
Quality

Assurance

of

Chemical

Measurements

JOHN KEENAN TAYLOR

Quality Assurance of Chemical Measurements

JOHN KEENAN TAYLOR



LEWIS PUBLISHERS, INC.

Library of Congress Cataloging-in-Publication Data

Taylor, John K. (John Keenan), 1912-
Quality assurance of chemical measurements.

Bibliography: p.

Includes index.

1. Chemical laboratories—Quality control.

I. Title.

QD51.T38 1987 542'.3 86-27334

ISBN 0-87371-097-5

3rd Printing 1988

2nd Printing 1987

**COPYRIGHT © 1987 by LEWIS PUBLISHERS, INC.
ALL RIGHTS RESERVED**

Neither this book nor any part may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, microfilming, and recording, or by any information storage and retrieval system, without permission in writing from the publisher.

LEWIS PUBLISHERS, INC.

121 South Main Street, P.O. Drawer 519, Chelsea, Michigan 48118

PRINTED IN THE UNITED STATES OF AMERICA

Preface

Chemical measurement data are often the basis for critical decisions on vital matters, ranging from the health of individuals, to the protection of the environment, to the production of safe, reliable, and useful products and services. Obviously, the data used for such purposes must be reliable, and there must be unequivocal evidence to prove it. The philosophy and procedures by which this is achieved and demonstrated are called quality assurance.

This book discusses the basic concepts of quality assurance as presented in a short course given by the author many times since 1979. It is based on the premise that a good understanding of the basic principles of chemical measurement is a necessary prerequisite to achieving accurate data and to designing and implementing a credible quality assurance program.

Credible data must be supported by probabilistic statements of the confidence that can be placed in it. This requires a systematic approach to measurement and to the attainment of statistical control of the measurement process by quality control procedures. The precision and accuracy of the data so produced can be evaluated by quality assessment techniques.

Not only the philosophy, but also practical approaches to quality assurance are discussed, and the statistical techniques vital to its various aspects are reviewed.

The book is written to provide guidance for the development of a credible quality assurance program and also for its implementation. The chapters are presented in a logical progression starting with the concept of quality assurance, the principles of good measurement, the principles of quality assurance, and the evaluation of measurement quality. Guidance is provided for the development of quality assurance programs and for the improvement of existing ones. Each chapter has a degree of independence so that it may be consulted, in isolation from the others, when its subject matter is of interest in a particular situation. An extensive appendix containing definitions of quality assurance terminology, a collection of useful statistical tables, outlines useful for guidance in the preparation of quality assurance program documents, study aids for those using the book for self instruction or as a text, and an extensive collection of abstracts of important quality assurance publications are also included. The abstracts also serve as the list for references cited in the text.

If the book achieves the above-mentioned objectives, it will have provided a valuable service to the producers and users of chemical measurement data.

However, it can serve another purpose as well—namely, in training analytical chemists. Most of modern analytical education is devoted to the theory and principles of measurement techniques, and such knowledge is a necessary foundation for reliable measurements. The present book supplements such information and provides guidance in the practice of the profession of analytical chemistry.

While the text focusses principally on chemical measurement, the author is confident that the material presented is widely applicable to the physical and biological sciences as well. The basic principles of measurement are the same, no matter what the subject area of application. In fact, he has developed quality assurance programs for high accuracy physical measurement and calibration programs that do not differ in kind, but only in detail, from the chemical programs described in this book. The biological scientist should also find the quality assurance principles enunciated useful in measurement programs.

Acknowledgments

The author is grateful to all of the excellent analytical chemists with whom he has been privileged to associate in various ways over many years, who have contributed to his education and have helped to mould his philosophy of good measurement. Unfortunately, most of them must go unnamed because of space limitations. The subject matter presented in the book is the result of the author's gleanings from many sources, including his long association with like-minded colleagues at the National Bureau of Standards (NBS), who have had measurement accuracy as their personal as well as institutional goals. He grew up under the tutelage of the late Dr. G.E.F. Lundell, one of the early deans of accurate chemical measurements. His concepts of the critical importance of sampling and the analytical sample were sharpened and increased by a year's sabbatical association with Professor Byron G. Kratochvil of the University of Alberta. His long personal involvement as a bench chemist, and later as a supervisor responsible for reference material analysis and certification, have provided practical insight to constructive planning and to the avoidance of measurement pitfalls.

The author was very fortunate to have worked under the late Leroy W. Tilton, who was a master metrologist and a pioneer in the application of statistics to experimental measurements. More recently, he has benefited from association with and guidance from the NBS Statistical Engineering Division, and especially from Mrs. Mary G. Natrella. His recent position as Coordinator for Quality Assurance of the NBS Center for Analytical Chemistry has provided the opportunity to put all of this past experience together in a systematic fashion as a quality assurance concept, which provides the substance for this book.



