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Review

High-performance liquid chromatographic methods for the determination of N-methylcarbamate pesticides in water, soil, plants and air

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ABSTRACT

High-performance liquid chromatographic methods of analysis for 31 N-methylcarbamate pesticides and 46 of their metabolites in water, soil, plant and air samples are reviewed. Consideration is given to extraction, clean-up, chromatographic separation and detection techniques including UV absorbance, fluorescence, electrochemical and mass spectrometric detection.

CONTENTS

1. INTRODUCTION

N-methylcarbamate (NMC) pesticides comprise an important class of pesticides noted for their relatively short persistence in the environment. Since their introduction in the 1950s they have been used worldwide on a large number of crops. Of the 31 NMCs included in this review (Table 1), one, ethidimuron, is a herbicide and the rest are insecticides, acaracides, nematicides or molluscicides. There are no fungi-

TABLE 1

N-METHYLCARBAMATE PESTICIDES INCLUDED IN THIS REVIEW

A = Acaricide; H = herbicide; I = insecticide; M = molluscicide; N = nematicide.

No.	Common name(s)	Trade name(s)	Class
1	Aldicarb	Temik	I, N, A
2	Aminocarb	Matacil	I, A, M
3	Bendiocarb	Ficam	I
4	BPMC, fenobucarb	Bassa, Baycarb, Osbac	I
5	Bufencarb	Bux	I
6	Butacarb		I
7	Butocarboxim	Drawin 755	I, A
8	Butoxycarboxim	Plant Pin	I, A
9	Carbanolate	Banol	I
10	Carbaryl	Sevin	I
11	Carbofuran	Furadan, Curaterr	I, N, A
12	Cloethocarb	Lance	I, N
13	CPMC	Hopcide, Etrofol	I
14	Dioxacarb	Famid, Elocron	I
15	Ethidimuron	Ustilan	H
16	Ethiofencarb	Croneton	I
17	Formetanate	Carzol, Dicarzol	A, I
18	Isoprocarb, MIPC	Mipsin, Etrofolan	I
19	Methiocarb, mercaptodimethur	Mesurol, Draza	I, A, M
20	Methomyl	Lannate	I
21	Mexacarbate	Zectran	I, M, A
22	–	Mobam	I
23	MPMC	Meobal	I
24	MTMC	Tsumacide, Metacrate	I
25	Oxamyl	Vydate	I, N, A
26	Promecarb	Carbamult	I
27	Propoxur, arprocarb, PHC	Baygon, Blattanex, Unden	I
28	Thiofanox	Dacamox	I, A
29	–	Tranid	I, A
30	Trimethacarb	Landrin	I
31	XMC	Macbal	I

cides in the group. A structural feature they have in common is a hydrolyzable N-methyl group, a feature that has been exploited for residue analysis. Also included in the review are 46 metabolites of NMC pesticides (Table 2), some of which have lost the N-methylcarbamate moiety.

High-performance liquid chromatography (HPLC) is the favoured technique for determination of NMC pesticides as a class since many of them lack the thermal stability necessary for gas chromatographic determination. It has now been 20 years since the first reports of HPLC determination of NMCs were published [1–3]. Since then a large body of literature has been produced on this subject and it seemed appropriate to review this literature for the interest of those working in this field.

This review will attempt to deal with all aspects of determination of NMC residues in water (Table 3), soil (Table 4), plants (Table 5) and air by HPLC, including extraction, clean-up, chromatographic separation and detection. An attempt has been made at comprehensiveness, but no doubt omissions have occurred. A number of papers which include advances in analytical technology but in which no application to environmental analysis was made are also included because of their possible relevance to workers in the field (Table 6). In Tables 3–6 the units ppm, ppb and ppt are reported as used in the references.

TABLE 2

METABOLITES OF N-METHYLCARBAMATE PESTICIDES INCLUDED IN THIS REVIEW

No.	Metabolite	Parent compound
32	Aldicarb sulphoxide	Aldicarb
33	Aldicarb sulphone (aldoxycarb)	Aldicarb
34	Aldicarb oxime	Aldicarb
35	Aldicarb sulphoxide oxime	Aldicarb
36	Aldicarb sulphone oxime	Aldicarb
37	Aldicarb nitrile	Aldicarb
38	Aldicarb sulphoxide nitrile	Aldicarb
39	Aldicarb sulphone nitrile	Aldicarb
40	4-Formamido-3-methylphenol	Aminocarb
41	4-Methylamino-3-methylphenol	Aminocarb
42	4-Formamido-3-methylphenyl N-methylcarbamate	Aminocarb
43	4-Amino-3-methylphenyl N-methylcarbamate	Aminocarb
44	4-Dimethylamino-3-methylphenol	Aminocarb
45	4-Methylamino-3-methylphenyl N-methylcarbamate	Aminocarb
46	Butocarboxim sulphoxide	Butocarboxim
47	Butocarboxim sulphone (butoxycarboxim)	Butocarboxim
48	1-Naphthol	Carbaryl
49	7-Hydroxycarbaryl	Carbaryl
50	6-Hydroxycarbaryl	Carbaryl
51	4-Hydroxycarbaryl	Carbaryl
52	5-Hydroxycarbaryl	Carbaryl
53	Methylolcarbaryl	Carbaryl
54	1,6-Dihydroxynaphthalene	Carbaryl
55	1,5-Dihydroxynaphthalene	Carbaryl
56	1,7-Dihydroxynaphthalene	Carbaryl
57	3-Hydroxycarbofuran	Carbofuran
58	3-Ketocarbofuran	Carbofuran
59	2,3-Dihydro-2,2-dimethyl-7-benzofuranol	Carbofuran
60	2,3-Dihydro-2,2-dimethyl-3,7-benzofurandiol	Carbofuran
61	2,3-Dihydro-2,2-dimethyl-3-oxo-7-benzofuranol	Carbofuran
62	Ethiofencarb sulphoxide	Ethiofencarb
63	Ethiofencarb sulphone	Ethiofencarb
64	Ethiofencarb phenol	Ethiofencarb
65	Ethiofencarb phenol sulphoxide	Ethiofencarb
66	Ethiofencarb phenol sulphone	Ethiofencarb
67	Methiocarb sulphoxide	Methiocarb
68	Methiocarb sulphone	Methiocarb
69	Methomyl oxime	Methomyl
70	4-Dimethylamino-3,5-xylenol	Mexacarbate
71	4-Methylformamido-3,5-xylyl N-methylcarbamate	Mexacarbate
72	4-Methylamino-3,5-xylyl N-methylcarbamate	Mexacarbate
73	4-Formamido-3,5-xylyl N-methylcarbamate	Mexacarbate
74	4-Amino-3,5-xylyl N-methylcarbamate	Mexacarbate
75	Oxamyl oxime	Oxamyl
76	Thiofanox sulphoxide	Thiofanox
77	Thiofanox sulphone	Thiofanox

