

TECHNIQUES AND INSTRUMENTATION IN ANALYTICAL CHEMISTRY — VOLUME 17

QUALITY ASSURANCE FOR ENVIRONMENTAL ANALYSIS

Method Evaluation within the Measurements
and Testing Programme (BCR)

Edited by

Ph. Quevauviller

E.A. Maier

B. Griepink

*European Commission, Measurements and Testing Programme,
rue de la Loi 200, B-1049 Brussels, Belgium*



1995

ELSEVIER

Amsterdam — Lausanne — New York — Oxford — Shannon — Tokyo

CONTENTS

Preface

by Ph. Quevauvillerxix

CHAPTER 1. QUALITY ASSURANCE FOR ENVIRONMENTAL ANALYSIS

by Ph. Quevauviller, E.A. Maier and B. Griepink

1.1.	Overview of quality assurance principles	2
1.1.1.	General	2
1.1.2.	Statistical control	2
1.1.3.	Comparison with results of other methods	3
1.1.4.	Use of certified reference materials	3
1.1.5.	Interlaboratory studies	4
1.2.	Sources of errors in environmental analyses	4
1.2.1.	Potential sources of error in inorganic analyses	4
1.2.1.1.	Sample digestion	5
1.2.1.2.	Other sample pre-treatment	6
1.2.1.3.	Final determination	6
1.2.2.	Potential sources of error in speciation analyses	7
1.2.2.1.	Extraction	7
1.2.2.2.	Derivatization	9
1.2.2.3.	Separation	10
1.2.2.4.	Detection	11
1.2.3.	Potential sources of error in organic analyses	12
1.2.3.1.	Pretreatment and extraction	12
1.2.3.2.	Clean-up and concentration	14
1.2.3.3.	Separation	15
1.2.3.4.	Final detection	18
1.2.3.5.	Calibration	19
1.3.	Conclusions	23
	References	23

CHAPTER 2. DEVELOPMENT OF ICPMS AND ID-ICPMS WITH THE DETERMINATION OF Pb AND Hg IN ENVIRONMENTAL MATRICES AS AN EXAMPLE

by M. Campbell

2.1.	Principle of isotope dilution	28
------	---	----

2.2.	Choice of instrumentation	28
2.3.	ID-ICP-MS	29
2.3.1.	Precision and performance	29
2.3.2.	Routine applications	30
2.3.3.	More complicated applications	32
2.3.4.	Speciation and metabolic studies	35
References	37

CHAPTER 3. DETECTION OF SOURCES OF ERROR IN THE DETERMINATION OF Cr IN ENVIRONMENTAL MATRICES BY FAAS AND ETAAS

by A. Sahuquillo, R. Rubio and G. Rauret

3.1.	Determination of chromium by FAAS	40
3.1.1.	State of the art	40
3.1.1.1.	Type of flame	40
3.1.1.2.	Effect of burner height	40
3.1.1.3.	Instrumental parameters	41
3.1.1.4.	Effect of the oxidation state	41
3.1.1.5.	Interferences in FAAS	41
3.1.1.6.	Conclusions	42
3.1.2.	Systematic study of chromium determination by FAAS	42
3.1.2.1.	Type of flame and burner height	42
3.1.2.2.	Interferences	48
3.1.2.3.	Releaser agents	49
3.1.2.4.	Conclusions	50
3.1.3.	Procedure	50
3.1.4.	Validation of the method	51
3.2.	Determination of chromium by ETAAS	51
3.2.1.	State of the art	51
3.2.1.1.	Background correction	52
3.2.1.2.	Effect of the interferences	52
3.2.1.3.	Type of graphite furnace and use of L'vov platform	53
3.2.1.4.	Effect of the oxidation state	53
3.2.1.5.	Calibration mode	53
3.2.1.6.	Conclusions	53
3.2.2.	Systematic study of chromium determination by ETAAS	54
3.2.2.1.	Instrumental conditions	54
3.2.2.2.	Interferences	55
3.2.3.	Procedures	57
3.2.4.	Validation of the method	57
3.3.	Conclusions	58
References	60

