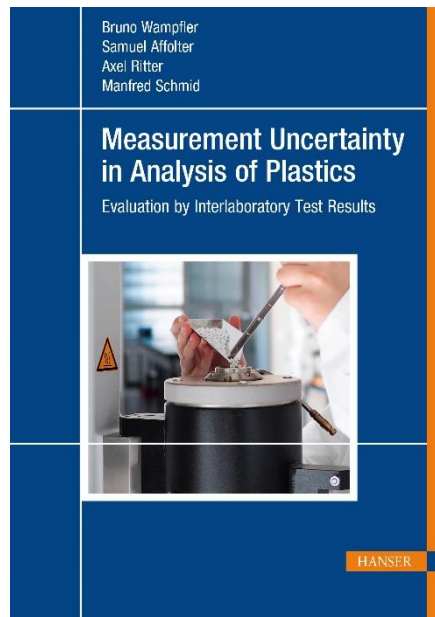


# HANSER



## Sample Pages

### Measurement Uncertainty in Analysis of Plastics

Bruno Wampfler, Samuel Affolter, Axel Ritter and Manfred Schmid

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# Contents

<b>Preface</b> .....	<b>VII</b>
<b>The Authors</b> .....	<b>IX</b>
<b>About the Use of this Book</b> .....	<b>XIII</b>
<b>List of Abbreviations</b> .....	<b>XVII</b>
<b>Equation Symbols</b> .....	<b>XXI</b>
<b>Glossary</b> .....	<b>XXIII</b>
<b>1 Introduction to Measurement Uncertainty</b> .....	<b>1</b>
1.1 Measuring – What Is It? .....	1
1.2 Measurement Uncertainty in Plastics Testing .....	4
1.3 Interlaboratory Comparisons .....	5
1.3.1 Terms and Parameters .....	6
1.3.2 Calculation of the Parameters .....	8
<b>2 Evaluation of the Measurement Uncertainty</b> .....	<b>13</b>
2.1 Explanatory Example .....	13
2.2 Modeling Approach According to GUM .....	14
2.3 Interlaboratory Comparisons and the Randomness of Systematic Influences .....	16
2.4 Evaluation of the Measurement Uncertainty Using Interlaboratory Comparison Data .....	19
2.4.1 Basic Equations .....	19

2.4.2	Additional Components . . . . .	21
2.4.3	Notes Regarding the Systematic Measurement Error (Bias) . . . .	22
2.5	Conclusion of the Explanatory Example . . . . .	23
2.6	Contribution of the Sampling . . . . .	24
2.6.1	Sampling and Interlaboratory Comparison . . . . .	25
2.6.2	Empirical Method . . . . .	27
2.7	Estimation Allowed! . . . . .	28
<b>3</b>	<b>Uncertainty Data in Practical Application . . . . .</b>	<b>31</b>
3.1	Assessment of Measurement Data . . . . .	31
3.1.1	Introduction . . . . .	31
3.1.2	Comparison of Results from Different Laboratories . . . . .	35
3.1.3	Comparison of Results from the Same Laboratory . . . . .	39
3.1.3.1	Critical Difference . . . . .	39
3.1.3.2	Reference Materials . . . . .	41
3.1.3.3	Failure Analysis . . . . .	42
3.1.4	Further Notes on the Evaluation of Measurement Data . . . . .	44
3.2	Reporting Uncertainty . . . . .	45
3.3	Explanations to the Precision Data Presented in the Following Chapters . . . . .	46
<b>4</b>	<b>Thermal Analysis . . . . .</b>	<b>53</b>
4.1	Differential Scanning Calorimetry (DSC) . . . . .	53
4.1.1	Principle of Measurement . . . . .	53
4.1.2	Interlaboratory Comparisons – Summary . . . . .	55
4.1.3	Glass Transition Temperature $T_g$ . . . . .	56
4.1.4	Change of the Specific Heat Capacity $\Delta c_p$ . . . . .	59
4.1.5	Crystallinity and Melting Characteristics of Thermoplastics . . .	60
4.1.6	Curing Reaction of Epoxy Resins . . . . .	61
4.2	Oxidative Induction Time and Temperature . . . . .	62
4.2.1	Principle of Measurement . . . . .	62
4.2.2	Results of Interlaboratory Comparisons . . . . .	64
4.3	Thermogravimetry (TGA) . . . . .	66
4.3.1	Principle of Measurement . . . . .	66

4.3.2	Results of Interlaboratory Comparisons – Summary	67
4.3.3	Content of Plasticizer	68
4.3.4	Content of Carbon Black	69
4.3.5	Ash Content	69
4.4	Dynamic Mechanical Analysis (DMA)	70
4.4.1	Principle of Measurement	70
4.4.2	Results of Interlaboratory Comparisons	72
4.5	Examples of Thermal Analysis	75
4.5.1	Adhesives: Comparison of Two Samples	75
4.5.2	OIT: Comparison of the Values of Two Laboratories	79
<b>5</b>	<b>Determination of the Molecular Weight</b>	<b>83</b>
5.1	Size Exclusion Chromatography (SEC)	83
5.1.1	Principle of Measurement	83
5.1.2	SEC in Organic Phase	85
5.1.3	SEC in Aqueous Phase	87
5.1.4	High Temperature SEC	87
5.1.5	Polydispersity	88
5.2	Melt Mass-Flow Rate (MFR)	88
5.2.1	Principle of Measurement	88
5.2.2	Results of Interlaboratory Comparisons	89
5.3	Solution Viscosity	90
5.3.1	Principle of Measurement	90
5.3.2	Results of Interlaboratory Comparisons	91
5.4	Examples to the Determination of the Molecular Weight	92
5.4.1	MFR: Testing the Sample for Specification and Inhomogeneity	92
5.4.2	Intrinsic Viscosity [ $\eta$ ] – Estimation of the Standard Uncertainty	94
<b>6</b>	<b>Quantification of Main and Secondary Components</b>	<b>99</b>
6.1	Elements	99
6.1.1	Halogens	99
6.1.1.1	Principle of Measurement	100
6.1.1.2	Results of Interlaboratory Comparisons	101

