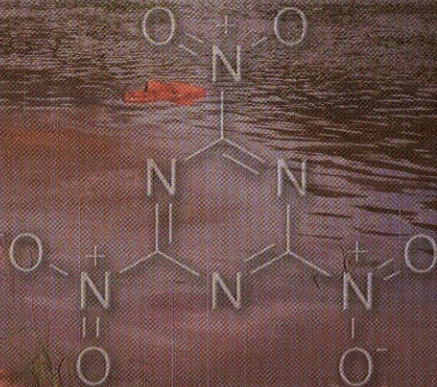


# Handbook of Environmental Analysis

Second Edition

Chemical Pollutants in  
Air, Water, Soil, and Solid Wastes



Pradyot Patnaik



CRC Press  
Taylor & Francis Group

# Contents

List of Tables	xxiii
Preface	xxvii
Preface to the First Edition	xxix
Acknowledgments	xxxi
Author	xxxiii
Glossary of Terms: Units, Conversions, and Abbreviations	xxxv

## PART I Analytical Techniques

1. Introduction	3
2. Precision and Accuracy of Analysis	7
Quality Assurance and Quality Control in Environmental Analysis	7
Precision and Accuracy	8
Control Charts	17
3. Analysis of Organic Pollutants by Gas Chromatography	21
Selection of Column	22
Detectors	25
Calibration	26
Calculations	27
External Standard Calibration	27
Alternative Calculation	29
Internal Standard Method	29
Routine Analysis	30
4. Analysis of Organic Pollutants by Gas Chromatography/Mass Spectrometry	31
Terms and Definitions	31
Application of Mass Spectrometry	32
Interpretation of Mass Spectra	33
Number of Carbon Atoms	35

“Nitrogen Rule”	36
Index of Hydrogen Deficiency	36
Determination of Molecular Formula	36
Chemical Ionization	38
Limitation of GC/MS Analysis	39
U.S. EPA Methods	39
Volatile Organics by Purge and Trap Method	40
Semivolatile Organics	41
Tuning	42
Compound Identification	44
Calibration	45
References	47
5. Extraction of Organic Pollutants and Sample Cleanup	49
Sample Extraction	49
Liquid–Liquid Extraction	49
<i>Solid Phase Extraction</i>	51
Soxhlet Extraction	51
Supercritical Fluid Extraction	52
Cleanup	52
Acid–Base Partitioning	53
Alumina Column Cleanup	54
Silica Gel Cleanup	54
Florisil Column Cleanup	55
Gel-Permeation Cleanup	55
Sulfur Cleanup	55
Permanganate–Sulfuric Acid Cleanup	56
6. Titrimetric Analysis	57
<i>Acid–Base Titration</i>	58
Calculation	61
Oxidation–Reduction Titrations	64
Standardization of Oxidants	68
Reducing Agent	69
Oxidation–Reduction Indicators	70
Iodometric Titration	71
Role of Potassium Iodide	74
Reducing Agent	74
Standardization of $\text{Na}_2\text{S}_2\text{O}_3$	75
Starch Indicator	76
Argentometric Titration	77
Complexometric Titrations	80
<i>Potentiometric Titration</i>	82
End Point Detection	83
7. Colorimetric Analysis	85

8.	Analysis of Metals by Atomic Absorption and Emission Spectroscopy	89
	Atomic Spectroscopy: An Overview	90
	Sample Digestion for Metals	91
	Atomic Absorption Spectrometry	92
	Chelation–Extraction Method	94
	Hydride Generation Method	95
	Cold Vapor Method for Mercury Determination	95
	Accuracy in Quantitation	96
	Standard Addition	97
	Atomic Emission Plasma Spectroscopy	98
	Inductively Coupled Plasma Mass Spectrometry	98
9.	Ion-Selective Electrodes Analysis	103
	Environmental Sample Analysis	104
	Standard Calibration Method	105
	Standard Addition Method	106
	Sample Addition Method	108
10.	Application of High-Performance Liquid Chromatography in Environmental Analysis	109
11.	Ion Chromatography	115
	References	119
12.	Air Analysis	121
	Sampling Plan	121
	Air Sampling	122
	Direct Collection of Air	122
	Use of Adsorbent Tubes	123
	Air Sampling for Particulates and Inorganic Substances	124
	Flow Rate	125
	Chemical Analysis	125
	Calculation	126
13.	Application of Immunoassay Techniques in Environmental Analysis	131
	Extraction	133
	Calculation	133