CHAPTER 4. ANALYSIS OF ENVIRONMENTAL AND BIOLOGICAL SAMPLES BY ATOMIC SPECTROSCOPIC METHODS

by M. Hoenig and M.F. Guns

4.1.	Preparation of samples	64
4.1.1.	Liquid samples	64

4.1.2.	Solid samples	64
4.1.2.1.	Dry ashing methods	64
4.1.2.2.	Wet digestion methods	65
4.1.2.3.	Direct analysis of solid and solid slurried samples	65
4.1.3.	Usual procedures	67
4.1.3.1.	Plants	67
4.1.3.2.	Animal tissues	67
4.1.3.3.	Soils, sediments and particulate matter	68
4.2.	Plasma atomic emission spectrometry	68
4.2.1.	Basic principles and instrumentation	68
4.2.2.	Interferences	69
4.2.2.1.	Transport interferences	69
4.2.2.2.	Chemical interferences	69
4.2.2.3.	Ionization interferences	69
4.2.2.4.	Spectral interferences	70
4.3.	Atomic absorption spectrometry	70
4.3.1.	Basic principles and instrumentation	71
4.3.2.	Flame atomization	72
4.3.2.1.	Nebulization	72
4.3.2.2.	Flames	73
4.3.2.3.	Flame microsampling	74
4.4.	Vapour generation techniques	74
4.4.1.	Hydride forming elements	74
4.4.2.	Mercury	74
4.4.2.1.	Determination	74
4.4.2.2.	Sources of errors	75
4.5.	Electrothermal atomization	75
4.5.1.	General considerations	75
4.5.2.	Atomizer	76
4.5.3.	Electrothermal program	76
4.5.4.	Interferences	77
4.5.4.1.	Spectral interferences	78
4.5.4.2.	Non-spectral interferences	80
4.5.5.	Role of the graphite	86
4.6.	Atomic absorption spectrometry / conclusions	86
	References	87

CHAPTER 5. VALIDATION OF NEUTRON ACTIVATION ANALYSIS TECHNIQUES

by K. Heydorn

5.1.	Critical review	90
5.1.1.	The BIPM philosophy	90
5.1.2.	Advantages of NAA	93
5.1.3.	Pitfalls	93
5.1.4.	Sample homogeneity	94
5.2.	Methods of validation	94
5.2.1.	Uncertainty budget	95
5.2.2.	Validation of computer programs	96
5.2.3.	Validation of the calibration function	99
5.3.	Practical validation	100
5.3.1.	Experimental results for validation	101

5.3.2. Verification and traceability	107
5.4. Conclusions	109
References	110

CHAPTER 6. FLOW-THROUGH (BIO)CHEMICAL SENSORS IN ENVIRONMENTAL ANALYSIS

by M.D. Luque de Castro and M. Valcárcel

6.1. Flow through (bio)chemical sensors based on integrated reaction and detection	118
6.1.1. Sensors based on an immobilized biocatalyst: biosensors	118
6.1.2. Sensors based on an immobilized non-biological catalyst	120
6.1.3. Immunosensors	122
6.1.4. Flow-through sensors based on consumption of the immobilized reagent	124
6.1.5. Sensors based on an immobilized regenerable reagent	126
6.2. Flow-through chemical sensors based on integrated separation and detection	127
6.2.1. Flow-through sensors based on integrated gas-diffusion and detection	128
6.2.2. Flow-through sensors based on integrated liquid-liquid separation and detection	131
6.2.3. Flow-through sensors based on integrated sorption and detection	134
6.2.4. Flow-through sensors for multideterminations based on integrated retention and detection	139
6.2.5. Ion-selective electrodes and ion-sensitive field-effect transistors	143
6.3. Flow-through chemical sensors based on integrated reaction, separation and detection	148
6.3.1. Flow-through (bio)chemical sensors based on integrated reaction, gas diffusion and detection	150
6.3.2. Flow-through sensors based on integrated reaction, liquid-liquid separation and detection	152
6.3.3. Flow-through (bio)chemical sensors based on integrated reaction, sorption and detection	154
6.4. Final remarks	158
References	159

CHAPTER 7. FIBER OPTICAL SENSORS APPLIED TO FIELD MEASUREMENTS

by C. Cámara, C. Pérez-Conde, M.C. Moreno-Bondi and C. Rivas

7.1. Determination of target compounds	167
7.2. Validity of sensors	168
7.3. Instrumentation and design	170
7.4. Water monitoring	173
7.4.1. pH sensors	174
7.4.2. Sensing cations and anions	177
7.4.3. Organochlorides, aromatic hydrocarbons and mineral oils	179
7.4.4. Pesticides	183
7.4.5. Seawater gases	184
7.5. Air pollution	185
7.5.1. Carbon monoxide and dioxide	185
7.5.2. Nitrogen oxides	186
7.5.3. Hydrogen sulphide and sulphur dioxide	187
7.5.4. Ammonia	187
7.5.5. Methane	188