6.1.2	Sulfur	101
6.1.2.1	Principle of Measurement	102
6.1.2.2	Results of Interlaboratory Comparisons	102
6.1.3	Nitrogen	103
6.1.3.1	Principle of Measurement	103
6.1.3.2	Results of Interlaboratory Comparisons	103
6.2	Compounds	104
6.2.1	Plasticizer	104
6.2.1.1	Principle of Measurement	104
6.2.1.2	Results of Interlaboratory Comparisons	105
6.2.2	Vinyl Acetate Content in Ethylene–Vinyl Acetate Copolymers	106
6.2.2.1	Principle of Measurement	106
6.2.2.2	Results of Interlaboratory Comparisons	107
6.2.3	Water	108
6.2.3.1	Principle of Measurement	108
6.2.3.2	Results of Interlaboratory Comparisons	109
6.3	Ash	110
6.3.1	Principle of Measurement	110
6.3.2	Results of Interlaboratory Comparisons	110
6.4	Examples for Quantitative Determination	112
6.4.1	Plasticizer: Extraction versus TGA	112
6.4.2	Bromine: XRF versus Titrimetry	114
<b>7</b>	<b>Quantification of Trace Components</b>	<b>119</b>
7.1	Elements: Metalloids, Heavy Metals and Bromine	119
7.1.1	Principle of Measurement	119
7.1.2	Results of Interlaboratory Comparisons	121
7.2	Stabilizers	124
7.2.1	Principle of Measurement	125
7.2.2	Results of Interlaboratory Comparisons	127
7.3	Residual Solvents	129
7.3.1	Principle of Measurement	129

7.3.2	Sample Preparation .....	130
7.3.3	Results of Interlaboratory Comparisons .....	131
7.4	Examples of Quantitative Trace Analysis .....	132
7.4.1	Correction of the Lead Content .....	132
7.4.2	Mini-Interlaboratory Test (Three Participants) .....	134
<b>8</b>	<b>Summary .....</b>	<b>139</b>
8.1	Data Overview .....	140
8.2	Reproducibility Precision .....	143
8.3	Repeatability Precision .....	144
8.4	Between-Laboratory Effects .....	145
8.5	Reporting Uncertainty .....	147
<b>Index</b>	<b>.....</b>	<b>149</b>



# Preface

Technical and scientific results should include information about measurement uncertainty. This statement is largely undisputed today, although such information is still missing in many documents. But how is the measurement uncertainty evaluated? The authors have learned from experience that analytical laboratories often shy away from time-consuming calculations for economic reasons, but also because of the complexity of the subject matter. Instead, they prefer an approximate estimate of the measurement uncertainty based on their experience, especially since the accreditation bodies of many countries accept such approaches. On the other hand, there is a great willingness to participate in interlaboratory comparisons. Such studies are considered very useful because one's own results can be compared with those of other participants. In addition, the results provide a valuable basis for measurement uncertainty.

There are also many laboratories that are confronted with changing questions, materials and analytes day after day and are always under time pressure. The authors have worked in such non-routine laboratories for a long time and some of them still do. It has been their experience that the available guidelines do not provide help in determining measurement uncertainty because the necessary data from long-term quality assurance are missing and precision data from interlaboratory tests cannot be found. Therefore, results are usually reported without measurement uncertainty or, at best, in the form of a rough estimate. To increase the amount and variety of precision data available, the authors organized interlaboratory tests in the field of plastics for more than two decades. Most participants were from industrial laboratories and performed the tests under daily conditions. The commitment of the laboratories resulted in a lot of data that has not yet been fully published.

The aim of this book is to make the collected data available, together with other precision data published in literature and standards, thereby facilitating the estimation of the measurement uncertainty in plastics analysis and, finally, to show how different measurement results should be interpreted using the uncertainty data. The easy-to-understand theoretical part of the book first introduces measurement uncertainty, followed by a description of how this uncertainty can be calcu-



lated from interlaboratory test results. An entire chapter is devoted to the question under which conditions a difference between two results is significant. In the main part of the book, the data found up to the end of 2021 are grouped thematically, presented graphically or in tabular form, and discussed in the accompanying text. Some different analytical methods dealing with the same measurand are compared under the aspect of measurement uncertainty. Examples at the end of the chapters show how the data can be used in everyday industrial applications.

The present book is primarily a translation of the German edition “Messunsicherheit in der Kunststoffanalytik – Ermittlung mit Ringversuchsdaten” (Uncertainty of Measurement in Plastic Analysis – Determination with Interlaboratory Test Data), which was published by Carl Hanser Verlag in 2017. Feedback from some readers about the lack of such an overview in English encouraged the authors to translate this book. The English version has been updated and expanded to include new findings and results from the literature and standards where appropriate.

The authors would like to thank the many laboratories in Europe that participated in the interlaboratory tests with a high level of expertise and thus made the book possible at all. The Swiss Federal Laboratories for Materials Science and Technology Empa provided us with a set of unpublished interlaboratory test data; many thanks for this. A special thanks is due to Dr. Petra Wampfler. Petra has contributed much to the understanding of Chapters 2 and 3 with her critical questions and useful hints. Last but not least, we would like to thank the Hanser Verlag for their constructive support, especially Dr. Mark Smith for editing the manuscript and proofreading the English translation, Melanie Lindwurm-Giordani for checking the manuscript and page proofs, and Conny Speckmaier for her production work on this book.

