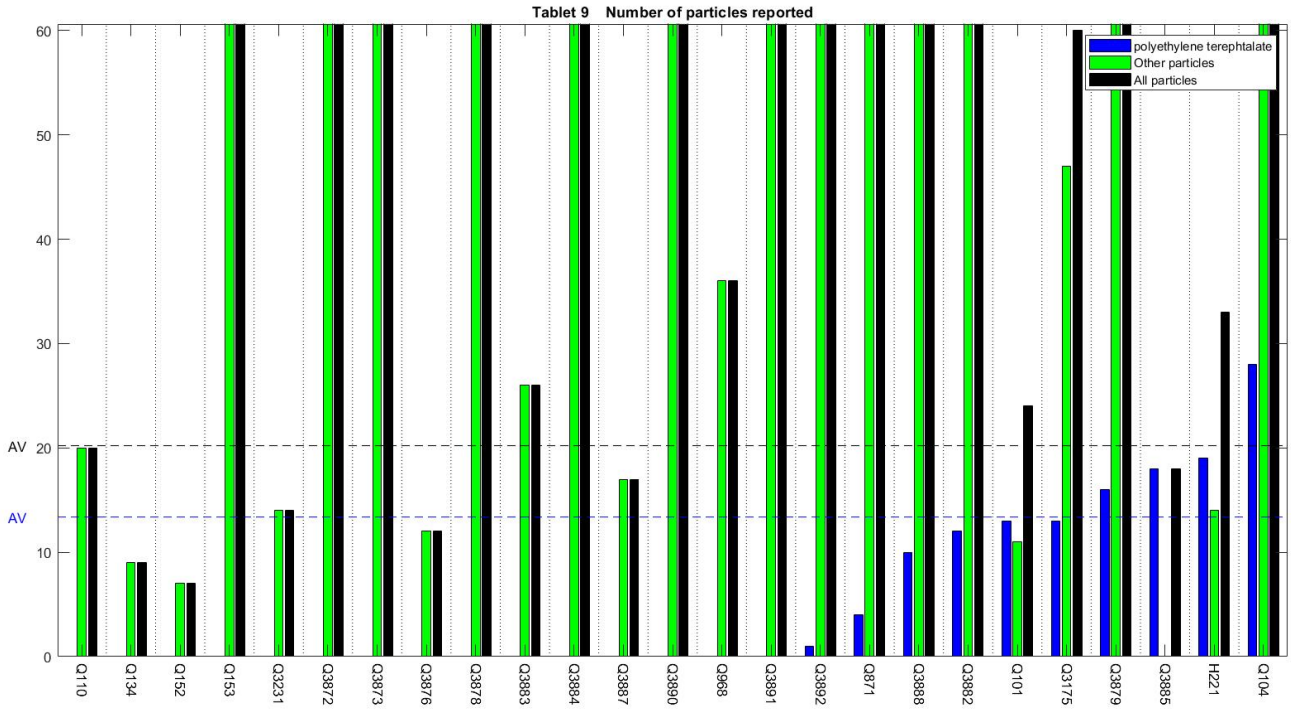


Figure 3-4 *Number of particles reported per laboratory for tablet position no. 9*

NB Some laboratories reported "> than" values for particles other than polyethylene terephathalate (PET) in position 9. This figure is cut off at 60 particles, to keep it informative for PET.

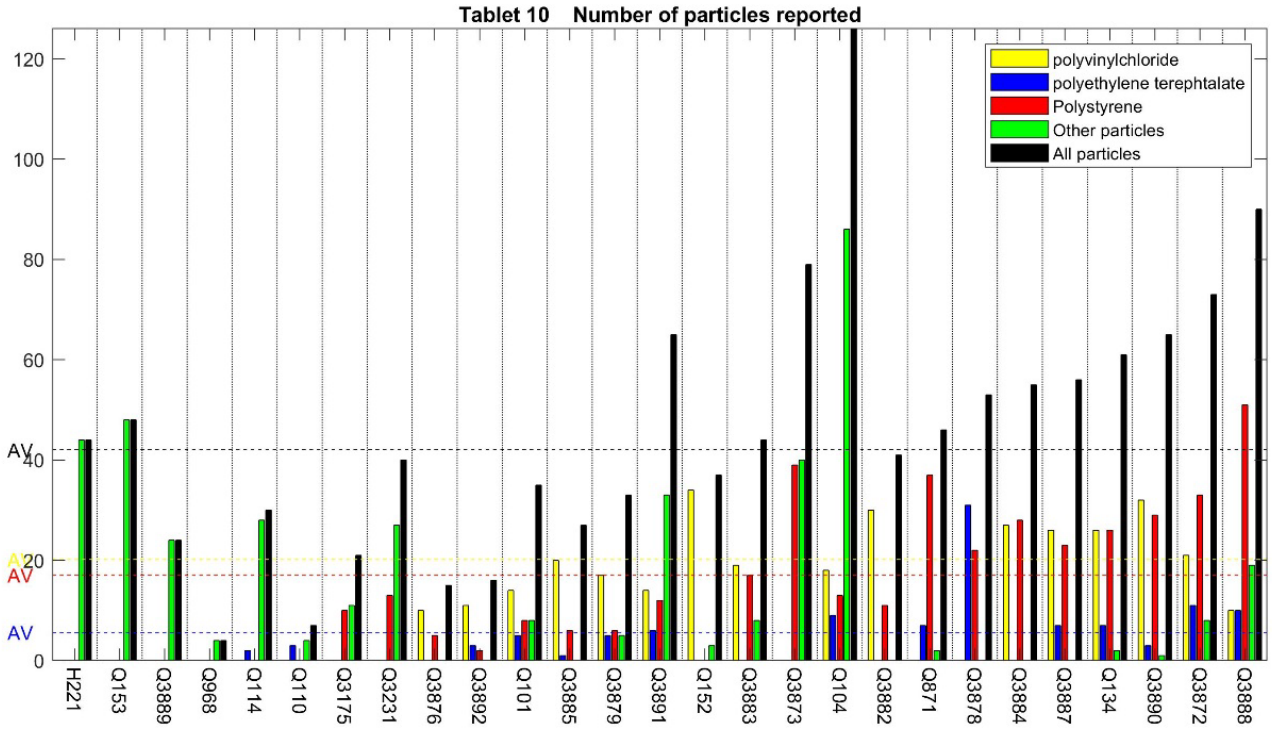


Figure 3-5 *Number of particles reported per laboratory for tablet position no. 10*

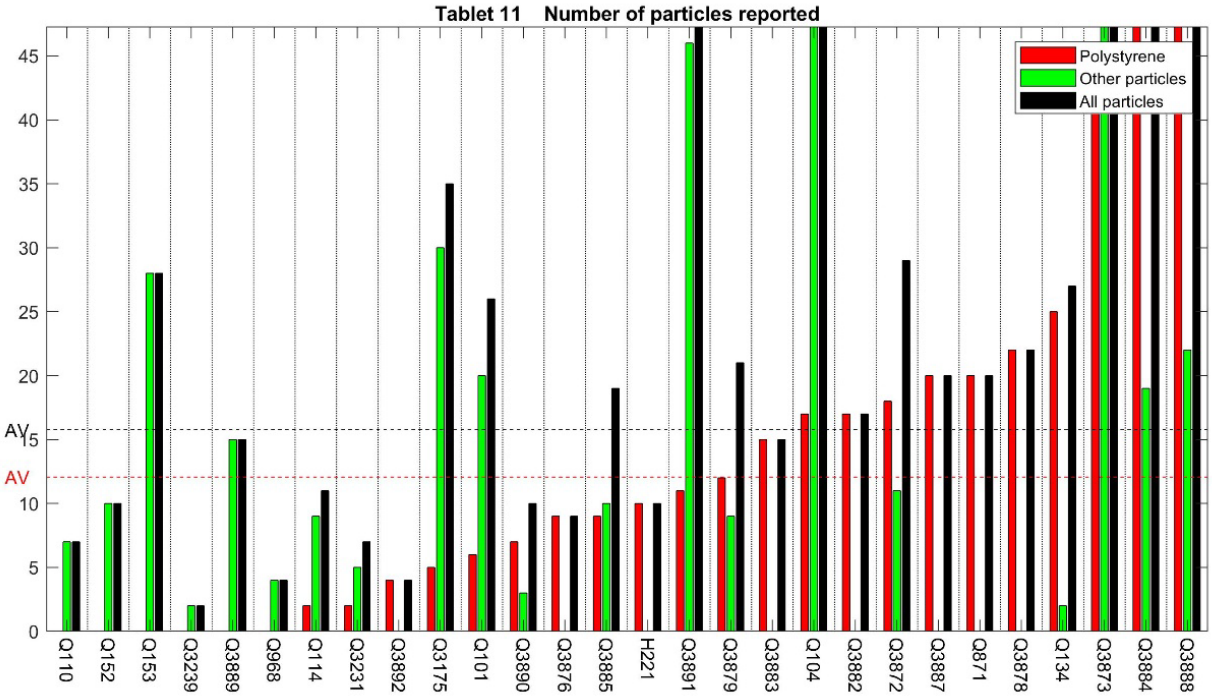


Figure 3-6 *Number of particles reported per laboratory for tablet position no. 11*

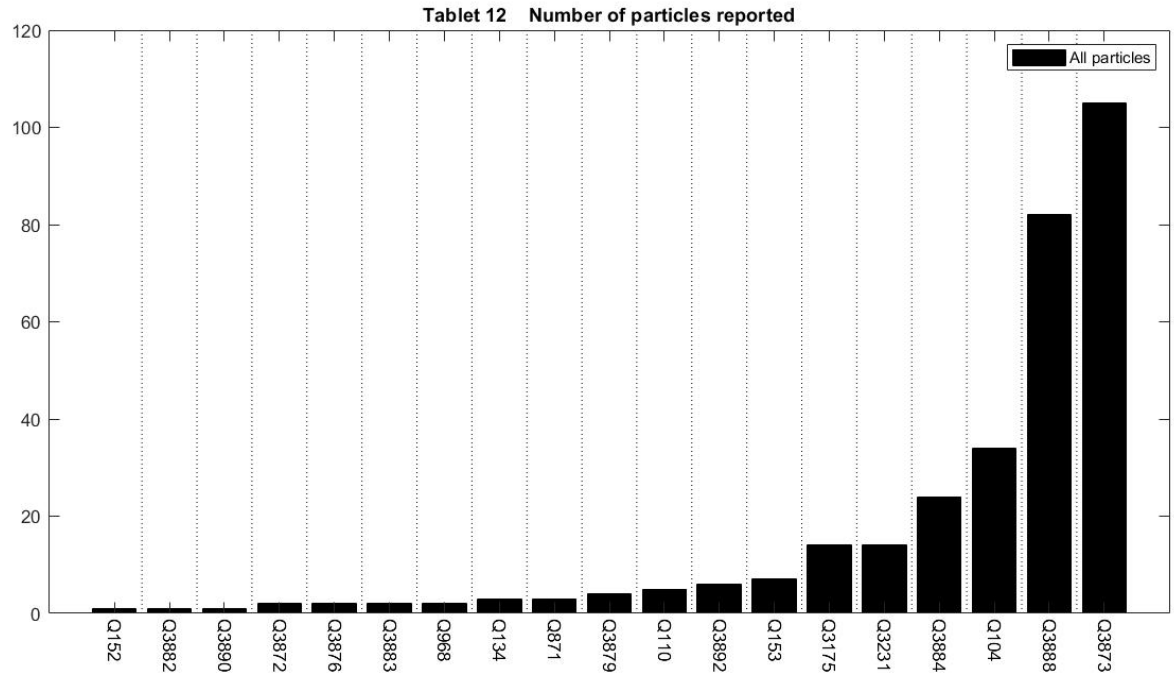


Figure 3-7 *Number of particles reported per laboratory for tablet position no. 12*

Table 3-6 summarises how well the polymers added to the tablets have been identified by the laboratories. Particles of the polymers added were reported by 77.8%-80.8% of the laboratories for tablet 7,8 and 11, i.e. the tablets that contained a single polymer. The polymers added were found by 55.5%-74.1% of the laboratories in tablet 10 that contained a mixture of three polymers. Just 43.5% of the laboratories submitted data on PET fibres in tablet 9. This tablet contained a more complex mixture of polymers owing

to the mode of preparation. It appears that the laboratories have more difficulties in identifying the particles as the number of polymers in the tablets increased.

Table 3-6 Summary of degree to which the polymers added are identified

Tablet	Polymer added	N labs reporting particles	N labs reporting particles for polymer added	% Labs reporting particles for polymer added
Position no. 7	**Polyethylene terephthalate**	26	20	80.8
Position no. 8	**Polyvinylchloride**	27	21	77.8
Position no. 9	**Polyethylene terephthalate**	23	10	43.5
Position no. 10	**Polyethylene terephthalate**	27	15	55.5
	Polystyrene	27	20	74.1
	Polyvinylchloride	27	16	59.3
Position no. 11	**Polystyrene**	28	22	78.6

In Table 3-7, a summary is given of how well laboratories identify the polymers added to the tablets. The maximum score is 7, as one polymer was added to tablets 7, 8, 9 and 11 and three polymers were added to tablet 10. The score summarises how many times laboratories provide a result for the polymer added and does not reflect how well the reported data are in terms of agreement with the assigned value.

Table 3-7 Summary of the identification of polymer particles by laboratories in tablets position nos. 7-11.

Number of polymers added to tablets in position nos. 7-11 correctly identified	Number of laboratories (N=28)
0 (0%)	2
1 (14%)	2
2 (29%)	1
3 (43%)	4
4 (57%)	4
5 (71%)	3
6 (86%)	6
7 (100%)	6

It is observed that 6 laboratories report data for the polymers added for all tablets, whereas 2 laboratories did not find the polymers added in any of the tablets. This may be due to different objectives and instrumentation for the measurement and thus of experience in determining the number of particles per polymer type.

Per tablet, the sum of the added polymer particles and the total number of particles reported is expected to be the similar (Section 2.6). In Figure 3-8, the relationship is depicted, and the correspondence is reasonably well.