7.5.6. Other air pollutants	188
7.6. Conclusions	189
References	189

CHAPTER 8. CHROMIUM SPECIATION IN ENVIRONMENTAL AND BIOLOGICAL SAMPLES

by K. Vercoetere and R. Cornelis

8.1. Different species of Cr and their toxicity	195
8.2. Cr speciation in water	197
8.2.1. Methods of final determination	197
8.2.1.1. Atomic absorption spectrometry, atomic emission spectrometry	198
8.2.1.2. Chemiluminescence	198
8.2.1.3. Electrochemical methods	198
8.2.1.4. Isotope dilution mass spectrometry (IDMS)	199
8.2.1.5. Inductively coupled plasma mass spectrometry (ICP-MS)	199
8.2.1.6. Neutron activation analysis	200
8.2.1.7. Spectrophotometry	200
8.2.2. Separation methods	201
8.2.2.1. Solvent extraction	201
8.2.2.2. Chromatography	202
8.2.2.3. Coprecipitation	204
8.3. Cr speciation in welding fumes	205
8.4. Cr speciation in biological samples	207
8.5. Use and availability of reference materials	208
8.6. Future developments	210
References	211

CHAPTER 9. DETERMINATION OF ALUMINIUM SPECIES IN NATURAL WATERS

by B. Fairman and A. Sanz-Medel

9.1. The toxic aluminium species in aquatic systems	216
9.2. Analytical methods for the speciation of aluminium	216
9.2.1. 8-Hydroxyquinoline extraction procedures	217
9.2.2. Driscoll methods	218
9.2.3. Chelex-100 based methods	222
9.2.4. Fluoride electrode methods	223
9.2.5. HPLC methods	223
9.2.6. ^{27}Al NMR studies	225
9.3. Water sampling for aluminium speciation analysis	225
9.3.1. To filter or not to filter	226
9.4. Validation of aluminium speciation analytical methods	227
9.5. Conclusions and future perspectives	229
References	231

CHAPTER 10. SELENIUM SPECIATION ANALYSES IN WATER AND SEDIMENT MATRICES

by C. Cámara, M.G. Cobo, M.A. Palacios, R. Muñoz and O.F.X. Donard

10.1	Selenium species in the environment	237
10.2	Analytical methodology - General remarks	240
10.3	Method validation	240
10.4	Stability of selenium species	241
10.5	Analytical methods for selenium speciation	245
10.5.1.	Fluorimetric methods	245
10.5.2.	Electrothermal atomic absorption spectrometry	247
10.5.3.	Hydride generation / atomic detectors	248
10.5.3.1.	Interferences	251
10.5.3.2.	Ethylation	251
10.5.4.	Hyphenated techniques	252
10.5.4.1.	Liquid chromatography / atomic detectors	252
10.5.4.2.	Gas chromatography	254
10.5.4.2.1.	Air samples	254
10.5.4.2.2.	Water samples	255
10.5.4.2.3.	Soil samples	256
10.5.4.2.4.	Biological samples	257
10.5.5.	Electrochemical methods	257
10.5.6.	Neutron activation analysis	259
References		259

CHAPTER 11. ANTIMONY SPECIATION IN WATER

by M.B. de la Calle-Gutiñas, Y. Madrid and C. Cámara

11.1.	Stability of antimony species	264
11.2.	Analytical methods for the determination of inorganic antimony	266
11.2.1.	Liquid-liquid extraction	266
11.2.1.1.	Spectrophotometric determination	266
11.2.1.2.	Detection by electrothermal atomic absorption spectrometry	269
11.2.2.	Complex formation with immobilized reagents	275
11.2.3.	Selective generation of antimony hydride	276
11.2.3.1.	By pH control	276
11.2.3.2.	Other methods	280
11.2.4.	Electroanalytical methods	281
11.3.	Conclusions	281
References		282