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# About the Use of this Book

From the point of view of measurement uncertainty, plastics analysis is a special case. In contrast to other fields of chemical analysis, many procedures are standardized and more and more accompanied by precision data from interlaboratory comparisons. Such precision data is the key to good estimation of measurement uncertainty. The other main approach, often called modeling approach or GUM approach, only works if the systematic influences can be identified and quantified with some reliability. And experience has shown that this is not the case in plastics analysis. This view is apparently shared by metrological institutes. The U.S. National Institute for Standards and Technology (NIST), for example, calculates the uncertainty of the reference material 1474b (MFR of PE) [1] not by the modeling approach, but based on linear interpolation of the data from two interlaboratory comparisons.

This book is intended to facilitate access to precision data and its use. For each important method of plastics analysis, results from several high-quality interlaboratory comparisons can be found. The tables and figures presented contain absolute or relative data, mostly in the form of the median with MAD (Median Absolute Deviation). MAD is a robust measure of the distribution of values and corresponds to about two-thirds of the standard deviation. An entire chapter is devoted to the critical difference between two analytical results and its dependence on the conditions under which it was obtained. However, the book does not address aspects of validation and quality assurance. It is assumed throughout this book that quality assurance and control measures are in place to ensure that the measurement process is stable and under control and the analytical method is fit for its intended purpose.

The present book is aimed primarily at the non-routine laboratory, which is confronted with different parameters and materials each and every day and therefore inevitably uses ad-hoc methods or standards developed for materials other than the one under investigation. It goes without saying that precision data is difficult to find under such circumstances. The book attempts to fill this gap and assists the analyst in finding suitable values. As far as possible, however, the analyst should

# 1

## Introduction to Measurement Uncertainty

Analyses on identical objects often yield different results when two or more laboratories are involved. This can lead to discussions between business partners. In such cases, knowledge of the measurement uncertainty helps to evaluate the differences and to take action. Furthermore, if testing results are provided with information on the measurement uncertainty, the client knows the limits within which he/she can rely on them.

Measurement uncertainty belongs to the concept of metrology. The term can only be understood in combination with other terms such as value of the measurand, traceability or recognized standard. Therefore, the first question to ask is: “What does it mean to measure?”

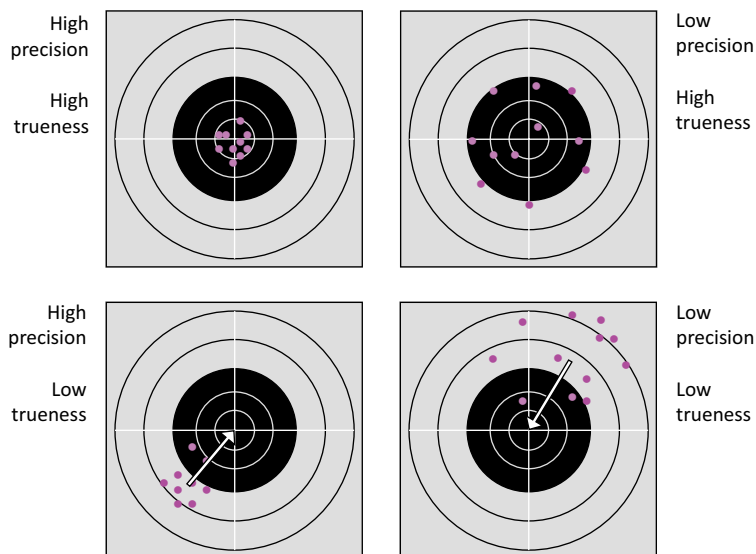
### ■ 1.1 Measuring – What Is It?

To measure means to compare. Thus, the length of a table is measured by comparing the table edge with a tape measure. Another example involves the content of alcohol in the blood. This concentration is determined by comparing the peak areas the gas chromatograph provides based on the alcohol content in the sample and in the reference solution. However, these two measurements only work if the measuring tape and the alcohol reference solution are correctly calibrated, that is, their values must be related to a recognized standard by an unbroken chain of comparison measurements with known uncertainty. One then speaks of traceability of the measurement value and says that the measured length of the table and the alcohol content are traceable on recognized standards.

A few decades ago, the aim of a measurement was to find the true value. If this had been achieved, different laboratories would have obtained identical results when analyzing the same measurement object. In spite of great effort, it was found again and again that the true value eluded measurement and thus remained unknown. In 1977, the topic was taken up by the world’s highest authority in metrology, the

Comité International des Poids et Mesures (CIPM). The committee initiated a development process which involved several metrological institutions and which finally resulted in the detailed Guide to the Expression of Uncertainty in Measurement (GUM) [1]. This guide appeared in 1995 and launched a paradigm shift. For the first time it was stated that the value of a measurand, that is, the true value, is always unknown and a measurement can only refer to observable values such as expected value, measurement value, distribution of the measured values or observable systematic deviation.

This approach can be illustrated in a simplified way using a target from sport shooting, where only observable values are involved (Figure 1.1). The target is given by the crosshair in the center and corresponds to the (agreed) expected value. Ten shots are fired and the pattern of holes in the target is evaluated. The focal point of the holes is close to the expected values for both of the targets situated above. Neither of the two rifles has any noticeable systematic deviation. This is not the case for the targets below. However, the magnitude and direction of the deviation are measurable and can be corrected by adjusting the sights of the rifle. The correction is made according to the white arrows illustrating the location of the focal points of the holes in relation to the expected value (crosshair). In contrast, the large random deviation (low precision) in the targets on the right side cannot be corrected. This distribution is system-related due to poor quality of the rifle or inability of the person shooting.



