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Identification of Carbamates by Particle Beam/Mass Spectrometry

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The possibility of analysing 33 carbamate pesticides and 14 of their transformation products was investigated utilizing flow injection particle beam/mass spectrometry (PBMS) with electron impact (EI) ionization and ammonia and methane positive and negative chemical ionization (CI). Optimum operating conditions of the interface and mass spectrometer in each mode were determined, with special attention given to spectrum quality; variables investigated included ion source temperature and ion source pressure in CI experiments. Ammonia, as a reagent gas, provided less fragmentation and better quantitative results than methane. The CI response was generally higher with positive ion detection (PCI) than with negative ion detection (NCI), but NCI was found to be highly selective for compounds such as aminocarb, asulam and thiophanate-methyl. As regards analyte detectability, EI performed best for most compounds, with the spectra providing relevant structure information. The response of more polar degradation products is generally larger by 2–3 orders of magnitude compared with the parent compounds. When analysing real samples, the combined use of CI for molecular mass determination and EI for structure elucidation is required. The spectral information from this study and additional chromatographic data were used for the determination of low- and sub-μg l^{-1} levels of the test carbamates in surface water.

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INTRODUCTION

Carbamate pesticides are widely used because the class of compounds covers a broad spectrum of activity with a high efficiency and a relatively low persistence. The presence of carbamates has been reported for many compartments of the environment[1] and, obviously, there is a need for analytical procedures for identification, confirmation or screening. Carbamates, in general, and their degradation products, in particular, are often quoted to be polar, involatile and thermally labile. Nevertheless, it is possible to use gas chromatography (GC) with mass spectrometric (MS) detection for their determination, albeit under specific conditions[1–6] or after derivatization.[7,8]

The use of liquid chromatography (LC) with MS for the analysis of carbamates in environmental samples with several LC/MS interfaces has also been reported (e.g. Refs 9–19). In LC/MS thermospray (TSP) is the most frequently used interface, but its generally reported good sensitivity often refers to the monitoring of only a single ion, e.g. $[M + H]^+$ or $[M + NH_4]^+$. In addition to this limitation, the lower mass range is often not monitored, because of the presence of abundant solvent cluster ions; a typical low cut-off mass lies in the range 160–180 u, i.e. above the molecular mass of some degradation products. Atmospheric pressure ionization (API) interfaces are rapidly gaining in popularity, mainly because of the reported excellent sensitivity and of the possibility of inducing additional fragmentation before mass analysis; thus, molecular mass and structural information can easily be obtained.[20–22] As with TSP, detection limits relevant to environmental analysis generally require the use of selected ion monitoring (SIM).[23] In addition, co-elution often obscures full-scan spectra with pre-analyser fragmentation in API of environmental samples. In other words, although TSP- and API-based detection can be applied for the carbamates, these methods do have some drawbacks. Given recent developments in on-line methods for trace-enrichment in LC/MS, it is feasible to use the generally less sensitive particle beam (PB) interface with LC/MS.

So far, PB has proved to be the only robust LC/MS type of interface which opens up the full identification power of electron impact (EI) ionization mass spectrometry. Similarly to GC/MS, PBMS is capable of generating solvent-independent chemical ionization (CI)

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spectra. CI with positive ion detection (PCI) is generally used to obtain molecular mass information for labile compounds which produce no, or only weak, molecular ions under EI conditions, whereas CI with negative ion detection (NCI) is usually employed to obtain selectivity and sensitivity for compounds with high electron affinity or acidity.[24,25] The generally low sensitivity of detection (typically 10–500 ng injected) and non-linearity of the response, particularly near the limit of detection, are reported to be major drawbacks of PBMS. The sensitivity of detection was successfully enhanced by the application of on-line trace enrichment.[26] The problem of non-linearity has not yet been overcome, although co-elution of analytes and a 'carrier compound' has been reported to provide a remedy in some cases (see, e.g., Refs 27 and 28).

Here, we report an investigation of on-line trace enrichment LC/PBMS of carbamates and some of their transformation products, using EI, PCI and NCI with methane or ammonia. The aim of this investigation was to establish the applicability and limitations of the use of each ionization mode, for the particular compounds, in order to provide a basis for the selection of the 'best' mode(s) for the identification of organic micro contaminants, e.g. in long-term monitoring programmes, and for structural elucidation of transformation products from fate studies (see, e.g., Ref. 29). In a follow-up study,[2] the results were applied in an automated method for the detection of carbamates and transformation products; the best performance was observed for 17 of these analytes, which were identified and detected at low- and sub-$\mu g\ l^{-1}$ levels in surface water.

EXPERIMENTAL

Instrumentation

An HP 1090 HPLC system (Hewlett-Packard, Waldbronn, Germany), equipped with an autosampler, six-port switching valve (Rheodyne, Cotati, CA, USA) and filter photometric detector, was used for LC and flow injection (FI) experiments. The LC separations were carried out on a 250 mm × 4.6 mm i.d. Supelco LC-18-DB analytical column packed with 5 μm Supelcosil C-18 (Supelco, Bornem, Belgium). Details of the automated on-line trace-enrichment procedure are given in Ref. 2.

PBMS detection was performed on an HP 5989A MS Engine, equipped with an HP 59980B PB interface and a 'high-energy dynode' (HED) detector. The connection of LC and PB was achieved by a 50 cm × 0.12 mm i.d. stainless-steel capillary. The helium flow of the PB nebulizer was optimized by a standard procedure and operated at the optimum flow rate of 2–2.5 1 min^{-1} (30–40 psi inlet pressure indication). The PB desolvation chamber was kept at 70 °C.

The mass spectrometer was operated at a source temperature of 200 °C and an analyser temperature of 100 °C, unless mentioned otherwise. The mass spectrometer was calibrated by the standard 'high-mass tune' option and using perfluorotributylamine (PFTBA); the HED voltage was kept constant at 10 kV, with the multiplier voltage set to 100 V above the tune value. EI spectra (70 eV ionization energy) were acquired in the mass range 65–350 u at a scan rate of 0.36 scan s^{-1}; the manifold pressure was maintained below 5×10^{-5} Torr (6.7×10^{-3} Pa) by regulating the PB helium flow. Under CI conditions, methane or ammonia was used as the reagent gas for PCI and NCI; the reagent gas pressure, measured by a fore vacuum ion gauge between the PB port valve and the ion source, was kept at 0.7–0.9 Torr (90–120 Pa) which corresponds to an indicated manifold pressure of $(1–2) \times 10^{-4}$ Torr [$(1.3–2.6) \times 10^{-2}$ Pa]. Spectra were acquired from 85 to 350 u at 0.32 scan s^{-1} in the PCI mode and from 50 to 350 u at 0.31 scan s^{-1} in the NCI mode.