CHAPTER 12. ARSENIC SPECIATION IN ENVIRONMENTAL MATRICES

by A. Amran, F. Lagarde, M.J.F. Leroy, A. Lamotte, C. Demesmay, M. Ollé, M. Albert, G. Rauret and J.F. López-Sánchez

12.1.	Critical review of existing methods	288
12.1.1.	Hydride generation method	288
12.1.1.1.	Hydride generation and separation	288

12.1.1.2.	Detection	289
12.1.2.	Liquid chromatography coupled with specific detectors	289
12.1.2.1.	Separation by ion-pair chromatography	290
12.1.2.2.	Separation by ion-exchange chromatography	290
12.1.2.3.	Detection by atomic absorption spectrometry	290
12.1.2.4.	Detection by inductively coupled plasma atomic emission spectrometry	291
12.1.2.5.	LC procedures involving hydride generation	291
12.1.2.6.	HPLC coupled to ICP-MS	292
12.2.	Means of validation	292
12.3.	Description of a validated technique	293
12.3.1.	Sample treatment	294
12.3.1.1.	Analysis of seafood materials	294
12.3.1.2.	Sediment analysis	294
12.3.2.	Arsenic speciation	296
12.3.2.1.	Procedures used: Laboratory 1	296
12.3.2.2.	Procedures used: Laboratory 2	297
12.3.2.3.	Procedures used: Laboratory 3	299
12.4.	Conclusions	301
	References	303

CHAPTER 13. MERCURY SPECIATION IN BIOLOGICAL MATRICES

by I. Drabæk and Å. Iverfeldt

13.1.	Means of validation	308
13.1.1.	Extraction	309
13.1.2.	Separation	310
13.1.3.	Derivatization	311
13.1.4.	Detection	311
13.1.5.	Primary calibrants	312
13.2.	Critical review of derivatization methods	312
13.3.	Advices on how to take up Hg speciation analyses	314
13.4.	Conclusions	315
	References	316

CHAPTER 14. SPECIATION ANALYSIS OF ORGANOLEAD COMPOUNDS. STATUS AND FUTURE PROSPECTS

by R. Łobiński, W.M.R. Dirkx, J. Szpunar-Łobińska and F.C. Adams

14.1.	Sources and concentrations of interest of organolead compounds	320
14.1.1.	Atmosphere	320
14.1.2.	Air gaseous phase	321
14.1.3.	Air aerosol	323
14.1.4.	Atmospheric deposits	323
14.1.5.	Hydrosphere	324
14.1.6.	Sediments, soil and dusts	325
14.1.7.	Biological materials	325
14.1.8.	Miscellaneous	326
14.2.	Sample handling prior to measurement	326

14.2.1.	Sampling and storage	326
14.2.1.1.	Air	326
14.2.1.2.	Water samples	328
14.2.1.3.	Sediments and soils	329
14.2.1.4.	Biological materials	330
14.2.2.	Extraction	330
14.2.3.	Preconcentration	331
14.2.4.	Derivatization of ionic organolead compounds	331
14.3.	Instrumental aspects of the determination of organolead compounds	332
14.3.1.	Gas chromatography based hyphenated techniques	332
14.3.1.1.	Sample introduction	332
14.3.1.2.	Separation of the analytes	333
14.3.1.3.	Transfer lines	336
14.3.2.	Detection techniques	336
14.3.2.1.	Atomic absorption spectrometry (AAS)	336
14.3.2.2.	Atomic emission spectrometry (AES)	337
14.3.2.3.	Mass spectrometry (MS)	340
14.3.3.	Liquid chromatography (LC) based hyphenated techniques	340
14.3.3.1.	LC-AAS coupling	340
14.3.3.2.	LC-MS coupling	342
14.3.4.	Electrochemical techniques	342
14.3.5.	Summary of characteristics of hyphenated techniques used for organolead speciation analysis	344
14.4.	Analysis of environmental materials	344
14.4.1.	Analysis of water samples	344
14.4.2.	Sediments, soil and dust	347
14.4.3.	Biological tissues	349
14.5.	Accuracy	349
14.5.1.	Contamination risk	349
14.5.2.	Losses	351
14.5.3.	Calibrants	351
14.5.4.	Validation of the results	351
14.6.	Conclusions	352
	References	352