## PART II Specific Classes of Substances and Aggregate Properties

14.	Aldehydes and Ketones	137
	Derivatization with 2,4-Dinitrophenylhydrazine	139
	Chromatographic Columns and Conditions	141
	Sample Collection and Holding Time	141
	Air Analysis	141

15. Alkalinity	145
Calculation	145
16. Bromide	147
<i>Phenol Red Colorimetric Method</i>	147
Procedure	148
Reagents	148
<i>Titrimetric Method</i>	148
Determination of Bromide Plus Iodide	149
Procedure	149
Determination of Iodide	150
Calculation	150
17. Chloride	153
<i>Mercuric Nitrate Titrimetric Method</i>	153
Procedure	154
Reagents	154
<i>Argentometric Titrimetric Method</i>	155
Procedure	155
Reagents	156
<i>Automated Ferricyanide Colorimetric Method</i>	156
Procedure	156
Reagents	157
<i>Gravimetric Determination of Chloride</i>	157
Procedure	157
Calculation	158
18. Cyanate	159
Calculation	159
Procedure	160
19. Cyanide, Total	161
<i>Silver Nitrate Titrimetric Method</i>	161
Procedure	162
Reagents	162
<i>Colorimetric Method</i>	162
Procedure	163
Preparation of Cyanide Standards and Calibration Curve	165
Reagents	166
Determination of Cyanide in Soil, Sediment, and Solid Waste	166
Cyanides in Aerosol and Gas	167
20. Cyanide Amenable to Chlorination	169
Procedure	169
Alternative Procedure	170
Reagents	171
21. Emerging Pollutants: Nonionic Surfactants—Alkylphenols and Their Ethoxylates	173
Structures	174

Sample Extractions and Analysis: General Discussion	175
SPE–LC/MS Method (Liquid Chromatography Tandem Mass Spectrometry (LC-MS/MS))	178
SPE–GC/MS Method	179
References	182
22. Emerging Pollutants: Organophosphate Flame Retardants, Plasticizers, and Lubricants	183
Analysis of Indoor Dust	188
References	188
23. Emerging Pollutants: Pharmaceuticals and Personal Care Products	191
U.S. EPA Method 1694	191
Summary of the Method	191
Sample Preparation	195
Sample Cleanup	201
LC-MS/MS Analysis	201
Qualitative Determination and Quantification	202
Quality Assurance/Quality Control	203
Sample Collection, Preservation, and Holding Time	204
References	204
24. Emerging Pollutants: Steroids and Hormones	207
Outline of the Procedure	207
Sample Collection, Preservation, and Storage	209
GC Conditions	210
MS Conditions	210
Calibration and Quantitation	211
Quality Control	215
References	215
25. Fluorides	217
Colorimetric SPADNS Method	217
Procedure	218
Automated Colorimetric Method	218
26. Haloacetic Acids	219
Alternative Methods	220
References	222
27. Halogenated Hydrocarbons	223
Solvent Extraction	225
Sample Collection and Preservation	228
Internal Standards/Surrogates and Tuning Compounds	229
Air Analysis	229

28. Hardness	233
Hardness Determinations	234
Calculation	234
Titration	234
29. Herbicides: Chlorophenoxy Acid	235
Analysis	235
Sample Extraction	235
Hydrolysis	236
Esterification	237
Gas Chromatographic Analysis	238
Air Analysis	240
30. Herbicides: Glyphosate	243
Water Analysis	243
HPLC Method	243
Sampling and Storage	244
Detection Limit	244
Miscellaneous Methods for Analysis of Glyphosate Residues in Water, Soil, Sludge, Fruit, and Vegetable Extracts	245
References	246
31. Hydrocarbons	247
Analysis	248
Total Petroleum Hydrocarbons	248
Gasoline Range Organics	249
Diesel Range Organics	250
32. Hydrocarbons, Polynuclear Aromatic	253
HPLC Columns and Conditions	255
GC Columns and Conditions	255
MS Conditions	255
Sample Extraction and Cleanup	255
Air Analysis	257
Reference	258
33. Nitrogen (Ammonia)	259
Sample Distillation	259
Reagents	260
Titrimetric Method	260
Reagents	261
Colorimetric Nesslerization Method	262
Procedure	262
Calculation	262
Reagents and Standards	263
Colorimetric Phenate Method	264
Procedure	264
Calculation	264
Reagents and Standards	265

