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ANALYSIS OF SELECTED PESTICIDES BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY–MASS SPECTROMETRY

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SUMMARY

A Finnigan 4500 mass spectrometer was modified to perform direct liquid introduction high-performance liquid chromatography–mass spectrometry (DLI-HPLC–MS). The HPLC–MS analysis of some 25 pesticides, including carbamates, chlorinated carboxylic acids and methyl ureas is described. The qualitative appearance of the spectra as well as detection limits are presented for both positive and negative ion detection. In most cases DLI-HPLC–MS, using an 1:100 split, provided molecular weight information with sub-microgram detection limits and greatly increased specificity over HPLC detection.

INTRODUCTION

Analytical procedures for a number of pesticides are rather limited by virtue of their thermal lability [gas chromatographic (GC) methods] and lack of sensitivity and specificity (spectrophotometric methods). The thermal lability of the pesticides has, in certain cases, been overcome through derivatization[1,2]. However, most workers have attacked the problem of thermal lability through the use of high-performance liquid chromatography (HPLC). HPLC, while providing suitable separation of most pesticides, is still hindered by the lack of a specific and sensitive detector for a number of pesticides[3–6]. Ultraviolet (UV)[7] or electrochemical HPLC detection[8] often provide adequate sensitivity, but do not provide the specificity necessary for analysis of moderately complex sample matrices. Post-column fluorometric labeling techniques[9] sometimes overcome the selectivity problem; however, this solution is effective for only a limited number of pesticides. HPLC–mass spectrometry (MS) is a method which can be used for the analysis of most pesticides, with adequate sensitivity and excellent specificity.

A number of HPLC–MS interfaces have been developed for introducing the HPLC effluent into the mass spectrometer[10–15]. Of these, two are commercially available; the direct liquid introduction (DLI) interface and the mechanical transport interface (moving belt). Pesticides analyzed on the moving belt include both carbamates and ureas[16,17]. While some pesticides analyzed on the belt produce molecular

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ions, most show low mass fragments due to decomposition when the sample is desorbed from the belt. For this reason, the DLI interface has proven successful in the analysis of triazines and organophosphorus pesticides[18,19]. In DLI-HPLC–MS, the sample is nebulized and does not require heating. Thus, less decomposition of the analyte is observed. Research discussed here explore the applicability of DLI-HPLC–MS to the analysis of carbamate, acid, oxime, urea, and acetanilide pesticides.

EXPERIMENTAL

The HPLC system consisted of a 6000A pump (Waters Assoc., Milford, MA, U.S.A.), a UK-6 injector (Waters Assoc.) and a 440 UV detector (Waters Assoc.) at 254 nm. A C_{18} reversed-phase column with 5 μm particle size and 15 cm × 4.6 mm I.D. dimensions was used to perform the separations. The mobile phase was acetonitrile–water (60:40) at a flow-rate of 1.5 ml/min.

The HPLC–MS interface was a Hewlett-Packard DLI probe (Hewlett-Packard, Palo Alto, CA, U.S.A.) which is the variable split type. The usual split ratio is 1:100 which allows approximately 10–30 μl/min of mobile phase to enter the mass spectrometer.

The mass spectrometer was a Finnigan 4500 (Finnigan, Sunnyvale, CA, U.S.A.) equipped with an INCOS data system. The instrument was modified for HPLC–MS by the addition of a Vespel® desolvation chamber (Fig. 1). The desolvation chamber fits snugly on a removable ion volume and can be installed without breaking vacuum to allow for changing from GC–MS to HPLC–MS and back to GC–MS in a matter of minutes. The Vespel is an excellent insulator so no other electrical isolation is needed between the source and DLI probe. Also, no water cooling is required, since the Vespel is a poor conductor of heat. The source pressure is controlled by the position of the DLI probe with respect to the desolvation chamber. As the probe moves closer to the desolvation chamber the source pressure increases. About 2–3 mm distance between the probe tip and desolvation changer is

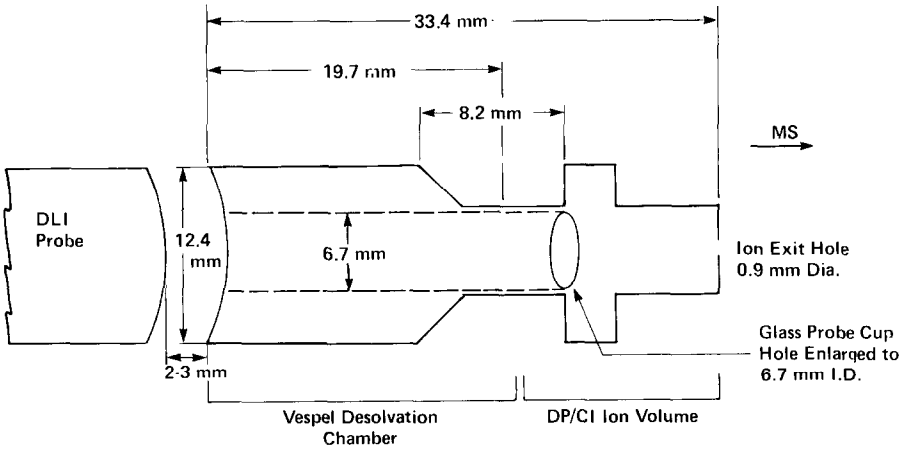


Fig. 1. Schematic drawing of Vespel desolvation chamber and ion volume used to interface the DLI probe to the Finnigan 4500 mass spectrometer.