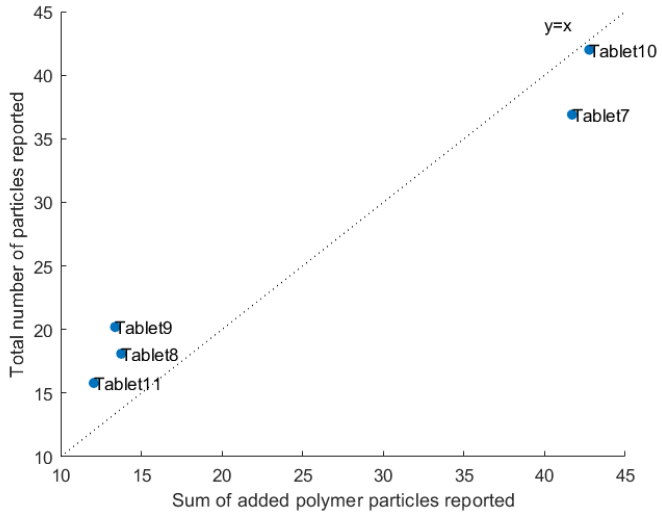


Figure 3-8 *Relationship between sum of added polymer particles and total number of particles.*

3.3 Youden analysis

The tablets 7, 8, 10 and 11 are made up with polymers from the same batches, i.e. the composition of the substrate is identical. The only differences are the weights of the polymers added, as summarised in the Table 3-8. This implies that the tablets 7, 8 and 11 may be considered as Youden pairs with tablet 10. The ratio given in the table represents the expected ratio of the results of laboratories when their results for the polymer in tablet 10 are plotted against those obtained in tablet x and measurements are carried out in consistently.

Table 3-8. Summary of amounts of polymers added to tablets in position no. 7,8,10 and 11

Tablet	Mass added to tablets (mg)		
	PET	PVC	PS
Position no. 7	0.556		
Position no. 8		0.056	
Position no. 10	0.090	0.090	0.090
Position no. 11			0.074
Ratio Tablet 10/tablet x	**0.162**	**1.620**	**1.218**

PET Polyethylene terephthalate PVC Polyvinylchloride PS Polystyrene

The two-sample plot (Youden plot) for polystyrene in tablet 10 versus tablet 11 is given in Figure 3-9. The dotted line represents the concentrations expected for tablet 10 (y-axis) given the concentrations in tablets 11 (x-axis) using the ratio listed in Table 3-8.

Youden split level experiments require that the two samples have a similar composition and have a small difference, typically 1-5%, in the value of the measurand. The composition of the tablets is in our case similar, the difference in the number of particles is relatively high. Calculations on the within- and between laboratory variances are presented here in an approximate sense and outlined for polystyrene in tablets 10 and 11. The approach taken is based on papers of Lischer (1984) and Shirono et al (2013).

Only laboratories i that report non-zero values for both $x_{PS\ tablet\ 11,i}$ and $x_{PS\ tablet\ 10,i}$ are taken into account. We construct the sums $v_i = \frac{(x_{PS\ tablet\ 11,i} + x_{PS\ tablet\ 10,i})}{2}$ and the differences $w_i = \frac{(x_{PS\ tablet\ 11,i} - x_{PS\ tablet\ 10,i})}{2}$. The variances of these terms are $Var[w_i] = \frac{1}{2}\sigma_r^2$ respectively $Var[v_i] = \frac{1}{2}\sigma_r^2 + \sigma_L^2$. The term $\hat{\sigma}_r$ reflects the average within laboratory and within-sample errors, the term $\hat{\sigma}_L$ the average between-laboratory and

between sample errors. The variances $Var[v_i]$ and $Var[w_i]$ have been calculated with our robust model. The results of the calculations for all Youden pairs is given in Table 3-9 and include $\hat{\sigma}_R$ calculated as $\hat{\sigma}_R = \sqrt{\hat{\sigma}_r^2 + \hat{\sigma}_L^2}$.

Table 3-9 Youden statistics showing values for tablet position nos. 7,8 and 10

Polymer	PET	$\hat{\sigma}_r$	$\hat{\sigma}_R$	$\hat{\sigma}_L$
PET	Tablets 7 and 10	11.69	12.78	5.15
PVC	Tablets 8 and 10	5.67	7.95	5.58
PS	Tablets 11 and 10	4.48	11.57	10.67

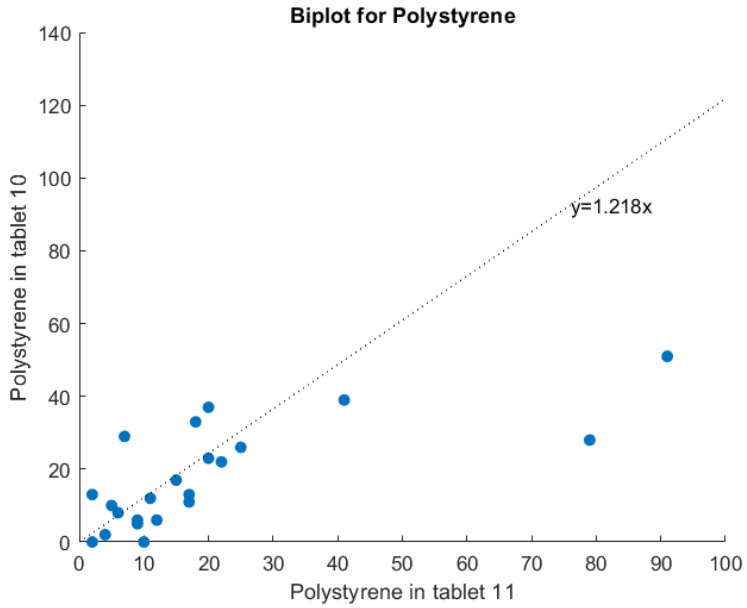


***Figure 3-9** Biplot for polystyrene (PS) showing the relationship between the reported number of PS particles in tablets position nos. 10 and 11.*

The results for PS (Figure 3-9) appear to be linearly correlated, in particular for the results in the left lower section. The slope agrees well with the ratio of amounts in tablets 11 and 10 as represented by the dotted line. A robust linear regression using a bisquare algorithm forcing the intercept to be zero yields a slope equal to 1.05 +/- 0.14 (df=19, R^2=0.53). This finding points to the occurrence of systematic differences between the laboratories.

The two-sample plot for PVC (Figure 3-10) exhibits a more complicated picture. The variances σ_r^2 and σ_L^2 have a comparable magnitude. The results for laboratories that report non-zero values for both tablets are more of less contained in circular area. This indicates that random errors dominate.

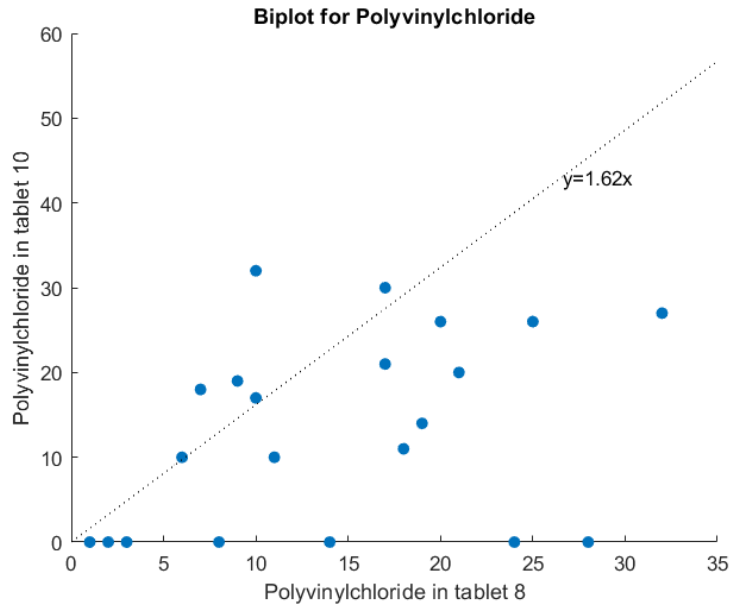


Figure 3-10 *Biplot for Polyvinylchloride (PVC) showing the relationship between the reported number of PVC particles in tablets position nos. 10 and 8.*

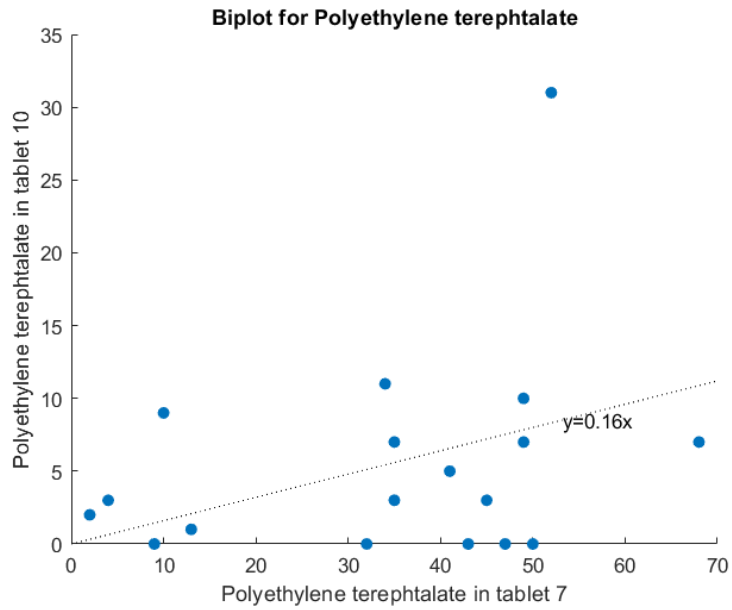


Figure 3-11 *Biplot for Polyethylene terephthalate (PET) showing the relationship between the reported number of PET particles in tablets position nos. 10 and 7.*

The two-sample plot for PET in Figure 3-11 shows that several laboratories identified PET particles in tablet 7 but not in tablet 10. The results of the remaining laboratories appear to be linearly correlated. A robust linear regression using a bisquare algorithm forcing the intercept to be zero yields a slope equal to 0.14 +/- 0.070 (df=14, R2=0.55). The observed slope agrees well with the ratio 0.16 of the PET particles in tablets 7 and 10. In this case, a group of laboratories with systematic differences appears to be present, while other laboratories have analytical difficulties as they do not measure PET particles in tablet 10 (n=5) or report a high number in this tablet (n=1).

The systematic differences observed for PS and PET may result from the application of different methodologies, different practices in the application of methods based on similar principles, or systematic errors. In this study no correlation could be found between methodology and accuracy of results reported.

In Figure 3-12, two sample plots are given for the total number of particles in tablets 7,8,10 and 11. Tablet 9 has been omitted in view of the issue with small particles (Section 2.2). The two sample plots suggest that systematic differences between laboratories may occur as the correlations are weak. Further analysis has not been carried out given the diversity of methods used and the less well specified nature of the measurand.

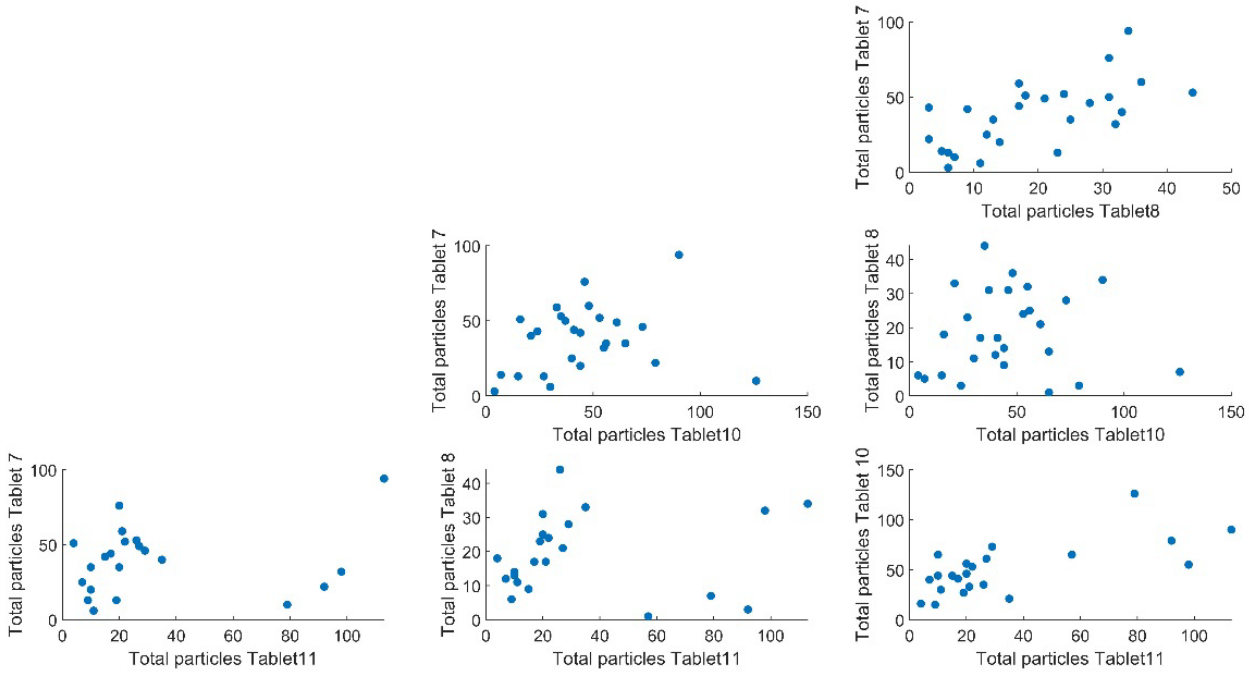


Figure 3-12 *Biplot for 'total particles' showing the relationship between 'total particles' in tablet position no. 8 to 11.*

3.4 Z-scores

Z-scores are provided separately for the polymers added to the tablets and the total number of particles and can be found in Appendix B. A summary of the statistics for the polymers added to the tablets is given in Table 3-10. The table also provides the assigned values and the standard deviations used to calculate the z-scores. The summary statistics for the total number of particles is given in Table 3-11.

In Appendix B, graphical representations of the data and z-scores are given. Per tablet the following information is provided:

- A box and whisker plot depicting the range of z-scores reported. In this plot, also the Assigned value, the zones discussed in section 2.6 and illustrated in Figure 2-4, and the number of z-scores per zone-section are given. It is noted that the horizontal range of the plots is restricted so that outliers as identified by the box-and-whisker procedures are not plotted.

- Bar graphs with z-scores, i.e. z-score plots. The laboratories are sorted from low to high z-scores. Laboratories that did not report particles for the polymer added are marked with NR.

Tables with the z-scores of the individual laboratories are also given in Appendix B.

