

# Principles of Environmental Sampling



*ACS Professional Reference Book*

# *Principles of Environmental Sampling*

---

Lawrence H. Keith, Editor

---



*ACS Professional Reference Book*

AMERICAN CHEMICAL SOCIETY 1988



Library of Congress Cataloging-in-Publication Data

Principles of environmental sampling/Lawrence H. Keith,  
editor.

p. cm.

Includes bibliographies and indexes.

ISBN 0-8412-1173-6. ISBN 0-8412-1437-9 (pbk.)

1. Pollution—Measurement. 2. Environmental  
chemistry. 3. Environmental monitoring. 4. Quality  
assurance.

I. Keith, Lawrence H., 1938–. II. American Chemical  
Society.

TD193.P75 1987

628.5'0287—dc19

87-22975

CIP

Copyright © 1988

American Chemical Society

All Rights Reserved. The appearance of the code at the bottom of the first page of each chapter in this volume indicates the copyright owner's consent that reprographic copies of the chapter may be made for personal or internal use or for the personal or internal use of specific clients. This consent is given on the condition, however, that the copier pay the stated per copy fee through the Copyright Clearance Center, Inc., 27 Congress Street, Salem, MA 01970, for copying beyond that permitted by Sections 107 or 108 of the U.S. Copyright Law. This consent does not extend to copying or transmission by any means—graphic or electronic—for any other purpose, such as for general distribution, for advertising or promotional purposes, for creating a new collective work, for resale, or for information storage and retrieval systems. The copying fee for each chapter is indicated in the code at the bottom of the first page of the chapter.

The citation of trade names and/or names of manufacturers in this publication is not to be construed as an endorsement or as approval by ACS of the commercial products or services referenced herein; nor should the mere reference herein to any drawing, specification, chemical process, or other data be regarded as a license or as a conveyance of any right or permission, to the holder, reader, or any other person or corporation, to manufacture, reproduce, use, or sell any patented invention or copyrighted work that may in any way be related thereto. Registered names, trademarks, etc., used in this publication, even without specific indication thereof, are not to be considered unprotected by law.

PRINTED IN THE UNITED STATES OF AMERICA

*Principles  
of  
Environmental Sampling*

## About the Editor



Lawrence H. Keith has been involved with the principles and problems of environmental chemistry for over 20 years. Beginning with the U.S. Environmental Protection Agency and continuing with Radian Corporation, he has contributed to environmental sampling and analysis involving method developments, the priority pollutant list, national drinking water surveys, chlorinated dioxin and dibenzofuran analyses, and many other similar programs. He is an author of over 50 papers and a dozen books encompassing the areas of environmental chemistry, expert systems, and chemical health and safety.

A member of the American Chemical Society (ACS) since college days, Dr. Keith has served as past chairman of the Environmental Chemistry Division and the Central Texas Section. He is an ACS delegate to the U.S. National Committee as part of the International Association for Water Pollution Research and Control; chairman of the ACS Committee on Environmental Improvement, Subcommittee on Environmental Monitoring and Analysis; and board member of the *Journal of Chemical Health and Safety*. At Radian Corporation in Austin, TX, Dr. Keith serves as a Senior Program Manager and Principal Scientist.

---

## Preface

---

**T**he goal of this book is to ensure consideration of the many variables and special techniques that are needed to plan and execute reliable sampling activities. Specific needs will dictate which techniques are actually incorporated in sampling plans and which are rejected; the key point is to be certain that those variables and techniques not selected were rejected because of the sampling goals rather than because of being overlooked.

Obtaining reliable environmental samples is a difficult process. Generally, the objective is to take representative samples of a heterogeneous and changing piece of our world in order to analyze for components that constitute a very tiny fraction of the samples (often at or below the parts-per-billion level). Other complicating factors are that the matrix is usually very complex, thereby facilitating analytical interferences such as masking and false positives. And once the sample is taken, other interferences can be introduced during transport or preservation. Furthermore, the analytes of interest are sometimes unstable. No wonder sampling is often considered to be the weakest link in the chain of planning–sampling–analysis–reporting activities.

This discussion shows that the reliability of the overall data cannot be greater than that of the reliability of the weakest part of the chain of events constituting an environmental sampling and analysis effort. What good is a precise analytical report if the samples are not representative of their source?

The American Chemical Society (ACS) Committee on Environmental Improvement recognized this problem and sponsored a symposium upon which this book is based, in conjunction with the Divisions of Agrochemistry, Analytical Chemistry, and Environmental Chemistry, to bring together a distinguished group of experienced scientists to present the benefits of their knowledge in this field. The group was charged with presenting their advice and recommendations on *what* should be considered when planning an environmental sampling task. This information is different from that on *how* to conduct environmental sampling, which is very detailed and specific depending on the objectives. However, some procedures almost always should be followed, and these do represent “how to” recommendations for conducting specific tasks.