used in normal operations. At this position, the source pressure was 0.65 torr and the analyzer pressure was $2.5 \cdot 10^{-5}$ torr as measured with a thermocouple and ion gauge, respectively. No modifications to the probe vacuum lock were required. The entrance hole for the glass-probe cup of a direct probe CI ion volume was drilled to the same inside diameter as the remainder of the ion volume tube.

The mass spectrometer was operated in the CI mode at an electron energy of 100 eV, emission current of 0.3 mA, and a source temperature of 180°C. The instrument was scanned from 150 to 500 a.m.u. at 2 sec per scan. The low mass of 150 a.m.u. was dictated by the numerous cluster ions observed at lower masses[20]. The HPLC solvent served as the CI reagent gas.

The pesticides were obtained from the Environmental Protection Agency Reference Standard Repository (Research Triangle Park, NC, U.S.A.). Standard solutions were prepared in acetonitrile or acetonitrile–water (60:40). The stated purities of these pesticides ranged from 95 to 100%. The solvents used were HPLC-grade acetonitrile (Burdick & Jackson Labs., Muskegon, MI, U.S.A.) and reagent-grade deionized water. The acetonitrile was filtered through a 0.5-μm filter and the water through a 0.45-μm filter (Millipore, Bedford, MA, U.S.A.).

RESULTS AND DISCUSSION

Optimization of HPLC–MS interface

The DLI probe was adjusted daily to produce a straight 4–5 cm long solvent jet. Once inserted into the mass spectrometer, the position of the probe was adjusted to produce the best solvent cluster ions (m/z 83, 95 for positive ion CI, m/z 81 negative ion CI) as the optimal setting for the sample[21]. The resulting source pressure was 0.65 torr. The optimal source pressure (probe position), temperature, and repeller voltage had been previously determined for a number of carbamate pesticides[22].

Qualitative appearance of the mass spectra of the pesticides

Tables I, II, III and IV list the ions of greater than 5% relative abundance and their proposed identity with both negative and positive ion detection for carbamate, chlorinated carboxylic acid, methylurea and oxime, and acetanilide classes of pesticides, respectively. These pesticides were analyzed individually with quantities of 1 to 5 μg injected on-column (10–100 ng into the source) to obtain acceptable quality spectra and to assess the purity of the individual compounds. Each mass and intensity assignment was obtained from averaging at least six scans and subtracting background on either side of the peak. The mass spectra usually exhibited molecular weight information with few fragments and some solvent clustering. A more detailed description of the mass spectra for the various classes of pesticides is given below.

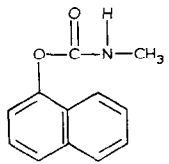
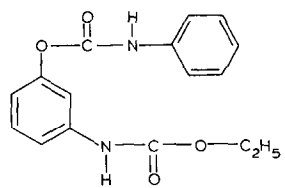
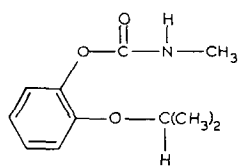
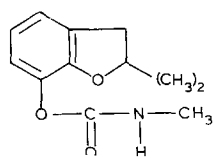
Carbamate pesticides

All carbamates except benomyl exhibited protonated molecular ions $[M+H]^+$ and sample–acetonitrile cluster ions $[M+H+CH_3CN]^+$ in the positive ion detection mode (Table I). The carbamates can be represented by: R_1–O–CO–NH–R_2, where R_1 and R_2 are the alkyl side chains or substituted aromatic rings. The fragment ions observed for carbamates were usually formed through simple cleavages resulting in the loss of R_1 or R_2 groups. The negative ion spectra for these pesticides usually

TABLE I

STRUCTURE, MOLECULAR WEIGHT, MASS AND INTENSITY, AND PROPOSED ION IDENTIFICATION FOR BOTH POSITIVE AND NEGATIVE ION DETECTION OF CARBAMATE PESTICIDES

RA = Relative abundance.