Table 3-10. Summary statistics for added polymers in tablets (position no. 7-11) for z-score assessment

Tablet	Polymer type	N labs	Assigned value	Robust SD of study	Standard uncertainty	SD used to calculate z-scores (12.5% of AV)
Position no. 7	**Polyethylene terephthalate**	20	41.7	12.0	3.4	5.2
Position no. 8	**Polyvinylchloride**	21	13.8	9.1	2.5	1.7
Position no. 9	**Polyethylene terephthalate**	10	13.4	6.1	2.4	1.7
Position no. 10	**Polyethylene terephthalate**	15	5.5	4.0	1.3	0.7
	Polystyrene	20	17.1	13.3	3.7	2.1
	Polyvinylchloride	16	20.2	9.3	2.9	2.5
Position no. 11	**Polystyrene**	22	12.1	9.1	2.4	1.5

SD standard deviation

Table 3-11. Summary statistics for total number of particles in tablets (position no. 7-11) for z-score assessment

Tablet	Polymer type	N labs	Assigned value	Robust SD of study	Standard uncertainty	SD used to calculate z-scores (12.5% of AV)
Position no. 7	**Total number of particles**	26	36.9	21.0	5.1	4.6
Position no. 8	**Total number of particles**	27	18.1	9.1	2.2	2.3
Position no. 10	**Total number of particles**	27	42.0	24.3	5.8	5.3
Position no. 11	**Total number of particles**	28	15.8	12.8	3.0	2.0

SD standard deviation

NB. Statistic results for position 9 are not given, as some labs reported "> values" , which can not be statistically evaluated. Therefore the assigned value will be underestimated.

4 Discussion

The number of laboratories that participated and were able to submit data before the deadline (*n*=30) in this ILS round was sufficient for proper statistical treatment. Overall, an agreement was found among laboratories in the weight of the preproduction pellets in the larger size range of 2-4 mm (position nos.1-6), with RSDs <33%. The reported weights were similar to the homogeneity test of NIVA. This exercise mainly focussed on polymer identification of larger particles and showed that the polymer type was correctly identified in 85% of the distributed pellets. The polymer identification of the relatively large preproduction pellets is considered as a relatively straight forward analysis, nevertheless not all labs were able to identify all six samples correctly.

The results given in the Tables 3-6 and 3-7 do not reflect the how well the reported data are in terms of agreement with the assigned value. The quantitative analysis of the number of particles of the polymers added in the tablets varied largely among the laboratories (RSD 29%-78%, see Table 3-3). This highlights the difficulties when both identifying and counting different polymer fragments and fibres. Table 3-4 shows that the results for the total number of particles in tablets 7-11 exhibit a higher variation than added to the tablets (Table 2-3). The higher variation for total particles may be due to the less well-defined factors and to the inclusion of particles arising from contamination in the laboratory or during the production process or the polymer or fibre materials used.

The number of participants using Py-GC-MS was unfortunately too low (*n*=2) to perform statistics with. Several laboratories are currently validating Py-GC-MS as an option to analyse microplastics and it is our expectation that more 'MS'-labs will join the next round. Both mass based and spectrophotometric methods are expected to be used for the analysis of microplastics, depending on the purpose of scientific studies or monitoring projects.

For some participants the term "sample pre-treatment' might have been confusing, as "no" was often filled in for the question whether sample pre-treatment while pre-treatment actually was used. Likewise, it was in some cases unclear whether staining Nile red was considered as a sample pre-treatment or analytical method. For future reference, with the term "sample pre-treatment" will include all extraction, purification, clean-up and modification (including Nile red staining) steps that haven been taken prior analysis.

Although the study is unique by combining identification and quantification of small microplastic particles in the size range of 150-300 µm and the number of participants, the results of this ILS are compared to one other study. The variation between laboratories was similar to (50%) 12 laboratories in a study organised by the Japanese Research Institute for Applied Mechanics (Isobe et al. 2019.). Although in this study only the number of plastic particles were separated in plastics and non-plastics the RSD between the 12 laboratories for the smaller fraction (<1 mm) was around 50%. However, it should be taken into consideration that most of the particles in the Japanese study were between 400 and 1000 µm and in our study between 150-300 µm. In addition, FTIR was predominantly used in the Japanese study, while in our study a variety of methods and techniques were used which add to the complexity and variation between the laboratories.

5 Conclusions

Thirty laboratories provided data for the first ILS round on microplastics analysis, which included six preproduction pellets and six dissolvable tablets to which different polymers and fibres were added. A variety of different identification and quantification methods (n=7) were used to identify the polymer type and to report the number and/or mass of the plastics particles or fibres.

The type of polymer was correctly reported in most cases, both in the pellets as in the tablets. While the weight of the pellets was in good agreement among laboratories, the number or particles in the tablets varied considerably (RSD between laboratories 29-78%) and was dependent on the number of particles or fibres, the polymer type. The RSD's for polymers in tablets that contained a single plastic type (tablets 7,8 and 11) were lower than those for the tablets 9 and 10 that contained mixtures of polymers. Six laboratories reported data for the polymers added to each tablet, two laboratories did not find the added polymers in all 5 tablets.

The mode of preparation of the tablets enable a Youden type of analysis. Systematic between-laboratory effects are found for PS for the sample pair tablet 11-tablet 10 and to a lesser extent for PET in the pair tablet 7-tablet 10. Random errors dominate for PVC as regards to the Youden pair tablet 8-tablet 10. Two-sample plots of the total number of particles (Figure 3-12) are not conclusive regarding systematic and/or random effects.

The first round of the development exercise has resulted in a first assessment of the state of the art of microplastic analysis. The study also highlighted the complexity and the need for harmonisation in terms of reporting and used methods and techniques. This first round will be followed by a second round with increasing complexity. The next round will focus on the extraction of microplastics from more complex samples (e.g. sediments and fish).

The results of this first round and subsequent next round will be discussed in a workshop planned after the second round.

Tentative Timeline 2020

5 December 2019	Announcement of second development exercise
31 January 2020	Deadline registration
6 April 2020	Dispatch of test materials
1 July 2020	Deadline for returning results
12 October 2020	Draft Report
23 October 2020	Final Report
28 October 2020	Second workshop

6 References

W.P. Cofino, J. Molenaar, P. Torfs, Evaluating Proficiency tests, Wiley Online Library, https://doi.org/10.1002/9781118445112.stat04068.pub2.

W. P. Cofino, I. H.M. van Stokkum, D. E. Wells, F.Ariese, J-W. M. Wegener, R. A.L. Peerboom, A new model for the inference of population characteristics from experimental data using uncertainties. Application to interlaboratory studies, Chemom. Intell. Lab. Syst 53 (2000) 37-55.

A. Isobe, N. T. Buenaventura, S. Chastain, S. Chavanich, A. Cózar, M. DeLorenzo, P.l Hagmann, H. Hinata, N. Kozlovskii, A. L. Lusher, E. Martí, Y. Michida, J. Mu, M. Ohno, G. Potter, P. S. Ross, N. Sagawa, W. Joon Shim, Y. Kyoung Song, H. Takada, T. Tokai, T. Torii, K. Uchida, K. Vassillenko, V.Viyakarn, W. Zhang, An interlaboratory comparison exercise for the determination of microplastics in standard sample bottles, Marine Pollution Bulletin, 46 (2019) 831-837. https://doi.org/10.1016/j.marpolbul.2019.07.033.

P. Lischer, Robust Statistical Methods in Interlaboratory Analytical Studies. In: Rieder H. (eds) Robust Statistics, Data Analysis, and Computer Intensive Methods. Lecture Notes in Statistics, 109 (1996). Springer, New York, United States of America.

J. Molenaar, W P. Cofino, P.J.J.F. Torfs, Efficient and robust analysis of interlaboratory studies, Chemom. Intell. Lab. Syst 175 (2018) 65-73.

K. Shirono, K. Iwase, H. Okazaki,M, Yamazawa, K. Shikakume, N. Fukumoto,M. Murakami, M. Yanagisawa,T. Tsugoshi, A study on the utilization of the Youden plot to evaluate proficiency test results, Accred Qual Assur 18 (2013) 161–174.

Statistical Methods for Use in Proficiency Testing by Interlaboratory Comparison, ISO 13528:2015.

Appendices

A. Reported data and graphical output

B. Numerical z-score values per tablet position no. 7-11 and graphical output

C. Additional method information

D. NDA statistics

Appendix A Reported type and number of plastic particles per participants and graphical output

Table A-1 ***Type, weight and number of plastic particles reported for position no. 1***

Laboratory	No. polycarbonate	No. Polyimide	No. PMMA/PVC blend	Weight (mg) polycarbonate	Weight (mg) Polyimide	Weight (mg) PMMA/PVC blend
H221	3			45.5		
Q101						
Q104	3			45.7		
Q110	3					
Q114	3			45.5		
Q134	3			44.2		
Q152	3			50.9		
Q153	3			46.5		
Q871	3					
Q968						
Q3175						
Q3231	3			43.3		
Q3239	3			54.0		
Q3872	3			51.9		
Q3873	3			48.5		
Q3876	3			45.5		
Q3877		3			47.0	
Q3878	3			50.5		
Q3879	3			44.6		
Q3882	3					
Q3883	3			48.9		
Q3884	3			42.3		
Q3885	3			47.7		
Q3887	3			44.4		
Q3888	3					
Q3889			3			45.3
Q3890	3			47.5		
Q3891	3			50.5		
Q3892	3			47.7		
Q3894	3			53.0		
N labs reporting	25	1	1	21	1	1
Average	3.0	3.0	3.0	47.5	47.0	45.3
Standard deviation	0.0			3.3		

Table A-2 Type, weight and number of plastic particles reported for position no. 2

Laboratory	No. Polystyrene	No. poly (methyl metacrylate)	No. acrylonitrile butadiene styrene	Weight (mg) polystyrene	Weight (mg) poly (methyl metacrylate)	Weight (mg) acrylonitrile butadiene styrene
H221	3			64.3		
Q101						
Q104	3			60.6		
Q110	3					
Q114	3			66.2		
Q134	3			63.1		
Q152		3			66.9	
Q153	3			64.6		
Q871	3					
Q968						
Q3175						
Q3231	3			64.5		
Q3239	3			78.4		
Q3872	3			60.3		
Q3873	3			61.8		
Q3876			3			63.1
Q3877			3			65.9
Q3878	3			66.9		
Q3879	3			67.2		
Q3882	3					
Q3883	3			62.9		
Q3884	3			67.9		
Q3885	3			66.5		
Q3887	3			63.0		
Q3888	3					
Q3889	3			64.7		
Q3890	3			65.8		
Q3891	3			67.2		
Q3892	3			68.8		
Q3894	3			64.5		
N labs reporting	24	1	2	20	1	2
Average	3.0	3.0	3.0	65.5	66.9	64.5
Standard deviation	0.0			3.8		2.0

Table A-3 Type, weight and number of plastic particles reported for position no. 3

Laboratory	No. Polypropylene	No. Unknown	Weight (mg) polyproylene	Weight (mg) unknown
H221	3		104.3	
Q101				
Q104	3		88.0	
Q110	3			
Q114	3		106.4	
Q134	3		104.2	
Q152	3		72.1	
Q153	3		83.9	
Q871	3			
Q968				
Q3175				
Q3231	3		100.2	
Q3239	3		107.6	
Q3872	3		81.0	
Q3873	3		88.7	
Q3876	3		121.2	
Q3877	3		82.2	
Q3878	3		109.2	
Q3879	3		83.7	
Q3882	3			
Q3883	3		84.1	
Q3884	3		106.6	
Q3885	3		98.9	
Q3887			87.0	
Q3888	3			
Q3889		3		78.5
Q3890	3		124.4	
Q3891	3		78.2	
Q3892	3		105.5	
Q3894	3		114.8	
N labs reporting	21	1	22	1
Average	3.0	3.0	96.9	78.5
Standard deviation	0.0		14.6	

Table A-4 Type, weight and number of plastic particles reported for position no. 4

Laboratory	No. polyester	No. Polyethylene terephthalate	No. Polystyrene	Weight polyester	Weight Polyethylene terephthalate	Weight polystyrene
H221	3			67.3		
Q101						
Q104		2	1		37.4	0.5
Q110		3				
Q114		3			61.0	
Q134		3			51.4	
Q152		3			53.3	
Q153		3			61.8	
Q871		3				
Q968						
Q3175						
Q3231		3			60.0	
Q3239		3			57.4	
Q3872		3			57.2	
Q3873	3			57.2		
Q3876		3			58.3	
Q3877		3			61.2	
Q3878	3			57.3		
Q3879		3			59.3	
Q3882		3				
Q3883		3			54.2	
Q3884		3			63.9	
Q3885		3			61.0	
Q3887		3			54.7	
Q3888		3				
Q3889		3			59.6	
Q3890		3			63.8	
Q3891		3			60.3	
Q3892		3			58.7	
Q3894		3			54.5	
N labs reporting	3	24	1	3	20	1
Average	3.0	2.96	1.0	60.6	57.5	0.5
Standard deviation	0.0	0.20		5.8	5.8	

Table A-5 Type, weight and number of plastic particles reported for position no. 5

Laboratory	No. Low density polyethylene	No. high density polyethylene	No. Polyethylene	Weight low density polyethylene	Weight high density polyethylene	Weight polyethylene
H221	3			74.9		
Q101						
Q104	3			70.5		
Q110	3					
Q114		3			76.7	
Q134	3			74.6		
Q152	3			68.3		
Q153	3			75.6		
Q871			3			
Q968						
Q3175						
Q3231			3			79.2
Q3239			3			66.0
Q3872	3			77.0		
Q3873	3			66.9		
Q3876	3			83.7		
Q3877	3			84.8		
Q3878		3			80.5	
Q3879		3			76.9	
Q3882		3				
Q3883	3			80.9		
Q3884	3			116.9		
Q3885		3			75.5	
Q3887		3			77.2	
Q3888	3					
Q3889	3			79.4		
Q3890	3			80.3		
Q3891		3			88.5	
Q3892			3			79.1
Q3894		3			68.0	
N labs reporting	15	8	4	13	7	3
Average	3.0	3.0	3.0	79.5	77.6	74.8
Standard deviation	0.0	0.0	0.0	12.5	6.1	7.6

Table A-6 Type, weight and number of plastic particles reported for position no. 6

Laboratory	No. Polystyrene	Weight (mg) polystyrene
H221	3	1.20
Q101		
Q104	4	2.40
Q110	3	
Q114	4	2.32
Q134	3	2.47
Q152	3	1.88
Q153	4	2.00
Q871	3	
Q968		
Q3175		
Q3231	3	3.20
Q3239	3	1.51
Q3872	3	1.60
Q3873	3	2.34
Q3876	3	3.26
Q3877	3	2.84
Q3878	3	1.90
Q3879	3	1.30
Q3882	4	
Q3883	3	1.85
Q3884	3	0.90
Q3885	4	2.90
Q3887	3	1.70
Q3888	3	
Q3889	6	2.98
Q3890	2	1.07
Q3891	3	2.30
Q3892	3	3.10
Q3894	3	1.20
N labs reporting	27	23
Average	3.3	2.10
Standard deviation	0.7	0.73

Table A-7 Type and number of plastic particles reported for tablet in position no. 7