TABLE 3

HPLC METHODS USED TO DETERMINE N-METHYLCARBAMATE PESTICIDES IN WATER SAMPLES

CC = Column chromatography; EC = electrolytic conductivity; EL = electrochemical; FL = fluorescence; LLE = liquid–liquid extraction; LLP = liquid–liquid partitioning; MS = mass spectrometry; SPE = solid-phase extraction.

Chemical(s)	Extraction technique	Clean-up technique	Recovery (%)	Det.	Detection limit	Ref.
1, 5, 6, 9, 10, 14, 16, 17, 19, 20, 22, 26, 27, 30	LLE/dichloromethane	None	–	FL	–	4
10	LLE/dichloromethane	CC/Florisil	99.7	UV	–	5
1, 32–35	LLE/dichloromethane	Hexane wash	–	MS	0.3–0.6 ppb	6
3	LLE/dichloromethane	CC/Florisil	65–70	UV	1.8 μg/g	7
1, 4, 10, 11, 18, 20, 24, 27, 57	LLE/dichloromethane	None	62–109	UV	5–10 ng/g	8
4, 10, 11, 20, 25, 27	LLE/dichloromethane or SPE/C_{18}	None	98	MS	1 ppb	9
11	LLE/dichloromethane	None	94–100	UV	0.001 ppm	10
11	LLE/dichloromethane	None	82	UV	0.05 ppm	11
1, 11, 32, 33, 57, 58	LLE/dichloromethane	SPE/silica	>83	UV	1 ppb	12
25, 75	LLE/dichloromethane	None	92–98	UV	1 ppb	13
1, 2, 4, 10, 11, 19–21, 25, 27, 32, 33, 75	LLE/dichloromethane or SPE/C_{18}	None	19–93	MS	8–320 ng	14
10	LLE/chloroform	CC/silica	70–85	UV	1–2 ng	15
10	LLE/chloroform	None	–	MS	10–20 ppt	16
10	LLE/chloroform	Normal-phase HPLC	70–85	UV MS	1–2 ng	17
1, 20, 25, 32, 33	LLE/chloroform	None	77–95	FL UV	0.2 ng 10 ng	18
10	LLE/toluene or benzene	None	96	UV	5 ng	19
10, 20	LLE/hexane	None	–	EC	–	20
20, 69	LLE/ethyl acetate	LLP/dichloromethane	93.7	UV EL[a]	1–2 ng 0.1 ng	21
2, 40–45	SPE/XAD-4 resin	LLP/ethyl acetate	76–84	UV FL	0.5 ppb 0.05 ppb	22
1, 32, 33	SPE/XAD-2 resin	None	92–96	UV	12 ng	23
10, 11, 20, 48	SPE/C_{18} or direct injection	None	94–107	UV	0.9 ng	24
10, 48	SPE/C_{18} or direct injection	None	97–100	UV	–	25
1	SPE/C_{18}	None	97–115	UV	10 ppb	26
27	SPE/C_{18}	None	92–99	UV	20 ppb	27
11, 57–61	SPE/C_{18}	None	86–113	UV	0.4 μg/l	28
10, 48–56	SPE/C_{18}	None	99.8	UV	0.5 ng/ml	29
11	SPE/C_{18}	None	–	UV	0.04 ppb	30
11	SPE/C_{18}	None	94.5	UV	0.033 μg/ml	31
1, 32, 33	SPE/C_8	None	52–90	FL	2.5 ng	32
21, 70	Direct injection	None	–	UV	–	33
2, 4, 10	Direct injection	None	–	EL	0.14 ng	34
11, 57–61	Direct injection	None	–	UV	1–5 ppb	35
1, 2, 10,19, 20, 27	Direct injection	None	–	FL	0.1–0.85 ng	36
1, 32–39	Direct injection	None	–	UV	1–2 ng	37
1, 32, 33	Direct injection	None	–	UV	1–2 ng	38
1, 10, 11, 20, 25, 32, 33, 57	Direct injection	None	87–106	FL	0.5 ng	39
2	Direct injection	None	–	EL	53 pg	40
2, 10	Direct injection	None	–	EL	–	41
1, 10, 11, 19, 20, 25, 27, 32, 33, 57	Direct injction	None	94–98	FL	–	42
1, 11, 20, 25, 32, 33, 57	Direct injection	None	77–138	FL	0.3–0.6 ng	43

TABLE 3 *(continued)*

Chemical(s)	Extraction technique	Clean-up technique	Recovery (%)	Det.	Detection limit	Ref.
1, 10, 11, 19, 20, 25, 27, 32, 33	Direct injection	None	–	FL	0.7–26 ng	44
20, 25	Direct injection	None	–	FL	1 ng	45
11	Direct injection	None	99–105	UV	0.03 μg/ml	46
10	On-line trace enrichment/C_{18}	None	104–106	FL	0.4–2.0 ng	47
1, 32, 33	On-line trace enrichment/C_8	None	71–80	FL	70 ng/l	48
10, 11, 27	On-line trace enrichment/C_8 or C_{18}	None	–	UV	10–70 pg/ml	49

[a] Electrochemical detector was used for methomyl oxime only.

2. EXTRACTION

2.1. Water samples

Residues of NMCs are commonly extracted from water using liquid–liquid extraction or solid-phase extraction on C_{18} cartridges. The first report of HPLC analysis of NMCs in water was by Frei *et al.* [4] who used liquid–liquid extraction with dichloromethane followed by passage through anhydrous sodium sulphate and evaporation. This general approach has been followed using dichloromethane,

TABLE 4

HPLC METHODS USED TO DETERMINE N-METHYLCARBAMATE PESTICIDES IN SOIL SAMPLES

CC = Column chromatography; EL = electrochemical; FL = fluorescence; LLP = liquid–liquid partitioning; MS = mass spectrometry.

