

Contents

Preface to First Edition	xvii
Preface to Second Edition	xix
Part I General principles and techniques	
1 Introduction	1
F.W. FIFIELD and P.J. HAINES	
1.1 Environmental science and analytical chemistry	3
1.2 Analytical chemistry	4
1.3 Overall analytical processes	6
1.3.1 Defining the aims of an analytical programme	7
1.3.2 Selection of an analytical method	7
1.3.3 Sampling, sample handling and pretreatment	7
1.3.4 Analytical measurements	10
1.3.5 Method validation and quality assurance	10
1.3.6 Data assessment and interpretation	11
1.3.7 Safety	11
2 Analytical environmental data: assessment and interpretation	13
F.W. FIFIELD	
2.1 Introduction	13
2.2 Basic concepts and definitions	13
2.2.1 True result	13
2.2.2 Population	14
2.2.3 Statistical sample	14
2.2.4 Error	14
2.2.5 Accuracy	14
2.2.6 Precision	15
2.2.7 The range, or spread of data	15
2.2.8 Distribution curves	16
2.2.9 The mean	16
2.2.10 The mode	16
2.2.11 The median	16
2.2.12 Degrees of freedom	17
2.2.13 Standard deviation	17
2.2.14 The variance	18
2.2.15 Confidence levels and confidence limits	18
2.3 The nature and origin of errors	18
2.3.1 Types of errors	19
2.4 Frequency distributions	21
2.4.1 Normal and Student <i>t</i> distributions	22
2.4.2 Other distributions	23
2.5 Assessment and interpretation of analytical results	23
2.5.1 Introduction	23
2.5.2 Data reliability	23

2.5.3	Precision comparisons	25
2.5.4	The assessment and comparison of means	27
2.5.5	Graphical methods	29
2.5.6	Detection limits	34
	Further reading	35
	Self-study exercises	35
	Answers	35
	<i>Chemical principles</i>	
	3 Chemical principles	36
	P.J. HAINES	
3.1	Introduction	36
3.1.1	Periodicity	38
3.1.2	Atomic spectra	39
3.1.3	Nature of the electron	40
3.1.4	Population of energy levels	43
3.2	Atomic orbitals and chemical bonds	43
3.2.1	Ionic bonds	43
3.2.2	Covalent molecules	45
3.2.3	Polyatomic molecules	47
3.2.4	Metal compounds and complexes	50
3.2.5	Chains, rings and networks	53
3.3	Molecular energy levels	57
3.3.1	Energy of assemblies of molecules	58
3.4	Enthalpies of formation and reaction	59
3.5	Entropy and free energy	60
3.6	Free energy and equilibrium	61
3.7	The effects of temperature	63
3.8	Application to equilibria	63
3.8.1	Phase equilibria	63
3.8.2	Ions in solution	64
3.8.3	Solubility	64
3.8.4	Acid-base equilibria	66
3.8.5	Oxidation-reduction equilibria	67
3.8.6	Electrochemical reactions	67
3.8.7	Complexation	69
3.9	Reaction kinetics	70
3.10	Examples of reaction kinetics	71
3.10.1	Radioactive reactions	71
3.10.2	Ionic reactions	72
3.10.3	Solid-state reactions	72
3.10.4	Photochemical reactions	72
3.11	Summary	73
	Further reading	73
	Self-study exercises	74
	Answers	74
	<i>Titrimetry and gravimetry</i>	
	4 Titrimetry and gravimetry	76
	F.W. FIFIELD	
4.1	Introduction	76
4.2	Titrimetry	76
4.2.1	Introduction	76
4.2.2	Acid-base titrations	78
4.2.3	Complexometric titrations	81
4.2.4	Redox titrations	86
4.3	Gravimetry	88
4.3.1	Principles	88