Laboratory	acrylonitrile butadiene styrene	blue fiber	brown fiber	Cellulose	Cellulose fiber black	Cotton (blue fibres)	Cellulose fiber white	light blue piece	low density polyethylene	polymethylmethacrylate	polyacrylic	Polyamide	polyepoxide	Polyester	Polyethylene	polyethylene terephthalate	Polypropylene	Polystyrene	polytetrafluoroethylene	Polyurethane	Polyvinylchloride	red fiber	rubber	Unknown	Total no. particles
H221														20											20
Q101				12												41	< 3	< 3							53
Q104					< 4		< 2									10									10
Q110																4								10	14
Q114																2								4	6
Q134																49									49
Q152																50									50
Q153																47								13	60
Q871																68	3	5							76
Q968		1						2																	3
Q3175			2	31		6																1			40
Q3231														21				1					3		25
Q3239																									
Q3872															2	34	1	9							46
Q3873										1		1				9		11							22
Q3876										11								1			1				13
Q3877																									
Q3878																52									52
Q3879	1															41	1	16							59
Q3882																43	1								44
Q3883														42											42
Q3884																32									32
Q3885																13									13
Q3887																35									35
Q3888									13	4	1		1			49	2	15	1	8					94
Q3889																43									43
Q3890																35									35
Q3891																>5									
Q3892																45		4			2				51
Q3894																									
No. of reporting labs	1	1	1	2	1	1	1	1	1	3	1	1	1	3	1	21	5	9	1	1	2	1	1	3	26
Average	*1*	*1*	*2*	*22*		*6*		*2*	*13*	*5.3*	*1*	*1*	*1*	*28*	*2*	**42**	**1.4**	**7.5**	*1*	*8*	*1.5*	*1*	*3*	*9.0*	**36.9**
Standard deviation				*13*						*5.1*				*12*		**12**	**0.9**	**7.1**			*0.7*			*4.6*	**21.0**

Average and standard deviation derived by only the numerical values (i.e. non-numerical values such as <4 are excluded). The robust means and standard deviations of the number of particles per determinand have been calculated with robust NDA statistics, when more than 3 numerical observations were reported and are indicated in bold. In case of 3 or less numerical observations, estimates of means are calculated straightforwardly and given in italics. Note that the uncertainty in means and standard deviations is high with low numbers of particles.

Table A-8 Type and number of plastic particles reported for tablet in position no. 8

Laboratory	blue fiber	blue piece	Cellulose	Cellulose fiber black	Cellulose fiber white	Ethylene vinylacetate	green fiber	Hemicellulose fibers yellow	light blue piece	Low density polyethylene	polymethylmethacrylate	polyacrylate	Polyamide	Polycarbonate	Polyethylene	polyethylene terephthalate	Polypropylene	Polystyrene	Polyurethane	Poly vinylChloride	red fiber	red piece	unknown	white and brown piece	Zein	Total no. of particles
H221																				14						14
Q101			5														20			19						44
Q104				< 4	< 2															7						7
Q110																				3			2			5
Q114																				2			9			11
Q134						1														20						21
Q152																							31			31
Q153																							36			36
Q871																	1	2		28						31
Q968		2							2													1		1		6
Q3175	8		20				1														3		1			33
Q3231															2			2		8						12
Q3239																										
Q3872												2			4	1	3	1		17						28
Q3873											1		1							1						3
Q3876																				6						6
Q3877																										
Q3878																				24						24
Q3879										3						1	1	2		10						17
Q3882																				17						17
Q3883																				9						9
Q3884																				32						32
Q3885																2				21						23
Q3887																				25						25
Q3888										8						3	8	2	2	11						34
Q3889								< 50															3			3
Q3890										1							1	1		10						13
Q3891														> 215											1	1
Q3892																				18						18
Q3894																										
No. of reporting labs	1	1	2	1	1	1	1	1	1	3	1	1	1	1	2	4	6	6	1	21	1	1	6	1	1	27
Average	*8*	*2*	*13*			*1*	*1*		*2*	*4*	*1*	*2*	*1*		*3*	**1.5**	**1.4**	**1.7**	*2*	**13.8**	*3*	*1*	**3.5**	*1*	*1*	**18.7**
Standard deviation			*11*							*3.6*					*1.4*	**0.8**	**1.3**	**0.6**		**9.1**			**5.7**			**14.6**

Average and standard deviation derived by only the numerical values (i.e. non-numerical values such as <4 are excluded). The robust means and standard deviations of the number of particles per determinand have been calculated with robust NDA statistics, when more than 3 numerical observations were reported and are indicated in bold. In case of 3 or less numerical observations, estimates of means are calculated straightforwardly and given in italics. Note that the uncertainty in means and standard deviations is high with low numbers of particles.

Table A-9 Type and number of plastic particles reported for tablet in position no. 9

Laboratory	acrylonitrile butadiene styrene	black fibre	Blue/purple fibre	Butylstearate	Cellulose	Cellulose fiber black	Cellulose fibre red	Cellulose fiber white	Ethylene-vinyl acetate	Fluorescent particles	grey fibre	Hemicellulose fibre (indigo)	Low density polyethylene	Metacrylate polymere	Nylon	polymethyl methacrylate)	Polyamide	polybutadiene acrylonitrile	Polyester	Polyethylene	polyethylene terephthalate	polyoxymethylene	Polypropylene	Polystyrene	polytetrafluoroethylene	Polyurethane	Polyvinylchloride	red/orange fibre	Styrene-isoprene styrene	fibres	Total no. of particles
H221																					19			14							33
Q101					11																13										24
Q104						10		235													28			16240							16,513
Q110		6	2								1																	11			20
Q114																															
Q134									1															8							9
Q152															7																7
Q153										122																					122
Q871																					4		1	>1000							5
Q968		11	1																									24			36
Q3175			15					22													13			9				1			60
Q3231																								14							14
Q3239																															
Q3872																			23					39							62
Q3873	9																			43			4	1275							1,331
Q3876																														12	12
Q3877																															
Q3878														1					16										>400		17
Q3879																					16		1	>1000							17
Q3882				5																	12			156							173
Q3883																			26					> 1							26
Q3884																								> 12.8 mio							
Q3885																					18										18
Q3887																												17			17
Q3888													11		2			1			10		9	393	1	13					440
Q3889							< 30	< 30				< 30																			
Q3890																			26					>30000							26
Q3891																								>350							
Q3892																	2			3	1	1	2	2,352			2				2,363
Q3894																															
No. of reporting labs	1	2	3	1	1	1	1	3	1	1	1	1	1	1	1	1	1	1	4	2	10	1	5	15	1	1	1	4	1	1	23
Average	*9*	*8.5*	*6*	*5*	*11*	*10*		*129*	*1*	*122*	*1*		*11*	*1*	*2*	*7*	*2*	*1*	**25.2**	*23.0*	**13.4**	*1*	**1.7**	**40.5**	*1*	*13*	*2*	**13.9**		*12*	**20.2**
Standard deviation		*3.5*	*7.8*					*151*											**2.1**	*28.3*	**6.1**		**1.4**	**114.0**				**9.6**			**18.3**

Average and standard deviation derived by only the numerical values (i.e. non-numerical values such as <4 are excluded). The robust means and standard deviations of the number of particles per determinand have been calculated with robust NDA statistics, when more than 3 numerical observations were reported and are indicated in bold. In case of 3 or less numerical observations, estimates of means are calculated straightforwardly and given in italics. Note that the uncertainty in means and standard deviations is high with low numbers of particles.

Table A-10 Type and number of plastic particles reported for tablet in position no. 10

Laboratory	acrylonitrile butadiene styrene	Black fiber	Blue fiber	Cellulose	Cellulose fiber black	Cellulose fiber white	Crystaline particles	Grey fiber	Grey piece	High density polyethylene	Low-density polyethylene	polymethylmethacrylate	Polyamide	polybutylmethacrylate	Polycarbonate	Polyester	Polyethylene	polyethylene terephthalate	Polypropylene	Polystyrene	Polytetrafluoroethylene	Polyurethane	Polyvinylchloride	red fiber	TiO2	Unknown	Total particles
H221																44											44
Q101				8														5	< 3	8			14				35
Q104					1	85												9		13			18				126
Q110																		3								4	7
Q114																		2								28	30
Q134											1							7	1	26			26				61
Q152																							34			3	37
Q153																										48	48
Q871																		7	2	37							46
Q968		2						1	1																		4
Q3175			3			6														10				2			21
Q3231																8				13						19	40
Q3239																											
Q3872																	8	11		33			21				73
Q3873	1											1					30		8	39							79
Q3876																				5			10				15
Q3877																											
Q3878																		31		22							53
Q3879																		5	5	6			17				33
Q3882																				11			30				41
Q3883																8				17			19				44
Q3884																				28			27				55
Q3885																		1		6			20				27
Q3887																		7		23			26				56
Q3888	1						17			7	8			1				10	6	51	2	1	10				90
Q3889													1														24
Q3890															30			3		29			32				65
Q3891																		6		12			14		3		65
Q3892																		3		2			11				16
Q3894																											
No. of reporting labs	2	1	1	1	1	2	1	1	1	1	2	1	1	1	1	3	2	15	6	20	1	1	16	1	1	5	27
Average	*1*	*2*	*3*	*8*	*1*	*46*	*17*	*1*	*1*	*7*	*4.5*	*1*	*1*	*1*	*30*	*20*	*19*	**5.5**	**4.4**	**17.1**	*2*	*1*	**20.2**	*2*	*3*	**18.5**	**42.0**
Standard deviation						*56*					*4.9*					*21*	*16*	**4.0**	**3.9**	**13.3**			**9.25**			**20.9**	**24.3**

Average and standard deviation derived by only the numerical values (i.e. non-numerical values such as <4 are excluded). The robust means and standard deviations of the number of particles per determinand have been calculated with robust NDA statistics, when more than 3 numerical observations were reported and are indicated in bold. In case of 3 or less numerical observations, estimates of means are calculated straightforwardly and given in italics. Note that the uncertainty in means and standard deviations is high with low numbers of particles.

Table A-11 Type and number of plastic particles reported for tablet in position no. 11

Laboratory	acrylonitrile butadiene styrene	black and white piece	Black fibre	Blue fibre	brown fiber	Cellulose	Cellulose fiber white	Cellulose fiber black	ethylene-vinyl acetate	green fiber	grey fiber	Low-density polyethylene	Nylon fiber	Nylon plastic - white particles	poly(butylmethacrylate)	polymethylmethacrylate	polyacrylonitrile styrene	Polyamide	Polycarbonate	Polyester	Polyethylene	Polyethylene oxydized	polyethylene terephthalate	polypropylene	Polysiloxane	Polystyrene	polystyrene éthylacrylate	Polyurethane	polyvinylchloride	TiO2	Unknown	Total particles
H221																										10						10
Q101						16																		4		6						26
Q104							62	< 4																		17						79
Q110			2	2																											3	7
Q114																										2					9	11
Q134												1			1											25						27
Q152																10																10
Q153																															28	28
Q871																										20						20
Q968		1		1	1						1																					4
Q3175				5			21			2													2			5						35
Q3231									2									3								2						7
Q3239																																
Q3872																	1				7		2			18	1					29
Q3873	1															2					45			3		41						92
Q3876																										9						9
Q3877																																
Q3878																										22						22
Q3879												5				1								2		12			1			21
Q3882																										17						17
Q3883																										15						15
Q3884									1							2						3	1	4	1	79		2	5			98
Q3885																							10			9						19
Q3887																										20						20
Q3888	1											8							1				5	7		91						113
Q3889													1	3						11												15
Q3890																				1				1		7			1			10
Q3891																			40				2			11			2	2		57
Q3892																										4						4
Q3894																																
N labs reporting	2	1	1	3	1	1	2	1	2	1	1	3	1	1	1	4	1	1	2	2	2	1	6	6	1	22	1	1	4	1	3	27
Average	*1*	*1*	*2*	*2.7*	*1*	*16*	*42*		*2*	*2*	*1*	*4.7*	*1*	*3*	*1*	**1.7**	*1*	*3*	*21*	*6*	*26*	*3*	**1.8**	**3.1**	*1*	**12.1**	*1*	*2*	**1.3**	*2*	*13.3*	**15.8**
Standard deviation	*0*			*2.1*			*29*		*0.7*			*3.5*				**0.7**			*28*	*7.1*	*27*		**0.6**	**1.5**		**9.1**			**0.7**		*13.1*	**12.8**

Average and standard deviation derived by only the numerical values (i.e. non-numerical values such as <4 are excluded). The robust means and standard deviations of the number of particles per determinand have been calculated with robust NDA statistics, when more than 3 numerical observations were reported and are indicated in bold. In case of 3 or less numerical observations, estimates of means are calculated straightforwardly and given in italics. Note that the uncertainty in means and standard deviations is high with low numbers of particles.