Chemical(s)	Extraction solvent	Clean-up technique	Recovery (%)	Det.	Detection limit	Ref.
25, 75	Methanol	None	98.6	UV	–	50
11, 57, 58	Methanol	Hexane wash	89–94	UV	30 ng	51
25	Methanol	None	95.5	UV	2 ng	52
10, 25	Methanol	CC/Florisil	–	MS	1–2 ng	53
11, 59	Methanol–water (4:1)	None	–	UV	–	54
11	Methanol–water (2:1)	None	93–97	UV	0.1 μg/g	46
7, 46, 47	Methanol–water (1:1)	CC/silica	81–96	UV	0.3 μg/g	55
11	Methanol–water (2:1)	LLP/dichloromethane	82.4	UV	0.05 ppm	11
1, 20, 25, 32, 33	Acetone or water	LLP/chloroform (acetone extracts only)	83–99	FL UV	0.2 ng 10 ng	18
1, 5, 6, 9–11, 14, 17, 19, 20, 22, 26, 27, 30	Acetone	CC/silica	–	FL	–	4
11, 57	Acetone	LLP/dichloromethane and CC/silica	90–96	UV	–	56
10, 11, 25, 27	Acetone–dichloromethane	CC/Florisil	–	MS	1 ng	57
10, 11, 25, 27, 48	Acetone–dichloromethane	CC/Florisil or SPE/Florisil or SPE/aminopropyl silica	98–110	UV	5 ng	58
10	Acetone–water	LLP/dichloromethane and CC/Florisil	106	UV	–	5
11	Acetonitrile	LLP/dichloromethane and CC/silica	90–100	UV	0.02 ppm	10
25, 75	Dichloromethane	SPE/silica	92	UV	1 ppb	13
1, 4, 10, 11, 18, 20, 24, 27, 57	Acidic ammonium acetate	LLP/dichloromethane and CC/Florisil	59–100	UV	0.05–0.1 μg/g	8
4, 10, 11, 27	Water	LLP/dichloromethane	–	MS	0.1 ppb	9

TABLE 5

HPLC METHODS USED TO DETERMINE N-METHYLCARBAMATE PESTICIDES IN PLANT SAMPLES

CC = Column chromatography; EC = electrolytic conductivity; EL = electrochemical; FL = fluorescence; GPC = gel permeation chromatography; LLP = liquid–liquid partitioning; MS = mass spectrometry; SPE = solid-phase extraction; TLC = thin-layer chromatography.

Chemical(s)	Extraction solvent	Clean-up technique	Recovery (%)	Det.	Detection limit	Ref.
2, 9–11, 19, 21, 27, 30	Acetone	LLP/dichloromethane–hexane and CC/Florisil	>70	UV	0.004–0.1 ppm	59
11, 57, 58	Acetone	LLP/dichloromethane–hexane and CC/Florisil	68–110	UV	0.02–0.05 ppm	60
11, 57, 58	Acetone	LLP/dichloromethane–petroleum ether and CC/Florisil	–	UV	–	61
10	Acetone	LLP/dichloromethane–hexane and CC/Florisil	90–91 78–81	UV FL	30–50 ppb 10 ppb	62 63
11, 57, 58	Acetone	LLP/dichloromethane–hexane and CC/Florisil	50–65	FL	0.01 ppm	64
1, 7, 32, 33, 46, 47	Acetone	Petroleum ether wash, LLP/chloroform and CC/silica or TLC	75–91	FL	0.02–0.1 μg/g	65
20, 25	Acetone	LLP/dichloromethane–petroleum ether and CC/Florisil	–	MS	50 ng	66
10	Acetone	LLP/dichloromethane–petroleum ether and CC/Florisil	93	FL	–	67
11	Acetone	LLP/dichloromethane–hexane and SPE/silica	91	UV	0.011 μg/g	68
1, 5, 19, 20, 25, 27, 32	Acetone	LLP/dichloromethane–petroleum ether	69–110	MS	0.025–1 ppm	69
10, 11, 16, 19, 26, 27	Acetone	LLP/dichloromethane and CC/Florisil	94–106	EL	0.5–2 ng	70
11, 57, 59–61	Acetone	LLP/chloroform, evaporation, dissolution in precipitating solution, LLP/cabon tetrachloride	60–100	UV	–	71
10	Acetone	LLP/chloroform, evaporation, dissolution in precipitating solution, LLP/carbon tetrachloride	72–81	UV FL	–	72
1–3, 5, 7, 9–11, 14–16, 18–21, 25–30, 32, 33, 46–48, 57, 67, 68, 76, 77	Acetone–dichloromethane–petroleum ether	SPE/aminopropyl-bonded silica	47–102	FL	0.025–0.5 ng	73
1–3, 5, 7, 9–12, 14–16, 18–21, 25–30, 32, 33, 46, 47, 57, 58, 67, 68, 76, 77	Acetone–dichloromethane–petroleum ether	SPE/aminopropyl-bonded silica	–	FL	1–10 ppb	74
10	Acetone–methanol	LLP/dichloromethane	78–104	UV	0.05 μg/g	75
10	Acetone–methanol	Add acetonitrile to separate aqueous layer, LLP/chloroform, CC/Florisil	–	–	5 ng	19
1, 3, 4, 7, 8, 10, 11, 14, 16, 18–20, 24–28, 30, 32, 33, 46, 57, 62, 63, 67, 68	Acetonitrile or dichloromethane/water	LLP/hexane and CC/Florisil or SPE (unspecified phase)	59–108	FL	40–80 ng/g	76