**Figure 1.1** Illustration of precision and trueness using the target model

Note: High precision corresponds to small random deviation and vice versa. The arrows mark the amount by which the systematic deviation can be corrected.



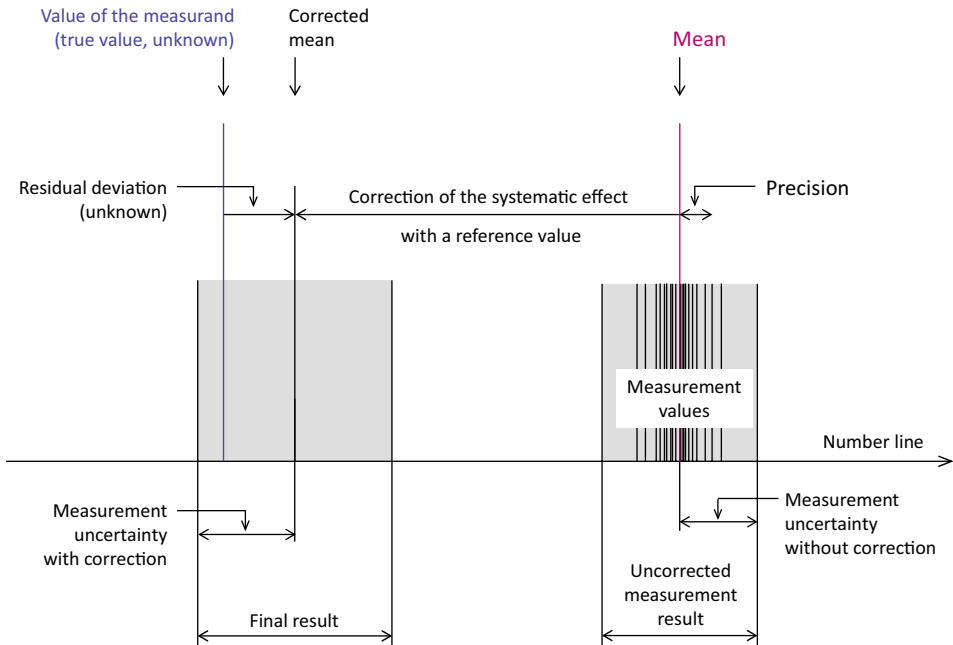
In metrology, there is no crosshair that can be used to measure a systematic deviation or the trueness of results. Trueness control is performed with the help of reference values, whose carriers include reference procedures, reference materials and interlaboratory comparisons. The precision, on the other hand, can be calculated directly from the individual results and specified as an imprecision in the form of a standard deviation, a variance or a coefficient of variation.

The path from a measurement to the final result can be described by the following steps (Figure 1.2):

1. The measurement is carried out. The result consists of the mean of the individual values and the measurement uncertainty determined (Figure 1.2, right).
2. If systematic effects are detected, for example by measurement on a reference material, the cause of the deviation is sought and eliminated. If elimination is not possible, the result is corrected by the deviating value [1]. Figure 1.2 shows a correction of the mean value to a lower value. The correction leads to a higher trueness of the result.
3. The uncertainty of the correction is calculated and integrated into the measurement uncertainty. Therefore, the uncertainty becomes larger compared to the uncorrected result.
4. The final result consists of the interval given by the corrected mean and the measurement uncertainty obtained after correction (Figure 1.2, left).

The measurement uncertainty stands for the informative power or usefulness of a result. The smaller the measurement uncertainty, the better the result is suited to identify differences to limit values, specifications or third-party results. Therefore, great importance should be attributed to the measurement uncertainty in the validation of analytical procedures.

Since Figure 1.2 does not address accuracy and trueness, some comments on these terms need to be made. Accuracy is an umbrella term that comprises trueness and precision. Both accuracy and trueness are qualitative terms used, for example, to express that a result is more or less accurate or has a higher or lower trueness. However, they cannot be quantified [2].



**Figure 1.2** Modern metrology focuses exclusively on observable values: measurement values, measurable systematic effects, measurement uncertainty

## ■ 1.2 Measurement Uncertainty in Plastics Testing

A wide body of standards is available for the testing of plastics, which increasingly includes precision data from interlaboratory comparisons. This gives the testing of plastics a considerable advantage over other chemical-analytical disciplines, because the measurement uncertainty can be assessed much more easily on the basis of interlaboratory comparison data. Ideally, data are available that correspond exactly to the desired combination of method and material. If this is not the case, the measurement uncertainty can be estimated using interlaboratory data based on the same method but on other materials with similar properties (cf. Section 2.7). Such an estimate is often more reliable than the modeling approach described in Section 2.2.

The present book lists medians, each based on several interlaboratory tests and provide these with a dispersion measure. Such medians are broadly based and are intended to provide a valuable starting point for roughly and quickly estimating a measurement uncertainty in the absence of other data. The selection must also

take into account whether the interlaboratory test data are linked to specific, well-defined standard procedure or are based on values from different procedures. In the former case, a smaller measurement uncertainty tends to be expected than in the latter.

ISO 9924-1 [3] draws attention to an important point which is generally valid in chemical analysis and which is also included in similar form in many other standards:



The parameters of interlaboratory comparisons should not be used for acceptance or rejection of any group of materials without documentation that the parameters are applicable to the particular group of materials and the specific test protocols of the test method.

## ■ 1.3 Interlaboratory Comparisons

The project structure of an interlaboratory comparison consists of an organizer and several participants. In the field of plastics, the participants are laboratories. The organizer prepares a sufficient amount of material in sufficient homogeneity and draws up a procedure on how to condition and analyze the sample. He/she sends a sample and a copy of the procedure to each participant of the interlaboratory comparison. The participants carry out the required number of analyses on the sample and submit the individual results to the organizer. The organizer evaluates the results and prepares a report for the participants. The report contains the results of each participant in anonymized form and provides the specific parameters of the interlaboratory comparison, including an appropriate discussion.