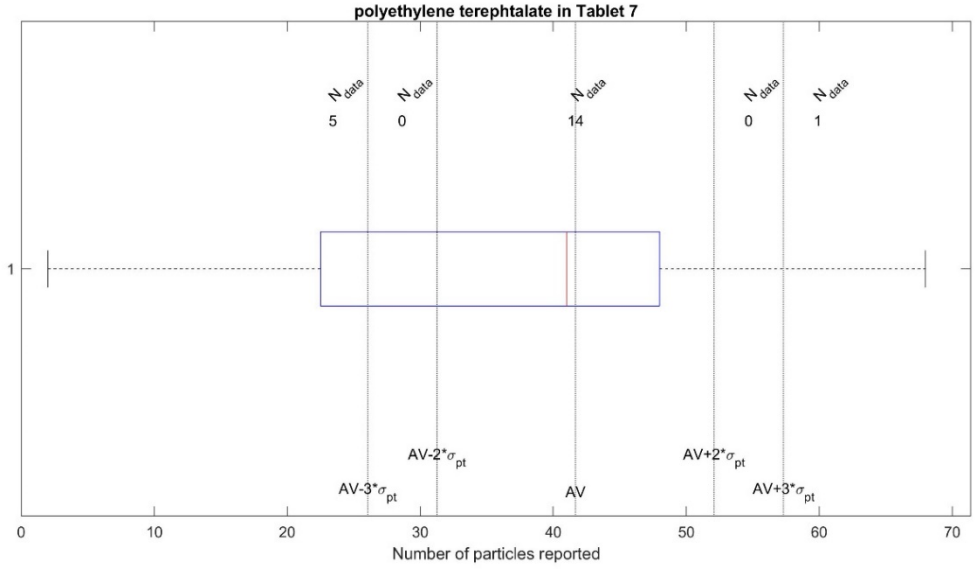
Table A-12 Type and number of plastic particles reported for tablet in position no. 12

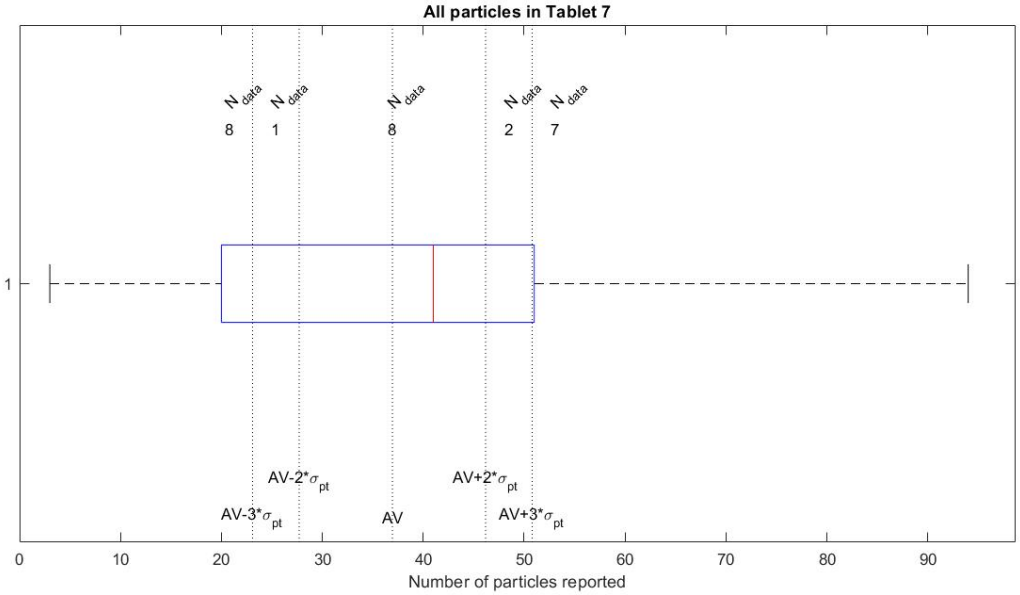
Laboratory	Polystyrene	Cellulose fiber white	Cellulose fiber black	orange fibre	red fibre	black fibre	grey fibre	Unknown	polyethylene terephthalate	blue fiber	Polyamide	Polypropylene	Ethylene-vinyl acetate	Acrylates	Rubber	Polyethylene	Polymethylmethacrylate	polyvinyl chloride acetate	Polyester	Low density polyethylene	Polyurethane	Poly-n-Butyl Metacrylate	polytetrafluoroethylene	polyvinylidene fluoride	Total particles
H221																									
Q101																									
Q104	< 2	34	< 4																						34
Q110				1	1	2	1																		5
Q114																									
Q134	3																								3
Q152								1																	1
Q153								7																	7
Q871	3																								3
Q968						2																			2
Q3175		8			1				1	4															14
Q3231	2										2	5	3	1	1										14
Q3239																									
Q3872	1											1													2
Q3873	25											4				75	1								105
Q3876	2																								2
Q3877																									
Q3878																									
Q3879									1			2						1							4
Q3882	1																								1
Q3883	1																		1						2
Q3884	11								1			6								3	1	2			24
Q3885																									
Q3887																									
Q3888	29								7			20								18	3		4	1	82
Q3889																									
Q3890	1																								1
Q3891																									
Q3892	6																								6
Q3894																									
N labs reporting	13	2	1	1	2	2	1	2	4	1	1	6	1	1	1	1	1	1	1	2	2	1	1	1	19
Average	**1.9**	*21*		*1*	*1*	*2*	*1*	*4*	**1.6**	*4*	*2*	**3.7**	*3*	*1*	*1*	*75*	*1*	*1*	*1*	*11*	*2*	*2*	*4*	*1*	**3.2**
Standard deviation	**1.9**	*18*			*0*	*0*		*4*	**2.7**			**2.7**								*11*	*1*				**3.9**

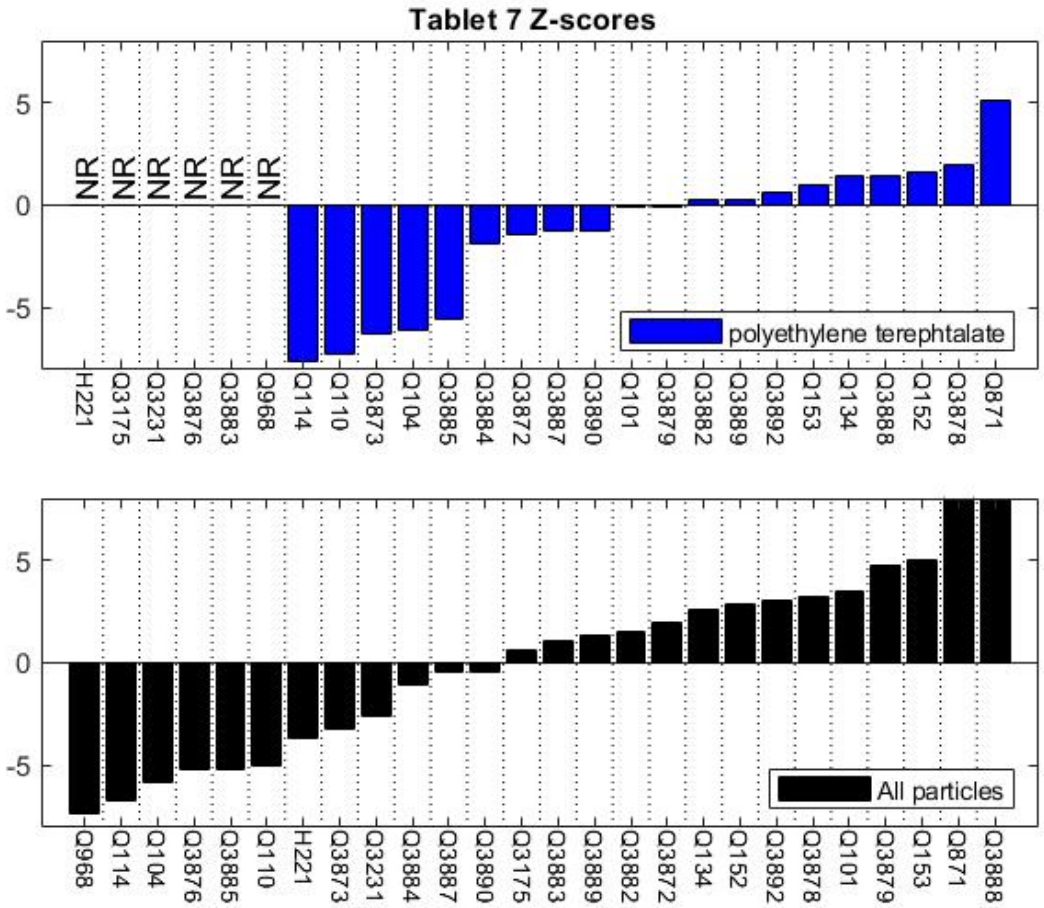
Average and standard deviation derived by only the numerical values (i.e. non-numerical values such as <4 are excluded). The robust means and standard deviations of the number of particles per determinand have been calculated with robust NDA statistics, when more than 3 numerical observations were reported and are indicated in bold. In case of 3 or less numerical observations, estimates of means are calculated straightforwardly and given in italics. Note that the uncertainty in means and standard deviations is high with low numbers of particles.

Appendix B Numerical z-score values per tablet position no. 7-11and graphical output

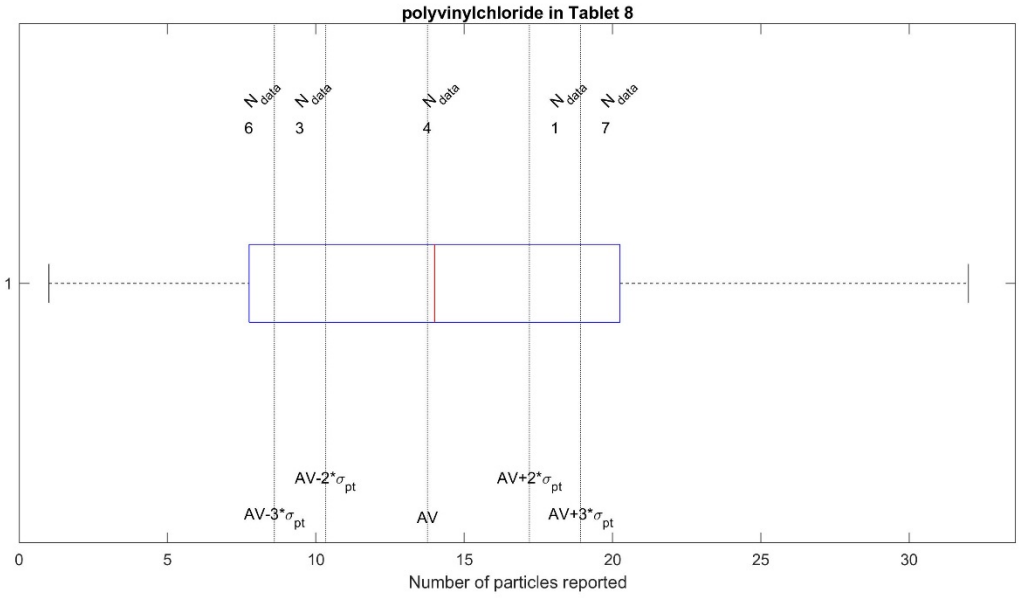
Tablet 7

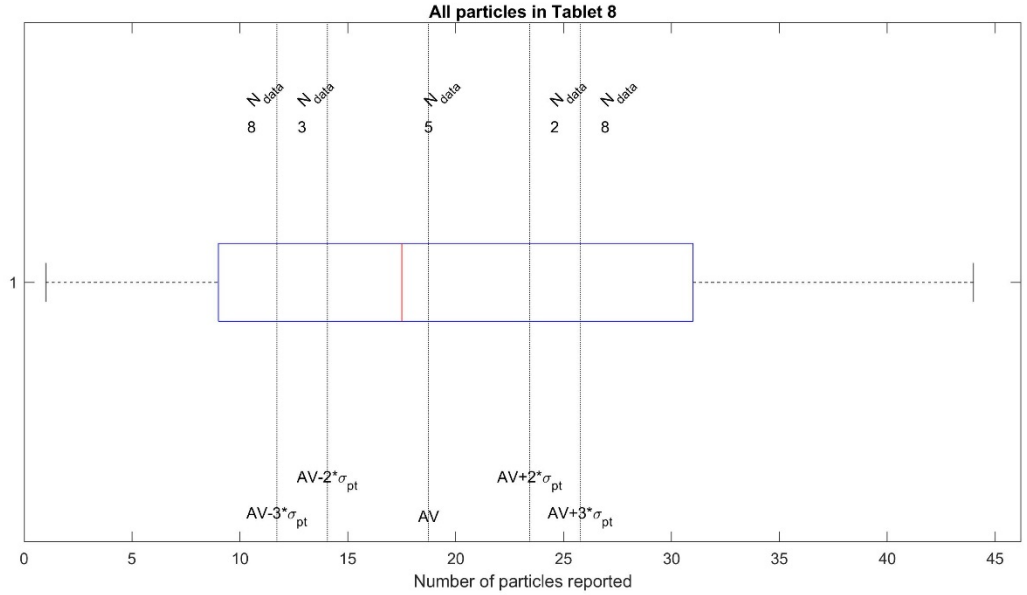


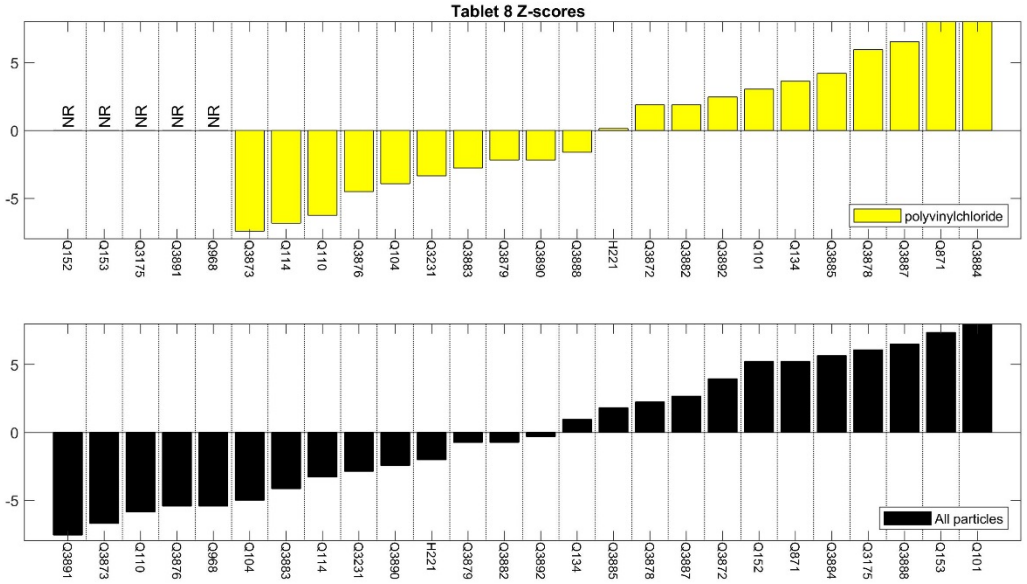



Tablet 7 Z-scores
5
0
-5
NR NR NR NR NR NR
polyethylene terephtalate
H221 Q3175 Q3231 Q3876 Q3883 Q968 Q114 Q110 Q3873 Q104 Q3885 Q3884 Q3872 Q3887 Q3890 Q101 Q3879 Q3882 Q3889 Q3892 Q153 Q134 Q3888 Q152 Q3878 Q871
5
0
-5
All particles
Q968 Q114 Q104 Q3876 Q3885 Q3883 Q110 H221 Q3873 Q3231 Q3884 Q3887 Q3890 Q3175 Q3883 Q3889 Q3882 Q3872 Q134 Q152 Q3892 Q3878 Q101 Q3879 Q153 Q871 Q3888