TABLE 5 *(continued)*

Chemical(s)	Extraction solvent	Clean-up technique	Recovery (%)	Det.	Detection limit	Ref.
10	Acetonitrile	LLP/dichloromethane	80–85	UV	0.02 μg/g	77
1, 10, 11, 19, 20, 25	Acetonitrile	Add NaCl, centrifuge, take acetonitrile layer for SPE/C_{18} or CC/Florisil	72–107	FL	–	78
32	Acetonitrile	Add NaCl, centrifuge, take acetonitrile layer	74–76	FL	0.2 ppm	79
17	Acetonitrile (acidified)	Wash with dichloromethane (acidic conditions), LLP/dichloromethane (basic conditions), LLP/0.1 *M* sulphuric acid, LLP/dichloromethane (basic conditions)	>80	UV	0.02–0.05 μg/g	80
10	Benzene or petroleum ether	None	77–115 61–85	UV	0.005 ppm	81
10	Chloroform	LLP/acetonitrile, CC/Florisil	75–100	UV	–	5
10	Chloroform	CC/silica, SPE/C_{18}	95–104	UV	3 ng	82
11, 59–61	Chloroform or 0.25 *M* HCl	None	–	UV	2–4 ng	83
2, 10	Dichloromethane	CC/alumina-silver nitrate	80–90	UV	0.02 ppm	84
16, 62–66	Dichloromethane	None	35–103	UV	–	85
1, 32, 33	Dichloromethane	SPE/silica	86–96	UV	20–38 ng	86
4, 10, 11, 16, 18, 19, 27	Dichloromethane	None	–	FL	0.1 ng	87
2, 5, 10, 27	Dichloromethane	On-line clean-up (column switching)	55–100	UV	0.025–0.25 ppm	88 89
5, 10, 27	Dichloromethane	On-line clean-up (column switching)	67–100	UV	0.01–0.1 μg/g	90
10, 11, 27	Dichloromethane	LLP/acetonitrile, on-line clean-up (column switching)	71–89	FL	1.6 ng	91
1, 2, 10, 11, 21, 27, 57	Dichloromethane	None	–	FL	0.2–50 ng	92
5, 27	Dichloromethane	None	–	UV MS	–	93
10, 11, 48, 57	Dichloromethane (acidified)	CC/silica	–	UV FL	–	94
20, 69	Ethyl acetate	LLP/dichloromethane	101.4	UV EL[a]	1–2 ng 0.1 ng	21
1, 2, 5, 10, 11, 14, 17, 19, 20, 26, 27	Ethyl acetate	Transfer to water–methanol by evaporation, wash with *n*-pentane, LLP/chloroform, CC/Florisil	70–90	UV	20–1000 ng	95
1, 10, 11, 19, 20, 25, 27, 32, 33	Ethyl acetate	CC/alumina	–	FL	0.7–26 ng	44
20, 25	Ethyl acetate	Transfer to water by evaporation, wash with hexane, LLP/chloroform	61–81	UV	–	96
10, 20	Hexane–isopropanol	None	–	EC	–	20
10	Methanol	CC/Florisil	97	UV	0.05 μg/g	97
1, 10, 11, 19, 20, 25, 27, 32, 33, 57	Methanol	LLP/dichloromethane, GPC, SPE/Nuchar-Celite	52–97	FL	5–10 ppb	98
25, 75	Methanol	SPE/C_{18}; or hexane wash and CC/XAD-2 resin; or HPLC clean-up on C_{18}	90–99	UV	0.05 ppm	50

(Continued on p. 96)

TABLE 5 *(continued)*

Chemical(s)	Extraction solvent	Clean-up technique	Recovery (%)	Det.	Detection limit	Ref.
25	Methanol	None	87–103	UV	–	99
1	Methanol	Oxidation to aldicarb sulphone, LLP/dichloromethane, SPE/silica	–	UV	–	100
10, 48	Methanol	On-line clean-up (column switching)	86–97	UV	0.1 μg/g	101
1, 5, 10, 11, 19, 20, 25, 32, 33, 57, 67	Methanol	LLP/acetonitrile, wash with 20% NaCl and petroleum ether, LLP/dichloromethane, CC/Celite-Nuchar	55–103	FL	–	102
1, 5, 10, 11, 19, 20, 25, 33, 57	Methanol	LLP/acetonitrile, wash with 20% NaCl and petroleum ether, LLP/dichloromethane, CC/Celite-Nuchar	79–103	FL	–	103
1, 3, 5, 10, 11, 14, 18–20, 25, 27, 32, 33, 57, 58, 67	Methanol	LLP/acetonitrile, wash with 20% NaCl and petroleum ether, LLP/dichloromethane, CC/Celite-Nuchar	99	FL	–	104
10, 11	Methanol	LLP/acetonitrile, wash with 20% NaCl and petroleum ether, LLP/dichloromethane, CC/Celite-Nuchar	102–108	FL	–	105
5, 10, 11, 18, 19, 57	Methanol	LLP/acetonitrile, wash with 20% NaCl and petroleum ether, LLP/dichloromethane, CC/Celite-Nuchar	99	EL	0.4–0.7 ng	106
25	Methanol	LLP/dichloromethane, SPE/Florisil	86–94	UV	2 ng	107
25	Methanol	SPE/Nuchar-Attaclay	90–94	FL	0.02 μg/g	108
20	Methanol	None	80–90	UV	1 μg	109
10, 11, 19	Water	Hydroxylapatite removal of proteins, SPE/C_{18}	78–93	FL	0.01 ppm	110
20	Water + surfactant	LLP/dichloromethane	–	FL	–	111
17	Water–acetonitrile (acidified)	None	94	UV	–	112
11, 57	Water–dichloromethane with acid digestion	CC/silica-carbon-attaclay and CC/silica	77–85	UV	–	113
7, 46, 47	Water–methanol	CC/silica	73–105	UV	0.3 μg/g	55
20, 25	Matrix solid-phase dispersion isolation	None	72–129	FL	20 ppb	45
1, 32, 33	Centrifugation	None	–	FL	–	114
14	–	–	–	UV	4 ng	115
10	–	None	–	UV	0.002 ppm	116

[a] Electrochemical detector was used for methomyl oxime only.

chloroform, toluene, benzene, hexane, or ethyl acetate [5–21] (Table 3). In two studies [8,11] the water sample was acidified to pH 3 before extraction. In three other studies [12–14] NaCl or Na_2SO_4 was added to the water sample before extraction. Recoveries were generally good; however, since solubilities of the NMCs can vary quite dramatically, recoveries of individual NMCs may vary for any one method. Aldicarb sulphoxide in particular is extremely water soluble and recovery using liquid–liquid or solid-

TABLE 6

METHODS FOR DETERMINATION OF N-METHYLCARBAMATE PESTICIDES WHICH WERE NOT APPLIED TO ANALYSIS OF ENVIRONMENTAL SAMPLES

AA = Autoanalyzer; EL = electrochemical; FL = fluorescence; MS = mass spectrometry.

