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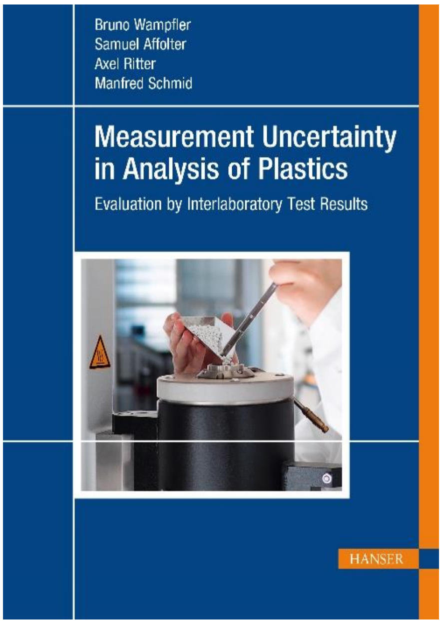

Sample Pages

Measurement Uncertainty in Analysis of Plastics

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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 calculated 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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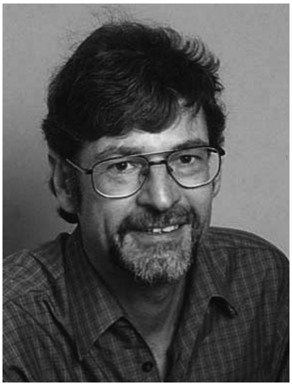

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About the Use of this Book

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 dependance 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

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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.

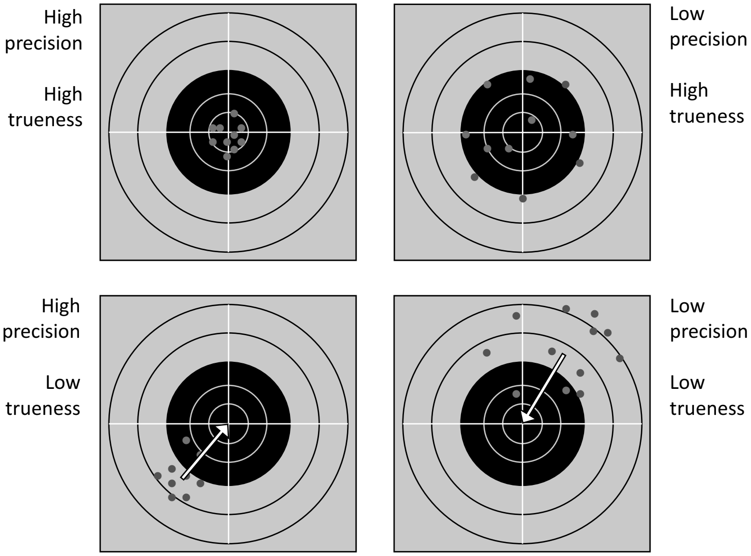

Figure 1.1 Illustration of precision and trueness using the target model
Note: High precision corresponds to small random deviation and vice versa. The arrows mark the amount by which the systematic deviation can be corrected.

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].

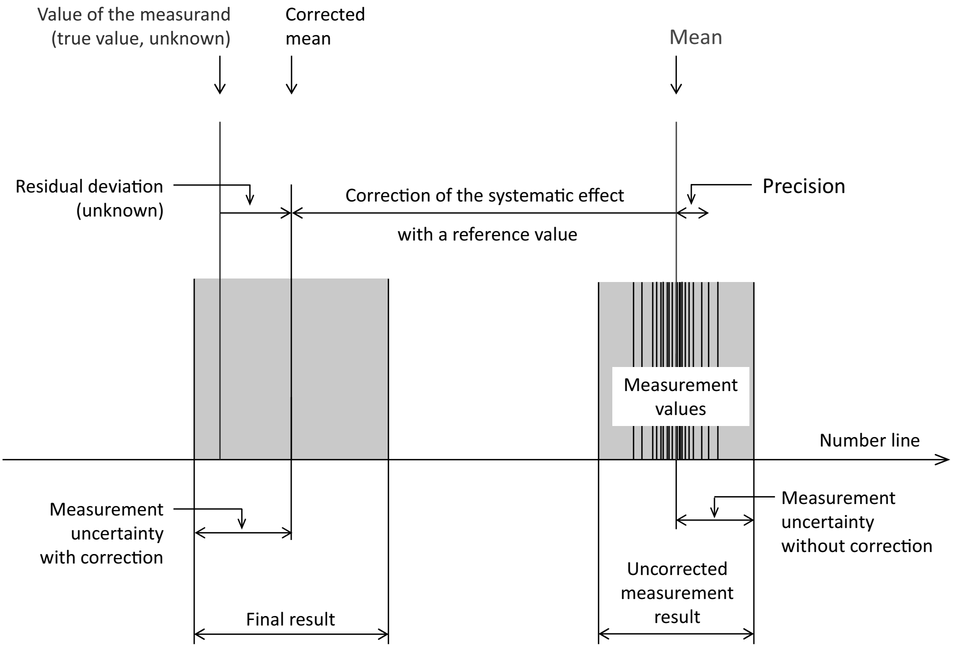

Figure 1.2 Modern metrology focuses exclusively on observable values: measurement values, measurable systematic effects, measurement uncertainty