Ion-Selective Electrode	266
Procedure	267
Reagents and Standards	268
34. Nitrogen (Nitrate)	269
Cadmium Reduction Method	269
Procedure	270
Apparatus, Reagents, and Standards	271
Miscellaneous Reduction Method	271
Nitrate Electrode Method	272
Procedure	272
Reagents	272
35. Nitrosamines	273
Extraction	274
Analysis	275
Air Analysis	275
References	277
36. Oil and Grease	279
Partition-Gravimetry Method	280
Partition-Infrared Method	281
Solid Phase Partition-Gravimetric Method	282
Hydrocarbons	283
Sample Collection and Preservation	284
References	284
37. Oxygen Demand, Biochemical	285
Graphical Calculation	287
Method	287
Measurement of Dissolved Oxygen	288
Iodometric or Winkler Method	288
Electrode Method	289
Kinetics of BOD Reaction	290
Reference	291
38. Oxygen Demand, Chemical	293
Sample Treatment	296
Colorimetric Analysis	297
39. Oxyhalides	299
Analysis of Oxyhalides by U.S. EPA Methods	299
U.S. EPA Method 300.1	299
U.S. EPA Method 317.0	301
Interference	301
Sample Collection, Preservation, and Storage	302
Quality Control	302
Miscellaneous Methods	303
References	303



40. Pesticides: Carbamate, Urea, and Triazine	305
Carbamate Pesticides	306
LC Columns	306
Chromatographic Conditions	307
Hydrolysis Conditions	307
Postcolumn Derivatization Conditions	308
Fluorometer Conditions	308
<i>Extraction</i>	308
Urea Pesticides	309
Column	310
Liquid Chromatograph	310
Mass Spectrometer	310
Precision and Accuracy	311
Triazine Pesticides	311
Sample Extraction	312
41. <i>Pesticides: Organochlorine</i>	315
Sample Extraction	315
Analysis	318
Air Analysis	322
References	322
42. Pesticides: Organophosphorus	323
Analysis of Aqueous and Solid Samples	324
Sample Extraction	327
<i>Air Analysis</i>	329
43. pH and Eh	331
Eh	333
44. Phenols	337
Extraction	338
Analysis	339
Derivatization	339
Air Analysis	342
45. Phosphorus	343
Analysis	343
Sample Presentation	343
Colorimetric Analysis	345
Interference	346
Calibration Standards	346
Ion Chromatography	346
46. Phthalate Esters	349
Air Analysis	351

47. Polychlorinated Biphenyls	353
Quantitation	355
Sample Extraction and Cleanup	356
Alternate Analytical Methods	357
Air Analysis	357
48. Polychlorinated Dioxins and Dibenzofurans	359
Analysis	359
Sample Extraction and Cleanup	360
Acid-Base Partitioning	360
Alumina Cleanup	360
Silica Gel Cleanup	361
Carbon Column Cleanup	361
GC/MS Analysis	361
Sample Preservation and Holding Time	362
References	362
49. Radioactivity	363
Units of Measurement	363
Instruments for Measuring Radioactivity	365
Gas-Flow Proportional Counters	365
Alpha Scintillation Counters	366
Liquid Scintillation Counters	366
Alpha Spectrometers	367
Gamma Spectrometers	368
Determination of Gross Alpha and Gross Beta Radioactivity	368
Evaporation Method	369
Gross Activity of the Sample	369
Activity of Dissolved and Suspended Matter	370
Activity of Semisolid Samples	371
Cociprecipitation Method for Gross Alpha Activity	372
Procedure	373
Specific Radionuclides	373
Radium	374
Precipitation Method and Alpha Counting	374
Precipitation and Emanation Method to Measure	
Radium as Radon-222	375
Sequential Precipitation Method	377
Measurement of Radium-224 by Gamma Spectroscopy	377
Radon	378
Uranium	379
Determination of Total Alpha Activity	379
Determination of Isotopic Content of Uranium Alpha Activity	380
Radioactive Strontium	381
Tritium	383
Radioactive Iodine	384
Precipitation Method	385