Certain principles of planning, sample design, and quality control prevail over all the special considerations that matrix variations impose. These principles are discussed in the first section. Special matrix requirements (e.g., sampling equipment and techniques, and preservation) are then discussed along

with the principles of sampling that involve them. These topics are discussed in sections involving water; air and stacks; biota; and solids, sludges, and liquid wastes.

This book also serves as the basis for an ACS short review on the subject. This review will not be as detailed as this work and will be a companion to the ACS short review "Principles of Environmental Analysis" (*Anal. Chem.* **1983**, *55*, 2210–2218).

LAWRENCE H. KEITH

---

# Contents

---

Contributors xv

Preface xxiii

## *Planning and Sample Design*

1. Overview of the Sampling Process 3  
Michael J. Barcelona  
*Review of the Literature* 4  
*Elements of Environmental Sampling Protocols* 10
2. Sampling for Tests of Hypothesis When Data Are Correlated in Space and Time 25  
Leon E. Borgman and William F. Quimby  
*Model Assumptions* 27  
*Important Considerations* 30  
*Advantages and Disadvantages* 32  
*Hypothesis Testing* 35  
*Hypothesis Testing within the Random Sampling Framework* 38  
*Covariance Structure for Geostatistical Procedures* 38  
*Some Approximate Nonparametric Tests for Geostatistical Data* 40  
*Abbreviations and Symbols* 42
3. Nonparametric Geostatistics for Risk and Additional Sampling Assessment 45  
Andre G. Journel  
*Probabilistic Assessment of Uncertainty* 46  
*Spatial Distributions* 50  
*Determination of the Cumulative Distribution Function*  
*Uncertainty Model* 53  
*Criteria for Estimation of the Unknown* 57  
*Risk and Additional Sampling Assessment* 61  
*Summary* 70  
*Abbreviations and Symbols* 71



4. Geostatistical Approaches to the Design of Sampling Regimes 73  
     George T. Flatman, Evan J. Englund, and Angelo A. Yfantis  
     *Geostatistics* 74  
     *Random or Spatial Variables* 74  
     *Semivariograms for Quantifying Spatial Correlation* 75  
     *Sample Support and Estimation Blocks* 78  
     *Primary or Semivariogram Sampling* 78  
     *Secondary or Map-Making Sampling* 80
5. Defining Quality Assurance and Quality Control Sampling Requirements: Expert Systems as Aids 85  
     Lawrence H. Keith, M. Timothy Johnston, and David L. Lewis  
     *Knowledge Engineering* 86  
     *The User Interface* 87  
     *Statistical Calculations* 90  
     *The Expert System in Operation* 91  
     *Directions for Further Research* 96

### *Quality Assurance and Quality Control*

6. Defining the Accuracy, Precision, and Confidence Limits of Sample Data 101  
     John K. Taylor  
     *Data Requirements* 102  
     *Statistical Considerations* 104  
     *Quality Assurance of Sampling* 105  
     *Conclusion* 106  
     *Abbreviations and Symbols* 107
7. Defining Control Sites and Blank Sample Needs 109  
     Stuart C. Black  
     *Blank Selection* 109  
     *Control Selection* 112  
     *Conclusion* 116
8. Assessing and Controlling Sample Contamination 119  
     David L. Lewis  
     *Sources of Contamination* 120

- Effects of Contamination* 123  
*Use of Blanks To Assess and Control Contamination* 125  
*Control Charts for Blanks* 130  
*Conclusions* 141  
*Abbreviations and Symbols* 143
9. Storage and Preservation of Environmental Samples 145  
 M. P. Maskarinec and R. L. Moody  
*Experimental Design* 146  
*Results and Discussion* 151  
*Abbreviations and Symbols* 154
10. Evaluating and Presenting Quality Assurance Sampling Data 157  
 Franklin Smith, Shrikant Kulkarni, Lawrence E. Myers,  
 and Michael J. Messner  
*Evaluating Quality Assurance Procedures for Collecting Sampling Data* 158  
*Presenting Quality Assurance Sampling Data* 164  
*Abbreviations and Symbols* 167

## Sampling Waters

11. Sampling Waters: The Impact of Sample Variability on Planning and Confidence Levels 171  
 U. M. Cowgill  
*Problems Associated with Sampling* 172  
*Nature of Samples and Problems Associated with Sample Collection* 180  
*Planning and Desired Confidence Level of Chemical Results* 188
12. Assessment of Measurement Uncertainty: Designs for Two Heteroscedastic Error Components 191  
 Walter S. Liggett  
*Measurement Error Model* 194  
*Multibatch Design for Error Assessment* 195  
*Estimation of the Error Properties* 196  
*Required Sample Sizes* 199  
*Some Generalizations* 205  
*Abbreviations and Symbols* 207