4.3.2 Gravimetric procedures	88
Further reading	90
5 Separation techniques	91
F.W. FIFIELD	
5.1 Introduction	91
5.2 Solvent extraction	91
5.2.1 Introduction	91
5.2.2 Solvent extraction of analytes from environmental samples	91
5.2.3 Separation of mixtures by solvent extraction	92
5.3 Chromatography	96
5.3.1 Introduction	96
5.3.2 Characteristics of chromatograms	97
5.3.3 High-performance liquid chromatography	100
5.3.4 Ion-exchange chromatography	103
5.3.5 Thin-layer and paper chromatography	106
5.3.6 Gas chromatography	108
5.4 Electrophoresis	112
5.4.1 Introduction	112
5.4.2 Capillary electrophoresis (CE)	112
5.5 Other separation techniques	115
5.5.1 Supercritical fluid chromatography (SFC)	115
5.5.2 Gel permeation chromatography (GPC)	115
5.5.3 Distillation and volatilisation	115
5.5.4 Precipitation	116
Further reading	116
Self-study exercises	116
Answers	117
6 General principles of spectrometry	118
P.J. HAINES	
6.1 Introduction	118
6.2 Energy levels	118
6.3 Types of transition	118
6.3.1 Lasers	119
6.4 Molecular dissociation	121
6.5 Electromagnetic radiation	122
6.6 The electromagnetic spectrum	124
6.7 Interaction of species with electromagnetic radiation	124
6.8 Absorption laws	128
6.9 Spectrometric instrumentation	129
6.9.1 Single-beam spectrometer	130
6.9.2 Double-beam spectrometer	131
6.9.3 Fourier-transform instruments	132
Further reading	133
7 Atomic spectrometry	134
F.W. FIFIELD	
7.1 Introduction	134
7.2 Flame emission spectrometry	135
7.2.1 The chemical flame	135
7.3 Plasma emission spectrometry	138
7.3.1 Introduction	138
7.3.2 Inductively coupled plasma-atomic emission spectrometry (ICP-AES)	138

7.4	Inorganic mass spectrometry	142
7.4.1	Introduction	142
7.4.2	Inductively coupled plasma-mass spectrometry (ICP-MS)	142
7.5	X-ray emission techniques	143
7.5.1	Introduction	143
7.5.2	Electron probe microanalysis	143
7.5.3	X-ray fluorescence spectrometry	147
7.6	Atomic absorption spectrometry	148
7.6.1	Introduction	151
7.6.2	Sharp-line radiation	151
7.6.3	AAS measurements	151
7.6.4	Flame AAS	152
7.6.5	Electrothermal AAS	153
7.7	Atomic fluorescence spectrometry	154
7.8	Use of atomic spectrometry	156
Further reading		
Self-study exercises		
Answers		

8 Molecular spectrometry

P.J. HAINES

8.1	Introduction	161
8.2	Ultraviolet and visible spectrophotometry	161
8.2.1	Instrumentation	161
8.2.2	Band spectra	162
8.2.3	Polyatomic organic molecules	163
8.2.4	Solvent effects	164
8.2.5	Metal complexes	165
8.2.6	Applications	165
8.2.7	UV fluorescence methods	166
8.2.8	Combined separation and UV techniques	168
8.3	Infrared spectrometry	168
8.3.1	Sampling	169
8.3.2	Infrared absorption	170
8.3.3	Polyatomic molecules	172
8.3.4	Combinations of infrared and separation techniques	175
8.3.5	Applications of infrared spectrometry in environmental analysis	175
8.4	Nuclear magnetic resonance spectrometry (NMR)	177
8.4.1	Instrumentation	178
8.4.2	Solvents for NMR work	179
8.4.3	The chemical shift	179
8.4.4	The peak area	182
8.4.5	Spin-spin coupling	182
8.4.6	Applications of NMR	186
8.5	Mass spectrometry (MS)	187
8.5.1	Instrumentation	187
8.5.2	Isotopic composition and accurate masses	190
8.5.3	Nitrogen rule	190
8.5.4	Fragmentation	191
8.5.5	Applications of mass spectrometry	192
8.6	Structure elucidation	194
Further reading		
Self-study exercises		
Answers		