Ion-Exchange Method	386
Distillation Method	387
Radioactive Cesium	389
Preparation of Ammonium Phosphomolybdate, $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$	
Reagent Solution	390
References	390
50. Semivolatile Organic Compounds	393
Sampling and Storage	410
References	410
51. Silica	413
Gravimetric Method	413
Procedure	414
Ammonium Molybdate Colorimetric Method	414
Procedure	415
Reagent	416
52. Sulfate	417
Gravimetric Method	417
Interference	418
Procedure	418
Calculation	418
Turbidimetric Method	419
Procedure	419
Calculation	419
Reagents	419
53. Sulfide	421
Analysis of Sulfide in Water	422
Screening Test for Sulfide	422
Sample Pretreatment	423
Analysis of Dissolved Sulfide in Water	423
Iodometric Method	424
Procedure	424
Calculation	424
Reagents	425
Methylene Blue Colorimetric Method	426
Procedure	427
Methylene Blue Solution: Preparation and Standardization	428
Standardization	428
Reagents	429
54. Sulfite	431
Iodometric Method	431
Interference	432
Procedure	432
Calculation	432
Reagents	433

Colorimetric Method	433
Procedure	434
Calculation	435
Reagents	435
55. Surfactant: Anionic	437
Reagents	437
Analysis	439
Sample Analysis	439
Calculation	439
Interference	440
56. Thiocyanate	441
Colorimetric Method	441
Interference	441
Procedure	442
Calculation	442
<i>Reagents and Calibration Standards</i>	442
Spot Test for Thiocyanate	443
Procedure	443
Reagents	444
57. <i>Volatile Organic Compounds</i>	445
Water Analysis	445
Apparatus	446
GC and MS Conditions	447
Soil, Sediments, and Solid Wastes	448
U.S. EPA's SW Methods	448
Air Analysis	452
U.S. EPA Method TO-14A	454
U.S. EPA's Solid Wastes 846 Methods	458
NIOSH Method 2549	459
GC Column and Conditions	459
MS Conditions	459
References	462

### PART III Selected Individual Compounds

58. Acetaldehyde	467
Analysis of Aqueous Sample	467
Air Analysis	468
59. Acetone	469
Analysis of Aqueous Samples	469
Air Analysis	470
60. Acetonitrile	471
Analysis of Aqueous and Nonaqueous Samples	471
Air Analysis	472

61. Acrolein	473
Analysis of Aqueous and Nonaqueous Samples	473
Air Analysis	473
62. Acrylonitrile	475
Analysis of Aqueous and Nonaqueous Samples	475
Air Analysis	476
63. Aniline	477
Description	477
Analysis of Aqueous and Nonaqueous Samples	477
Air Analysis	478
64. Arsine	479
Air Analysis	479
65. Asbestos	481
Analysis	481
Analysis of Aqueous Samples	481
Air Analysis	482
66. Benzene	485
Analysis of Aqueous and Nonaqueous Samples	485
Air Analysis	486
67. Benzidine	487
Analysis of Aqueous and Nonaqueous Samples	487
68. Benzyl Chloride	489
Description	489
Analysis of Aqueous and Nonaqueous Samples	489
Air Analysis	490
69. 1,3-Butadiene	491
Air Analysis	491
70. Captan	493
Analysis of Aqueous and Nonaqueous Samples	493
71. Carbon Disulfide	495
Description	495
Analysis of Aqueous and Nonaqueous Samples	495
Air Analysis	495
72. Carbon Monoxide	497
Air Analysis	497
73. Carbon Tetrachloride	499
Analysis of Aqueous and Nonaqueous Samples	499
Air Analysis	499