The system was controlled and data were acquired by using an HP UX 98578X data system, running on an HP/UNIX Series 9000/345 computer. Later in the experimental work, MS Chemstation software (G1034C, DOS Series) running under Microsoft Windows on an HP Vectra 486/66X computer was used instead. A user macro program was used to facilitate calculation of the signal-to-noise (S/N) ratios.

Chemicals and reagents

Standards of pesticides were obtained from Riedel-de Haën (Seelze, Germany), the US Environmental Protection Agency Repository for Toxic and Hazardous Materials (USEPA, Research Triangle Park, NC, USA) and Dr. Ehrenstorfer (Augsburg, Germany). Some of the *N*-methylcarbamates were a gift from Dr. A. de Kok (Food Inspection Service, Alkmaar, The Netherlands). All compounds were at least of 95% purity. HPLC-grade acetonitrile was obtained from Westburg (Leusden, The Netherlands) and HPLC-grade water, methanol, acetic acid and ammonium acetate from J. T. Baker (Deventer, The Netherlands). Helium, for the PB nebulizer and for degassing of solvents (Hoekloos, Schiedam, The Netherlands), was of 99.99999% purity; the purities of methane and ammonia reagent gases from the same producer were 99.99995% and 99.9996%, respectively.

Procedures

Standard solutions (200 mg l^{-1}) of all compounds were prepared in methanol. These stock solutions were stored in the dark, at −18 °C, and diluted with eluent to appropriate concentrations in mixtures and samples prior to analysis. With the exception of benomyl and thiophanate-methyl, the compounds showed no degradation during the 1 year period of the study.

The pH of the ammonium acetate solution used in the LC eluent was adjusted to 5 by adding acetic acid. An LC gradient, composed of methanol (A) and 0.1 M aqueous ammonium acetate (B), was used at a flow rate of 0.4 ml min^{-1}; the linear gradient applied was programmed from 10% (v/v) to 90% A in 45 min and then back to 10% A in 5 min. Because the concentration of ammonium acetate in the LC eluent gradually decreases with this gradient, it should be mentioned that despite

reported beneficial effects of ammonium acetate in the LC eluent on PBMS,[27] only a slight (1.5–2-fold) enhancement of signal was observed at best in our experiments. FI of 1–25 μl volumes was performed with an eluent consisting of 50% A and 50% B (v/v). Details of the analytical procedure and automation of the system are reported in Ref 2.

The calculation of S/N values was automated by a self-compiled macro program which (i) searched detected peaks for the most abundant ion (base peak), (ii) created an appropriate extracted ion chromatogram, (iii) calculated the value of the signal maximum (peak height) from a 1 min region around the top of the chromatographic peak and (iv) compared it with the maximum noise (peak height) from a 1 min region in the early part of the flow injectogram. Special precaution was taken to select a representative region for noise calculations which was subsequently used for all analytes; the amounts injected were 500 ng.

RESULTS AND DISCUSSION

Structure elucidation of carbamates by LC/PBMS

The information content of EI, PCI and NCI spectra of 33 carbamates and 14 of their transformation products was studied with the aim of proposing an analytical strategy for the unambiguous identification of the analytes when found in real samples. EIMS is a valuable tool in environmental analysis, as both the molecular ion and abundant fragments can be used to characterize compounds. Since carbamates, like many environmental pollutants, are of anthropogenic origin, EI spectra are often available in common spectral libraries and library searches can be of great use. PCI typically provides relevant additional or confirmatory information on the molecular mass of the analytes of interest. The sensitivity of detection in PCI depends on the proton affinity of the compound and on the degree of fragmentation; the latter can be influenced by a proper choice of the reagent gas. We chose to use methane or ammonia, which represent the two extremes of the commonly accessible proton affinity scale. As regards the use of methane, it is noted that methanol penetrates into the source and that, effectively, the acidity of protonated methanol might pose the real upper limit in our experiments. NCI was studied because several carbamates may be expected to give a better response in this mode than in EI or PCI and, thus, to be detectable with more selectivity.

To facilitate discussion, the compounds studied were divided into four classes, according to structural features. The carbamates and their degradation products, which are basically *N*-substituted carbamic acid esters (RO—C(O)—NR′R″), were divided into three subclasses, the general structures of which are shown in Fig. 1: *N*-methyl aryl carbamates (class 1), *N*-methyl oxime carbamates (class 2) and *N*-substituted aryl ester carbamates (class 3). All other compounds, triallate, pirimicarb and its degradation products V and VI and 1-naphthol, were grouped in class 4. Molecular structures of individual compounds are given in Fig. 2.

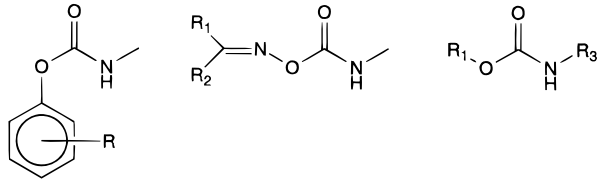

Figure 1. General structures of the three classes of carbamate pesticides distinguished.

Electron impact ionization

EI spectra of 33 carbamates and 14 of their degradation products were obtained by FI of 5 μg of each compound (25 μl of a 200 mg l^{-1} methanol solution); each analyte was injected three times. When the absolute amount injected was reduced to 500 ng (2.5 μl of a 200 mg l^{-1} solution or 25 μl of a 20 mg l^{-1} solution), chlorpropham and triallate did not show any response and the amounts of thiofanox, promecarb, degradation product V, isoprocarb and butocarboxim were at the limit of detection (S/N = 2–3). Table 1 gives relevant data on the EI spectra of all compounds. For the sake of brevity, only the five most abundant ions from the EI spectra are reported; if a low-abundance molecular ion signal was observed in addition to these five peaks, its intensity is reported as well. In the case of aldicarb sulfone, an ion at *m/z* 223 is observed, which we attribute to self-protonation. Although we did not assign compositions to all reported peaks, an attempt was made to identify most fragment ions. Peaks which were found to be related to compound structures by common fragmentation mechanisms[30–32] are labelled '+' in Table 1, and all other peaks are labelled '−'. EI spectra are briefly discussed below.

The spectra of class 1 compounds mostly show molecular ions, $M^{+\cdot}$, whereas the loss of methyl isocyanate, CH_3NCO, from $M^{+\cdot}$ generally leads to intense $[M - 57]^{+\cdot}$ signals. Some of the class 1 compounds show fragmentation reactions which are characteristic of a specific side-chain, e.g. *m/z* 107 in the spectra of ethiofencarb ($[M - CH_3NCO - CH_3CH_2S]^{+\cdot}$), its sulfoxide ($[M - CH_3NCO - CH_3CH_2SO]^{+\cdot}$) and sulfone ($[M - CH_3NCO - CH_3CH_2SO_2]^{+\cdot}$). Class 2 compounds all show extensive fragmentation in their mass spectra and a molecular ion signal is often absent. The fragmentation of class 2 compounds is all but straightforward, as is illustrated by the large differences in the spectra of the structurally similar aldicarb and aldicarb sulfoxide. Class 3 compounds typically show abundant isocyanate ions, $[R_2NCO]^{+\cdot}$, which result from the loss of an alcohol molecule, R_1OH, from the carbamate ester moiety; only chlorpropham and propham exhibit abundant anilinium ions (*m/z* 127 and 93), formed by a McLafferty rearrangement with additional transfer of a hydrogen atom from the isopropyl group ('double McLafferty rearrangement').