161

7.4	Inorganic mass spectrometry	142
7.4.1	Introduction	142
7.4.2	Inductively coupled plasma-mass spectrometry (ICP-MS)	142
7.5	X-ray emission techniques	143
7.5.1	Introduction	143
7.5.2	Electron probe microanalysis	147
7.5.3	X-ray fluorescence spectrometry	148
7.6	Atomic absorption spectrometry	151
7.6.1	Introduction	151
7.6.2	Sharp-line radiation	151
7.6.3	AAS measurements	152
7.6.4	Flame AAS	153
7.6.5	Electrothermal AAS	154
7.7	Atomic fluorescence spectrometry	156
7.8	Use of atomic spectrometry	157
Further reading		
Self-study exercises		
Answers		160
8 Molecular spectrometry		161
P.J. HAINES		
8.1	Introduction	161
8.2	Ultraviolet and visible spectrophotometry	161
8.2.1	Instrumentation	161
8.2.2	Band spectra	161
8.2.3	Polyatomic organic molecules	163
8.2.4	Solvent effects	164
8.2.5	Metal complexes	165
8.2.6	Applications	165
8.2.7	UV fluorescence methods	166
8.2.8	Combined separation and UV techniques	168
8.3	Infrared spectrometry	168
8.3.1	Sampling	169
8.3.2	Infrared absorption	170
8.3.3	Polyatomic molecules	172
8.3.4	Combinations of infrared and separation techniques	175
8.3.5	Applications of infrared spectrometry in environmental analysis	175
8.4	Nuclear magnetic resonance spectrometry (NMR)	177
8.4.1	Instrumentation	178
8.4.2	Solvents for NMR work	179
8.4.3	The chemical shift	179
8.4.4	The peak area	182
8.4.5	Spin-spin coupling	182
8.4.6	Applications of NMR	186
8.5	Mass spectrometry (MS)	187
8.5.1	Instrumentation	187
8.5.2	Isotopic composition and accurate masses	190
8.5.3	Nitrogen rule	190
8.5.4	Fragmentation	191
8.5.5	Applications of mass spectrometry	192
8.6	Structure elucidation	194
Further reading		201
Self-study exercises		201
Answers		202

9 Measurement of ionising radiations and radionuclides	203
F.W. FIFIELD	
9.1 Introduction	203
9.2 Ionising radiations and radioactivity	203
9.2.1 Alpha radiation (α)	204
9.2.2 Beta radiation (β^- or β^+)	204
9.2.3 Gamma radiation (γ)	205
9.2.4 Internal conversion (ic)	206
9.2.5 Radioactive decay	207
9.2.6 Units of radioactivity and radiation measurement	209
9.3 The detection and measurement of radiation	210
9.3.1 Gas ionisation detectors	211
9.3.2 Semiconductor detectors	212
9.3.3 Sodium iodide detectors	213
9.3.4 Organic scintillators	215
9.3.5 Liquid scintillation counting	215
9.3.6 Detection by films	217
9.3.7 The importance of autoradiographic techniques in environmental analysis	219
9.3.8 Concentration and separation of radionuclides	219
Further reading	219
10 Electroanalytical techniques	220
E. BUCKLEY-DHOOT	
10.1 Introduction	220
10.2 Electrochemical principles	220
10.3 Potentiometric techniques	222
10.3.1 Introduction and theory	222
10.3.2 Practical considerations and applications	224
10.3.3 Potentiometric titrations	233
10.3.4 Current developments	234
10.4 Voltammetric and controlled potential techniques	234
10.4.1 Introduction	234
10.4.2 Theory	235
10.4.3 Practical considerations and applications	236
10.4.4 Techniques	240
10.5 Electrochemical detection in flowing streams	246
10.5.1 Introduction	246
10.5.2 Potentiometric measurements in flowing streams	247
10.5.3 Voltammetric measurement in flowing streams	247
10.6 Other electroanalytical techniques	249
10.6.1 Introduction	249
10.6.2 Conductometry	249
10.6.3 Coulometry	250
10.6.4 Electrogravimetry	250
Further reading	251
Self-study exercises	251
Answers	252
11 Thermal methods of analysis	253
P.J. HAINES	
11.1 Introduction	253
11.2 Definitions	253
11.3 General apparatus	254

Part II Specific applications 307

13 Speciation	309
G.L. CHRISTIE	
13.1 The importance of speciation	309
13.2 Definition of speciation	309
13.3 The determination of trace metal speciation	309
13.3.1 Computer modelling	309
13.3.2 Experimental determination of speciation	314
13.4 Concluding remarks	324
Further reading	325
14 The analysis of atmospheric samples	326
C.K. LAIRD	
14.1 Introduction	326
14.2 Atmospheric analyses	327
14.2.1 Measurements of atmospheric composition	327
14.2.2 Emission measurements	327
14.2.3 Indoor and workplace atmospheres	328
14.3 Techniques for gas analysis	328
14.3.1 Gas chromatography	328
14.3.2 Spectrometric methods	328
14.3.3 Electrochemical sensors	336
14.3.4 Chemical methods and detector tubes	336
14.3.5 Diffusion tubes and diffusion denuder tubes	337
14.4 Sampling	339
14.4.1 Ambient air	339
14.4.2 Emissions	340
14.5 Calibration of gas analysers	341
14.6 Determination of the main air pollutants and oxygen	343
14.6.1 Carbon monoxide	343
14.6.2 Nitrogen oxides	344
14.6.3 Ozone	345
14.6.4 Sulphur dioxide	346
14.6.5 Volatile organic compounds	347
14.6.6 Oxygen	348
14.7 Determination of some other air pollutants	351
14.7.1 Methane	351
14.7.2 Chlorofluorocarbons	351
14.7.3 Organic nitrates	351
14.7.4 Nitrous oxide	352
14.7.5 Toxic organic micropollutants	352
14.7.6 Hydroxyl and hydroperoxyl radical	353
14.7.7 Combustible gases	353
14.8 Sampling and analysis of particles and aerosols	353
14.8.1 Sampling particles and aerosols	354
14.8.2 Particle and aerosol composition	359
Further reading	359
References	359
15 Trace elements	360
N.I. WARD	
15.1 Trace elements in the environment	360
15.2 Natural levels and chemical forms	362