John K. Taylor is an analytical chemist of many years of varied experience. All of his professional life has been spent at the National Bureau of Standards, from which he recently retired after 57 years of service.

Dr. Taylor received his BS degree from George Washington University and MS and PhD degrees from the University of Maryland. At the National Bureau of Standards, he served first as a research chemist, and then managed research and development programs in general analytical chemistry, electrochemical analysis, microchemical analysis, and air, water, and particulate analysis. The development of reliable sampling plans was another area of interest. The development and certification of reference materials was a major activity throughout his career at NBS. For the past seven years, he coordinated the NBS Center for Analytical Chemistry's program in quality assurance, and conducted research activities to develop advanced concepts to improve and assure measurement reliability. He provided advisory services to other government agencies as part of his official duties.

As a part of his recent activities, he has developed a comprehensive short course—Quality Assurance of Chemical Measurements—that has been presented some 75 times to a cumulative audience of over 3200 persons.

Dr. Taylor has edited three books, and has written over 200 research papers in analytical chemistry, some 20 of which have dealt with various aspects of the quality assurance of measurements.

Dr. Taylor is the recipient of several awards for his accomplishments in analytical chemistry, including the Department of Commerce Silver and Gold Medal Awards. He is a past chairman of the Washington Academy of Sciences and the ACS Analytical Chemistry Division, and is currently chairman of ASTM Committee D 22 on Sampling and Analysis of Atmospheres.

Table of Contents

Preface	iii
CHAPTER 1. Introduction to Quality Assurance	1
CHAPTER 2. Precision, Bias, and Accuracy	7
Axioms	8
Corollaries	9
Sources of Error	9
Errors of Rounding	10
Influence of Uncertainty on Decision	10
CHAPTER 3. Statistical Control	13
CHAPTER 4. Statistical Techniques	15
Basic Requirements	15
Distributions	17
Statistics of Measurements	18
Estimation of Standard Deviation	20
Estimation of Standard Deviation from Replicate Measurements	21
Estimation of Standard Deviation from Duplicate Measurements	22
Estimation of Standard Deviation from the Range	23
Pooling Estimates of Standard Deviations	24
The Analysis of Variance	25
Do Two Estimates of Precision Differ?	25
What are the Confidence Limits for an Estimate of a Standard Deviation?	26
Confidence Interval for a Mean	27

Does a Measured Value Differ from an Expected Value?	28
Do the Means of Two Measured Values Disagree Significantly?	29
Statistical Tolerance Intervals	31
Pooling Means to Obtain a Grand Average	32
Outliers	33
Rejection for an Assignable Cause	34
Rule of the Huge Error	34
Statistical Tests	35
Dixon Test for Outlying Observations	35
Grubbs Test for Outlying Observations	36
Youden Test for Outlying Laboratories	37
Cochran Test for Extreme Values of Variance	38
Statistics of Control Charts	38
Control Limits	38
Central Line Considerations	38
Agreement With Established Value	38
Has the Central Line Changed?	39
Use of Random Number Tables	39
 CHAPTER 5. Chemical Analysis as a System	41
Systematic Approach to Analysis	41
Effective Problem Solving	41
 CHAPTER 6. The Model	45
Importance of a Model	45
Development of a Model	46
Data Quality Objectives	47
 CHAPTER 7. Planning	49
General Aspects of Planning	49
Development of an Experimental Plan	51
Content of a Measurement Plan	51
 CHAPTER 8. Principles of Sampling	55
Initial Considerations	55
Sampling Plan	58
Peer Review	59
Training	60
Sample Management	60
Problem of Subsampling	61
Critical Matters Related to Samples	61
Quality Assurance of Sampling	62

Sample Uncertainties	62
Stratification	63
Holding Time	63
Statistical Considerations in Sampling	64
Measurement Situations	64
Statistical Sampling Plan	65
Basic Assumptions	66
Guidance in Sampling	66
Cost Considerations	68
Minimum Size of Increments in a Well-Mixed Sample	68
Size of Sample in Segregated Materials	69
Acceptance Testing	70
Matrix-Related Sampling Problems	72
Sampling Gases	73
Sampling Liquids	73
Sampling Solids	74
Sampling Multiphases	74
 CHAPTER 9. Principles of Measurement	 75
Terminology	75
Measurement is a Comparison Process	77
Principles of Chemical Measurement	77
Figures of Merit	78
Precision	78
Sensitivity	79
Limit of Detection and Limit of Quantitation	79
Short-term and Long-term Standard Deviation	83
Bias	83
Selectivity	84
Other Considerations	84
Importance of an SOP	85
Ruggedness Testing	85
Standardization of Methods	87
Selection of Appropriate Methodology	90
Guidelines for Selecting Instrumentation	91
Internal vs External Services	92
 CHAPTER 10. Principles of Calibration	 95
What Needs to be Calibrated	96
Requirements for Calibration	96
Frequency of Calibration	97
Mode of Calibration	97
Linear Relationships	98