Of the 47 analytes studied, 28 had reference spectra in a commercially available EI spectral library.[33] When using default settings of search strategy parameters, 25 compounds matched well with spectra from this library (fit quality between 50 and 90%), despite the fact that

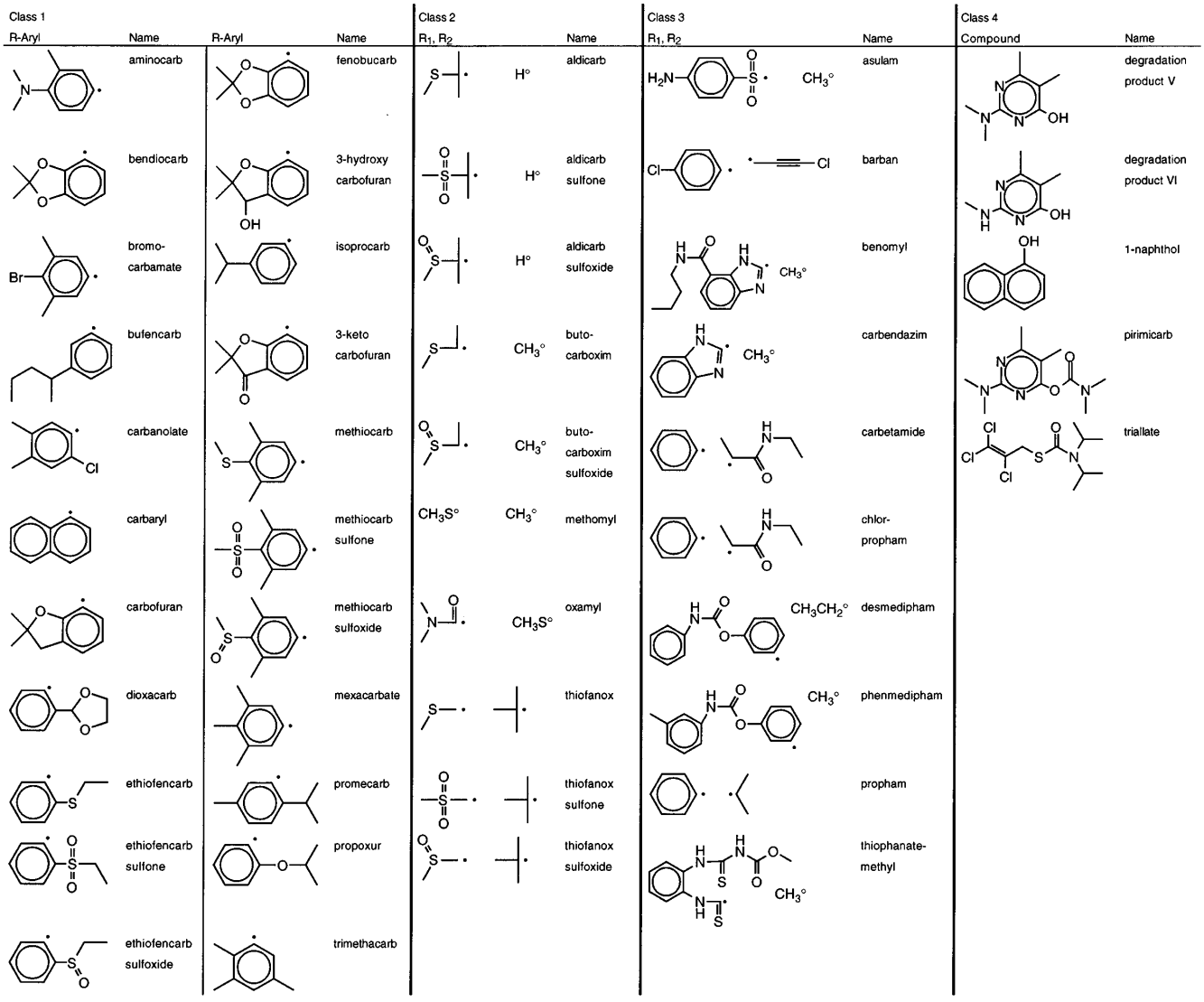

Figure 2. Structures of the compounds investigated.

the library spectra were generally obtained under different inlet conditions. In all these cases, the analytes were mentioned as the first hit, whether searched after FI or after LC separation. Marked differences with the spectra of the commercial library were observed in three instances only, viz. with methomyl (*m/z* 88 instead of 'library' *m/z* 87), oxamyl (*m/z* 98 instead of 'library' *m/z* 99) and thiofanox (large differences in relative abundances of ions). To avoid future problems, e.g. in the automation, compound spectra obtained from FI experiments were compiled in a user library. No relevant influences of changes in the chromatographic conditions, e.g. the eluent composition, on the spectra of the carbamates were observed throughout the 12 month period and the library was successfully used for the identification of carbamates in LC/PBMS studies.

Chemical ionization

The unambiguous identification of carbamates requires molecular mass information, which is often not clearly present in EI spectra (or even absent); molecular ion signals were present in 29 out of the 47 spectra. Molecular mass information can usually be obtained by using CI; in our experimental set-up this requires the introduction of a reagent gas, the availability of a proper tune file and a readjustment of the PB interface. On the basis of other reports on PCI of carbamates (see, e.g., Refs 3, 10 and 34–36), methane CI is expected to yield protonated molecules and sometimes abundant fragmentation, whereas ammonia CI might produce protonated molecules and ammonium adduct ions. With both reactant gases, protonated molecules should be observed for most carbamates. NCI of carbamates has not been systematically investigated, although there are indications from APCI experiments that NCI is not so well suited for carbamates.[13] In order to investigate the feasibility of CI for carbamate detection with a PB inlet system, we tested 33 analytes (shown in Table 2), under PCI and NCI conditions using methane and ammonia. Special attention was devoted to the influence of ion source temperature and gas pressure on the appearance of spectra.