15.3	Trace element contamination and pollution	368
15.3.1	Air particulates	368
15.3.2	Natural waters	370
15.3.3	Soils and sediments	371
15.3.4	Plants	373
15.3.5	Animals and humans	374
15.4	Sampling and sample preparation	375
15.4.1	Atmospheric samples	377
15.4.2	Water samples	378
15.4.3	Soils and sediments	379
15.4.4	Plants	381
15.4.5	Biological tissues and fluids	382
15.4.6	Sample digestion methods	383
15.5	Methods of analysis	384
15.6	Selected important examples	388
15.6.1	Lead	388
15.6.2	Aluminium	390
	Further reading	392
16 Environmental radiation and radioactivity		393
F.W. FIFIELD		
16.1	Introduction	393
16.2	The hazards of ionising radiations and their assessment	394
16.3	Natural sources of radiation	395
16.3.1	Radionuclides of geological origin	395
16.3.2	Radionuclides resulting from cosmic rays	401
16.4	Artificial sources of radiation	402
16.4.1	Radiation and radioactivity in research and medicine	402
16.4.2	Nuclear power	402
16.5	Radiogenic dating	407
16.5.1	Geological dating	408
16.5.2	Carbon dating	408
16.5.3	Tritium dating	409
16.5.4	Lead-210 dating	409
16.5.5	Thermoluminescence and electron spin resonance dating	410
	Further reading	410
17 Contaminated landsites		411
F.W. FIFIELD		
17.1	Introduction	411
17.2	The nature of contaminated sites	412
17.2.1	Origins of contamination	412
17.2.2	Physical characteristics of landsites	412
17.3	Assessments	414
17.3.1	Investigational plan	415
	Further reading	418
18 The analysis of water		419
F.W. FIFIELD		
18.1	Introduction	419
18.2	pH, acidity and alkalinity	421
18.3	Dissolved oxygen and oxygen demand	422
18.4	Total organic carbon	424
18.5	Metals	424

18.6	Dissolved salts	425
18.7	Trace organics	426
18.8	Radioactivity and radionuclides in water	427
18.9	Water surveys and sampling	427
	Further reading	428

19 The determination of trace amounts of organic compounds **429**

C.J. WELCH

19.1	Introduction	429
19.2	Sample preparation	431
19.2.1	Maceration, dissolution and extraction	432
19.2.2	Partition	433
19.2.3	Concentration of the analyte	436
19.3	Chromatography	437
19.3.1	Gas chromatography	438
19.3.2	High-performance liquid chromatography	439
19.3.3	Capillary (zone) electrophoresis	439
19.3.4	Quantitation	439
19.4	Screening analysis	440
19.5	GC applications: pesticide analysis	441
19.6	HPLC: trace analysis	443
19.7	HPLC applications	445
19.7.1	Aromatic hydrocarbons	445
19.8	GC/HPLC applications	446
19.8.1	Trace organic analysis in water	446
19.8.2	Analysis of organic materials in soil and sediments	449
19.8.3	Analysis of amines	449
	Further reading	450

20 Ecotoxicology **452**

R. MANLEY

20.1	Introduction	452
20.2	Toxicant behaviour in living organisms	452
20.3	Dose-response relationships of toxicants	454
20.4	Toxicants and the environment	460
20.5	Toxicity testing	461
20.5.1	Bioassays	463
20.6	Ecological risk assessment	468
	Further reading	470

Glossary **471**

Index **480**