

Bruno Wampfler
Samuel Affolter
Axel Ritter
Manfred Schmid

Measurement Uncertainty in Analysis of Plastics

Evaluation by Interlaboratory Test Results



HANSER

Bruno Wampfler
Samuel Affolter
Axel Ritter
Manfred Schmid

Measurement Uncertainty in Analysis of Plastics

Evaluation by Interlaboratory Test Results

HANSER
Hanser Publishers, Munich

Bruno Wampfler, Luzern, Switzerland
Samuel Affolter, Buchs, Switzerland
Axel Ritter, Urnäsch, Switzerland
Manfred Schmid, St. Gallen, Switzerland



MIX
Papier aus verantwortungs-
vollen Quellen
FSC® C083411

Distributed by:
Carl Hanser Verlag
Postfach 86 04 20, 81631 Munich, Germany
Fax: +49 (89) 98 48 09
www.hanserpublications.com
www.hanser-fachbuch.de

The use of general descriptive names, trademarks, etc., in this publication, even if the former are not especially identified, is not to be taken as a sign that such names, as understood by the Trade Marks and Merchandise Marks Act, may accordingly be used freely by anyone. While the advice and information in this book are believed to be true and accurate at the date of going to press, neither the authors nor the editors nor the publisher can accept any legal responsibility for any errors or omissions that may be made. The publisher makes no warranty, express or implied, with respect to the material contained herein.

The final determination of the suitability of any information for the use contemplated for a given application remains the sole responsibility of the user.

All rights reserved. No part of this book may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying or by any information storage and retrieval system, without permission in writing from the publisher.

© Carl Hanser Verlag, Munich 2022
Editor: Mark Smith
Production Management: Cornelia Speckmaier
Cover concept: Marc Müller-Bremer, www.rebranding.de, Munich
Cover image: © Carl Hanser Verlag GmbH & Co. KG
Cover design: Max Kostopoulos
Typesetting: Eberl & Koesel Studio GmbH, Altusried-Krugzell, Germany
Printed and bound by CPI books GmbH, Leck
Printed in Germany

ISBN: 978-1-56990-812-9
E-Book ISBN: 978-1-56990-813-6

Contents

Preface	VII
The Authors	IX
About the Use of this Book	XIII
List of Abbreviations	XVII
Equation Symbols	XXI
Glossary	XXIII
1 Introduction to Measurement Uncertainty	1
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
2 Evaluation of the Measurement Uncertainty	13
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
3	Uncertainty Data in Practical Application	31
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
4	Thermal Analysis	53
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 Δc_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
5	Determination of the Molecular Weight	83
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 [η] – Estimation of the Standard Uncertainty	94
6	Quantification of Main and Secondary Components	99
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
7	Quantification of Trace Components	119
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
8	Summary	139
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
Index	149

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.

The Authors



Dr. Bruno Wampfler

- Apprenticeship as air-conditioning technician, planning of ventilation and air-conditioning systems in several companies (1964–1976)
- Studies in chemistry at the University of Geneva and ETH Zurich (PhD in inorganic chemistry)
- Scientific assistant in a state office for environmental protection (1985–1986)
- Project manager in process and product optimization at Empa St. Gallen, Switzerland, followed by various management functions (1986–2010)
- Initiator and owner of the Eureka project UncertaintyManager (software for the evaluation of the measurement uncertainty in analytical chemistry)
- Retired since 2011

**Prof. Dr. Samuel Affolter**

- Studies in chemistry at ETH Zurich (PhD in organometallic chemistry)
- Head of chemical-analytical and physical-mechanical materials testing at Huber + Suhner, Herisau, Switzerland (1989–1994)
- Head of polymer analysis at Empa St. Gallen (1994–2001)
- Lecturer in chemistry and plastics technology at the NTB University of Applied Sciences, Buchs, Switzerland, head of the polymer laboratory at the Institute for Micro and Nanotechnology MNT (2001–2019)
- Head of polymer chemistry and lecturer in plastics technology at OST Eastern Switzerland University of Applied Sciences, IWK Institute for Materials Technology and Plastics Processing, Rapperswil, Switzerland (since 2019)

**Dr. Axel Ritter**

- Studies in chemistry at the Technical University of Munich (PhD in organic chemistry)
- Chemist at Empa St. Gallen in the fields of analytics and polymer chemistry, Laboratory of Advanced Functional Fibers and Textiles: project manager in product development (1989–2012)
- Chemist at EMS-EFTEC AG, Romanshorn, Switzerland, quality assurance and regulatory affairs (2012–2014)
- Chemist at intracosmed AG, Urnäsch, Switzerland, quality assurance and regulatory affairs (2014–2018)
- Chemist at Alpinamed AG, Freidorf, Switzerland, laboratory manager (since 2018)

**Dr. Manfred Schmid**

- Apprenticeship as chemistry laboratory technician at Metzeler Kautschuk AG, Munich
- Studies in chemistry at the University of Bayreuth, Germany (PhD in polymer chemistry)
- Activity in polyamide research at EMS-Chemie AG, Domat-Ems, Switzerland (1991–1997)
- Project manager in the fields of plastics analysis and biopolymers at Empa St. Gallen (1997–2008)
- Head of R&D in the field of selective laser sintering at inspire AG, St. Gallen (since 2008)