Table 1. Major peaks and their relative intensities in the FI/PB-EI mass spectra of 33 carbamates and 14 of their transformation products

Compound[a] (M_r)	$M^{+\cdot}$	*m/z* (% relative abundance, identified)[b] Fragment ions				
Class 1						
Aminocarb (208)	208 (18, +)	151 (100, +)	150 (82, +)	136 (45, +)	120 (19, −)	
Bendiocarb (223)	223 (17, +)	166 (60, +)	151 (100, +)	126 (57, −)	108 (8, +)	
Bromocarbamate (257, ^{79}Br)	257 (1, +)	200 (100, +)	121 (87, +)	91 (31, −)	77 (19, −)	
Bufencarb (221)		164 (33, +)	135 (13, +)	122 (48, +)	121 (100, +)	107 (24, +)
Carbanolate (213, ^{35}Cl)		156 (77, +)	141 (25, +)	121 (100, +)	91 (28, −)	77 (28, −)
Carbaryl (201)	201 (5, +)	144 (100, +)	115 (42, +)	89 (5, +)	72 (4, −)	
Carbofuran (221)	221 (6, +)	164 (100, +)	149 (55, +)	131 (16, +)	122 (15, +)	
Dioxacarb (223)		166 (81, +)	149 (18, +)	121 (100, +)	107 (14, −)	73 (35, +)
Ethiofencarb (225)	225 (3, +)	168 (37, +)	139 (3, +)	107 (100, +)	77 (12, −)	
Ethiofencarb sulfone (257)		200 (12, +)	171 (1, +)	136 (2, −)	107 (100, +)	77 (14, −)
Ethiofencarb sulfoxide (241)		184 (4, +)	168 (7, +)	164 (6, −)	107 (100, +)	77 (20, −)
Fenobucarb (207)		121 (100, +)				
3-Hydroxycarbofuran (237)	237 (5, +)	180 (54, +)	162 (18, +)	151 (21, +)	147 (27, −)	137 (100, −)
Isoprocarb (193)	193 (2, +)	136 (84, +)	121 (100, +)	103 (11, +)	91 (11, −)	77 (9, −)
3-Ketocarbofuran (235)	235 (3, +)	178 (100, +)	163 (33, +)	137 (29, −)	110 (19, +)	92 (8, −)
Methiocarb (225)	225 (9, +)	168 (100, +)	153 (63, +)	109 (37, −)	91 (12, −)	
Methiocarb sulfone (257)	257 (1, +)	200 (96, +)	185 (55, +)	137 (58, −)	121 (100, +)	91 (30, −)
Methiocarb sulfoxide (241)	241 (10, +)	184 (72, +)	169 (100, +)	153 (32, −)	123 (23, −)	107 (89, −)
Mexacarbate (222)	222 (41, +)	165 (100, +)	164 (57, +)	150 (50, +)	134 (42, −)	
Promecarb (207)	207 (3, +)	150 (72, +)	135 (100, +)	107 (5, +)	91 (11, +)	
Propoxur (209)	209 (2, +)	152 (27, +)	110 (100, +)	92 (3, +)	81 (5, +)	
Trimethacarb (193)	193 (3, +)	136 (100, +)	121 (59, +)			
Class 2						
Aldicarb (190)		144 (33, +)	115 (79, +)	100 (84, +)	89 (100, +)	68 (94, +)
Aldicarb sulfone[c] (222)	223 (1, +)	143 (15, +)	122 (3, +)	86 (100, +)	81 (12, +)	68 (55, +)
Aldicarb sulfoxide (206)		191 (1, +)	143 (14, +)	131 (5, +)	86 (100, +)	68 (63, +)
Butocarboxim (190)		144 (18, +)	117 (2, +)	87 (26, +)	75 (29, +)	71 (100, +)
Butocarboxim sulfoxide (206)		149 (6, +)	143 (7, +)	92 (9, +)	86 (100, +)	68 (20, +)
Methomyl (162)	162 (2, +)	144 (2, +)	115 (3, +)	105 (100, +)	88 (33, +)	
Oxamyl (219)	162 (44, +)	145 (25, +)	115 (25, +)	98 (85, +)	72 (100, +)	
Thiofanox (218)		115 (83, +)	99 (58, +)	84 (100, +)	73 (67, −)	
Thiofanox sulfone (250)		93 (5, −)	92 (64, −)	91 (100, −)	89 (3, −)	
Thiofanox sulfoxide (234)		84 (100, +)	69 (42, −)			
Class 3						
Asulam (230)	230 (13, +)	198 (69, +)	156 (100, +)	108 (61, −)	92 (97, +)	
Barban (257, ^{35}Cl)	257 (9, +)	222 (40, +)	153 (100, +)	125 (30, +)	90 (28, −)	
Benomyl (290)		191 (85, +)	159 (100, +)	146 (16, −)	132 (16, +)	105 (25, −)
Carbendazim (191)	191 (97, +)	159 (100, +)	146 (19, −)	132 (18, +)	105 (27, −)	
Carbetamide (236)	236 (7, +)	165 (32, +)	119 (100, +)	91 (29, +)	72 (2, +)	
Chlorpropham[d] (213, ^{35}Cl)	213 (51, +)	171 (23, +)	154 (25, +)	127 (100, +)	99 (9, −)	
Desmedipham (300)	300 (<1, +)	181 (62, +)	122 (34, −)	119 (100, +)	109 (43, +)	
Phenmedipham (300)	300 (<1, +)	167 (68, +)	133 (100, +)	122 (22, −)	104 (44, −)	91 (14, −)
Propham[d] (179)		137 (20, +)	119 (20, +)	93 (100, +)	77 (13, +)	
Thiophanate-methyl (342)	342 (18, +)	191 (40, −)	159 (38, −)	150 (100, +)	73 (58, −)	
Class 4						
Degradation product V (167)	167 (100, +)	153 (53, +)	138 (58, +)	123 (27, +)	69 (22, −)	
Degradation product VI (153)	153 (100, +)	124 (44, +)	110 (5, −)	96 (15, −)	69 (23, −)	
1-Naphthol (144)	144 (100, +)	115 (63, +)				
Pirimicarb (238)	238 (27, +)	193 (2, +)	166 (100, +)	138 (5, −)	72 (52, +)	
Triallate (305, ^{35}Cl)		145 (13, +)	143 (12, +)	128 (23, +)	86 (100, +)	70 (17, −)

[a] Amount injected 500 ng unless indicated otherwise.
[b] '+' if identified, '−' if not.
[c] $[M + H]^+$ instead of $M^{+\cdot}$.
[d] Amount injected 5 μg.