13. Modern Sampling Equipment: Design and Application 209  
Lorance H. Newburn  
*Water Sampling History* 210  
*Sampler Evaluations* 210  
*Ideal Sampler Features* 212  
*Sampler Characteristics* 214  
*User Knowledge* 216  
*Sample Intake Position* 216
14. Preservation Techniques for Organic and Inorganic Compounds in Water Samples 221  
Jerry Parr, Mark Bollinger, Owen Callaway, and Kathy Carlberg  
*General Practices for Minimizing Changes* 222  
*Preservation Process* 225  
*Coordination of Activities* 227  
*Holding-Time Considerations* 229
15. Sampling Groundwater Monitoring Wells: Special Quality Assurance and Quality Control Considerations 231  
Robert T. Kent and Katherine E. Payne  
*Hydrogeologic Controls on Groundwater Monitoring* 232  
*Sampling Strategy* 236  
*Laboratory Test Methods* 244  
*Summary* 245  
*Abbreviations* 245
16. Techniques for Sampling Surface and Industrial Waters: Special Considerations and Choices 247  
James E. Norris  
*Sediment Sampling* 248  
*Fish Sampling* 249  
*Sampling of Industrial Wastewater Discharges* 249  
*Sampling of Surface Waters: Receiving Streams* 251
17. Groundwater Sampling 255  
James S. Smith, David P. Steele, Michael J. Malley, and Mark A. Bryant  
*Groundwater Properties* 256  
*Techniques for Proper Groundwater Sampling* 257

## *Sampling Air and Stacks*

18. Effects of Environmental Measurement Variability  
on Air Quality Decisions 263  
John G. Watson  
*Types of Air Quality Decisions* 264  
*Air Quality Models* 265  
*Uses of Measurements in Models* 267  
*Quantifying Uncertainty* 268  
*Using Uncertainty in Making Decisions* 271  
*Conclusions and Future Research* 273
19. Airborne Sampling and In Situ Measurement of Atmospheric  
Chemical Species 275  
Roger L. Tanner  
*Separation of Phases* 276  
*Sampling of Condensed Phases* 277  
*Continuous Gas-Phase Techniques* 278  
*Continuous Aerosol Techniques* 281  
*Time Resolution Considerations* 282  
*Comparison of Real-Time and Integrative Measurements* 283
20. Sampling for Organic Compounds 287  
John B. Clements and Robert G. Lewis  
*Volatility* 288  
*Volatile Organic Compounds* 288  
*Semivolatile Organic Compounds* 292  
*Nonvolatile Organic Compounds* 294
21. Aerometric Measurement Requirements for Quantifying Dry  
Deposition 297  
B. B. Hicks, T. P. Meyers, and D. D. Baldocchi  
*Needs for Intensive (Research) Measurement* 299  
*Needs for Routine Measurement (Monitoring)* 303  
*Conclusions* 310  
*Abbreviations and Symbols* 311  
*Appendix—Summary of Existing Networks Providing Data on Dry  
Deposition in the United States* 312

22. Quality Control Infusion into Stationary Source Sampling 317

James A. Peters

*Data Quality Objectives* 318

*Source Types and Compositions* 319

*Hazardous Air Pollutants* 321

*Reporting and Documentation* 328

*Abbreviations* 332

## *Sampling Biota*

23. Coping with Sampling Variability in Biota: Percentiles and Other Strategies 337

Richard Albert and William Horwitz

*Proper Sampling* 339

*Variance and Confidence Intervals* 343

*Confidence Intervals for Percentile Estimates* 347

*Conclusion* 349

*Abbreviations and Symbols* 350

*Appendix* 351

24. Sample Size: Relation to Analytical and Quality Assurance and Quality Control Requirements 355

John B. Bourke, Terry D. Spittler, and Susan J. Young

*Preliminary Considerations* 355

*Distribution* 356

*Sample Size* 357

*Size Reduction* 358

*Case History* 359

*Current Study* 360

25. Composite Sampling for Environmental Monitoring 363

Forest C. Garner, Martin A. Stapanian, and Llewellyn R. Williams

*Potential Advantages* 364

*Potential Limitations* 365

*Composite Sampling for Classification* 366

*Reducing Variance* 370

*Increasing Sensitivity* 371

*Achieving Confidentiality* 371

|                                  |     |
|----------------------------------|-----|
| <i>Discussion</i>                | 372 |
| <i>Abbreviations and Symbols</i> | 373 |