Tests for Linearity	101
Calibration Uncertainties	103
Intercalibration	106
Additional Remarks	106
 CHAPTER 11. Principles of Quality Assurance	 107
 CHAPTER 12. Principles of Quality Control	 111
Competence	111
Suitable Facilities and Equipment	112
Good Laboratory and Good Measurement Practices	112
Standard Operations Procedures	113
Distinction Between GLPs, GMPs, and SOPs	114
Protocols for Specific Purposes	115
Contents of a PSP	116
Other Quality Control Techniques	118
Inspection	118
Documentation	119
Training	120
The Quality Control System	121
 CHAPTER 13. Blank Correction	 123
Sources of Blanks	123
Control of Blanks	123
Evaluation of Blanks	124
Statistical Treatment of the Blank	125
Significance	126
 CHAPTER 14. Control Charts	 129
Format	129
Control Limits	131
Evaluating Control Limits	132
Control Samples	133
Frequency of Control Measurements	133
Identification of Population	136
Strategy of Use	136
Assignment of Uncertainty	138
Range Control Charts	139
Approach	139
Use of Range Control Charts	141
Subspan Range Control Charts	141
Range Performance Charts	141
Range Ratio Control Charts	143
Collateral Control Charts	144

Critical Collateral Measurement Control Charts	144
Recovery Control Charts	145
Other Useful Control Charts	145
Additional Remarks	145
Blinds vs Double Blinds	146
 CHAPTER 15. Principles of Quality Assessment	 147
Internal Techniques	147
External Techniques	149
Qualitative Identification	150
Other Techniques	150
 CHAPTER 16. Evaluation Samples	 153
Prime Requirements	153
Types of Evaluation Samples	153
Liquid Samples	155
Solid Samples	155
Gas Samples	155
Stability of Mixtures	156
Subsampling	156
Integrity of Evaluation Samples	157
 CHAPTER 17. Reference Materials	 159
Role of Reference Materials	159
Uses of Reference Materials	160
Certification of Reference Materials	163
 CHAPTER 18. Traceability	 165
Chemical Traceability	165
Standards Prepared by the Analyst	167
Standards Prepared by Others	167
Physical Standards	167
Reference Materials Produced by NBS	167
Reference Materials Produced by Others	168
Traceability of Analytical Results	169
Concept of the National Measurement System	169
 CHAPTER 19. Quality Audits	 173
Internal Audits	173
Internal Systems Audits	173
Internal Performance Audits	174
Mechanism	174
Corrective Actions	175
External Audits	175

Independent Audits	175
Forms	176
Personal Quality Assurance Profile	177
Laboratory Quality Assurance Profile	179
Quality Assurance Survey	181
Quality Assurance Practices Check List	182
Quality Assurance Training Profile	185
 CHAPTER 20. Quality Circles	187
Organization	187
Objectives	187
Operation	188
Reporting	189
Agenda	191
 CHAPTER 21. Validation	193
Validation of Samples	193
Validation of Methodology	193
Validation of Data	195
 CHAPTER 22. Reporting Analytical Data	197
Minimum Requirements	197
Data Limitations	198
Numerical Values	199
Limits of Uncertainty for Data	199
Significant Figures	200
Guidelines for Reporting Results of Measurements	202
Guidelines for Combining Data Sets	203
Arbitrary Reporting Procedures	203
Reporting Low-Level Data	203
Report Format	205
 CHAPTER 23. An Improved Approach to Performance	
Testing	209
Premises	209
Advance Estimation of Precision	210
Performance Testing Plan	211
Diagnosis	211
Feedback	212
Consensus Values	213
Statistical Treatment of Data	213
 CHAPTER 24. Correction of Errors and/or Improving Accuracy	215