Thermal decomposition is commonly known to occur in GC/MS of carbamates (see, e.g., Refs 3 and 4) and it has also been reported to occur in PBMS of some carbamates;[13] therefore, the ion source temperature may be a critical parameter. In addition, the ion source temperature might give rise to 'tailing' of the chromatographic peak; this phenomenon was confirmed by the present experiments, as reported by Betowski *et al.*[37] The tailing is attributed to retarded evaporation of the analyte upon ion source wall impact of the particle

Table 2. Major peaks and their relative intensities in PCI and NCI spectra of 35 carbamates and their degradation products in FI/PBMS[a]

Compound	PCI *m/z*	PCI *I*(%)[b] NH_3	PCI *I*(%)[b] CH_4	ID[c]	NCI *m/z*	NCI *I*(%)[b] NH_3	NCI *I*(%)[b] CH_4	ID
Class 1								
Aminocarb	209	38	56	P1	150	100	100	N2
	152	100	100	P3				
Bendiocarb	224		67	P1	165	100	100	N2
	167		100	P3				
Bromocarbamate	275	100		P2	199	100	100	N2
	258	25	95	P1				
	201		100	P3				
Carbaryl	240	3			157	31	100	
	219	100		P2	143	100	65	N2
	202	15	25	P1				
	162	12		P4				
	145	10	100	P3				
Carbofuran	239	62		P2	177	45		
	222	69	60	P1	163	100	100	N2
	182	100		P4				
	165		100	P3				
3-Hydroxycarbofuran	255	10		P2	235		16	
	238	1	20	P1	194		20	
	220		19	P11	179	100	100	N2
	198	11		P4				
	181	4	53	P3				
	163	100	100	P5				
	147		5					
	115		4					
Dioxacarb	241	21		P2	180		36	
	224	10	19	P1	178		87	
	195		1		165	100	100	N2
	184	10		P4	122		11	
	167	100	100	P3	121		16	
	162	1						
	151		2	P7				
	139	3						
	123		10					
	122	31						
Ethiofencarb	243	100		P2	167	100	100	N2
	226	27	43	P1	107	30	58	
	183	25		P15				
	169	28	63	P3				
	166		31	P12				
	164		26					
	155	6						
	109		100	P13				
	107		35					
Isoprocarb	211	100		P2	135	100	100	N2
	194		100	P1				
Methiocarb	243	100		P2	285	2	13	
	226	27	20	P1	167	100	100	N2
	214	4			165		37	
	169	19	100	P3				
Butocarboxim sulfoxide	224	2		P2	142	13	28	
	207		3	P1	132	32	11	
	167	5		P4	116	12	21	
	150	18	20	P3	85	30	43	
	134	100	21	P7	74	100	100	N5
	132		10	P5				
	118	48	100					
	116		33					
	93		14					
	86	17	60					
Methomyl	180	23		P2				
	163	24		P1				
	90	100		P7				
Oxamyl	237	4		P2	161	20		N2
	180	9		P4	147		63	
	163	10	3	P3	111	52	58	
	147	16	2	P7	74	100	100	N5
	140		13					
	133	12						
	116	100	25					
	99							
Class 3								
Asulam	248	5		P2	155	100	100	N4
	233	2						
	231		100	P1				
	216	12						
	190	100						
	173	5						
	109	11						
Barban	275	100		P2	222	11		
	239	78			204		25	
	222	18	4		193	100	48	
	180		2		170	12		
	154		7		126	65	100	
	128		100	P14	104		10	
	94		13		94		16	
Benomyl	192	100	100		226	11		
	99	1			190	100		N1
					158	31		
Carbendazim	209	1		P2	226	13		
	192	100	100	P1	190	100		N1
	99	2			158	34		
Carbetamide	254	2		P2	235	28	13	N1
	237	9	11	P1	159	73	100	
	219		1	P11	143	18		
	192		1		116	100	52	
	158		2					
	135	81		P10				
	120		36	P8				
	118	100	100	P9				

Methiocarb sulfone	275	1		P2	214		100			116		15						
					199		18	N2		102		24						
	235	1			151					94		8						
	218	100		P4	135	18			Chlorpropham	216		100						
	201	1		P3	79		16	N6		214		78	P1					
Promecarb	265	43			270		13		Desmedipham	233	1			194	10			
	225	100		P2	261		40			199	100		P10	180	100	9	N8	
	208		26	P1	217		32			182	32	63	P9	159	67	34		
	151		100	P3	202		20			148		12		149		100		
					176		20			120		100	P8	134	68	11	N9	
					149	100		N2		110	26							
					135		100			88		14						
					126		20		Phenmedipham	241	2			173	100	46		
Propoxur	227	77		P2	151	100	100	N2		185	100		P10	166	77	8	N8	
	210	100		P1						174		3		149		100		
Class 2										168	22	20	P9	134	61	14	N9	
Aldicarb	118	100		P7	74	100	100	N5		162		2						
Aldicarb sulfone	240	24		P2	221		1	N1		134		100	P8					
	223		<1	P1	146	17	12	N3		110	21							
	189		32		79	100	100	C6		108		6						
	183	23		P4	74	16	8	N5	Thiophanate-methyl	252		1		58	100	100	N7	
	165	100	72	P6						250	3							
	150	95	100	P7						192	100	4						
	148		52	P5						160	5							
	140	6	4							151	6	3						
	115		11							118		32						
	89	5								116		21						
Aldicarb sulfoxide	86		14							115		18						
	224	2		P2	143	14				103	26							
	173				130	18	18	N3		102		100						
	167	2		P4	116	20	14			93		8						
	149	100	44	P6	85	32	45			88		9						
	134	13		P7	74	100	100	N5	*Class 4*									
	132		100	P5					Pirimicarb	239	100	100	P1	280	11			
	91		8							225	1			237	100		N1	
	89	6								152		28	P3	223	76			
Butocarboxim	86		10						1-Naphthol	145		100	P1	285	11			
	118	100		P7	74	100		N5						157	75			
														156		100		
														143	100	65	N1	
									Degradation product V	168	100		P1	180	30			
														166	100		N1	
									Degradation product VI	169	33							
										154	100		P1	166	63			
										118	6			152	100		N1	

[a] Conditions: ion source 200 °C, quadrupole 100 °C, indicated CI gas pressure 0.7 Torr; 500 ng injected.
[b] Intensity relative to base peak.
[c] ID, proposed identification following:

P1 $[M+H]^+$
P2 $[M+NH_4]^+$
P3 $[M+H-MeNCO]^+$
P4 $[M+NH_4-MeNCO]^+$
P5 $[M+H-(MeNHC(O)-OH]^+$
P6 $[M+NH_4-(MeNHC(O)-OH)]^+$
P7 $[M+H-CH_2{=}NH-CO_2]^+$
P8 $[RC_6H_4NCO+H]^+$
P9 $[M+H-RC_6H_4NCO]^+$
P10 $[M+NH_4-RC_6H_4NCO]^+$
P11 $[M+H-H_2O]^+$
P12 $[M+H-RXH]^+$, X = S, H
P13 $[M+H-MeNCO-RXH]^+$, X = S, H
P14 $[RC_6H_4NH_2+H]^+$
P15 $[M+NH_4-RXH]^+$, X = S, H
N1 $[M-H]^-$
N2 $[M-H-MeNCO]^-$
N3 $[M-H-(MeNHC(O)-OH)]^-$
N4 $[M-(MeNHC(O)-OH)]^-$
N5 $[CH_3NHCO_2]^-$
N6 $[CH_3SO_2]^-$
N7 $[NCS]^-$
N8 $[M-H-RNCO]^-$
N9 $[M-H-RNCO-XOH]^-$