## 26. Considerations for Preserving Biotic Samples 375

Terry D. Spittler and John B. Bourke

|                                         |     |
|-----------------------------------------|-----|
| <i>Timing of Sample Movement</i>        | 376 |
| <i>Visual Clues</i>                     | 376 |
| <i>Component Segregation</i>            | 377 |
| <i>Necessary Homogeneous Reductions</i> | 377 |
| <i>Knowledge of the Analyte</i>         | 377 |
| <i>Containers and Stability</i>         | 378 |
| <i>Storage Stability Assessment</i>     | 379 |
| <i>Packing and Transport</i>            | 380 |

## *Sampling Solids, Sludges, and Liquid Wastes*

## 27. Sampling Variability in Soils and Solid Wastes 385

Elly K. Triegel

|                                               |     |
|-----------------------------------------------|-----|
| <i>Sources of Variability</i>                 | 386 |
| <i>Goals of the Sampling Program</i>          | 387 |
| <i>Ranking of Variables</i>                   | 388 |
| <i>Design of the Sampling Plan</i>            | 389 |
| <i>Sampling Method</i>                        | 391 |
| <i>Significance of the Observed Variation</i> | 392 |
| <i>Increasing the Level of Confidence</i>     | 393 |

## 28. Relations of Sampling Design to Analytical Precision Estimates 395

Larry J. Holcombe

|                                    |     |
|------------------------------------|-----|
| <i>Pilot Study</i>                 | 397 |
| <i>Variance Component Analysis</i> | 401 |
| <i>Sampling Designs</i>            | 401 |
| <i>Conclusions</i>                 | 405 |
| <i>Abbreviations and Symbols</i>   | 406 |

## 29. Preservation Techniques for Samples of Solids, Sludges, and Nonaqueous Liquids 409

Larry I. Bone

|                                    |     |
|------------------------------------|-----|
| <i>Prior Planning Is Essential</i> | 410 |
|------------------------------------|-----|

*Standard Preservation Techniques* 411

*Preservation of Samples of Volatile Organic Compounds* 412

30. Sampling and Analysis of Hazardous and Industrial Wastes: Special Quality Assurance and Quality Control Considerations 415

Larry P. Jackson

*Institutional Problems* 416

*Technical Problems* 418

*Abbreviations* 423

## *Glossary and Indexes*

Glossary 427

Affiliation Index 435

Subject Index 435

---

## Contributors

---

- Albert, Richard      page 337  
*Center for Food Safety and Applied Nutrition*  
*Food and Drug Administration*  
*Washington, DC 20204*
- Baldocchi, D. D.      page 297  
*Atmospheric Turbulence and Diffusion Division*  
*National Oceanic and Atmospheric Administration*  
*Oak Ridge, TN 37831*
- Barcelona, Michael J.      page 3  
*Aquatic Chemistry—Water Survey Division*  
*Illinois Department of Energy and Natural Resources*  
*Champaign, IL 61820-7495*
- Black, Stuart C.      page 109  
*Environmental Monitoring Systems Laboratory*  
*U.S. Environmental Protection Agency*  
*Las Vegas, NV 89114*
- Bollinger, Mark      page 221  
*Rocky Mountain Analytical Laboratory*  
*A Division of Enseco, Inc.*  
*4955 Yarrow Street*  
*Arvada, CO 80002*
- Bone, Larry I.      page 409  
*Dow Chemical Company*  
*Baton Rouge, LA 70816*
- Borgman, Leon E.      page 25  
*Statistics Department*  
*University of Wyoming*  
*Laramie, WY 82071*



Bourke, John B.      pages 355, 375  
*Analytical Laboratories*  
*New York State Agricultural Experiment Station*  
*Cornell University*  
*Geneva, NY 14456*

Bryant, Mark A.      page 255  
*Harding Lawson Associates*  
*5580 Havana Street, Suite 5A*  
*Denver, CO 80239*

Callaway, Owen      page 221  
*Rocky Mountain Analytical Laboratory*  
*A Division of Enesco, Inc.*  
*4955 Yarrow Street*  
*Arvada, CO 80002*

Carlberg, Kathy      page 221  
*Rocky Mountain Analytical Laboratory*  
*A Division of Enesco, Inc.*  
*4955 Yarrow Street*  
*Arvada, CO 80002*

Clements, John B.      page 287  
*Environmental Monitoring Systems Laboratory*  
*U.S. Environmental Protection Agency*  
*Research Triangle Park, NC 27711*

Cowgill, U. M.      page 171  
*Mammalian and Environmental Toxicology*  
*Dow Chemical Company*  
*Midland, MI 48674*

Englund, Evan J.      page 73  
*Exposure Assessment Research Division*  
*U.S. Environmental Protection Agency*  
*Las Vegas, NV 89114-5027*