Chemical(s)	Detector	Detection limit	Ref.
1, 2, 5, 9–11, 19–22, 27, 30	UV	–	1
13, 18, 23, 24, 27, 31	UV	–	2
6, 11, 14, 17	FL	1–10 ng	3
1, 5, 9–11, 19–21, 27, 30, 32, 33, 48, 57	UV	1.1–61.3 ng	118
1, 5, 9–11, 19, 20, 23, 25–27, 30	IR	–	119
10	FL	–	120
1, 2, 10, 11, 19, 20, 27	FL	0.1 ng (methomyl)	121
1, 2, 10, 17, 19–21, 25, 48	UV	–	122
1, 32–35	UV	<1 μg/l	123
11, 59	UV	–	124
10	UV	*ca.* 0.04 μg	125
11, 57–59	UV	–	126
10, 27	UV	–	127
10, 11	UV	–	128
11, 57–61	UV	–	129
21, 70–74	UV	–	130
10, 48	UV	<3.5 ng	131
10, 11, 19, 20, 27, 48, 57	FL	–	133
1, 3, 5, 10, 11, 19, 20, 25, 27, 30, 32, 33, 48, 57, 67, 68	FL	10 ppb	134
3, 10, 11, 48, 57	FL	–	135
1, 19, 20, 27	FL	0.4–1 ng	136
1, 2, 10, 11, 13, 17–21, 25–27, 32, 33	FL	0.9–1.3 ng	137
1, 5, 10, 11, 19, 20, 25, 27, 32, 33, 57	FL	0.1 ng	138
10, 19, 27, 30	EL	1–1000 ng	139
	UV	1.2–13.6 ng	
1–3, 10, 19, 20, 32, 33	EL	5–100 pg	140
10	EL	0.03 ng	141
1, 2, 11, 20, 21, 23, 26, 27	MS	2.5–27.2 ng	142
	UV	1.1–18.2 ng	
1, 4, 10, 11, 27	MS	2–6 ng	143
4, 10, 11, 27	MS	40–50 ng	144
1, 4, 10, 11, 20, 25, 27	MS	0.02–2 μg	145
20	MS	–	146
1, 10, 11, 20, 25, 32, 33, 57	MS	–	147
10	MS	–	148
14	AA	200 ng	149

phase extraction may be poor. In the last-mentioned study [14] recoveries ranged from 19% for aldicarb sulphoxide to 93% for methiocarb using liquid–liquid extraction with dichloromethane, and from 10% for aldicarb sulphoxide to 98% for methiocarb using solid-phase extraction on C_{18}.

The first report of solid-phase extraction of an NMC from water for HPLC analysis was by Brun and McDonald [22] who used XAD-4 resin to extract aminocarb from lake water and rain water, achieving recoveries of 76–84%. Narang and Eadon [23] used XAD-2 resin to extract aldicarb and its oxidation products from drinking water and achieved recoveries of 92–96%. Other studies employing solid-phase extraction of water samples have used C_{18} [24–31] or C_8 [32] cartridges. In most cases recovery was over 85%.

Several HPLC studies have employed direct injec-

tion of unextracted, unconcentrated water samples [24,25,33–46]. This circumvents the extraction and clean-up steps with their inherent possibility of loss of analyte, but may not provide the detection limits required for environmental samples.

On-line trace enrichment of NMC residues on a precolumn prior to determination on an analytical column has been utilized by several workers to improve detection limits. She *et al.* [47] concentrated carbaryl residues on a C_{18} precolumn. Chaput [48] concentrated 10-ml water samples containing residues of aldicarb and its oxidation products on a C_8 precolumn. Marvin *et al.* [49] concentrated carbaryl, carbofuran and propoxur from 100-ml water samples on C_8 or C_{18} precolumns in a completely automated HPLC system.

2.2. Soil samples

Extraction of NMCs from soil is accomplished using solvent extraction [4,5,8–11,13,18,46,50–58] (Table 4). In most cases, recovery was better than 80%. Some of the earlier methods involved the use of chloroform or benzene, a practice which of course is no longer recommended for health reasons. De Bertrand *et al.* [58] compared four extraction solvents: methanol, and 1:1 mixtures of acetone–dichloromethane, acetone–methanol and acetone–ethyl acetate. The best recovery of carbaryl, carbofuran, oxamyl and propoxur was obtained with acetone–dichloromethane (1:1) (102%). Methanol extraction produced a co-extractive which prevented determination of oxamyl. Dekker and Houx [18] extracted subsoils with water and topsoils with acetone and found acetone to be better for methomyl and oxamyl and water to be better for aldicarb sulphoxide, another reflection of aldicarb sulphoxide's water solubility.

2.3. Plant samples

The solvent chosen to extract residues of NMC pesticides from plant tissue depends not only on the solubility of the chemical, but also on the nature of the information required. For example, the determination of dislodgeable residues for the purpose of establishing safe re-entry times for workers after crops have been sprayed requires a surface extraction of residues. On the other hand, determination of residues in fruits or vegetables to ensure the safety of food for consumers normally requires homogenization of the whole sample to extract the total residue.

A number of solvents have been used for the extraction of NMC residues from plant tissue ranging in polarity from water to petroleum ether [5,19,20, 44,45,50,55,59–116] (Table 5). The most effective strategy is to choose the solvent, whenever possible, such that the recovery of analytes is maximized and extraction of co-extractives is minimized. For highly water-soluble compounds such as formetanate and butocarboxim the water content of the extraction solvent may be increased [55,112], thus minimizing the amount of potentially interfering co-extracted material. Similarly, relatively non-polar solvents such as dichloromethane may efficiently extract less polar compounds without removing an excess of plant pigments. Unfortunately, compounds of intermediate polarity such as oxamyl are most effectively extracted in a solvent such as methanol which also removes an abundance of co-extractives. In such a situation an efficient clean-up step is normally required before determination.

The most inclusive study of extraction of NMCs from plant tissue was that of De Kok *et al.* [73], who determined recoveries of 21 NMC pesticides and 10 of their metabolites in a wide range of crops. They used an extraction solvent consisting of acetone–dichloromethane–petroleum ether (1:1:1) for fruits and vegetables. Recovery of NMCs was almost invariably better than 70%, but recovery of the most polar metabolites, butocarboxim sulphoxide and aldicarb sulphoxide, was always less than 60%.