beam, as it is corroborated by a decrease in the chromatographic peak width with an increase in the source temperature.[37] A selection of 19 carbamates were used to study the effect of the source temperature (range 125–250 °C at 25 °C intervals) on the ammonia PCI mass spectra; FI experiments were performed with three injections of 500 ng of each compound. Two typical examples of the influence of thermal degradation on spectra are shown in Fig. 3. With carbendazim, the abundance of the $[M + H]^+$ ion [Fig. 3(A)] decreases at higher temperatures, whereas the intensity of the major fragment ion peak, *m/z* 119, reaches a maximum at 225 °C. In contrast, the $[M + H]^+$ ion abundance of 3-hydroxycarbofuran [Fig. 3(B)] can be considered to be constant in the range 125–225 °C, whereas the main fragment ion, *m/z* 163, has a maximum abundance at around 225 °C. The two minor fragment ions, *m/z* 198 and 147, are present in the spectra only between 125 and 175 °C. Essentially, as concerns the quality of spectra, each analyte was observed to have its own optimum source temperature; as a compromise, 200 °C was used throughout further experiments, with the observation that tailing was insignificant at this source temperature.

The reagent gas pressure is known to influence CI mass spectra; the effect is due to a possible shift in the reactant gas equilibria and to increased thermalization of excited ions at higher pressures. Desorption CI experiments in the positive ion mode indicate that the pressure dependence of the ion abundances of some carbamates is large in the pressure regime commonly used for GC/CIMS and LC/PB-CIMS.[36] This may result in a large variation of the ion abundances and, thus, in unreliable PB-PCI data. To study the effect in more detail, five representative carbamates (aminocarb, carbaryl, carbofuran, dioxacarb and pirimicarb) were introduced, via FI, at seven different source pressures and at three ion source temperatures (125, 175 and 225 °C) (for details, see Ref. 36). For the five compounds studied the maximum total ion current occurs at indicated fore vacuum pressures between 0.7 and 0.9 Torr and at a source temperature of 225 °C. For all compounds except carbofuran, the relative peak intensities in the mass spectra were found to be nearly the same (differences in signals of all ions were less than 5%) in the pressure domain tested. The ion signal intensity of the base peak of carbofuran (fragment, *m/z* 165) increased by ~10% on changing the source pressure from 0.7 to 0.9 Torr (fore vacuum indication); however, the abundances of the other ions in the spectra (*m/z* 182 and 222) did not alter with pressure. Therefore, an indicated source pressure between 0.7 and 0.9 Torr was used throughout the experiments reported here.

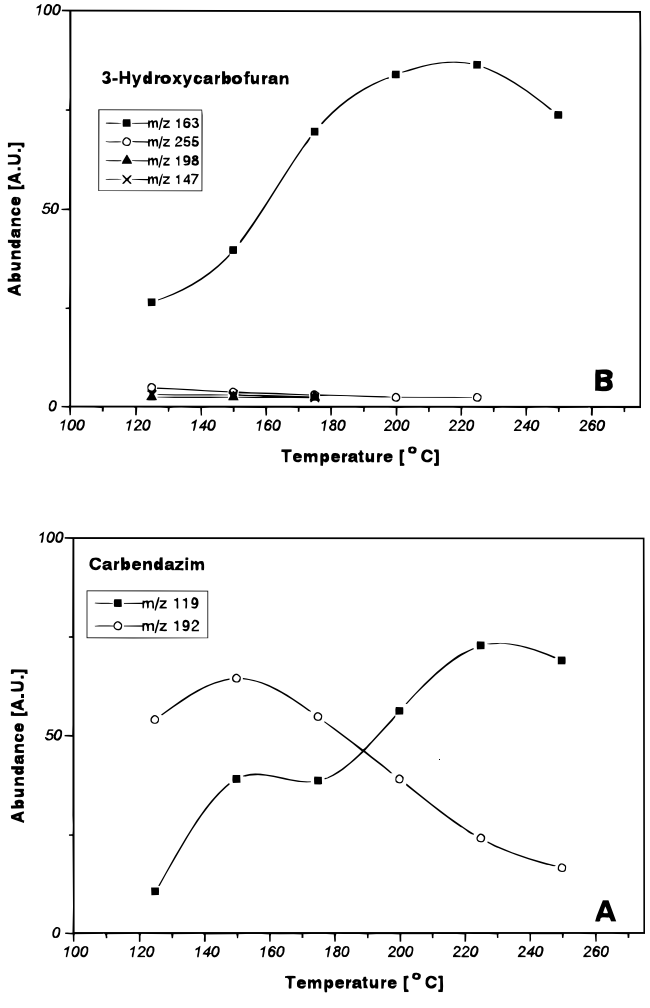

Figure 3. Ion abundance as function of ion source temperature in FI/PBMS under ammonia PCI conditions. (A) Carbendazim; (B) 3-hydroxycarbofuran.

PCI. The ammonia and methane PCI spectra of 33 carbamates were obtained by FI/PBMS. Typical spectra of ethiofencarb are shown in Fig. 4 and a summary of the spectra is given in Table 2. The behaviour of carbamates under PCI conditions has been reported by other workers.[3,10,34–36,38–40] Most compounds show $[M + H]^+$ and $[M + NH_4]^+$ ions in their ammonia PCI spectra, but fairly intense fragmentation occurs with many compounds. As is to be expected, the methane PCI spectra show even more abundant fragmentation. Although it proved impossible to assign ion compositions to all signals in the various PCI spectra, several conclusions can be drawn. Most fragment ions are formed by the loss of an isocyanate neutral from protonated or ammoniated molecules. These primary fragmentations are sometimes accompanied by the loss of a small molecule, e.g. H_2O, HCl or CH_3CH_2SH; such secondary fragmentations provide some information about the non-carbamate groups in the analytes. A further important fragmentation is the loss of *N*-methylcarbamic acid, $CH_3NHCOOH$ (75 u), from $[M + H]^+$ and from $[M + NH_4]^+$. Most *N*-methyl oxime carbamates lose 73 u from the protonated (or ammoniated) molecule; this is probably due to the subsequent loss of methanimine, CH_2NH and carbon dioxide, CO_2. The PCI mass spectra of the three high molecular mass carbamates (desmedipham, phenmedipham and thiophanate-methyl) show only low-mass fragments and no signals indicative of the molecular mass. In general, ammonia PCI yields molecular mass information for most of the test analytes (24 out of 33) and should therefore be preferred over methane PCI.