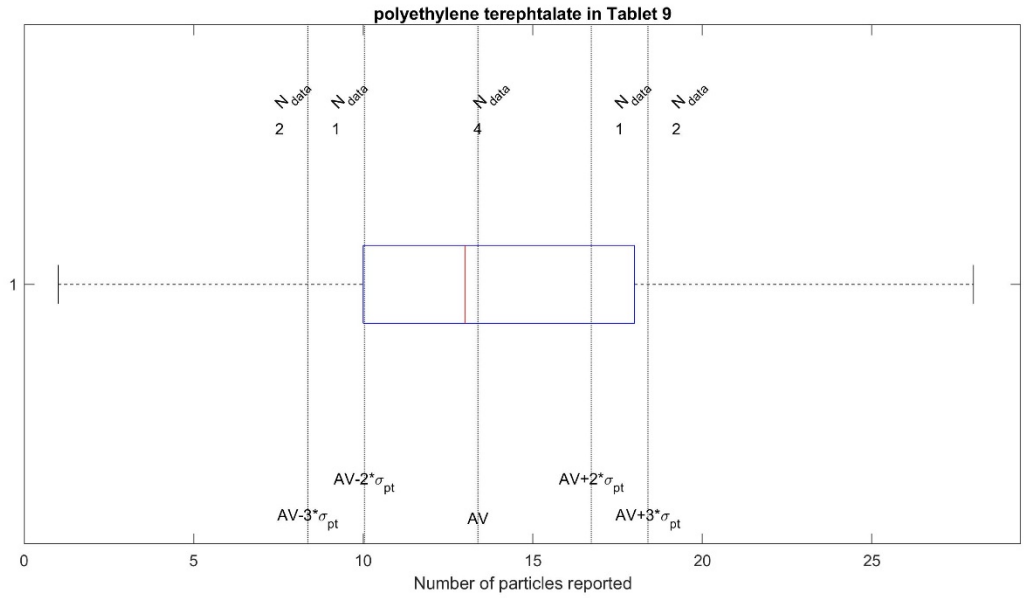
Tablet 8

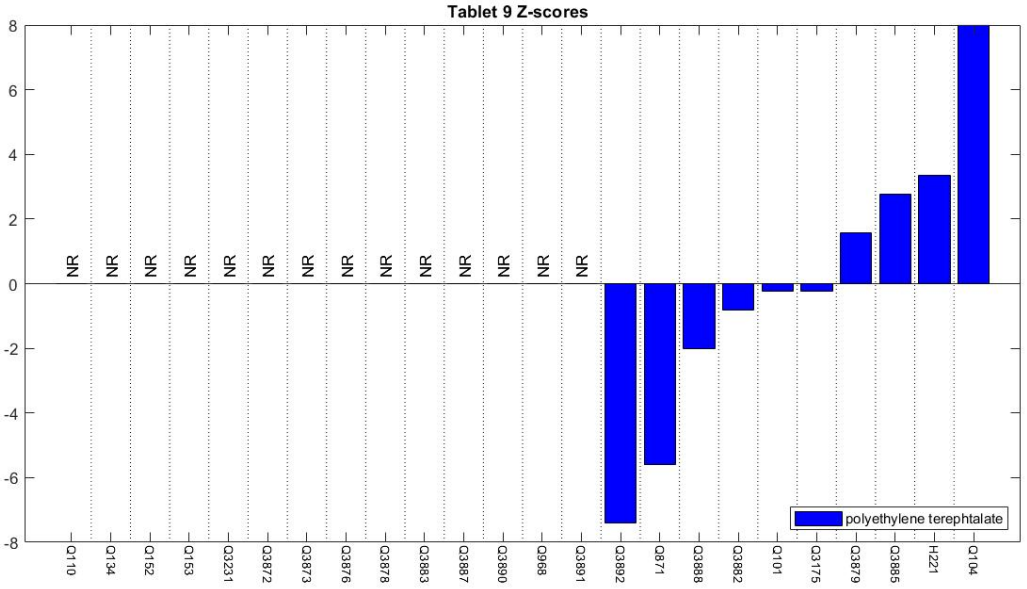

polyvinylchloride in Tablet 8
N data 6
N data 3
N data 4
N data 1
N data 7
1
AV-2*σpt
AV+2*σpt
AV-3*σpt
AV
AV+3*σpt
0 5 10 15 20 25 30
Number of particles reported


All particles in Tablet 8
N data
8
N data
3
N data
5
N data
2
N data
8
1
AV-2*σpt
AV+2*σpt
AV-3*σpt
AV
AV+3*σpt
0
5
10
15
20
25
30
35
40
45
Number of particles reported

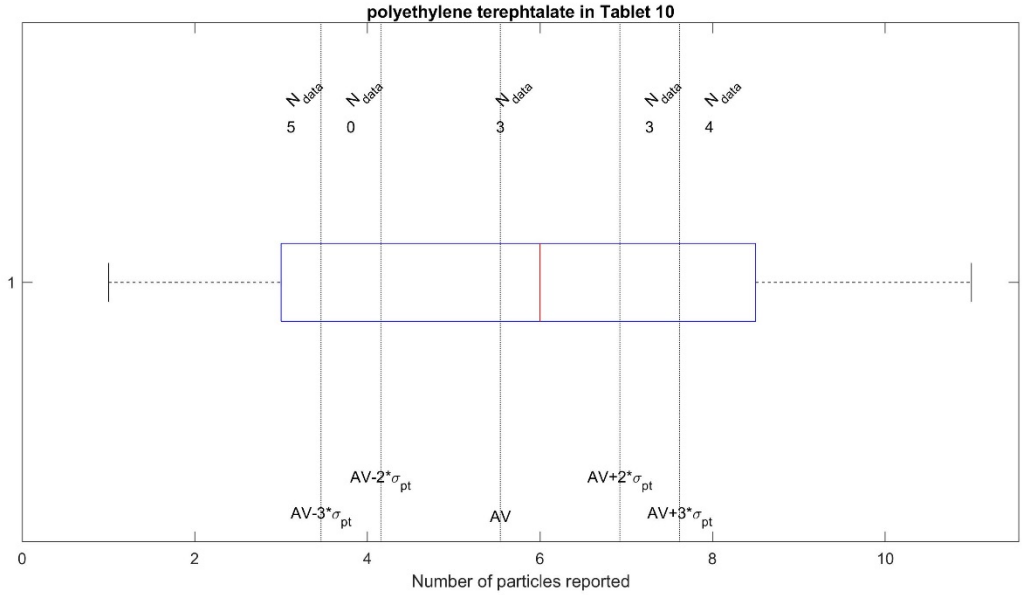

Tablet 8 Z-scores
5
0
-5
NR
NR
NR
NR
NR
polyvinylchloride
Q152
Q153
Q3175
Q3891
Q968
Q3873
Q114
Q110
Q3876
Q104
Q3231
Q3883
Q3879
Q3890
Q3888
H221
Q3872
Q3882
Q3892
Q101
Q134
Q3885
Q3878
Q3887
Q871
Q3884
5
0
-5
All particles
Q3891
Q3873
Q110
Q3876
Q968
Q104
Q3883
Q114
Q3231
Q3890
H221
Q3879
Q3882
Q3892
Q134
Q3885
Q3878
Q3887
Q3872
Q152
Q871
Q3884
Q3175
Q3888
Q153
Q101

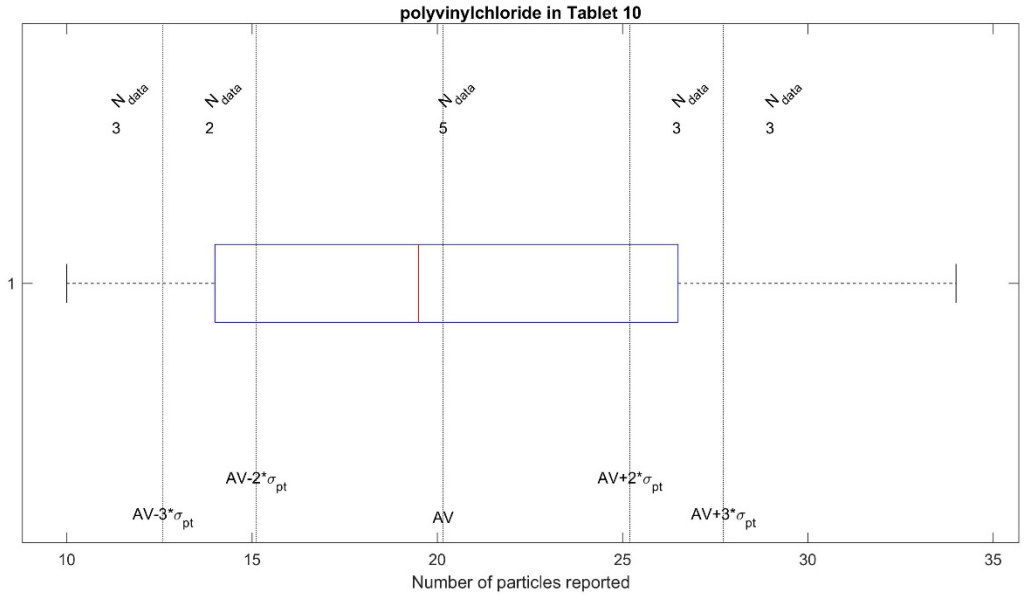
Tablet 9

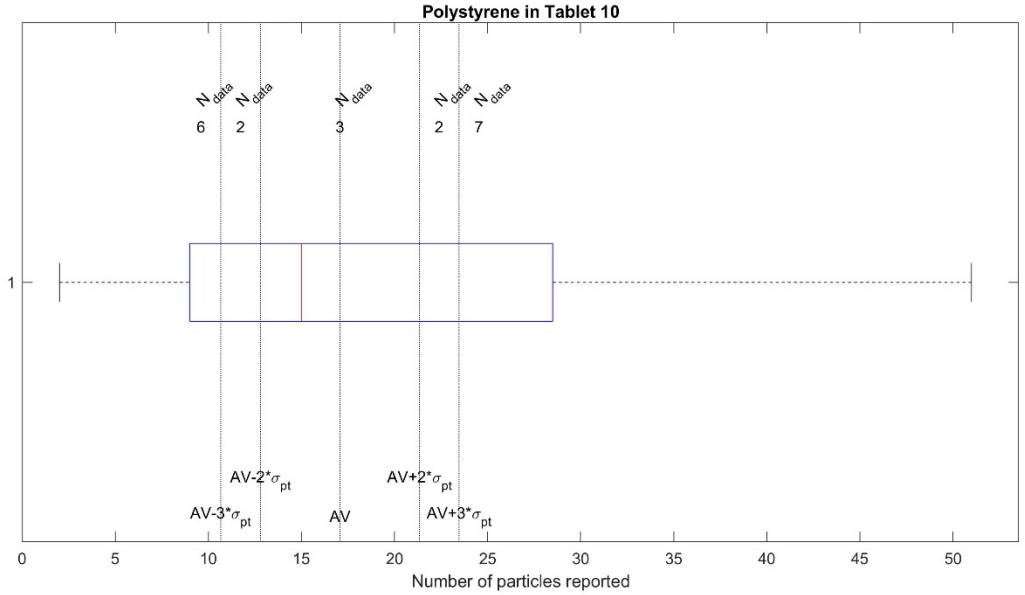

polyethylene terephtalate in Tablet 9
N data
2
N data
1
N data
4
N data
1
N data
2
AV-2*σpt
AV-3*σpt
AV
AV+2*σpt
AV+3*σpt
Number of particles reported

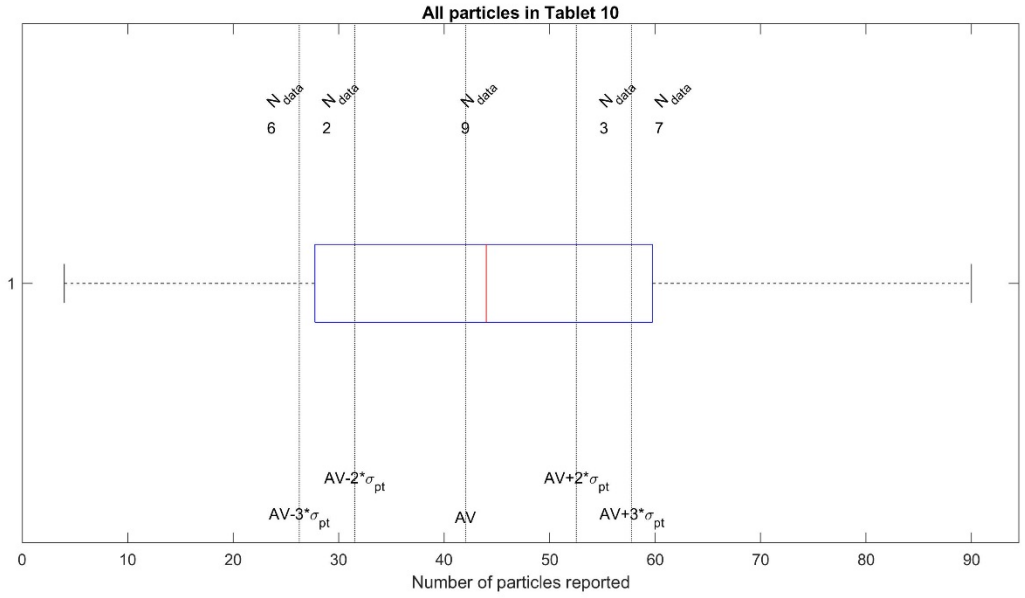

Tablet 9 Z-scores
NR
polyethylene terephtalate
Q110
Q134
Q152
Q153
Q3231
Q3872
Q3873
Q3876
Q3878
Q3883
Q3887
Q3890
Q968
Q3891
Q3892
Q871
Q3888
Q3882
Q101
Q3175
Q3879
Q3885
H221
Q104

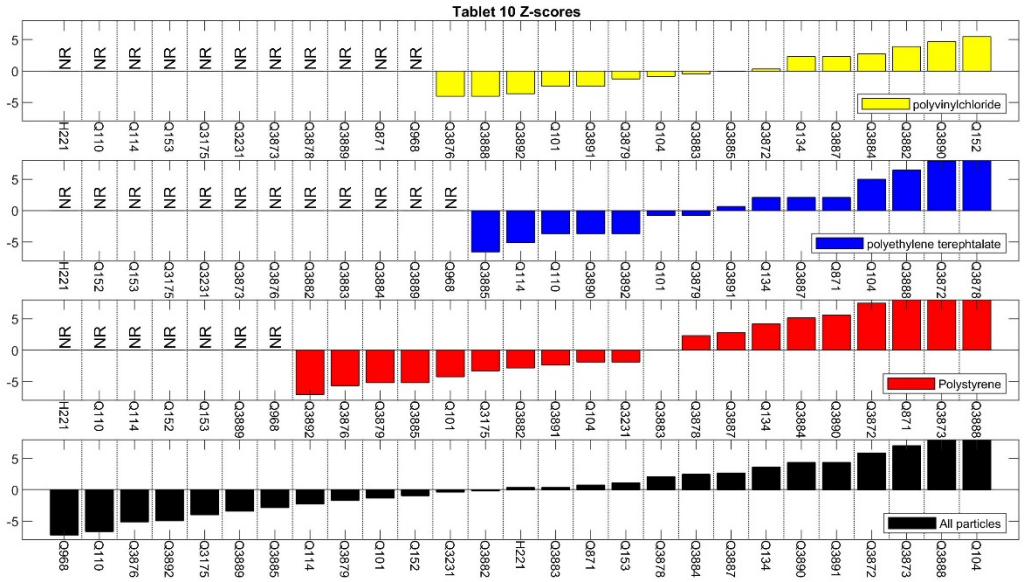
Tablet 10


polyethylene terephtalate in Tablet 10
N data
5
N data
0
N data
3
N data
3
N data
4
1
AV-2*σpt
AV+2*σpt
AV-3*σpt
AV
AV+3*σpt
0
2
4
6
8
10
Number of particles reported