■ 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.

$$s_R = \sqrt{s_L^2 + s_r^2} \tag{1.1}$$

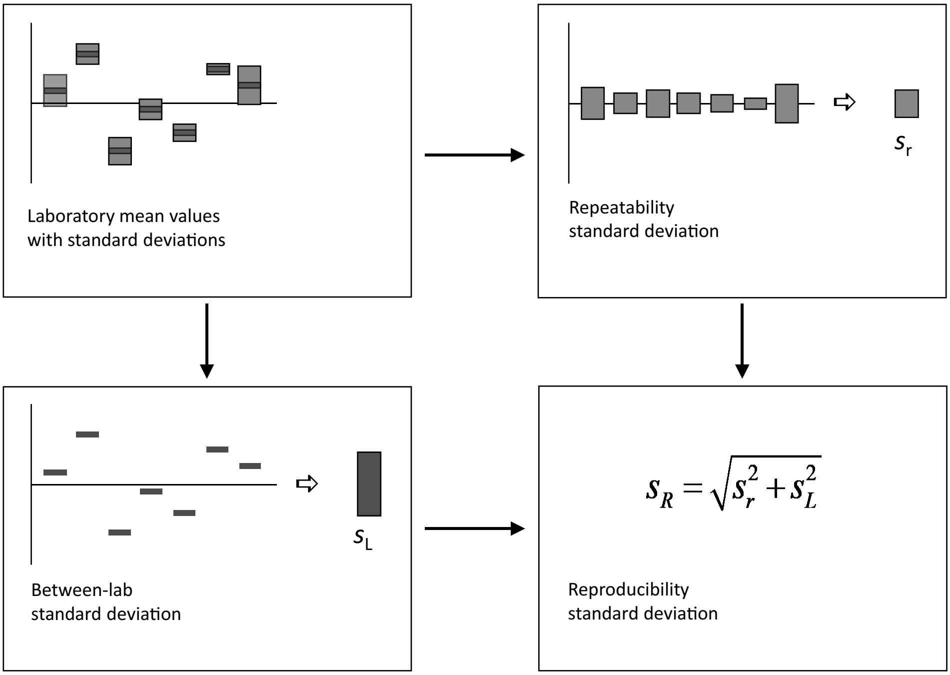

Figure 1.3 Relationship between the key parameters from interlaboratory comparisons

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).

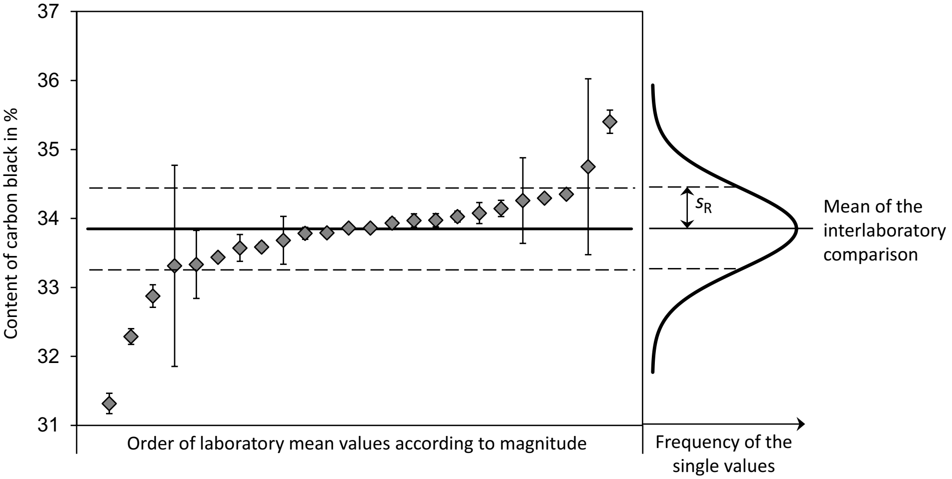

Figure 1.4 Typical interlaboratory test plot based on the example of the determination of carbon black in plastics
If the frequency of the single values is plotted to the right, a normal distribution with the reproducibility standard deviation results.

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.

$$y_j = \frac{1}{n}\sum_{i=1}^{n} y_{ji} \tag{1.2}$$

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:

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