Fundamentals of Environmental Sampling and Analysis

Chunlong (Carl) Zhang

University of Houston-Clear Lake
Fundamentals of Environmental Sampling and Analysis
Each generation has its unique needs and aspirations. When Charles Wiley first opened his small printing shop in lower Manhattan in 1807, it was a generation of boundless potential searching for an identity. And we were there, helping to define a new American literary tradition. Over half a century later, in the midst of the Second Industrial Revolution, it was a generation focused on building the future. Once again, we were there, supplying the critical scientific, technical, and engineering knowledge that helped frame the world. Throughout the 20th Century, and into the new millennium, nations began to reach out beyond their own borders and a new international community was born. Wiley was there, expanding its operations around the world to enable a global exchange of ideas, opinions, and know-how.

For 200 years, Wiley has been an integral part of each generation’s journey, enabling the flow of information and understanding necessary to meet their needs and fulfill their aspirations. Today, bold new technologies are changing the way we live and learn. Wiley will be there, providing you the must-have knowledge you need to imagine new worlds, new possibilities, and new opportunities.

Generations come and go, but you can always count on Wiley to provide you the knowledge you need, when and where you need it!

William J. Pesce
President and Chief Executive Officer

Peter Booth Wiley
Chairman of the Board
Fundamentals of Environmental Sampling and Analysis

Chunlong (Carl) Zhang
University of Houston-Clear Lake
To
My Parents

To My Wife Sue and
Two Sons
Richard and Arnold
Contents

Preface xvii

1. Introduction to Environmental Data Acquisition 1

1.1 Introduction 1
  1.1.1 Importance of Scientifically Reliable and Legally Defensible Data 2
  1.1.2 Sampling Error vs. Analytical Error During Data Acquisition 4

1.2 Environmental Sampling 5
  1.2.1 Scope of Environmental Sampling 5
  1.2.2 Where, When, What, How, and How Many 6

1.3 Environmental Analysis 6
  1.3.1 Uniqueness of Modern Environmental Analysis 7
  1.3.2 Classical and Modern Analytical and Monitoring Techniques 7

References 9

Questions and Problems 10

2. Basics of Environmental Sampling and Analysis 11

2.1 Essential Analytical and Organic Chemistry 11
  2.1.1 Concentration Units 11
  2.1.2 Common Organic Pollutants and Their Properties 14
  2.1.3 Analytical Precision, Accuracy, and Recovery 16
  2.1.4 Detection Limit and Quantitation Limit 17
  2.1.5 Standard Calibration Curve 18

2.2 Essential Environmental Statistics 20
  2.2.1 Measurements of Central Tendency and Dispersion 20
  2.2.2 Understanding Probability Distributions 21
  2.2.3 Type I and II Errors: False Positive and False Negative 25
## Contents

2.2.4 Detection of Outliers 26  
2.2.5 Analysis of Censored Data 28  
2.2.6 Analysis of Spatial and Time Series Data 29  

2.3 Essential Hydrology and Geology 30  
2.3.1 Stream Water Flow and Measurement 30  
2.3.2 Groundwater Flow in Aquifers 31  
2.3.3 Groundwater Wells 32  

2.4 Essential Knowledge of Environmental Regulations 35  
2.4.1 Major Regulations Administered by the U.S. EPA 35  
2.4.2 Other Important Environmental Regulations 35  

References 37  
Questions and Problems 39  

3. Environmental Sampling Design 45  

3.1 Planning and Sampling Protocols 45  
3.1.1 Data Quality Objectives 46  
3.1.2 Basic Considerations of Sampling Plan 48  

3.2 Sampling Environmental Population 49  
3.2.1 Where (Space) and When (Time) to Sample 49  
3.2.2 Obtain Representative Samples from Various Matrices 49  

3.3 Environmental Sampling Approaches: Where and When 52  
3.3.1 Judgmental Sampling 52  
3.3.2 Simple Random Sampling 53  
3.3.3 Stratified Random Sampling 54  
3.3.4 Systematic Sampling 56  
3.3.5 Other Sampling Designs 57  

3.4 Estimating Sample Numbers: How Many Samples are Required 61  

References 63  
Questions and Problems 63  

4. Environmental Sampling Techniques 69  

4.1 General Guidelines of Environmental Sampling Techniques 69  
4.1.1 Sequence of Sampling Matrices and Analytes 70  

viii Contents
## 4. Techniques for Sampling Various Media: Practical Approaches and Tips