Identification of Problems	215
Improvement of Performance	217
Editing Data	221
 CHAPTER 25. Laboratory Evaluation	 225
Generic Guidelines for Evaluation	225
Accreditation	226
Self-Evaluation	228
 CHAPTER 26. The Quality Assurance Program	 231
Approaches to Quality Assurance	231
Quality Assurance Policy	234
Planning for Quality Assurance	234
Development of a QA Program	236
Quality Assurance Manual	238
Federally Mandated Quality Assurance Programs	239
Public Health Service	239
Food & Drug Administration	241
Environmental Protection Agency	242
Nonfederally Mandated Quality Assurance Programs	243
Quality Assurance for Measurement Programs	244
Relating Personnel to Quality Assurance	244
 Appendix A. Terminology Used in Quality Assurance	 245
 Appendix B. Quality Assurance Program Documentation	 255
B.1 Example Quality Assurance Program Document	255
B.2 Outline for Use in Preparing an SOP for a Measurement Method	262
B.3 Outline for Use in Preparing an SOP for Calibration	263
B.4 Outline for Use in Preparing a GLP or GMP	263
 Appendix C. Statistical Tables	 265
C.1 Use of Range to Estimate Standard Deviation	265
C.2 Z-Factors for Two-Sided Confidence Intervals for the Normal Distribution	266
C.3 Student t Distribution	267
C.4 Factors for Computing Two-Sided Confidence Intervals for ξ	268
C.5 Factors for Computing Two-Sided Confidence Intervals for a Normal Distribution	269
C.6 Critical Values for the F Test	269
C.7 Values for Use in the Dixon Test for Outliers	270

C.8	Values for Use in the Grubbs Test for Outliers	271
C.9	Values for Use in the Youden Test for Outliers	272
C.10	Values for Use in the Cochran Test for Extreme Variance	273
C.11	Short Table of Random Numbers	274
Appendix D.	Study Aids	277
D.1	Seventy-Five Terms Commonly Used in Discussing Quality Assurance	278
D.2	Seventy-Five Topics Related to Quality Assurance	279
D.3	Quality Assurance Problems	282
D.4	Subject-Problem Identification Template	288
Appendix E.	Annotated Bibliography of Selected Publications on Quality Assurance of Measurements	289
Index	325

List of Figures

Figure 1.1	Production process quality assurance	3
Figure 1.2	Measurement process quality assurance	3
Figure 2.1	Unbiased measurement processes	8
Figure 2.2	Biased measurement processes	8
Figure 2.3	Influence of analytical uncertainty	11
Figure 4.1	Some gross deviations from randomness	16
Figure 4.2	Typical distributions of the means of random measurements/samples	18
Figure 4.3	Confidence intervals for sigma	19
Figure 4.4	Computed 50% confidence intervals for the mean	20
Figure 5.1	Chemical measurement system	42
Figure 5.2	Chemical problem solving	43
Figure 6.1	Items for consideration when developing a model	46
Figure 7.1	Items for consideration when planning a measurement program	50
Figure 8.1	Items for consideration when developing a sampling plan ..	56
Figure 8.2	Estimation of holding time	64
Figure 9.1	Basic statistics for a method of measurement	79
Figure 9.2	Useful range for a method of measurement	80
Figure 9.3	Uncertainty of measurement close to the limit of detection	82
Figure 9.4	Approaches that may be used to standardize methodology.	88
Figure 9.5	Procedures used for collaboratively testing a method of measurement	89
Figure 9.6	Steps that may be used when selecting methodology for a specific purpose	91
Figure 10.1	Linear fit of a theoretical relationship	99
Figure 10.2	Linear fit of a limited data set	100
Figure 10.3	Joint confidence ellipse for slope and intercept	101
Figure 10.4	Linear functional relationship when both X and Y axes are affected by measurement errors	102
Figure 10.5	Propagation of calibration uncertainty	104
Figure 10.6	Uncertainty of the spiking mode of calibration	105
Figure 11.1	Basic elements of quality assurance	108
Figure 12.1	Quality control by inspection	118
Figure 12.2	Quality control system	121

Figure 14.1 Typical control charts	130
Figure 14.2 X-bar control chart with warning limits and control limits .	130
Figure 14.3 Setting and revising control limits	133
Figure 14.4 Length of run concept for frequency of measuring control samples	134
Figure 14.5 Identification of rare events	137
Figure 14.6 Range control chart	140
Figure 14.7 Subspan control chart	142
Figure 14.8 Range performance chart	142
Figure 14.9 Range ratio control chart	143
Figure 15.1 The quality assessment system	151
Figure 17.1 Measurement compatibility by intercalibration, using an SRM	161
Figure 17.2 Interpreting SRM measurements	162
Figure 18.1 The national measurement system	170
Figure 20.1 Mode of operation of a quality circle	188
Figure 22.1 Rationale for combining data sets	204
Figure 24.1 Ishikawa's cause-effect diagram	216
Figure 24.2 Youden plot to identify measurement problems	219
Figure 24.3 Types of analytical bias	220
Figure 24.4 Template depicting sources of measurement blunders	221
Figure 24.5 Template depicting sources of measurement imprecision ...	222
Figure 24.6 Template depicting sources of measurement bias	223
Figure 25.1 Laboratory appraisal process	228
Figure 26.1 Building blocks for developing a laboratory quality assurance program	235