74. Chloroacetic Acid	501
Analysis of Aqueous Samples	501
Air Analysis	502
75. Chlorobenzene	505
Analysis of Aqueous and Nonaqueous Samples	505
Air Analysis	506
76. Chloroform	507
Analysis of Aqueous and Nonaqueous Samples	507
Air Analysis	508
77. 2-Chlorophenol	509
Analysis of Aqueous and Nonaqueous Samples	509
Air Analysis	510
78. Cumene	511
Analysis of Aqueous and Nonaqueous Samples	511
Air Analysis	512
79. Cyanogen	513
Air Analysis (Suggested Method)	513
80. Cyanuric Acid	515
Analysis of Aqueous and Nonaqueous Samples	515
Air Analysis	516
81. Diazomethane	517
Air Analysis	517
82. Diborane	519
Air Analysis	519
83. Dichlorobenzene	521
Analysis of Aqueous and Nonaqueous Samples	521
Air Analysis	522
84. 1,1-Dichlorethylene	523
Analysis of Aqueous and Nonaqueous Samples	523
Air Analysis	523
85. 2,4-Dichlorophenol	525
Analysis of Aqueous and Nonaqueous Samples	525
Air Analysis	526
86. Diethyl Ether	527
Analysis of Aqueous Samples	527
Air Analysis	527

87.	2,4-Dinitrotoluene	529
	<i>Analysis of Aqueous and Nonaqueous Samples</i>	529
88.	2,6-Dinitrotoluene	531
	<i>Analysis of Aqueous and Nonaqueous Samples</i>	531
89.	Epichlorohydrin	533
	<i>Analysis of Aqueous and Nonaqueous Samples</i>	533
	Air Analysis	534
90.	Ethylbenzene	535
	<i>Analysis of Aqueous and Nonaqueous Samples</i>	535
	Air Analysis	536
91.	Ethyl Chloride	537
	<i>Analysis of Aqueous Samples</i>	537
	Air Analysis	537
92.	Ethylene Chlorohydrin	539
	<i>Analysis of Aqueous Sample</i>	539
	Air Analysis	539
93.	Ethylene Dibromide	541
	<i>Analysis of Aqueous and Nonaqueous Samples</i>	541
	Air Analysis	541
94.	Ethylene Glycol	543
	<i>Analysis of Aqueous and Nonaqueous Samples (Suggested Method)</i>	543
	Air Analysis	543
	Reference	544
95.	Ethylene Oxide	545
	Air Analysis	545
96.	Formaldehyde	547
	Water Analysis	547
	Air Analysis	547
97.	Freon 113	549
	<i>Analysis of Aqueous Samples</i>	549
	Air Analysis	549
98.	Hydrogen Cyanide	551
	<i>Analysis of Aqueous Samples</i>	551
	Air Analysis	551
	Reference	552
99.	Hydrogen Sulfide	553
	Air Analysis	553

100.	Hydroquinone	555
	Analysis of Aqueous and Nonaqueous Samples	555
	Air Analysis	555
101.	Isophorone	557
	Analysis of Aqueous and Nonaqueous Samples	557
102.	Methane	559
	Analysis of Aqueous Samples and Sludge Digester Gas	559
	Air Analysis	560
103.	Methyl Bromide	561
	Analysis of Aqueous Samples	561
	Air Analysis	561
104.	Methyl Chloride	563
	Analysis of Aqueous and Nonaqueous Samples	563
	Air Analysis	563
105.	Methylene Chloride	565
	Analysis of Aqueous and Nonaqueous Samples	565
	Air Analysis	565
106.	Methyl Iodide	567
	Analysis of Aqueous Samples	567
	Air Analysis	567
107.	Methyl Isobutyl Ketone	569
	Analysis of Aqueous and Nonaqueous Samples	569
	Air Analysis	570
108.	Methyl Isocyanate	571
	Air Analysis	571
109.	Methyl Methacrylate	573
	Analysis of Aqueous Samples	573
	Air Analysis	573
110.	Nitrobenzene	575
	Analysis of Aqueous and Nonaqueous Samples	575
	Air Analysis	575
111.	Nitrogen Dioxide	577
	Air Analysis	577
112.	Pentachlorophenol	579
	Analysis of Aqueous and Nonaqueous Samples	579
	Air Analysis	580
113.	Phosgene	581
	Air Analysis	581