A novel technique that was used on very small samples (0.5 g) was that of matrix solid-phase dispersion isolation [45]. Instead of using a solvent to extract the analytes, this technique involved blending a small amount of homogenized sample with C_{18} sorbent (40-μm particle size), transfering the mixture to a glass chromatography column and eluting the analytes with dichloromethane. This essentially combined extraction and column chromatographic clean-up, but would appear to be useful only for very small samples.

2.4. Air samples

Only one method for HPLC determination of airborne NMC pesticide residues was found [117].

This method employed a glass absorption tube packed with 10% Carbowax 400 on 80/100 mesh Supelcoport to absorb airborne propoxur. Air was sampled at a rate of 5 l/min for a number of hours and absorbed propoxur was eluted from the absorption tube with methanol. Recoveries were better than 85%.

3. CLEAN-UP

Most environmental sample extracts will require a preliminary clean-up procedure before determination by HPLC. The extent of clean-up required is dependent on the type of sample being analyzed, the detection limit required and the detection technique employed. As might be expected, about 80% of the methods reported for analysis of water samples summarized in Table 3 did not require clean-up of samples or extracts. On the other hand, almost all methods for soil and plant samples summarized in Tables 4 and 5 required at least some clean-up. Selective detection techniques such as fluorescence or mass spectrometry may minimize the need for clean-up by ignoring co-eluting co-extractives. The need for clean-up is indicated when it is not possible to separate an analyte from an interfering co-extractive on the HPLC column at the required level of sensitivity. It may also be desirable to clean-up samples in order to prolong the life of HPLC columns or prevent contamination of detectors.

The goal of clean-up is to remove as much interfering co-extracted material and as little of the analyte(s) as possible. Development of a clean-up method is often difficult since co-extractive compounds most similar to the analyte are those which are most likely to interfere with analysis, and also the most difficult to remove without also removing the analyte. Also, as was the case for the extraction step, the range of polarities of NMC pesticides makes it difficult to develop one clean-up procedure which is equally effective for all.

The clean-up techniques most commonly employed for extracts containing residues of NMC pesticides are liquid–liquid partitioning or a chromatographic clean-up such as column chromatography or solid-phase extraction (SPE). Many methods require a combination of both. Surprisingly, only one report of the use of gel permeation chromatography as a clean-up method for NMC determination was found [98]. A useful strategy, in the case of chromatographic clean-up techniques, is to employ a different stationary phase in the clean-up step than will be used in the determination step. For example, a Florisil SPE clean-up may be effective prior to determination on a C_{18} column.

The most inclusive clean-up method for HPLC determination of NMC pesticides was that reported by De Kok *et al.* [73]. This simple method employed an aminopropyl-bonded silica SPE column for clean-up of a dichloromethane extract of 21 NMC pesticides and 10 metabolites. Recovery from the clean-up step was quantitative, but losses occurred in the extraction step as previously mentioned.

Several methods [88–91,101] employed an on-line clean-up of plant extracts using a precolumn and column switching to direct fractions of interest from the precolumn to the analytical column. This useful approach essentially permits automation of column chromatographic or SPE clean-up steps.

Two methods [71,72] utilized an ammonium chloride–orthophosphoric acid solution to precipitate methyl anthranilate and other interfering plant materials. Another [110] used a column packed with hydroxylapatite, a form of calcium phosphate, to remove protein from vegetable extracts.

4. CHROMATOGRAPHIC SEPARATION

Most HPLC methods for NMC pesticides have employed reversed-phase chromatography with C_{18} or C_8 columns and aqueous mobile phases. Some methods employed normal-phase LC on silica columns [3,4,10,16,19,59,60–64,66,75,84,88–90,93,95, 101,118,119]. Nondek *et al.* [120] used an alumina column with an *n*-heptane–2-propanol mobile phase. Almost all normal-phase methods were reported before 1984. Diol [89,90] and nitrile [6,89,90] stationary phases have also been used in the normal-phase mode and cyclohexyl [28,79] and phenyl [82,121] stationary phases in the reversed-phase mode.

Sparacino and Hines [118] studied retention and resolution of 14 NMC pesticides and metabolites in normal- and reversed-phase modes on a variety of columns. Silica, cyanopropyl and propylamine columns were studied in normal-phase mode with two mobile phase systems (isopropanol–heptane and dichloromethane–heptane). C_{18} and ether phase

columns were studied in reversed-phase mode with three mobile phase systems (water–methanol, water–tetrahydrofuran and water–acetonitrile). Although normal-phase mode was for the most part satisfactory, reversed-phase mode gave generally superior results. The C_{18} column and water–acetonitrile mobile phase gave overall best performance in terms of resolution of the pesticides and UV transparency of the mobile phase. Aten and Bourke [122] reported retention volumes for eight NMCs on a C_{18} column with six different mobile phases.

Two methods [107,114] employed unmodified silica HPLC columns with aqueous (*i.e.*, reversed-phase) mobile phases with good success. This was especially useful for the isocratic separation of aldicarb and its oxidation products [114]. Another method [123] separated aldicarb and its oxidation and hydrolysis products isocratically on a cyanopropyl bonded stationary phase with a water–acetonitrile mobile phase.

Kikta *et al.* [124] explored the influence of column temperature on retention using a C_{18} column and found that at 27°C carbofuran could not be completely resolved from 2,3-dihydro-2,2-dimethyl-7-benzofuranol, a metabolite of carbofuran. At 70°C with a modified water–methanol ratio in the mobile phase the elution order was reversed and complete resolution was achieved.

5. DETECTION

5.1. UV absorbance

UV absorbance has been the most commonly used detection method in HPLC determination of NMC pesticides [1,2,118,122–131, and relevant references in Tables 3–5] probably because of its wide applicability and consequent presence in most HPLC systems. However, UV is subject to interference from sample co-extractives and also lacks sensitivity for some compounds, two factors which limit its usefulness for analysis of environmental samples. Sparacino and Hines [118] studied absorption maxima and extinction coefficients for 14 NMC pesticides and metabolites and found that with the exception of carbaryl (222 nm), methomyl (233 nm) and Mobam (223 nm) absorption maxima occurred at 202 nm or less. This is a region where plant co-extractives also commonly absorb strongly.

