

TABLE OF CONTENTS

Volume III

Chapter 1	
Carbamates.....	1
B. D. Ripley and A. S. Y. Chau	
Chapter 2	
The Substituted Urea Herbicides	183
A. E. Smith and R. Grover	
Chapter 3	
Triazine Herbicides	213
A. E. Smith, D. C. G. Muir, and R. Grover	
Index	241

Chapter 1

CARBAMATE PESTICIDES

Brian D. Ripley and Alfred S. Y. Chau

TABLE OF CONTENTS

I.	Introduction	3
II.	General Chemistry	5
	A. Nomenclature	6
	B. Chemical and Physical Properties	16
	C. Synthesis of Parent Compounds	22
	1. Aryl <i>N</i> -Methylcarbamates	22
	2. <i>N,N</i> -Dimethylcarbamates	24
	3. <i>N</i> -Phenylcarbamates	24
	4. Oxime <i>N</i> -Methylcarbamates	24
	5. Thiocarbamates	24
	6. Dithiocarbamates and Ethylenebisdithiocarbamates	25
III.	Mode of Action	26
	A. Insecticides	26
	B. Herbicides	27
	C. Fungicides	28
IV.	Environmental Persistence	29
	A. Aquatic Environment	29
	1. Water Quality Objectives	32
	B. Soil and Sediment	33
	C. Fish	36
	D. Plants	36
	E. Model Ecosystems	38
	F. Environmental Study	38
	G. Summary	40
V.	Degradation and Metabolic Processes	40
	A. Hydrolysis	41
	B. Oxidation	42
	C. Conjugation	43
	D. Typical Metabolic Pathways	44
	E. Synthesis of Carbamate Pesticide Metabolites	45
VI.	Residue Analysis	49
	A. Sampling and Sample Preservation	51
VII.	Extraction	66
	A. <i>N</i> -Methylcarbamates	66
	1. Water	66
	a. Typical Extraction Methods for Aqueous Samples	69
	i. Separatory Funnel Method	69
	ii. XAD-2 Resin Column	69

2. Soils and Sediment	69
3. Animal, Bird, and Fish Tissues	71
4. Plant Tissue	71
B. Aminophenyl <i>N</i> -Methylcarbamates	73
C. Oxime Carbamates	75
D. <i>N</i> -Phenylcarbamates	75
E. Thiocarbamate Herbicides	75
F. Dithiocarbamates and EBDC Fungicides	76
G. Concentration of Sample Extracts	76
VIII. Cleanup of Sample Extracts	76
A. Separation of the Parent Carbamates from Their Phenols	79
1. Typical Isolation of Carbamate Phenols	80
IX. Gas Chromatography (GC)	80
A. Gas Chromatographic Detectors	81
B. Direct GLC Determination of <i>N</i> -Methylcarbamates	82
C. Direct GLC of Carbamate Phenols	89
D. Direct GLC of Other Carbamates	90
X. Derivatization of <i>N</i> -Methylcarbamates	94
A. Derivatives of Intact <i>N</i> -Methylcarbamates	95
1. Typical Acylation of Intact <i>N</i> -Methylcarbamates	103
B. Derivatives of Hydrolysis Products of <i>N</i> -Methylcarbamates	103
1. Derivatization of Carbamate Phenols	104
a. Typical Methods for Derivatization of Carbamate Phenols	115
i. Pentafluorobenzylation	115
ii. Dinitrophenylation	116
iii. DNT, PFB, or DNP Ethers of Carbamate Phenols	116
2. Derivatization of Amine Hydrolysis Products of <i>N</i> -Methylcarbamates	116
C. Analytical Hydrolysis of <i>N</i> -Methylcarbamates	119
1. Typical Hydrolysis of <i>N</i> -Methylcarbamates to Isolate the Phenols	121
D. On-Column Reactions	121
XI. Derivatization of Other Carbamate Pesticides	123
A. Derivatization of the Intact Compound	124
B. Derivatization of Hydrolysis Products	124
C. Ethylenebisdithiocarbamate (EBDC) Fungicides and Ethylenethiourea (ETU)	129
XII. Other Determinative Methods	130
A. HPLC	130
B. TLC	136
C. Enzymatic Techniques	138
D. Fluorescence	141
E. Colorimetric Methods	143
1. Colorimetric Method for Dithiocarbamate and Ethylenebisdithiocarbamate Fungicides	145