114.	Pyridine	583
	Analysis of Aqueous and Nonaqueous Samples	583
	Air Analysis	584
115.	Pyrocatechol	585
	Analysis of Aqueous and Nonaqueous Samples	585
	Air Analysis	586
116.	Pyrogallol	587
	Analysis of Aqueous and Nonaqueous Samples	587
	Air Analysis	588
117.	Resorcinol	589
	Analysis of Aqueous and Nonaqueous Samples	589
	Air Analysis	590
118.	Stibine	591
	Air Analysis	591
119.	Strychnine	593
	Analysis of Aqueous and Nonaqueous Samples	593
	Air Analysis	594
120.	Styrene	595
	Analysis of Aqueous and Nonaqueous Samples	595
	Air Analysis	596
121.	Sulfur Dioxide	597
	Air Analysis	597
122.	Tetrachloroethylene	599
	Analysis of Aqueous and Nonaqueous Samples	599
	Air Analysis	600
123.	Tetraethyllead	601
	Analysis of Aqueous and Nonaqueous Samples	601
124.	Tetraethyl Pyrophosphate	603
	Analysis of Aqueous and Nonaqueous Samples	603
	Air Analysis	603
125.	Tetrahydrofuran	605
	Analysis of Aqueous Samples	605
	Air Analysis	606
126.	Toluene	607
	Analysis of Aqueous and Nonaqueous Samples	607
127.	Toluene-2,4-Diisocyanate	609
	Analysis of Aqueous and Nonaqueous Samples	609
	Air Analysis	610
	Reference	610

128.	<i>o</i> -Toluidine	611
	Analysis of Aqueous and Nonaqueous Samples	611
	Air Analysis	612
129.	1,1,1-Trichloroethane	613
	Analysis of Aqueous and Nonaqueous Samples	613
	Air Analysis	613
130	Trichloroethylene	615
	Analysis of Aqueous and Nonaqueous Samples	615
	Air Analysis	616
131.	2,4,6-Trichlorophenol	617
	Analysis of Aqueous and Nonaqueous Samples	617
	Air Analysis	618
132.	Vinyl Chloride	619
	Analysis of Aqueous Samples	619
	Air Analysis	619
133.	Xylene	621
	Analysis of Aqueous and Nonaqueous Samples	621
	Air Analysis	622
	Bibliography	625
	Appendix A: Some Common QC Formulas and Statistics	629
	Measurement of Precision	629
	Standard Deviation	629
	Relative Standard Deviation (RSD)	629
	Standard Error of Mean ( <i>M</i> )	630
	Relative Percent Difference (RPD)	630
	Measurement of Linearity of Data Points	630
	Correlation Coefficient ( $\gamma$ )	630
	Measurement of Accuracy	632
	Percent Spike Recovery by U.S. EPA Formula	632
	Percent Spike Recovery by Alternate Method	632
	Method Detection Limits for Organic Pollutants in Aqueous Samples	633
	Method Detection Limit (MDL)	633
	Appendix B: Sample Containers, Preservations, and Holding Times	635
	Appendix C: Preparation of Molar and Normal Solutions of Some Common Reagents	639
	Appendix D: Total Dissolved Solids and Specific Conductance:	
	Theoretical Calculations	641
	Total Dissolved Solids	641
	Conductivity	642

Appendix E: Characteristic Masses of Miscellaneous Organic Pollutants (Not Listed in Text) for GC/MS Identification	649
Appendix F: Volatility of Some Additional Organic Substances (Not Listed in Text) for the Purge and Trap Analysis	653
Appendix G: NIOSH Methods for Air Analysis	657
Appendix H: A Full List of NIOSH Analytical Methods for Indoor Air Analysis (Update 2006)	667
Appendix I: U.S. EPA Methods for Air Analysis	691
Appendix J: Inorganic Test Procedures for Analysis of Aqueous Samples: EPA, SM, and ASTM Reference Methods	697
Appendix K: U.S. EPA'S Analytical Methods for Organic Pollutants in Aqueous and Solid Matrices	705
Chemical Compound Index	731
CAS Index	755
Index	771