NCI. Ammonia and methane NCI spectra of the carbamate test set were obtained under the same condi-

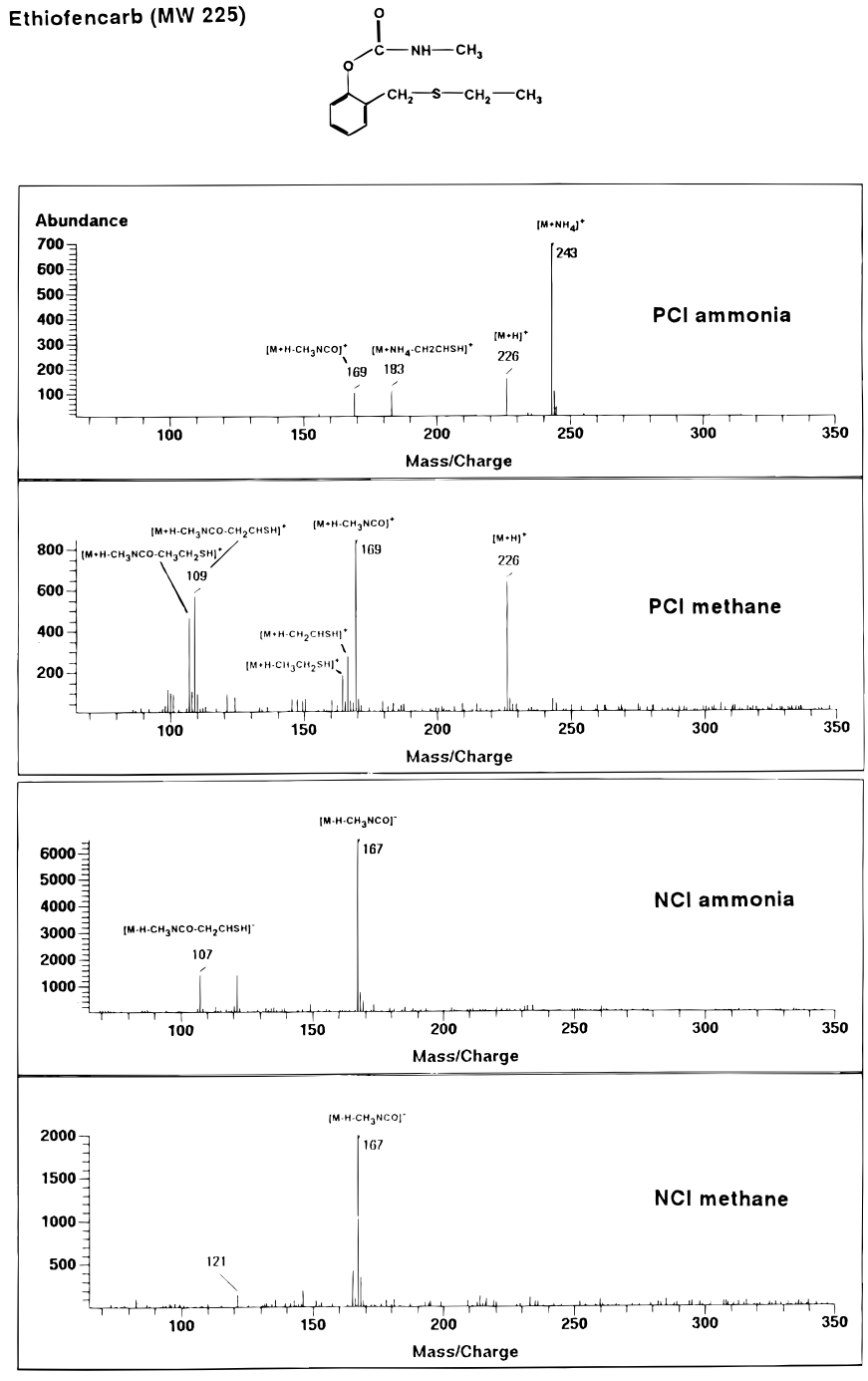

Figure 4. FI/PBMS under PCI and NCI conditions for 500 ng ethiofencarb, using ammonia and methane as reagent gases.

tions of pressure and source temperature as in PCI. Only a few carbamates, and all alcohol-type degradation products, show an $[M - H]^-$ signal in their spectrum, most compounds showing extensive fragmentation. In many cases no composition can be assigned to fragment ions, unless rearrangements are assumed to occur, e.g. for the formation of the thiocyanate anion from thiophanate-methyl. Adduct ion signals were observed for eight compounds, but the composition of the adduct ions is clear only in the case of carbendazim chloride adduct (m/z 226, ^{35}Cl). The *N*-methyl aryl carbamates typically lose methyl isocyanate, CH_3NCO, after deprotonation, to give $[M - 58]^-$ ions. The chloride adduct ion formation and net loss of 58 u is in line with the findings of other investigators.[8] *N*-Substituted carbamic acid, $RNHC(O)O^-$, is a typical fragment for many other carbamates, e.g. the *N*-methyl oxime carbamates produce *N*-methylcarbamate, $CH_3NHC(O)O^-$, at m/z 74. Although some characteristic structure information may be derived from NCI spectra, molecular mass information is only rarely obtained.

From the results of PCI and NCI FI/PBMS, we conclude that ammonia CI, particularly ammonia PCI, is

the best complementary technique to EI for the compounds under investigation.

Comparison of sensitivity of EI, PCI and NCI detection

The sensitivity of detection of CI generally is higher than that of EI, because fragmentation is suppressed. However, the fragmentation of carbamates under CI conditions is fairly extensive and one's expectations should not be too optimistic. To investigate the sensitivity of the different modes of detection, S/N ratios were determined. FI analysis of 32 test analytes was performed within one day and at the same mass spectrometer multiplier voltage. The maximum signal intensity was determined from the ion chromatogram of the mass spectrum base peak, and compared with the noise level in an early part of the FI chromatogram. The peak-to-peak S/N ratio, obtained from 500 ng injections, was then normalized to the EI S/N ratio; the results are given in Table 3, with the highest S/N ratios indicated in bold type.

For 13 carbamates and degradation product VI, higher S/N ratios are obtained in the EI mode. Ammonia PCI provides the highest S/N ratios for another ten carbamates. Methane PCI generally gives lower, or even much lower, S/N ratios than ammonia PCI and EI. Actually, methane PCI gives a higher S/N ratio for promecarb and chlorpropham (not shown) only; the latter compound does not show up in either EI or NCI. Ammonia NCI gives better S/N ratios than EI for nearly the same compounds as does ammonia PCI, while methane NCI yields poor results, the single exception being thiophanate-methyl. As regards ammonia NCI, high sensitivity and selectivity can be obtained for four of the present test compounds, viz. aminocarb, asulam, thiophanate-methyl and degradation product V. The fact that combination of EI and

Table 3. Signal-to-noise (S/N) ratios of 32 carbamates in FI/PBMS under EI, PCI and NCI conditions