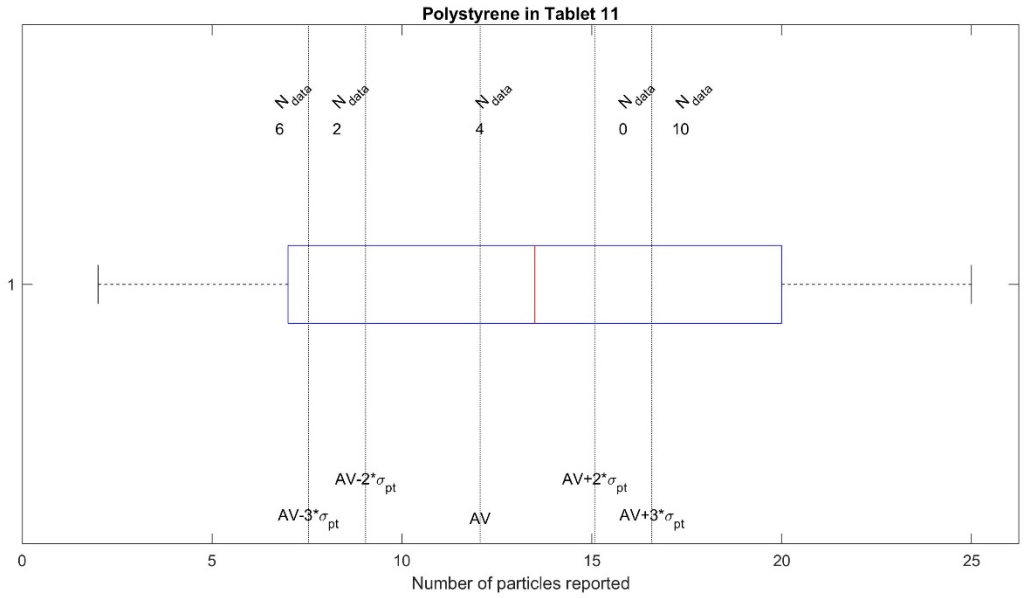

polyvinylchloride in Tablet 10
N data
3
N data
2
N data
5
N data
3
N data
3
1
AV-2*σpt
AV+2*σpt
AV-3*σpt
AV
AV+3*σpt
10
15
20
25
30
35
Number of particles reported

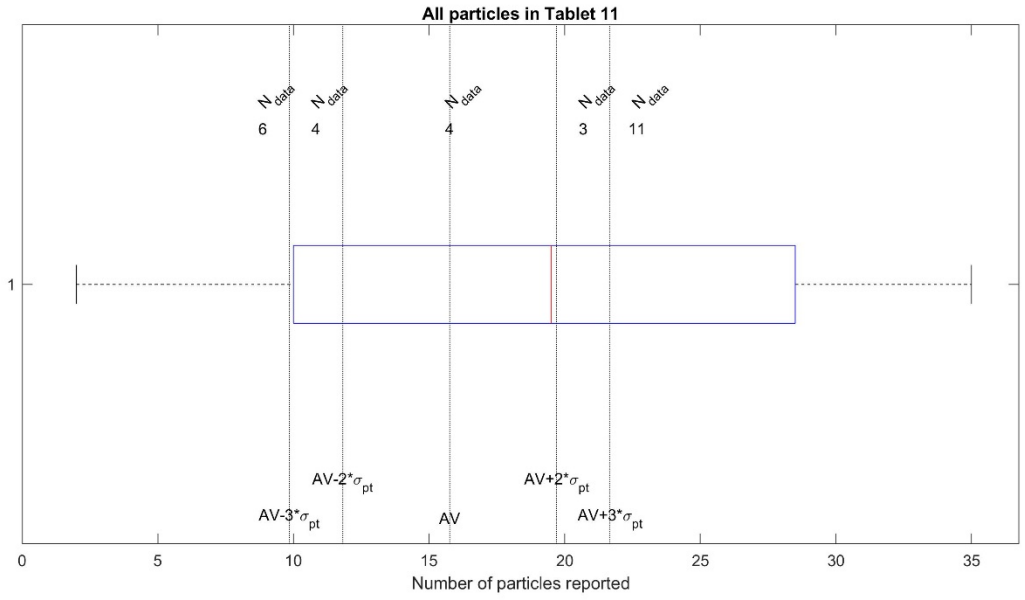

Polystyrene in Tablet 10
N data
6
N data
2
N data
3
N data
2
N data
7
1
AV-2*σpt
AV+2*σpt
AV-3*σpt
AV
AV+3*σpt
0
5
10
15
20
25
30
35
40
45
50
Number of particles reported

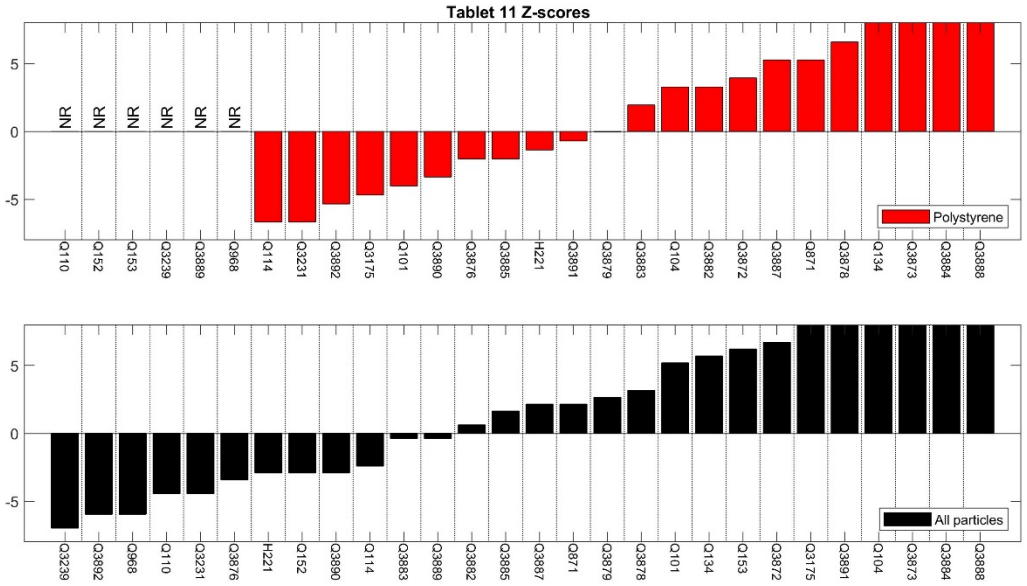

All particles in Tablet 10
N data
6
N data
2
N data
9
N data
3
N data
7
1
AV-2*σpt
AV+2*σpt
AV-3*σpt
AV
AV+3*σpt
0
10
20
30
40
50
60
70
80
90
Number of particles reported


Tablet 10 Z-scores
polyvinylchloride
polyethylene terephtalate
Polystyrene
All particles

Tablet 11


Polystyrene in Tablet 11
N data
6
N data
2
N data
4
N data
0
N data
10
1
AV-2*σpt
AV+2*σpt
AV-3*σpt
AV
AV+3*σpt
0
5
10
15
20
25
Number of particles reported


All particles in Tablet 11
N data
6
N data
4
N data
4
N data
3
N data
11
1
AV-2*σpt
AV+2*σpt
AV-3*σpt
AV
AV+3*σpt
0
5
10
15
20
25
30
35
Number of particles reported



Z-scores per laboratory

The z-scores of the laboratories are summarised in table A-13 for the polymers.

Table A-13. Z-scores for tablets position nos. 7-11 for the polymers added and for laboratories that report numerical results for these

Laboratory Code	Determinand	Pos no. 7	Pos no. 8	Pos no. 9	Pos no. 10	Pos no. 11
H221	polyethylene terephthalate			3.36		
	Polystyrene					-1.37
	Polyvinylchloride		0.14			
Q101	polyethylene terephthalate	-0.13		-0.23	-0.78	
	Polystyrene				-4.25	-4.02
	Polyvinylchloride		3.05		-2.44	
Q104	polyethylene terephthalate	-6.08		8.74	5.00	
	Polystyrene				-1.91	3.28
	Polyvinylchloride		-3.93		-0.86	
Q110	polyethylene terephthalate	-7.23			-3.67	
	Polyvinylchloride		-6.26			
Q114	polyethylene terephthalate	-7.62			-5.11	
	Polystyrene					-6.67
	Polyvinylchloride		-6.84			
Q134	polyethylene terephthalate	1.41			2.11	
	Polystyrene				4.19	8.59

	Polyvinylchloride		3.63		2.32	
Q152	polyethylene terephthalate	1.60				
	Polyvinylchloride				5.49	
Q153	polyethylene terephthalate	1.02				
Q3175	polyethylene terephthalate			-0.23		
	Polystyrene				-3.31	-4.68
Q3231	Polystyrene				-1.91	-6.67
	Polyvinylchloride		-3.35			
Q3872	polyethylene terephthalate	-1.47			7.89	
	Polystyrene				7.47	3.94
	Polyvinylchloride		1.88		0.33	
Q3873	polyethylene terephthalate	-6.27				
	Polystyrene				10.28	19.20
	Polyvinylchloride		-7.42			
Q3876	Polystyrene				-5.66	-2.03
	Polyvinylchloride		-4.51		-4.03	
Q3878	polyethylene terephthalate	1.98			36.79	
	Polystyrene				2.31	6.60
	Polyvinylchloride		5.95			
Q3879	polyethylene terephthalate	-0.13		1.57	-0.78	
	Polystyrene				-5.19	-0.04
	Polyvinylchloride		-2.19		-1.25	
Q3882	polyethylene terephthalate	0.25		-0.82		
	Polystyrene				-2.84	3.28
	Polyvinylchloride		1.88		3.90	
Q3883	Polystyrene				-0.03	1.95
	Polyvinylchloride		-2.77		-0.46	
Q3884	polyethylene terephthalate	-1.86				
	Polystyrene				5.13	44.41
	Polyvinylchloride		10.60		2.71	
Q3885	polyethylene terephthalate	-5.50		2.76	-6.56	
	Polystyrene				-5.19	-2.03
	Polyvinylchloride		4.21		-0.06	
Q3887	polyethylene terephthalate	-1.28			2.11	
	Polystyrene				2.78	5.27
	Polyvinylchloride		6.53		2.32	
Q3888	polyethylene terephthalate	1.41		-2.02	6.45	

	Polystyrene				15.91	52.37
	Polyvinylchloride		-1.60		-4.03	
Q3889	polyethylene terephthalate	0.25				
Q3890	polyethylene terephthalate	-1.28			-3.67	
	Polystyrene				5.59	-3.36
	Polyvinylchloride		-2.19		4.70	
Q3891	polyethylene terephthalate				0.67	
	Polystyrene				-2.37	-0.70
	Polyvinylchloride				-2.44	
Q3892	polyethylene terephthalate	0.64		-7.40	-3.67	
	Polystyrene				-7.06	-5.35
	Polyvinylchloride		2.46		-3.64	
Q871	polyethylene terephthalate	5.05		-5.61	2.11	
	Polystyrene				9.34	5.27
	Polyvinylchloride		8.28			

Appendix C Additional method information

Table A-14 Additional method information

Methods for pellets in position 1-6	H221	Q101	Q104
Sample pretreatment (SP)			No
SP method			
SP other method than specified			
Further SP steps			
Further SP steps other than specified			
Further SP steps			
Further SP steps other than specified			
More details (i.e. mesh size etc.)			
Identification method	µFTIR		ATR-FTIR
Additional identification method	*in ATR mode*		
Quantification method	Gravimetric		ATR-FTIR
Additional Quantification method			
Methods based on published work	No		No
Reference			

Methods for pellets in position 1-6	Q110	Q114	Q134
Sample pretreatment (SP)	No		No
SP method			
SP other method than specified			
Further SP steps			
Further SP steps other than specified			

Further SP steps			
Further SP steps other than specified			
More details (i.e. mesh size etc.)			
Identification method	ATR-FTIR	ATR-FTIR	ATR-FTIR
Additional identification method			
Quantification method	ATR-FTIR	Gravimetric	Gravimetric
Additional Quantification method			
Methods based on published work	No	No	No
Reference			

Methods for pellets in position 1-6	**Q152**	**Q153**	**Q871**
Sample pretreatment (SP)		No	
SP method			
SP other method than specified			
Further SP steps		Other	
Further SP steps other than specified		*Staining using Nile red*	
Further SP steps		Filtration	
Further SP steps other than specified		*Use of lab controls*	
More details (i.e. mesh size etc.)		*regenerated cellulose, 0.2 micron*	
Identification method	µFTIR	ATR-FTIR	ATR-FTIR
Additional identification method		*Use of reference materials for validation*	
Quantification method	Gravimetric	Other	

Additional Quantification method	*counted particles*	*Fluorescence tagging of polymers using Nile red*	
Methods based on published work		Yes	No
Reference		*Maes et al., 2017, Scientific report*	

Methods for pellets in position 1-6	**Q968**	**Q3175**	**Q3231**
Sample pretreatment (SP)		No	No
SP method			
SP other method than specified			
Further SP steps			
Further SP steps other than specified			
Further SP steps			
Further SP steps other than specified			
More details (i.e. mesh size etc.)			
Identification method		µFTIR	ATR-FTIR
Additional identification method			
Quantification method			Gravimetric
Additional Quantification method			
Methods based on published work			Yes
Reference			*Primpke S. et al. 2018, Anal. Bioanal. Chem 410*

Methods for pellets in position 1-6	**Q3239**	**Q3872**	**Q3873**
Sample pretreatment (SP)	No	No	No
SP method			
SP other method than specified			

Further SP steps			
Further SP steps other than specified			
Further SP steps			
Further SP steps other than specified			
More details (i.e. mesh size etc.)			
Identification method	ATR-FTIR	Raman	Raman
Additional identification method			
Quantification method		Other	Other
Additional Quantification method		*Weighing scale*	*By eye*
Methods based on published work	Yes	No	Yes
Reference			*Horton et al. 2017. Marine Pollution Bulletin*