The scheme described above is set out in detail in the ISO/IEC 17043 standard [4] and relates to interlaboratory tests whose goal is proficiency testing, that is, trueness control. Participants see their benefit in the verification and optimization of analytical methods and in the demonstration of their competence. Laboratories accredited according to ISO/IEC 17025 [5] or bound to a governmental approval procedure must regularly participate in such proficiency testing. The EPTIS [6] database provides a good overview of upcoming PT schemes.

Interlaboratory comparisons are also carried out to validate newly developed national or international standard or to certify reference materials. Since the value of a reference material should have the lowest possible uncertainty, the certifying analyses are often carried out at great expense by specialized institutes that use expensive equipment for high precision measurements. Therefore, values of interlaboratory tests from the certification of reference materials are only conditionally suitable to serve as uncertainty of results from the daily work of a laboratory.

### 1.3.1 Terms and Parameters

Participants in interlaboratory comparisons are required to perform a prescribed number  $n$  of analyses under repeatability conditions.

**Repeatability conditions** according to VIM 2.20 [2] are fulfilled if the analyses are performed

- by the same person
- in the same place
- using the same method of analysis
- using the same devices and equipment
- on the same or similar objects within a short time

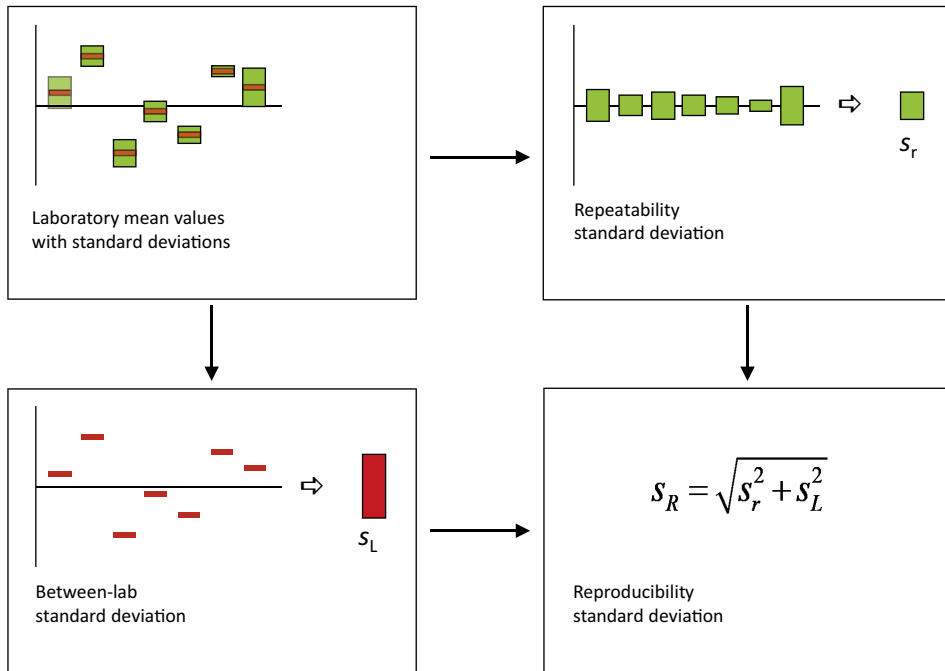
The repeatability standard deviation is a measure for the distribution of the values determined under repeatability conditions. When merging the results of the individual laboratories, one obtains an overall distribution based on reproducibility conditions.

**Reproducibility conditions** according to VIM 2.24 [2] are fulfilled if the analyses are performed

- by different persons
- in different laboratories
- using the same or different methods of analysis
- using different devices and equipment
- on the same or similar objects

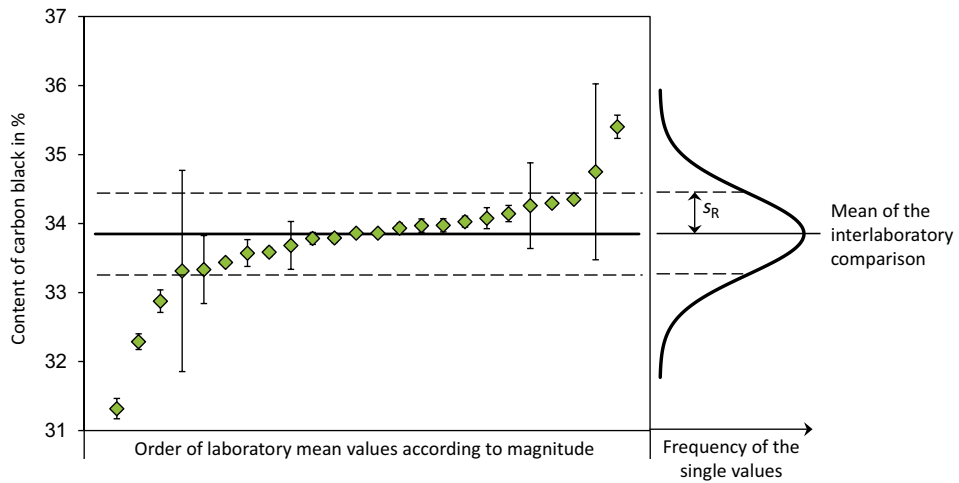
The between-lab standard deviation  $s_L$  and the reproducibility standard deviation  $s_R$  are two measures for the distribution of the values under reproducibility conditions. Figure 1.3 and Equation 1.1 illustrate the relationship between  $s_r$ ,  $s_L$  and  $s_R$ .