CHAPTER 15. SPECIATION ANALYSIS OF ORGANOTIN BY GC-AAS AND GC-AES AFTER EXTRACTION AND DERIVATIZATION

by *W.M.R. Dirkx, R. Łobiński and F.C. Adams*

15.1.	Instrumentation	360
15.1.1.	Gas chromatography	360
15.1.2.	Interface design	361
15.1.2.1.	GC - AES	361
15.1.2.2.	GC - quartz furnace AAS	361
15.1.2.3.	GC - graphite furnace AAS	363
15.1.3.	Detectors	365
15.1.3.1.	Atomic emission spectrometry	365
15.1.3.2.	Quartz furnace atomic absorption spectrometry	365
15.1.3.3.	Graphite furnace atomic absorption spectrometry	366
15.2.	Operational conditions	366
15.2.1.	GC related parameters	367
15.2.1.1.	Injections conditions	367

15.2.1.2.	Gas chromatographic separation	374
15.2.2.	Interface design	377
15.2.2.1.	Packed column - quartz furnace interface	377
15.2.2.2.	Megabore column - quartz furnace interface	378
15.2.2.3.	Megabore column - graphite furnace interface	379
15.2.2.4.	The GC - AES interface	380
15.2.3.	Detector design	380
15.2.3.1.	Quartz furnace atomic absorption spectrophotometer	380
15.2.3.2.	Graphite furnace atomic absorption spectrophotometer	382
15.2.3.3.	Atomic absorption spectrometer	387
15.3.	Analytical characteristics	389
15.3.1.	Instrumental detection limits	389
15.3.1.1.	Atomic emission spectrometry	389
15.3.1.2.	Atomic absorption spectrometry	389
15.3.2.	Experimental detection limits	391
15.3.3.	Reproducibility	392
15.3.4.	Dynamic range	392
15.4.	Sample handling	393
15.4.1.	Water samples	393
15.4.2.	Sediment samples	397
15.4.3.	Biological materials	397
15.5.	Accuracy of the analysis	400
15.5.1.	Preparation and quantification of calibrants	400
15.5.2.	Interferences	400
15.5.3.	Sources of errors	404
15.5.4.	Comparison studies	404
15.5.5.	Interlaboratory studies	406
15.6.	Conclusions	406
References		407

CHAPTER 16. HIGH PERFORMANCE LIQUID CHROMATOGRAPHY - ISOTOPE DILUTION - INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY FOR LEAD AND TIN SPECIATION IN ENVIRONMENTAL SAMPLES

by *S.J. Hill, A. Brown, C. Rivas, S. Sparkes and L. Ebdon*

16.1.	Overview of speciation methods for lead and tin	412
16.2.	Isotope dilution in HPLC-ICP-MS	413
16.3.	Practical considerations in ID-HPLC-ICP-MS	414
16.3.1.	Coupling HPLC to ICP-MS	414
16.3.2.	Potential problems with gradient elution HPLC-ICP-MS	420
16.3.3.	Organometallic calibrants for isotope dilution analysis	424
16.3.3.1.	Preparation of enriched lead isotope calibrants	424
16.3.3.2.	Preparation of enriched tin isotope calibrants	426
16.3.4.	Data processing in HPLC-ICP-MS and ID-HPLC-ICP-MS	426
16.3.5.	The determination of trimethyllead by HPLC-ICP-MS in a rainwater sample	428
16.4.	Evaluation of the ID-HPLC-ICP-MS technique	430
16.4.1.	Results	433
References		434

CHAPTER 17. SPECIATION OF ORGANOTIN COMPOUNDS IN ENVIRONMENTAL SAMPLES BY GC-MS

by R. Morabito, S. Chiavarini and C. Cremisini

17.1.	Analytical methods for the environmental analysis of organotins	437
17.1.1.	Extraction	438
17.1.2.	Derivatization	438
17.1.3.	Analytical techniques	439
17.2.	GC/MS analysis of organotins	439
17.2.1.	Which MS detector ?	440
17.2.2.	Gas chromatographic characteristics of organotins	440
17.2.3.	Mass spectral characteristics of organotins	443
17.3.	Analytical methods	452
17.3.1.	Reagents and materials	452
17.3.2.	Instrumentation	453
17.3.3.	Procedures	454
17.3.3.1.	Sediment and mussel samples	454
17.3.3.1.1.	Recovery tests from sediment samples	454
17.3.3.1.2.	Recovery tests from mussel samples	455
17.3.3.2.	Water samples	456
17.3.3.2.1.	Liquid/liquid extraction	456
17.3.3.2.2.	Solid phase extraction	457
17.3.3.3.	Remarks on the procedures	458
References		460