- **4.2.1 Surface Water and Wastewater Sampling** 84
- **4.2.2 Groundwater Sampling** 86
- **4.2.3 Soil and Sediment Sampling** 89
- **4.2.4 Hazardous Waste Sampling** 90
- **4.2.5 Biological Sampling** 92
- **4.2.6 Air and Stack Emission Sampling** 92

## 5. Methodology and Quality Assurance/Quality Control of Environmental Analysis

- **5.1 Overview on Standard Methodologies** 98
  - **5.1.1 The U.S. EPA Methods for Air, Water, Wastewater, and Hazardous Waste** 98
  - **5.1.2 Other Applicable Methods: APHA/ASTM/OSHA/NIOSH/USGS/AOAC** 103
- **5.2 Selection of Standard Methods** 108
  - **5.2.1 Methods for Sample Preparation** 109
  - **5.2.2 Methods for Physical, Biological, and General Chemical Parameters** 111
  - **5.2.3 Methods for Volatile Organic Compounds (VOCs)** 112
  - **5.2.4 Methods for Semivolatile Organic Compounds (SVOCs)** 113
  - **5.2.5 Methods for Other Pollutants and Compounds of Emerging Environmental Concerns** 113
- **5.3 Field Quality Assurance/Quality Control (QA/QC)** 115
  - **5.3.1 Types of Field QA/QC Samples** 116
  - **5.3.2 Numbers of Field QA/QC Samples** 118
- **5.4 Analytical Quality Assurance/Quality Control** 118
  - **5.4.1 Quality Control Procedures for Sample Preparation** 118
  - **5.4.2 Quality Control Procedures During Analysis** 119
6. Common Operations and Wet Chemical Methods in Environmental Laboratories

6.1 Basic Operations in Environmental Laboratories
   6.1.1 Labware Cleaning Protocols for Trace Analysis
   6.1.2 Chemical Reagent Purity, Standard, and Reference Materials
   6.1.3 Volumetric Glassware and Calibration
   6.1.4 Laboratory Health, Safety, and Emergency First Aid
   6.1.5 Waste Handling and Disposal

6.2 Wet Chemical Methods and Common Techniques in Environmental Analysis
   6.2.1 Gravimetric and Volumetric Wet Chemical Methods
   6.2.2 Common Laboratory Techniques

6.3 Analytical Principles for Common Wet Chemical Methods
   6.3.1 Moisture in Solid and Biological Samples
   6.3.2 Solids in Water, Wastewater, and Sludge (TS, TSS, TDS, VS)
   6.3.3 Acidity, Alkalinity, and Hardness of Waters
   6.3.4 Oxygen Demand in Water and Wastewater (DO, BOD and COD)
   6.3.5 Oil and Grease in Water and Wastewater
   6.3.6 Residual Chlorine and Chloride in Drinking Water
   6.3.7 Ammonia in Wastewater
   6.3.8 Cyanide in Water, Wastewater and Soil Extract
   6.3.9 Sulfide in Water and Waste

References
Questions and Problems

7. Fundamentals of Sample Preparation for Environmental Analysis

7.1 Overview on Sample Preparation
   7.1.1 Purpose of Sample Preparation
   7.1.2 Types of Sample Preparation

References
Questions and Problems
7.2 Sample Preparation for Metal Analysis 162

7.2.1 Various Forms of Metals and Preparation Methods 162
7.2.2 Principles of Acid Digestion and Selection of Acid 163
7.2.3 Alkaline Digestion and Other Extraction Methods 165

7.3 Extraction for SVOC and Non-VOC from Liquid or Solid Samples 168

7.3.1 Separatory Funnel and Continuous Liquid–Liquid Extraction (LLE) 168
7.3.2 Solid Phase Extraction 171
7.3.3 Solid Phase Microextraction 173
7.3.4 Soxhlet and Automatic Soxhlet Extraction (Soxtec) 174
7.3.5 Ultrasonic Extraction 176
7.3.6 Pressured Fluid Extraction 177
7.3.7 Supercritical Fluid Extraction 177
7.3.8 Comparison and Selection of Organic Extraction Methods 178

7.4 Post-Extraction Clean-up of Organic Compounds 179

7.4.1 Theories and Operation Principles of Various Clean-up Methods 179
7.4.2 Recommended Clean-up Method for Selected Compounds 181