F. Mass Spectrometry (MS).....	146
G. Other Spectroscopic Techniques	151
XIII. Confirmation of Residues.....	151
XIV. Appendix	152
References.....	154

Chapter 2

THE SUBSTITUTED UREA HERBICIDES

Allan E. Smith and Raj Grover

TABLE OF CONTENTS

I.	Introduction	184
A.	History	184
B.	Use Patterns	184
C.	Formulations and Application Rates.....	184
D.	Synthesis	190
E.	Physical Properties	191
F.	Chemical Properties	191
G.	Toxicological Properties	192
II.	Environmental Aspects	192
III.	Review of Analytical Procedures	193
A.	Colorimetry	194
B.	Gas Chromatography (GC)	196
C.	High-Performance Liquid Chromatography (HPLC).	197
D.	Discussion of Analytical Procedures	198
IV.	Analytical Methodology	199
A.	Extraction of Phenylurea Herbicides from Waters, Soils, and Plant Tissues.....	199
B.	GC Conditions for the Detection of Diuron.....	199
C.	HPLC Conditions for Urea Herbicides.....	201
D.	Standards	205
E.	Sample Collection	205
F.	Sample Preparation.....	206
G.	Confirmatory Techniques.....	206
V.	Detailed Analytical Procedures	206
A.	Colorimetric Screening for Qualitative Phenylurea Determination in Water.....	206
B.	Analysis of Diuron in Water by GC.....	207
C.	Analysis of Diuron in Sediment by GC	208
D.	Analysis of Diuron in Aquatic Vegetation and Biota by GC.....	208
E.	HPLC Procedure for Phenylureas in Water	208
F.	HPLC Procedure for Phenylureas in Sediments, Aquatic Plants, and Biota	208
	References.....	209

Chapter 3

THE TRIAZINE HERBICIDES

Allan E. Smith, Derek C. G. Muir, and Raj Grover

TABLE OF CONTENTS

I.	Introduction	214
A.	History	214
B.	Use Patterns	216
C.	Formulations and Application Rates.....	216
D.	Synthesis	216
E.	Physical Properties	219
F.	Chemical Properties	219
G.	Toxicological Properties	220
II.	Environmental Aspects	220
III.	Review of Analytical Procedures	222
A.	Spectrophotometry	222
B.	High-Performance Liquid Chromatography (HPLC).....	223
C.	Gas Chromatography (GC)	223
D.	Discussion of Analytical Procedures	224
IV.	Analytical Methodology	224
A.	Extraction of Triazine Herbicides from Water Samples	224
B.	Extraction of Triazine Herbicides from Soil and Sediment Samples ..	224
C.	Extraction of Triazine Herbicides from Plant Tissue	226
D.	Extraction of Triazine Herbicides from Animal and Fish Tissue	226
E.	Cleanup Procedures for Sediment, Plant, and Animal Extracts	226
F.	GC Columns.....	228
G.	GC Detectors	228
H.	Confirmatory Techniques.....	228
V.	Sample Collection, Preservation, and Preparation	229
A.	Introduction	229
B.	Sampling Apparatus	229
C.	Sampling Procedures.....	230
1.	Water.....	230
2.	Sediments	230
3.	Plant and Animal Samples	230
D.	Sample Preparation for Extraction	230
1.	Water.....	231
2.	Sediments	231
3.	Plant Material	231
4.	Fish Tissue	231
VI.	Detailed Analytical Procedures	231
A.	Analysis of Atrazine, Simazine, and Terbutryn in Water	231
1.	Reagents	231

2.	GC Conditions	231
3.	GC Determination	232
4.	Procedure	233
B.	Analysis of Atrazine, Simazine, and Terbutryn in Sediments.....	233
1.	Reagents	233
2.	GC Conditions	233
3.	Extraction Procedure	233
4.	Liquid-Liquid Partition Cleanup	233
5.	Column Cleanup	234
6.	GC Analysis	234
C.	Analysis of Atrazine, Simazine, and Terbutryn in Plant Tissue	234
1.	Reagents	234
2.	Apparatus.....	234
3.	GC Conditions	235
4.	Extraction Procedure	235
5.	Liquid-Liquid Partition Cleanup	235
6.	Column Cleanup	235
7.	GC Analysis and Calculations	235
D.	Analysis of Atrazine, Simazine, and Terbutryn in Fish Tissue	235
	References.....	236