Methods for pellets in position 1-6	**Q3876**	**Q3877**	**Q3878**
Sample pretreatment (SP)	No	No	No
SP method			
SP other method than specified			
Further SP steps			
Further SP steps other than specified			
Further SP steps			
Further SP steps other than specified			
More details (i.e. mesh size etc.)	*10µM*		
Identification method	µFTIR	Py-GC/MS	ATR-FTIR

Additional identification method			
Quantification method	Microscopy	Gravimetric	Other
Additional Quantification method			*Direct count from Petri dish*
Methods based on published work	No	Yes	No
Reference		*Fries et al 2013 Environmental Science Processes and Impacts*	

Methods for pellets in position 1-6	**Q3879**	**Q3882**	**Q3883**
Sample pretreatment (SP)	No	No	No
SP method			
SP other method than specified			
Further SP steps			
Further SP steps other than specified			
Further SP steps			
Further SP steps other than specified			
More details (i.e. mesh size etc.)			
Identification method	ATR-FTIR	µFTIR	ATR-FTIR
Additional identification method			*We futher analysed melting point for one sample, in order to identify whether it was a HDPE or LDPE*
Quantification method	ATR-FTIR	µFTIR	Gravimetric
Additional Quantification method			*samples were counted and weigthed*
Methods based on published work	No	No	Yes
Reference			

Methods for pellets in position 1-6	Q3884	Q3885	Q3887
Sample pretreatment (SP)	No	No	Yes
SP method			Filtration
SP other method than specified			
Further SP steps			
Further SP steps other than specified			
Further SP steps			
Further SP steps other than specified			
More details (i.e. mesh size etc.)			*300 micron and 10 micron*
Identification method	Raman	ATR-FTIR	Microscopy
Additional identification method	*µRaman*		*ATR-FTIR*
Quantification method	Gravimetric	Microscopy	Microscopy
Additional Quantification method			*gravimetric*
Methods based on published work		No	No
Reference			

Methods for pellets in position 1-6	Q3888	Q3889	Q3890
Sample pretreatment (SP)	Yes	No	No
SP method	Filtration		
SP other method than specified			
Further SP steps			
Further SP steps other than specified			
Further SP steps			
Further SP steps other than specified			

More details (i.e. mesh size etc.)	*Filtration on a square-shaped silicon filter 10x10mm, pores size 5µm*		
Identification method	ATR-FTIR	µFTIR	µFTIR
Additional identification method			*Raman*
Quantification method	µFTIR	Gravimetric	Gravimetric
Additional Quantification method			*visual inspection*
Methods based on published work	No	No	No
Reference			

Methods for pellets in position 1-6	**Q3891**	**Q3892**	**Q3894**
Sample pretreatment (SP)	No	No	No
SP method			Other
SP other method than specified			*Filtration*
Further SP steps			Other
Further SP steps other than specified			*Washing with Milli-Q water*
Further SP steps			
Further SP steps other than specified			
More details (i.e. mesh size etc.)	*samples were measured on the microscope slide*		*Preburned 0,7um fiberglass filter*
Identification method	Raman	ATR-FTIR	Py-GC/MS
Additional identification method			
Quantification method	Raman	Gravimetric	Gravimetric

Additional Quantification method			
Methods based on published work	Yes	No	Yes
Reference			

Methods for position 7-12	**H221**	**Q101**	**Q104**
Sample pretreatment (SP)		Yes	Yes
SP method	Filtration	Filtration	Filtration
SP other method than specified			
Further SP steps	Other		
Further SP steps other than specified	*Hydrogen peroxide treatment of filter*		
Further SP steps	Other		
Further SP steps other than specified	*Rinsing with MilliQ water of filter*		
More details (i.e. mesh size etc.)	*25 mm Al2O3 filters used, 0.2 µm mesh*	*10.0 um pore size, Hydrophilic PTFE membrane, 47 mm diameter*	*0.2 µm Anodisc filter and 10 µm stainless steel filter for Sample 8 only*
Identification method	µFTIR	µFTIR	µFTIR
Additional identification method	*in ATR mode*		*Focal Plane Array based microFTIR imaging, mainly in transmission mode*
Quantification method	Microscopy	Microscopy	Microscopy
If additional or other methods have been used, please specify			*Visual counts where representative particles validated with µFT-IR*
Additional Quantification method		No	Yes

Methods based on published work	*Strand, J., Feld, L., Murphy, F., Mackevica, A., & Hartmann, N. B. (2018). Analysis of microplastic particles in Danish drinking water. DCE scientifc report No. XXX*

Methods for position 7-12	**Q152**	**Q153**	**Q871**
Sample pretreatment (SP)	Yes	Yes	
SP method	Filtration	Filtration	
SP other method than specified			
Further SP steps	Other	Other	
Further SP steps other than specified	*Nile Red Staining*	*Staining using Nile Red*	
Further SP steps		Filtration	
Further SP steps other than specified		*Use of lab controls*	
More details (i.e. mesh size etc.)		*Regenerated cellulose filter 0.2 micron*	
Identification method	µFTIR	ATR-FTIR	µFTIR
Additional identification method		*Use of reference materials for validation*	
Quantification method	Other	Other	
If additional or other methods have been used, please specify	*Nile Red Staining/ counting*	*Fluorescence tagging of polymers using Nile Red*	
Additional Quantification method	Yes	Yes	No
Methods based on published work	*Maes, T. et al. A rapid-screening approach to detect and quantify microplastics based on fluorescent tagging with Nile Red. Sci. Rep. 7, 44501; doi: 10.1038/srep44501 (2017).*	*Maes et al., 2017, Scientific Report*	

Methods for position 7-12	Q968	Q3175	Q3231
Sample pretreatment (SP)	Yes	Yes	Yes
SP method	Filtration	Filtration	Filtration
SP other method than specified			
Further SP steps			
Further SP steps other than specified			
Further SP steps			
Further SP steps other than specified			
More details (i.e. mesh size etc.)	*1,6 µm*	*0,22µm*	*Anodisc 0.2 µm*
Identification method		µFTIR	µFTIR
Additional identification method			
Quantification method	Other	Microscopy	µFTIR
If additional or other methods have been used, please specify	*binocular magnifying*		
Additional Quantification method	Yes		Yes
Methods based on published work	*De Witte et al, 2014, Marine Pollution Bulletin*		*Liu, F. et al. 2019, Sci. Total Environ. 671*

Methods for position 7-12	Q3239	Q3872	Q3873
Sample pretreatment (SP)		Yes	No
SP method		Filtration	
SP other method than specified			
Further SP steps			
Further SP steps other than specified			
Further SP steps			
Further SP steps other than specified			
More details (i.e. mesh size etc.)			*5 um silver membrane filter*
Identification method		Raman	µFTIR
Additional identification method		*µFTIR (ATR)*	
Quantification method		Microscopy	µFTIR
If additional or other methods have been used, please specify			
Additional Quantification method		No	No
Methods based on published work			

Methods for position 7-12	Q3876	Q3877	Q3878
Sample pretreatment (SP)	Yes	No	Yes
SP method	Filtration		Filtration
SP other method than specified			
Further SP steps			
Further SP steps other than specified			
Further SP steps			
Further SP steps other than specified			
More details (i.e. mesh size etc.)	*10µM*		
Identification method	µFTIR	Py-GC/MS	µFTIR
Additional identification method			
Quantification method	µFTIR	Gravimetric	Microscopy
If additional or other methods have been used, please specify			
Additional Quantification method	No	Yes	No
Methods based on published work		*Fries et al 2013 Environmental Science Processes and Impacts*	

Methods for position 7-12	Q3879	Q3882	Q3883
Sample pretreatment (SP)	No	Yes	Yes
SP method		Filtration	Filtration
SP other method than specified			
Further SP steps	Filtration		
Further SP steps other than specified			
Further SP steps			
Further SP steps other than specified			
More details (i.e. mesh size etc.)	*Samples were filtred on a 0.2 µm alumine filter of 25 mm*	*mesh size 40µm*	*Anodisc Circle with Support Ring, 25 mm, 0.2 µm pore size.*
Identification method	µFTIR	µFTIR	ATR-FTIR
Additional identification method			
Quantification method	µFTIR	µFTIR	Microscopy
If additional or other methods have been used, please specify			
Additional Quantification method	No	No	Yes
Methods based on published work			

Methods for position 7-12	Q3884	Q3885	Q3887
Sample pretreatment (SP)	Yes		Yes
SP method	Filtration	Filtration	Filtration
SP other method than specified			
Further SP steps			
Further SP steps other than specified			
Further SP steps			
Further SP steps other than specified			
More details (i.e. mesh size etc.)	*0.2 µm*	*Mesh Size = 1.2µm*	*300 micron, 50 micron, and 10 micron*
Identification method	Raman	µFTIR	Microscopy
Additional identification method	*µRaman*		*ATR-FTIR*
Quantification method	Raman	Microscopy	Microscopy
If additional or other methods have been used, please specify	*µRaman*		
Additional Quantification method		No	No
Methods based on published work			

Methods for position 7-12	Q3888	Q3889	Q3890
Sample pretreatment (SP)	Yes	Yes	Yes
SP method	Filtration	Filtration	Filtration
SP other method than specified			
Further SP steps			
Further SP steps other than specified			
Further SP steps			
Further SP steps other than specified			
More details (i.e. mesh size etc.)	*Filtration on a square-shaped silicon filter 10x10mm, pores size 5µm*	*63 um and 0.4 um*	*0.1 µm, Anodisc 25 mm*
Identification method	µFTIR	µFTIR	µFTIR
Additional identification method			
Quantification method	µFTIR	Gravimetric	Microscopy
If additional or other methods have been used, please specify		*Microscopy*	*Image J analysis in case of sample 8*

Additional Quantification method	No	No	No
Methods based on published work			

Methods for position 7-12	**Q3891**	**Q3892**	**Q3894**
Sample pretreatment (SP)	Yes	Yes	
SP method	Filtration	Filtration	Filtration
SP other method than specified			*Preburned fiberglass filter*
Further SP steps			Other
Further SP steps other than specified			*Washing with Milli-Q water*
Further SP steps			
Further SP steps other than specified			
More details (i.e. mesh size etc.)	*carbonate filters 47mm, silver filters*	*0.2 µm inorganic filter membrane (anodisc)*	*0,7um fiberglass filter*
Identification method	Raman	µFTIR	Py-GC/MS
Additional identification method		*FTIR imaging in transmission mode, resolution 25x25 µm*	
Quantification method	Raman	µFTIR	Py-GC/MS
If additional or other methods have been used, please specify		*FTIR imaging in transmission mode, resolution 25x25 µm*	
Additional Quantification method		No	Yes
Methods based on published work			

Appendix D NDA statistics

Normal Distribution Approximation (NDA)

Interlaboratory studies like those of WEPAL-QUASIMEME frequently give rise to datasets that have complex distributions including excessive tailing and multiple modes. Consequently, sophisticated statistical methods are required to obtain meaningful assessments. A methodology is needed that does not rely on arbitrary outlier removal or subjective manual interpretations. The model that is chosen calculates population characteristics (mean and standard deviation) from experimental datasets as described by Cofino et al. (2000) and Molenaar et al. (2018).
The statistical principles of the model that we use to assess the data are outlined in two steps. Firstly, the full model is described, thereafter a description is given of the way the model is implemented for the assessment of the data in WEPAL and Quasimeme.

We assume that each laboratory i submits a result given by a probability density function q_i. We start thus from a set of probability density function q_i. i=1,....,N. We set ourselves to establish the average probably density function $\bar{q}$ that best describes the set.

It is insightful to make at this point an analogy with the calculation of the arithmetic mean of a set of data $a_i, i = 1, \dots, N$. The average $\bar{a}$ can be defined as the point that minimises the sum of the squared Euclidean distances $d(\bar{a}, a_i)$ to the given data. This can be accomplished by equating the first derivative of $\sum_{i=1}^{N} d^2(\bar{a}, a_i) = \sum_{i=1}^{N} (\bar{a} - a_i)^2$ with respect to $\bar{a}$ to zero. One readily finds the well known expression $\bar{a} = \frac{1}{N} \sum_{i=1}^{N} a_i$

In a similar manner, we construct the average probability density function $\bar{q}$ of the set of probability density functions $q_i, i = 1, \dots, N$. We define a measure $d(p, q)$ for the distance between two probability density functions p and q. We obtain $\bar{q}$ by minimising the sum of the square distances from each probability density function q_i to $\bar{q}$,thus by equating the first derivative of $\sum_{i=1}^{n} d(\overline{q}, q_i)^2$ with respect to $\bar{q}$ to zero. The calculation itself is extensive and not given here. The mean and standard deviation of the population are calculated using the first and second moments of the probability density function $\bar{q}$. The variance obtained from the second moment comprises both a within-laboratory and between-laboratory component.

In WEPAL and Quasimeme, laboratories report single data, we have no information about the underlying probability function. To cope with this problem we use a specific implementation of the model: the so-called Normal Distribution Approximation (NDA). The NDA approach is parametrised to reproduce the population characteristics of truly normal distributions, and is a robust method to evaluate interlaboratory studies.

The NDA approach has been devised using a set of normal distributions $q_i = N(\mu_i, \sigma), i = 1, \dots, N$. We assume thus that all normal distributions have the same standard deviation σ. The expected values μ_i are also taken to be normally distributed: $\mu_i = N(\bar{\mu}, S)$. It appears that the mean $\bar{\mu}$ and the standard deviation S of the normal distribution describing the population can be exactly reproduced when $\sigma = 0.78 * S$. In the NDA method, the standard deviation S is calculated directly from the total variance, no distinction between within-laboratory and between-laboratory components is made.

In practice, we have N laboratories each reporting a single value. This gives rise to a dataset $x_i, i = 1, \dots, N$. We calculate the population standard deviation from this dataset using the robust estimate *S=1.4826*MAD* (MAD: median of absolute standard deviations). The normal distributions associated with the data x_i are estimated by $q_i = N(x_i, 0.78S) = N(x_i, 1.156 * MAD)$. We calculate the average probability density function $\bar{q}$ of the set of normal distributions qi as described above. The mean and standard deviation of the interlaboratory study are obtained using the first and second moments of the average probability density function $\bar{q}$.

The NDA-mean (assigned value)

The NDA mean is centered around the highest density of values. Unless otherwise stated, the assigned value represents the consensus value of *all* data. Although *all* data are included in the assessment, those values that lie some distance from the NDA mean contribute less to the mean than values which occur at or near the mean.
With the NDA model, mean and standard deviation are calculated (under special conditions, see indicative values) using all reported data when at least 4 results are left after removal of reported 'lower than' (<) and 0 (=zero) values. No outliers are removed