7.5 Derivatization of Non-VOC for Gas Phase Analysis 182

7.6 Sample Preparation for VOC, Air and Stack Gas Emission 183

7.6.1 Dynamic Headspace Extraction (Purge-and-Trap) 183
7.6.2 Static Headspace Extraction 184
7.6.3 Azeotropic and Vacuum Distillation 185
7.6.4 Volatile Organic Sampling Train 186

References 187

Questions and Problems 187

8. UV-Visible and Infrared Spectroscopic Methods in Environmental Analysis 190

8.1 Introduction to the Principles of Spectroscopy 191

8.1.1 Understanding the Interactions of Various Radiations with Matter 191
8.1.2 Origins of Absorption in Relation to Molecular Orbital Theories 193
8.1.3 Molecular Structure and UV-Visible/Infrared Spectra 200
8.1.4 Quantitative Analysis with Beer-Lambert’s Law 204

8.2 UV-Visible Spectroscopy 206
8.2.1 UV-Visible Instrumentation 206
8.2.2 UV-VIS as a Workhorse in Environmental Analysis 208

8.3 Infrared Spectroscopy 211
8.3.1 Fourier Transform Infrared Spectrometers (FTIR) 211
8.3.2 Dispersive Infrared Instruments (DIR) 213
8.3.3 Nondispersive Infrared Instruments (NDIR) 214
8.3.4 Applications in Industrial Hygiene and Air Pollution Monitoring 214

8.4 Practical Aspects of UV-Visible and Infrared Spectrometry 215
8.4.1 Common Tips for UV-Visible Spectroscopic Analysis 215
8.4.2 Sample Preparation for Infrared Spectroscopic Analysis 216

References 217
Questions and Problems 218

9. Atomic Spectroscopy for Metal Analysis 220

9.1 Introduction to the Principles of Atomic Spectroscopy 221
9.1.1 Flame and Flameless Atomic Absorption 221
9.1.2 Inductively Coupled Plasma Atomic Emission 225
9.1.3 Atomic X-ray Fluorescence 227

9.2 Instruments for Atomic Spectroscopy 227
9.2.1 Flame and Flameless Atomic Absorption 227
9.2.2 Cold Vapor and Hydride Generation Atomic Absorption 229
9.2.3 Inductively Coupled Plasma Atomic Emission 232
9.2.4 Atomic X-ray Fluorescence 233

9.3 Selection of the Proper Atomic Spectroscopic Techniques 235
9.3.1 Comparison of Detection Limits and Working Range 235
9.3.2 Comparison of Interferences and Other Considerations 236

9.4 Practical Tips to Sampling, Sample Preparation, and Metal Analysis 240

References 243
Questions and Problems 243
10. Chromatographic Methods for Environmental Analysis 246

10.1 Introduction to Chromatography 247
   10.1.1 Types of Chromatography and Separation Columns 247
   10.1.2 Common Stationary Phases: The Key to Separation 249
   10.1.3 Other Parameters Important to Compound Separation 251
   10.1.4 Terms and Theories of Chromatogram 254
   10.1.5 Use of Chromatograms for Qualitative and Quantitative Analysis 258

10.2 Instruments of Chromatographic Methods 258
   10.2.1 Gas Chromatography 258
   10.2.2 High Performance Liquid Chromatography (HPLC) 260
   10.2.3 Ion Chromatography 264
   10.2.4 Supercritical Fluid Chromatography 265

10.3 Common Detectors for Chromatography 266
   10.3.1 Detectors for Gas Chromatography 267
   10.3.2 Detectors for High Performance Liquid Chromatography 272
   10.3.3 Detectors for Ion Chromatography 274

10.4 Applications of Chromatographic Methods in Environmental Analysis 275
   10.4.1 Gases, Volatile, and Semivolatile Organics with GC 276
   10.4.2 Semivolatile and Nonvolatile Organics with HPLC 278
   10.4.3 Ionic Species with IC 278

10.5 Practical Tips to Chromatographic Methods 279
   10.5.1 What Can and Cannot be Done with GC and HPLC 279
   10.5.2 Development for GC and HPLC Methods 280
   10.5.3 Overview on Maintenance and Troubleshooting 281

References 284

Questions and Problems 285

11. Electrochemical Methods for Environmental Analysis 289

11.1 Introduction to Electrochemical Theories 290
   11.1.1 Review of Redox Chemistry and Electrochemical Cells 290
   11.1.2 General Principles of Electroanalytical Methods 292
   11.1.3 Types of Electrodes and Notations for Electrochemical Cells 295