$$s_R = \sqrt{s_L^2 + s_r^2} \quad (1.1)$$



**Figure 1.3** Relationship between the key parameters from interlaboratory comparisons

Proficiency test reports usually contain diagrams in which the mean values of the laboratories are arranged in order of their magnitude (Figure 1.4). Normally distributed mean values form a typical point mirrored S-curve. The horizontal straight line through the point of symmetry is at the level of the mean value of the interlaboratory comparison. If the same graph is made with the individual values instead of the laboratory means and the frequency is plotted on one side, the result is a normal distribution whose standard deviation corresponds to the (experimental) reproducibility standard deviation  $s_R$ . The reproducibility standard deviation  $s_R$  is calculated according to Equation 1.7. Doubling  $s_R$  results in the 95% confidence interval, which is often additionally drawn in reports on either side of the mean. The uncertainty bars at the laboratory mean values show the standard deviation  $s_{rw}$  obtained from each laboratory under repeatability conditions (cf. Equation 1.3). From these standard deviations, the repeatability standard deviation  $s_r$  of the interlaboratory comparison is calculated (Equation 1.5). The third important parameter, the between-lab standard deviation  $s_L$  corresponds to the standard deviation of the mean values of the laboratories if the number of replicates per laboratory is sufficiently high (cf. Equation 1.6).



**Figure 1.4** Typical interlaboratory test plot based on the example of the determination of carbon black in plastics  
If the frequency of the single values is plotted to the right, a normal distribution with the reproducibility standard deviation results.

Laboratories often work under intermediate conditions that lie between the repeatability and reproducibility conditions explained above. A typical example is the control chart (Shewhart Chart), which is used for quality assurance of recurring analyses [7]. The control chart provides an overview of analytical control values that are entered and monitored over a longer time and often by different persons.

### 1.3.2 Calculation of the Parameters

The parameters are calculated according to Equation 1.2 to Equation 1.7 [8]. First, the mean and standard deviation are calculated from the  $n$  individual values obtained by each laboratory under repeatability conditions.

The result  $y_j$  obtained from the laboratory  $j$  is calculated according to Equation 1.2.

$$y_j = \frac{1}{n} \sum_{i=1}^n y_{ji} \quad (1.2)$$

$y_j$ : mean value determined by laboratory  $j$

$n$ : number of replicates

$y_{ji}$ :  $i$ -th individual value determined by laboratory  $j$

Standard deviation  $s_{rw}$  of the  $n$  values determined by laboratory  $j$  under repeatability conditions:

# Index

## Symbols

- 2-Butanone
- precision data 131

## A

- Acceptance of materials 5, 47
- Accuracy 3
- Adhesive
- reaction enthalpy 61
- Aluminum
- measurement principle 119
- precision data 122
- Antioxidant
- chemical structure 125
- GC 126
- HPLC 126
- measurement principle 125
- precision data 128, 129
- systematic effect 128, 129
- Arsenic
- measurement principle 119
- precision data 122
- Ash residue
- determination 66
- measurement principle 110
- precision data 68, 69, 111
- TGA vs. wet chemistry 112
- Atomic absorption spectrometry 120
- Axis intercept
- standard uncertainty 95

## B

- Baseline
- DSC 53
- Benzene
- precision data 131
- Between-lab standard deviation 6, 7, 9, 17, 19, 20, 27, 36, 37
- example 135
- Bias 21
- estimation 22, 23
- uncertainty estimation 22, 23
- Bromine
- precision data 124
- Bromine content
- determination 100
- measurement principle 100
- precision data 101
- Butyl acetate
- precision data 131

## C

- Cadmium
- measurement principle 119
- precision data 122, 124
- Calibration function 84
- Calorimeter 53
- Carbon black content
- determination 66
- precision data 68, 69
- Certified value 41
- Chlorine content
- determination 100

- measurement principle 100
  - precision data 101
  - Chromium
    - measurement principle 119
    - precision data 122, 124
  - Combined standard uncertainty 15, 17
  - Comparative analyses 28
  - Comparison
    - critical ratio, example 114
    - histogram 45
    - mean and median 44
    - mean and reference value 33, 44
    - reproducibility conditions 35
    - result and limit 32
    - two mean values 39, 44
    - two medians 44
    - two methods 45
    - two results 32, 33, 35
    - two results, example 112
    - two samples, example 75
    - under repeatability conditions 33, 34, 39
    - under reproducibility conditions 34
    - using critical difference 45
    - with a certified value 41
    - with a reference value 41
    - with reference value, example 132
  - Compatibility
    - reference value 46
  - Complex modulus 71
  - Compliance assessment 32
  - Confidence interval 16, 36, 40
  - Conformity
    - testing of a product 31
  - Conformity assessment 45
    - example 92, 94
  - Correction
    - systematic deviation 4
  - Correction factor
    - standard uncertainty 133
  - Correction of a result
    - example 132
  - Coverage factor 16, 35
    - and Student t-distribution 40
  - Critical difference 32, 35, 39
    - data overview 141
    - specific heat capacity 60
    - temperature by DSC 57
    - under repeatability conditions 40
  - Critical ratio 37, 39
    - data overview 142
    - development of the equation 48
    - example 136
  - Crystallinity 60
- ## D
- Deviation
    - random 16
    - systematic 16
  - Difference
    - critical 32, 35, 39
    - critical, data overview 141
    - under repeatability conditions 39
  - Differential scanning calorimetry 53
    - enthalpy difference 54
    - heat-flux 53, 54
    - interlaboratory comparison 55
    - power-compensated 54
    - precision data 55-61, 64-66
  - DMA. *See* dynamic mechanical analysis
  - DSC. *See* differential scanning calorimetry
  - Dynamic mechanical analysis
    - interlaboratory comparison 72
    - measurement principle 70
    - precision data 73-75
    - typical chart 73
  - Dynamic OIT. *See* oxidative induction temperature
- ## E
- Element analysis
    - purpose 99
  - Elugram 83, 84
    - baseline 84
  - Empirical approach 27
  - Endothermic process
    - DSC 53