In order to overcome these limitations some workers have employed derivatization of NMCs either before HPLC determination or on-line following chromatographic separation. Nelsen and Cook [11] improved the resolution of carbofuran from soil co-extractives by performing base and acid washes of soil extracts which converted carbofuran to its phenolic moiety. The phenol was well resolved from co-extractives. Any phenol initially present as a metabolite was removed in the initial base wash.

Li *et al.* [55] hydrolyzed butocarboxim and its oxidation products. This released methylamine which they derivatized with 1-fluoro-2,4-dinitrobenzene (FDNB) to form N-methyl-2,4-dinitroaniline which was determined by HPLC. Lauren and Agnew [83] reacted the phenolic metabolites of carbofuran with FDNB to form 2,4-dinitrophenyl ether derivatives and achieved detection limits of 2–4 ng. Pietrogrande *et al.* [82] hydrolyzed carbaryl and derivatized the resulting 1-naphthol with 4-aminoantipyrine. The derivative was determined by HPLC–UV at 460 nm, a wavelength at which co-extractive compounds are not likely to absorb. The detection limit was 3 ng.

A recent method reported by Tena *et al.* [131] employed a post-column derivatization reaction for UV detection of carbaryl and 1-naphthol. The post-column reaction required the delivery of three reagents to accomplish the hydrolysis of carbaryl with NaOH, diazotization of sulphanilic acid with $NaNO_2$ and coupling of 1-naphthol with diazotized sulphanilic acid. Derivatization provided stonger absorption at 280 nm and also allowed monitoring of the chromatogram at 506 nm, thus minimizing the possibility of interference from co-extractives. An interesting aspect of the method was that the flow cell of the UV detector was packed with C_{18} bonded silica (60–100 μm) which served to retain and concentrate the derivative in the flow cell and thereby allow determination at low concentration levels; the detection limit was <3.5 ng. In order to maximize sensitivity, a post-column pump was used to deliver water to the flow stream down stream from the reactor to dilute the aqueous acetonitrile mobile phase and favour retention of the derivative on the C_{18} solid-phase in the flow cell. A fifth reagent (acidified ethanol) was delivered when required, through a switching valve located just prior to the flow cell, to elute the derivative from the C_{18}

solid-phase after each peak had been completely integrated.

5.2. Fluorescence

Fluorescence detection is not nearly as widely applicable as UV detection, since most NMCs do not possess native fluorescence. However, for those which fluoresce, or can be made to fluoresce by derivatization, fluorescence detection offers a degree of selectivity and sensitivity often an order of magnitude or more over that offered by UV. Frei and co-workers [3,4] were the first to report the use of fluorescence detection for the determination of NMC pesticides. Fourteen NMCs were rendered fluorescent by derivatization with dansyl chloride prior to injection. Detection limits were between 1 and 10 ng. This approach was used to determine carbaryl [62,63] and carbofuran [64] residues in vegetables.

Moye and Wade [92] introduced a fluorometric enzyme inhibition detector for NMCs. In this system, the effluent from a reversed-phase LC column was incubated with cholinesterase, which was introduced via a post-column reagent-delivery pump, and the resulting partially inhibited cholinesterase was reacted with N-methyl indoxyl acetate to produce a fluorophore. The presence of a cholinesterase inhibitor was indicated by a reduction in the baseline fluorescence. Detection limits ranged from 0.2 ng for carbofuran to 50 ng for aldicarb.

A significant development occurred in 1977 when Moye *et al.* [121] introduced a post-column derivatization reaction for NMCs. Sodium hydroxide introduced by a post-column reagent delivery pump was used to hydrolyze the NMC at 90°C and release methylamine. This methylamine was subsequently reacted with a mixture of *o*-phthalaldehyde (OPA) and 2-mercaptoethanol, introduced by a second post-column pump, to form a highly fluorescent derivative identified as (1-hydroxyethylthio)-2-methylisoindole [132]. The detection limit for methomyl was as low as 0.1 ng.

In a series of studies, Krause refined the chromatographic and derivatization parameters [133, 134], introduced a complex extraction and clean-up procedure for crop samples [102] and validated the method through collaborative studies [103,104]. The method was rapidly adopted by a large number of workers for determination of various NMCs in a variety of substrates including water [18,32,39,42, 43,48], soil [18,76] and plant tissue [65,73,76,78,79, 87,91,98,110,111,114].

During this time there were also reports of the determination of naturally fluorescent aryl NMCs (aminocarb, carbaryl, carbofuran, 3-hydroxycarbofuran and Mobam) without derivatization [22,67,72, 94,105,135]. Detection of 0.5 ng carbaryl was reported [135].

In 1983 Nondek *et al.* [36,120] reported the use of a catalytic solid-phase reactor consisting of a column packed with an anion-exchanger resin maintained at 100–120°C for hydrolysis of NMCs. This reactor eliminated the need for the NaOH post-column reagent delivery pump and allowed detection of as little as 0.1 ng aldicarb and 0.85 ng methiocarb. She *et al.* [47] successfully used this technique with a less expensive anion exchanger to determine carbaryl in polluted water samples. Jansen *et al.* [136] miniaturized the solid-phase reactor to render it compatible with narrow-bore LC on 1 mm I.D. columns and observed detection limits of 0.4 ng for methomyl and 1.0 ng for propoxur. In a study which extended the application of the solid-phase reactor to determination of 22 NMC pesticides and 10 metabolites on crop samples De Kok *et al.* [74] used magnesium oxide in place of the anion exchanger and reduced reaction band broadening to zero.

Another approach to hydrolysis of NMCs prior to derivatization with OPA–2-mercaptoethanol was proposed by Miles and Moye [44,137] who employed a photolytic reactor consisting of a UV lamp inserted in the centre of a woven coil of PTFE tubing. This also eliminated the need for one post-column pump. Detection limits were about 1.0 ng.

A useful simplification of the post-column reaction technique which eliminated the need for both an NaOH post-column pump and solid-phase or photolytic reactors was reported by McGarvey [138]. In this approach the hydrolysis and derivatization steps were combined by the use of a single reagent, OPA–2-mercaptoethanol in 0.01 *M* KOH, which was delivered by a single post-column pump. The detection limit for eleven NMCs by the single-stage derivatization system was about 0.1 ng. Reproducibility of retention times and peak heights was also good, coefficients of variation averaging 0.2% and 2.3%, respectively. This technique has been

used to determine oxamyl in potatoes [108], and oxamyl and methomyl in crops and water [45].