CHAPTER 18. DEVELOPMENT OF SUPERCRITICAL FLUID EXTRACTION PROCEDURES FOR THE DETERMINATION OF ORGANOTIN COMPOUNDS IN SEDIMENT

by J.M. Bayona

18.1.	Fundamental aspects	466
18.1.1.	SFE instrumentation	467
18.1.2.	Speciation techniques	469
18.2.	Development of supercritical fluid extraction procedures	470
18.2.1.	Variables in SFE	470
18.2.2.	Method development	471
18.2.3.	Method validation	479
18.3.	Application and intercomparison between procedures	482
18.3.1.	Intercomparison between SFE and atmospheric pressure extraction procedure	482
18.3.2.	Application of the SFE procedures for the TBT extraction from real samples	483
18.4.	Conclusions	484
References		486

CHAPTER 19. HYDRIDE GENERATION FOR SPECIATION ANALYSES USING GC/AAS

by R. Ritsema, F.M. Martin and Ph. Quevauviller

19.1.	Hyphenated techniques using hydride generation	490
19.2.	The on-line hydride generation technique in combination with GC/AAS	491
19.2.1.	Reaction vessel	491
19.2.2.	Reducing conditions	491
19.2.3.	Stripping time/cryogenic focusing	493
19.2.4.	Gas chromatography	493
19.2.5.	Atomic absorption detection	493
19.3.	Sample pre-treatment	495
19.4.	Applications of hydride generation	495
19.5.	Interferences in hydride generation	496
19.5.1.	Spectral interferences	496
19.5.2.	Chemical interferences	496
19.5.2.1.	Interferences in organometallic speciation	497
19.5.2.2.	Interferences during redox speciation	498
19.6.	Other limitations	499
19.7.	Conclusions	500
	References	500

CHAPTER 20. SINGLE AND SEQUENTIAL EXTRACTION SCHEMES FOR TRACE METAL SPECIATION IN SOIL AND SEDIMENT

by A.M. Ure, C.M. Davidson and R.P. Thomas

20.1	General aspects of single and sequential extraction	506
20.1.1.	Functionally defined speciation in soils	506
20.1.2.	Operationally defined speciation	507
20.1.3.	Metal speciation in sediments	507
20.2.	Current methodologies	508
20.2.1.	Single-step extraction	508
20.2.2.	Sequential extraction procedures	509
20.3.	Justification and validation of speciation by extraction	509
20.3.1.	Validation of the relevance and specificity of extracting reagents	509
20.3.2.	Objective	511
20.4.	Development of agreed common extraction schemes	511
20.4.1.	Sampling soils for analysis and the preparation of bulk soil samples as candidate reference materials for certification of extractable contents	511
20.4.2.	Sediment sample preparation	513
20.4.3.	Temporal stability of air dried soil extractable contents	514
20.4.4.	Temporal stability of air dried sediment extractable contents	515
20.4.5.	Other factors affecting the validity and reliability of extraction procedures for speciation	516
20.4.6.	Validation of selective extraction procedures for metal speciation in soils and sediments	517
20.5.	Protocols for valid extraction procedures for the elements Cd, Cr, Cu, Ni, Pb and Zn	518
20.5.1.	Protocol for single-step extraction by 0.05 mol.l ⁻¹ EDTA	518
20.5.2.	Protocol for single-step extraction by 0.43 mol.l ⁻¹ acetic acid	519
20.5.3.	Protocol for BCR 3-step sequential extraction for sediment	519

20.6. Conclusions	520
References	521

CHAPTER 21. METHODS FOR THE DETERMINATION OF CHLORINATED BIPHENYLS IN AIR

by *M. Morosini and K. Ballschmiter*

21.1. Airborne chlorinated biphenyls	526
21.1.1. Filter and absorbent systems	528
21.1.1.1. Glass-fibre filters	528
21.1.1.2. Organic filters	528
21.1.1.3. Inorganic adsorbents	528
21.1.1.4. Carbon adsorbents	529
21.1.1.5. Polymeric adsorbents	529
21.1.2. Other sampling systems	530
21.1.2.1. Annular denuders	530
21.1.2.2. Electrostatic precipitators	530
21.1.2.3. Low-pressure cascade impactors	530
21.2. Deposition of chlorinated biphenyls	531
21.2.1. Dry depositions	531
21.2.2. Wet depositions	531
21.2.3. Vegetation samples	531
References	532