		S/N ratio[a]			
		PCI		NCI	
Compound	EI	NH_3	CH_4	NH_3	CH_4
Class 1					
Aminocarb	70	3.5	0.4	**11**	0.1
Bendiocarb	**50**	0.0	0.6	0.9	0.4
Bromocarbamate	**100**	0.1	0.05	0.06	0.04
Carbaryl	**750**	0.1	0.1	0.3	0.1
Carbofuran	**200**	0.1	0.1	0.1	0.01
3-Hydroxycarbofuran	**1870**	0.3	0.1	0.1	0.01
Dioxacarb	**710**	0.9	0.9	1.0	0.2
Ethiofencarb	**210**	0.2	0.05	0.4	0.1
Isoprocarb	2	**4.8**	1.5	3.1	0.3
Methiocarb	**200**	0.2	0.2	0.4	0.1
Methiocarb sulfone	1820	**1.1**	0.06	0.03	0.2
Promecarb	3	2.5	**3.0**	1.5	1.1
Propoxur	**40**	0.1	0.0	0.9	0.05
Class 2					
Aldicarb	6	**4.9**	0.0	2.7	0.7
Aldicarb sulfone	710	**1.1**	0.3	2.0	0.2
Aldicarb sulfoxide	300	**5.6**	1.3	2.9	0.6
Butocarboxim	3	**19**	0.0	1.4	0.0
Butocarboxim sulfoxide	1070	0.9	0.03	**2.2**	0.5
Methomyl	10	**1.7**	0.0	0.0	0.0
Oxamyl	260	0.9	0.6	**2.7**	1.0
Class 3					
Asulam	380	0.7	0.0	**27**	0.8
Barban	**490**	0.1	0.6	0.1	0.1
Benomyl	220	**1.6**	0.05	1.1	0.0
Carbendazim	360	**1.4**	0.1	1.0	0.0
Carbetamide	**1010**	0.1	0.02	0.8	0.07
Desmedipham	**670**	0.9	0.05	0.8	0.1
Phenmedipham	**1070**	0.6	0.4	0.3	0.9
Thiophanate-methyl	60	3.4	0.6	**57**	18
Class 4					
Degradation product V	2	10	0.0	**40**	0.0
Degradation product VI	**140**	0.7	0.0	0.8	0.0
1-Naphthol	12	0.0	0.7	**1.9**	0.3
Pirimicarb	220	**2.1**	0.1	0.05	0.0

[a] EI data are absolute S/N ratios, whereas CI data are relative S/N ratios, normalized to EI ratios; bold type indicates the higher S/N ratio, '0.0' indicates 'not detected'. Mass range scanned from 65 to 350 u (EI), 85 to 350 u (PCI) and 50 to 350 u (NCI); S/N ratios averaged from three 500 ng injections.

ammonia PCI yields the highest S/N ratios for 23 out of 32 compounds adds to the above-mentioned complementarity of EI and ammonia PCI for identification purposes.

The absolute S/N values for EI-mode PBMS (Table 3) show that the responses of the test analytes cover a range of 2–3 orders of magnitude, and that the same is true for the various CI modes tested. The (EI) responses apparently are largely independent of analyte structure. Large differences are observed within each class, e.g. in class 1 promecarb gives S/N 3 whereas that of carbaryl is 750; in class 3 propham and chlorpropham cannot be detected at all whereas desmedipham and phenmedipham have high S/N values of 670 and 1070, respectively. In all classes, an interesting effect is observed on comparing a parent carbamate and its oxidized products. Parent compounds (aldicarb and methiocarb, class 1; butocarboxim, ethiofencarb and thiofanox, class 2) invariably yield a much lower PBMS response than the corresponding sulfoxides and sulfones (see also Ref. 2). The same holds true for carbofuran and its 3-keto and 3-hydroxy transformation products. The structure difference between oxamyl and methomyl (dimethyl isocyanate instead of methyl group) also corresponds to a distinct (25-fold) enhancement of the PBMS signal for the more polar compound.

The results obtained in the PCI and NCI modes are similar to those reported for EI-mode PBMS. Probably the large response differences are primarily due to the lower volatility of the more polar compounds and a concomitantly more efficient transport through the PB interface. From a practical point of view, the effect significantly widens the applicability of PBMS for the analysis of very polar (oxidized) compounds. However, one should be aware that in gradient LC/PBMS studies of real samples the absolute S/N values are usually reduced owing to (i) a spectral noise from matrix compounds, (ii) an additional peak broadening compared with FI, especially in the reversed-phase LC of very polar or late-eluting compounds, (iii) exponential response curves and (iv) the fact that the more polar degradation products elute with a mobile phase containing a high percentage of water, i.e. conditions which are not favourable for obtaining the maximum PBMS response.[2]

CONCLUSION

Mass spectra of 33 carbamates and 14 of their transformation products were obtained by PBMS in the EI, PCI and NCI modes with methane or ammonia as reagent gas. The EI spectra of all analytes provided relevant structural information. Comparison with a commercially available spectral library showed good matching for 25 out of the 27 searchable analytes. Using a self-compiled library, EI [and also CI (see below)] spectra were found to be reproducible during the 1 year period of the study.

Whereas a follow-up study[2] showed that PB-EI mass spectra of carbamates are virtually independent of the experimental conditions, the relative abundance of ions in CI spectra was found to depend on the temperature of the ion source and on the reagent gas pressure. A source temperature of 200 °C and a pressure range of 0.7–0.9 Torr (indicated MS manifold fore vacuum on the MS Engine) were selected as a compromise in the analysis of the present set of compounds.

Ammonia PCI provided the best results in terms of specific molecular mass information, while extensive fragmentation was observed in most of the methane PCI and in all NCI spectra. As regards sensitivity of detection, EI is the best single choice. However, the additional use of ammonia PCI is recommended to obtain near-optimum identification and detection conditions for essentially the total set of compounds.

The FI/PBMS responses were invariably 2–3 orders of magnitude lower for parent carbamates than for their polar degradation (oxidized) products. This effect significantly widens the applicability of the PB interface for the analysis of very polar analytes, e.g. in degradation studies of pesticides in water. Assuming a typical exponential shape of PBMS calibration curves, absolute detection limits estimated from FI ought to vary in a range from $\sim$4 ng to 2 μg, i.e. the concentration detection limits would be 0.05–20 μg l^{-1} using a 100 ml sample and on-line solid-phase extraction (SPE). Here, one should also note that the above-mentioned signal enhancement can be significantly reduced in HPLC/PBMS, e.g. due to peak broadening of late-eluting compounds, gradient elution with a high percentage of water and adverse effects of the sample matrix.

A distinct advantage of using PBMS detection is that reproducible library-searchable EI and solvent-independent CI spectra can be obtained. The spectra generally provide structure and molecular mass information which is often absent in, e.g., thermospray MS[23] or depends strongly on operational parameters and solvents used in API-MS.[20,21] In other words, LC/PBMS is a valuable technique for the identification of (especially polar) unknowns and is complementary to GC/MS. This appraisal should help to stimulate ongoing attempts to improve the PB interface design and, thus, improve analyte detectability.[41]

Spectral information from this study was used in a recently developed automated on-line SPE/LC/PBMS method for the analysis of carbamates and their transformation products in surface water; the compounds could be identified from their full-scan spectra at low- and sub-$\mu g\, l^{-1}$ levels.[2]

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