- Enthalpy difference 54
  - DSC 54
- EPTIS database 5
- Ethanol
  - precision data 131
- Ethyl acetate
  - precision data 131
- Example
  - between-lab standard deviation 135
  - comparison of two results 112, 114
  - comparison of two samples 75
  - comparison with reference value 132
  - conformity assessment 92, 94
  - correction of a result 132
  - critical ratio 114, 136
  - determination of cadmium 13, 14, 18, 23
  - failure analysis 75
  - ICP-OES 13, 14, 18, 23
  - inhomogeneity 92
  - intrinsic viscosity 96
  - mean of an interlaboratory comparison 135
  - MFR 92
  - mini-interlaboratory comparison 134, 135
  - repeatability standard deviation 135
  - specification check 75
  - standard uncertainty 135
- Exothermic process
  - DSC 53
- Expanded uncertainty 16, 35
  - statement 45
- F**
- Failure analysis 42
  - example 75
  - standard uncertainty 43
- G**
- Glass transition temperature 56
  - and specific heat capacity 57
  - determination 57, 72
  - polyamide 57
  - precision data 55, 57-59, 75
  - standard uncertainty 57
- GUM 2
- GUM-approach. *See* modeling approach
- H**
- Heat capacity 56
- Heat flux
  - DSC 54
  - during glass transition 57
- Heavy metals
  - measurement principle 119
  - precision data 122-124
- Horwitz function 29
- I**
- ICP-MS 121
- ICP-OES 120
- Imprecision 3
- Influence
  - random 16
- Inhomogeneity 21, 25, 27, 93
  - example 92
  - repeatability standard deviation 26
- Injection volume 84
- Interlaboratory comparison 3, 5
  - differential scanning calorimetry 55
  - dynamic mechanical analysis 72
  - example 134
  - oxidative induction temperature 64
  - oxidative induction time 64
  - sampling 26
  - thermogravimetry 67
- Intermediate conditions 8, 43
- Intrinsic viscosity 91, 95
  - determination 96
  - example 94
  - standard uncertainty 96
- Isothermal OIT. *See* oxidative induction time

**L**

- Laboratory sample 25
- Lead
  - measurement principle 119
  - precision data 122, 124
- Light scattering
  - size exclusion chromatography 84
- Limit 32
- Loss factor 71
  - determination 72
- Loss modulus 71
  - determination 72
  - interlaboratory test plot 73
  - precision data 73
- Low temperature SEC 85, 86
  - LS detector 87

**M**

- MAD
  - and standard deviation 46
- Mark-Howink equation 91
- Mass-average molecular weight.
  - See molecular weight
- Mean of interlaboratory test
  - example 135
- Mean of the interlaboratory comparison 9
- mean value
  - comparison 44
- Measurand 2, 4
- Measurement result
  - comparison with a limit 32
- Measurement uncertainty 3
  - and within-lab reproducibility standard deviation 28
  - bias 21-23
  - comparative analyses 28
  - empirical approach 27
  - GUM-approach 14
  - inhomogeneity 21, 25
  - modeling approach 14
  - relevant contribution 15
  - rough estimation 28
  - sample preparation 25

- sampling 21, 25
- statement 45
- systematic deviation 21-23
- Type A contribution 16
- Type B contribution 16-18
- using precision data 28
- Mechanical strength 56
- Melt flow rate 88
- Melting characteristics
  - thermoplastics 60
- Melting enthalpy
  - precision data 56, 60
  - thermoplastics 60
- Melting peak 54
- Melting peak temperature
  - precision data 55
- Melt mass-flow rate 83, 88
  - example 92
  - precision data 89, 90
- Melt volume-flow rate 88
- Mercury
  - measurement principle 119
  - precision data 122, 124
- Metals
  - measurement principle 119
  - precision data 122-124
- Metrology 3
- MFR. See melt mass-flow rate
- Mini-interlaboratory comparison 29
- Modeling approach 14, 15
- Modulus of elasticity 56
- Molecular absorption coefficient 84
- Molecular weight 83
  - distribution 84
  - mass-average 83, 85, 86, 88
  - number-average 83, 85
  - precision data 85-88
  - viscosity-average 83, 91
  - z-average 83
- MVR. See melt volume-flow rate

**N**

- Nitrogen content
  - measurement principle 103
  - precision data 104

Normal distribution

- visual test 93

Number-average molecular weight.