CHAPTER 22. SAMPLE HANDLING AND DETERMINATION OF CARBAMATE PESTICIDES AND THEIR TRANSFORMATION PRODUCTS IN VARIOUS MATRICES

by *M. Honing, D. Barceló, B.L.M. van Baar and U.A.Th. Brinkman*

22.1. Sample preparation	537
22.1.1. Aqueous samples	537
22.1.2. Biological and soil samples	540
22.2. Column chromatography	542
22.2.1. Gas chromatography	542
22.2.2. Column liquid chromatography	544
22.2.3. Supercritical fluid chromatography	546
22.3. LC detection methods	546
22.3.1. Ultraviolet detection	546
22.3.2. Electrochemical detection	548
22.3.3. Fluorescence detection	548
22.3.4. Mass spectrometric detection	550
22.4. Conclusions	554
References	556

**CHAPTER 23. METHOD DEVELOPMENT FOR THE DETERMINATION OF
POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN
ENVIRONMENTAL MATRICES**

by *J. Jacob*

23.1.	Availability of reference materials	564
23.2.	Extraction of PAH	566
23.3.	Enrichment and clean-up	569
23.4.	Thin-layer chromatography (TLC)	570
23.5.	High-performance liquid chromatography (HPLC)	571
23.6.	Gas-liquid chromatography (GC)	576
	References	586

**CHAPTER 24. METHOD VALIDATION FOR THE DETERMINATION OF
DIOXINS**

by *T. Rymen*

24.1.	Review of existing methods for the determination of PCDD and PCDF	594
24.1.1.	Extraction	595
24.1.1.1.	Liquids	595
24.1.1.2.	Solids and sediments	596
24.1.1.3.	Solid sorbents and papers	596
24.1.1.4.	Soot, particulates and fly ash	597
24.1.1.5.	Biological samples	601
24.1.2.	Clean-up	601
24.1.2.1.	Acid/base clean-up	601
24.1.2.1.1.	In batch treatments	601
24.1.2.1.2.	Liquid chromatography on acid/base modified silica gel	601
24.1.2.2.	Treatment with AgNO ₃	602
24.1.2.3.	Liquid chromatography on silica gel	602
24.1.2.4.	Liquid chromatography on Florisil	604
24.1.2.5.	Liquid chromatography on neutral-, basic- or acidic-alumina	604
24.1.2.6.	Gel permeation chromatography	605
24.1.2.7.	Liquid chromatography on activated carbon	605
24.1.2.8.	High pressure liquid chromatography	605
24.1.2.9.	Clean-up procedures	606
24.1.3.	Instrumental analysis	606
24.1.3.1.	Capillary gas chromatography	606
24.1.3.2.	Mass spectrometry	613
24.1.3.3.	Data evaluation	616
24.2.	Quality control and method validation	616
24.2.1.	Internal quality control	616
24.2.1.1.	Blanks for standard preparation equipment	616
24.2.1.2.	Procedure blank	617
24.2.1.3.	Spiking standards of ¹³ C12-labelled compounds	617
24.2.1.4.	Calibration standard/detector linearity check	617
24.2.1.5.	Quality control of chromatographic capillary columns	618
24.2.1.6.	Extraction efficiency	618
24.2.1.7.	Recovery check	619
24.2.1.8.	Dioxin-dibenzofuran identification criteria	620

24.2.1.9.	Limits of detection (LD)	620
24.2.1.10.	Precision and accuracy	621
24.2.1.11.	Internal quality control systems	621
24.2.2.	Method validation	621
24.3.	Validated methods	625
24.3.1.	Analytical procedure for the quantitative determination of 2,3,7,8- chlorinated tetra-, penta- and hexachloro dioxins and dibenzofurans in municipal waste incinerator fly ashes	625
24.3.1.1.	Cleaning of glassware	625
24.3.1.2.	Materials and reagents	626
24.3.1.3.	Method blank	627
24.3.1.4.	Sample analysis	628
24.4.	Conclusions	633
	References	634
	Subject index	641