5.3. Electrochemical detection

Electrochemical detection is possible for analytes capable of being oxidized or reduced at moderate electrode potentials. It offers a degree of selectivity through adjustment of electrode potential, but has seen limited use for detection of NMC pesticides. Anderson and Chesney [34] studied oxidative electrochemical detection of aminocarb, BPMC and carbaryl at applied potentials of up to 1.2 V, but successfully detected only aminocarb which exhibited a detection limit of 140 pg. Alawi and Rüssel [21] determined methomyl oxime, but not methomyl, by electrochemical detection and observed a detection limit of 100 pg. Mayer and Greenberg [139] determined carbaryl, methiocarb, propoxur and trimethacarb at applied potentials of 1.31 to 1.37 V and observed detection limits ranging from 1–1000 ng. Only methiocarb and carbaryl exhibited potential for detection by this method at reasonable sensitivity.

Anderson *et al.* [40] determined aminocarb in water (detection limit 53 pg) using a microarray electrochemical detector. Olek *et al.* [70] determined six NMC pesticides in vegetables with detection limits of 0.5–2 ng. Thomas and Sturrock [140] could detect only aminocarb at an applied potential of 1.3 V but detected aldicarb, aminocarb, bendiocarb, carbaryl and methiocarb at 1.9 V. They were able to achieve a detection limit of 5 pg for aminocarb at 1.3 V and about 0.1 ng for the rest at 1.9 V. Von Nehring *et al.* [41] determined aminocarb and carbaryl at 1.25 and 1.3 V and Kawai *et al.* [141] determined carbaryl at 0.75 V (detection limit 0.03 ng).

Krause [106] used a post-column pump delivering NaOH solution to hydrolyze six NMC pesticides to their phenolic moieties and detected the phenols at 0.55 V. Detection limits in fruit and vegetable extracts ranged from 0.25 ng for carbaryl to 0.65 ng for bufencarb.

5.4. Mass spectrometry

Several workers have reported the use of mass spectrometry (MS) for detection of NMCs. The earliest reports [16,17] involved use of a fraction collector to collect carbaryl peaks as they were eluted from a UV detector and confirmation of their identity off-line using low- and high-resolution field desorption MS. Schmid *et al.* [93] used off-line electron impact MS to identify HPLC fractions containing bufencarb and propoxur.

Wright and co-workers [6,142] employed on-line HPLC–MS with a moving belt interface and a 2-propanol–hexane mobile phase and methane chemical ionization and obtained readily identifiable mass spectra. Detection limits ranged from 2.5 to 27.2 ng for nine NMCs. Cairns *et al.* [66] also used a moving belt interface with a hexane–isopropanol–dichloromethane mobile phase and methane chemical ionization mass spectrometry to determine methomyl and oxamyl. A protonated molecular ion was observed for methomyl (m/z 163) but not for oxamyl.

Voyksner and co-workers [9,143] applied on-line thermospray LC–MS to the determination of several NMCs using an aqueous methanol mobile phase and post-column addition of ammonium acetate for the ionization. Detection limits were in the range 1–8 ng. Voyksner and co-workers [144,145] also optimized conditions for direct liquid introduction LC–MS with an aqueous acetonitrile mobile phase and observed detection limits of 40–50 ng. Shalaby [146] employed on-line thermospray HPLC–MS for determination of methomyl with an aqueous acetonitrile or aqueous methanol mobile phase and post-column addition of ammonium acetate.

Bellar and Budde [14] determined 12 NMCs in water samples using on-line thermospray LC–MS with ammonium acetate in the aqueous acetonitrile mobile phase, and obtained detection limits ranging from 8 ng for methiocarb to 320 ng for carbaryl. Chiu *et al.* [147] used the same technique, except with methanol instead of acetonitrile in the mobile phase, and obtained detection limits in the low nanogram range. Bellar *et al.* [148] also used a particle beam interface for LC–MS determination of carbaryl and found that post-column addition of ammonium acetate solution resulted in enhanced positive ion abundance.

Liu *et al.* [69] used thermospray LC–MS with selected ion monitoring for determination of seven NMCs in fruits and vegetables, but obtained poor sensitivity for aldicarb, aldicarb sulphoxide, metho-

myl and oxamyl. Durand *et al.* [57] and Barceló *et al.* [53] studied the influence of different LC eluents in positive and negative ion mode thermospray LC–MS spectra of carbaryl, carbofuran, oxamyl and propoxur. They found that in positive ion (PI) mode the reversed-phase eluents produced a base peak corresponding to $[M + NH_4]^+$, but that relative intensities of other adduct ions varied with varying eluents. Thus the potential for positive identification by thermospray LC–MS may be extended by the use of different LC eluent mixtures. In negative ion (NI) mode carbaryl exhibited a base peak attributed to $[M - CONHCH_3 + CH_3COOH]^-$ and oxamyl a base peak attributed to $[M - CON(CH_3)_2 + HCOO]^-$. Sensitivity for carbaryl and oxamyl was 1.5 and 3 orders of magnitude better, respectively, in PI mode than in NI mode. Carbofuran and propoxur did not show any response in NI mode.

5.5. Other detection techniques

Ramsteiner and Hörmann [149] utilized a cholinesterase inhibition autoanalyzer for detection of dioxacarb and calculated a detection limit of 200 ng. The chief advantage of this method was that there was no interference from non-cholinesterase-inhibiting co-extractives.

In one study [20] chlorine selective electrolytic conductivity was evaluated for 37 pesticides including methomyl and carbaryl. The detector was found to be suitable for methomyl but unsuitable for carbaryl. It was speculated that adaptation of S- and N-selective electrolytic conductivity to HPLC would increase the potential applications of the system, but no subsequent related studies were found.

Another study of the behaviour of pesticides in normal-phase HPLC on a silica column [119] used IR detection at 5.75 μm to monitor 12 NMC insecticides. The study used 1-mg/ml pesticide standards and made no suggestion that IR would be suitable for trace analysis.

6. CONCLUSIONS

It is clear that a large and very diverse body of literature exists describing the determination of NMC pesticides by HPLC. This represents a well-developed field of study, but one in which, nonetheless, there is much room for further work. Of particular usefulness will be additional developments in sensitive and selective detection systems which minimize the need for clean-up of samples.

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