See molecular weight

## O

Onset temperature 54

Outlier 10

Oxidative induction temperature

- determination 63

- heat flux curve 63

- interlaboratory comparison 64

- precision data 65, 66

- vs. oxidative induction time 66

Oxidative induction time

- determination 62, 63

- heat flux curve 63

- interlaboratory comparison 64

- precision data 64

- standard uncertainty 64

- vs. oxidative induction temperature 66

## P

Peak temperature

- melting 54

Phase transition 53

Plasticizer content

- determination 66

- measurement principle 104

- precision data 68, 69, 105

- TGA vs. wet chemistry 106

Polydispersity 83, 85

- precision data 88

Polymer content

- determination 66

- precision data 68

Precision 2-4

Precision data

- 2-butanone 131

- aluminum 122

- antioxidant 128, 129

- arsenic 122

- ash residue 68, 69, 111

- benzene 131

- bromine 124

- bromine content 101

- butyl acetate 131

- cadmium 122, 124

- carbon black content 68, 69

- chlorine content 101

- chromium 122, 124

- differential scanning calorimetry

55-61, 64-66

- dynamic mechanical analysis 73-75

- ethanol 131

- ethyl acetate 131

- glass transition temperature 55,

57-59, 75

- heavy metals 122-124

- high temperature SEC 88

- lead 122, 124

- loss modulus 73

- mass-average molecular weight 85,

87, 88

- melting enthalpy 56, 60

- melting peak temperature 55

- mercury 122, 124

- metals 122-124

- MFR 89, 90

- MFR half die 89

- MFR multi weight procedure 89

- nitrogen content 104

- number-average molecular weight

86-88

- overview 141, 142, 146

- oxidative induction temperature 65

- oxidative induction time 64

- plasticizer content 68, 69, 105

- polydispersity 88

- polymer content 68

- reaction enthalpy 56, 61

- reaction peak temperature 55

- residual solvent 131

- SEC-LS 87

- specific heat capacity 60

- storage modulus 73, 74

- sulfur content 102

- thermogravimetry 68

- toluene 131
- trace metals 122–124
- vinyl acetate content 108
- viscosity number 91
- water content 110
- wet chemistry 101, 102, 104, 105, 108, 110, 111
- XRF 124
- xylene 131
- zinc 122
- Primary sample 25
- Product
  - testing for conformity 31
- Proficiency test
  - bias estimation 22, 23
- Proficiency testing 5
- Proficiency test report 7
- Prospection 27

## R

- Random deviation 2, 16
- Random influence 16
- Ratio
  - critical 37
  - critical, data overview 142
- Rayleigh ratio 84
- Reaction enthalpy
  - epoxy resins 61
  - precision data 56, 61
- Reaction peak temperature
  - precision data 55
- Reference material 3, 27, 41, 84
- Reference procedure 3
- Reference value 3
  - compatibility 46
  - use under repeatability conditions 41
  - use under reproducibility conditions 41
- Rejection of materials 5, 47
- Relative standard uncertainty 38
  - mass-average molecular weight 85
  - number-average molecular weight 86
- Repeatability 9
- Repeatability conditions 6, 17
  - critical difference 40

- Repeatability standard deviation 6, 7, 9, 19, 36
  - data overview 146
  - example 135
  - inhomogeneity 26
- Reproducibility 9
- Reproducibility conditions 6
- Reproducibility standard deviation 6–9, 17, 19, 27, 36
  - data overview 141, 142, 146
  - number-average molecular weight 86
- Residual deviation 4
- Residual solvent
  - measurement principle 129
  - precision data 131
- Results
  - comparison 33
- RI detector 84, 85
  - size exclusion chromatography 83
- Robust evaluation 10

## S

- Sample preparation
  - chemical 26
  - physical 25, 26
- Sampling 21, 27
  - proficiency testing 26
  - uncertainty sources 26
- Sampling plan 27
- SEC. *See* size exclusion chromatography
- SEC-light scattering 83
- Second virial coefficient 84
- Significant difference 35
- Size exclusion chromatography 83
  - LS detector 86
- Soil analysis 27
- Specification check
  - example 75
- Specific heat capacity 59
  - and glass transition temperature 57
  - precision data 60
- Specific refractive index increment 84, 86

- Standard deviation
  - and MAD 46
  - between-lab 17, 19, 20, 36, 37
  - repeatability 19, 36
  - repeatability conditions 8, 17
  - reproducibility 19
  - reproducibility conditions 17
  - reproducibility 36
  - within-lab 20
- standard uncertainty
  - example 135
- Standard uncertainty 19, 20, 35
  - axis intercept 95
  - combined 15, 17
  - correction factor 133
  - failure analysis 43
  - intermediate conditions 43
  - intrinsic viscosity 94
  - melting enthalpy 61
  - oxidative induction time 64
  - relative 37
  - temperature by DSC 62
  - under repeatability conditions 20
- Static OIT. *See* oxidative induction time
- Storage modulus 71
  - determination 72
  - interlaboratory test plot 73
  - precision data 73, 74
  - systematic effect 73
- Sulfur content
  - measurement principle 102
  - precision data 102
- Systematic deviation 2, 16
  - correction of 3
  - estimation 22, 23
- Systematic effect 3, 4
  - antioxidant 128, 129
  - storage modulus 73
- T**
- Tailing 84
- Temperature by DSC
  - standard uncertainty 62
- Temperature measurement
  - DMA 72
  - DSC 55
- Test sample 25
- Tetrahydrofuran
  - mobile phase 85
- Thermal analysis 53
- Thermogravimetry
  - interlaboratory comparison 67
  - precision data 68
  - typical diagram 67
- Tolerance interval 17
- Toluene
  - precision data 131
- Traceability 1
- Trace metals
  - measurement principle 119
  - precision data 122-124
- Trueness 2, 3
- Trueness control 5
- True value 1
- Type A contribution 16
- Type B contribution 16-18
- U**
- Ubbelohde viscometer 90
- Uncertainty
  - expanded 16, 35
- UV detector 84
  - size exclusion chromatography 83
- V**
- Vinyl acetate content
  - measurement principle 106
  - precision data 108
- Viscosity detector 83
- Viscosity in solution 83
- Viscosity number 83, 90
  - example 94
  - precision data 91
  - standard uncertainty 91

**W**

Water content

- measurement principle *108*
- precision data *110*

Wet chemistry

- precision data *101, 102, 104, 105, 108, 110, 111*

Within-lab reproducibility standard deviation

- intermediate conditions *28*

Within-lab standard deviation *20*

**X**

X-ray fluorescence spectrometry *121*

- precision data *124*

Xylene

- precision data *131*

**Z**

Zinc

- measurement principle *119*
- precision data *122*