Compound	*Structure*	*Mol.wt.*	*Positive ion*			*Negative ion*		
			m/z	*RA (%)*	*Proposed identification*	*m/z*	*RA (%)*	*Proposed identification*
Carbaryl		201	185	4		161	100	
			186	11	$[M+H-CH_4]^+$	227	<1	$[M+CN]^+$
			202	86	$[M+H]^+$			
			203	13				
			243	100	$[M+H+CH_3CN]^+$			
			244	16				
Desmedipham		300	182	100	$[M+H-C_6H_5NCO]^+$	150	13	$[C_6H_4CO_2NHNH]^-$
			197	3		159	47	
			223	47	$[M+H-C_6H_6]^+$	160	13	
			235	3		179	13	$[M-C_6H_5NH-C_2H_5]^-$
			260	3		180	100	$[M-C_6H_5NHCO]^-$
			276	4		181	17	
			301	4	$[M+H]^+$	218	11	
			342	2	$[M+H+CH_3CN]^+$	264	10	
						265	10	
						266	9	
Propoxor		209	194	5	$[M+H-CH_4]^+$	151	100	$[OC_6H_4OCONH]^-$
						152	10	
			210	100	$[M+H]^+$	161	8	
			211	13		178	2	$[M-H-2CH_3]^-$
			251	5	$[M+H+CH_3CN]^+$			
						192	2	
						235	1	$[M+CN]^-$
Carbofuran		221	206	5	$[M+H-CH_4]^+$	163	100	$[M-CONHCH_3]^-$
			222	100	$[M+H]^+$	164	14	
			223	14		181	11	
			263	4	$[M+H+CH_3CN]^+$	201	4	
						204	6	
						218	2	

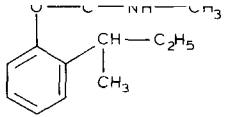
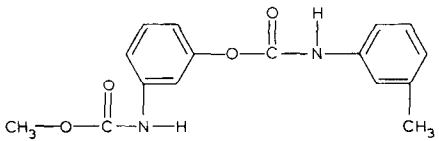
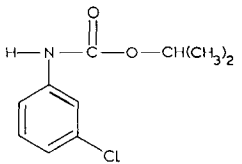
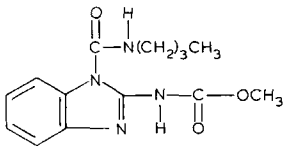
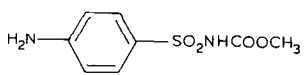
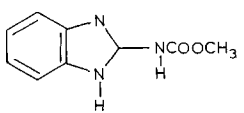
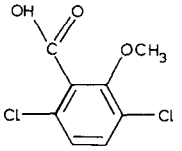
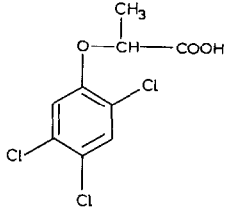
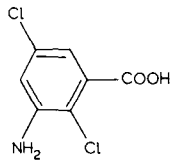
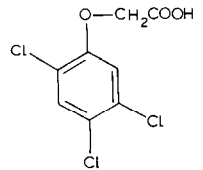
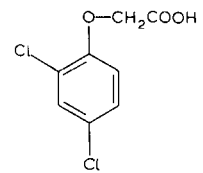
			249	17	$[M+H+CH_3CN]^+$	206	2	$[M-H]^-$
Phenmedipham		300	168	100	$[CH_3C_6H_4NCO]^+$	150	100	$[CH_3C_6H_4NHCO_2]^-$
						187	5	
			209	14	$[M+H-C_6H_5CH_3]^+$	221	29	
						299	12	$[M-H]^-$
			301	2	$[M+H]^+$			
Chlorprophram		213	170	1	$[M+H-CH_2(CH_3)_2]^+$	212	100	$[M-H]^-$
			213	5	$[M]^+$	213	12	
			214	100	$[M+H]^+$	214	33	
			215	12		238	1	$[M-H+CN]^-$
			216	33				
			255	29	$[M+H+CH_3CN]^+$			
			257	10				
Benomyl		290	159	100		158	200	
						190	100	$[M-CONH(CH_2)_3CH_3]$
			174	18		191	15	
						192	10	
			192	4				
Asulam		230	151	14		155	100	$[M-HNHCO_2CH_3]^-$
			152	11		156	9	
			153	19		229	<1	$[M-H]^-$
			158	9				
			214	8	$[M+H-NH_3]^+$			
			231	100	$[M+H]^+$			
			232	9				
			272	3	$[M+H+CH_3CN]^+$			
Carbendazim		191	160	36	$[M+H-CH_3OH]^+$	190	100	$[M-H]^-$
			161	10		191	4	
			162	17	$[M+H-CH_2O]^+$			
			163	16				
			174	100				
			175	12				
			177	37	$[M+H-CH_3]^+$			
			189	29	$[M-2H]^+$			
			192	6	$[M+H]^+$			
			233	25	$[M+H+CH_3CN]^+$			

TABLE II

STRUCTURE, MOLECULAR WEIGHT, MASS AND RELATIVE INTENSITY, AND PROPOSED ION IDENTIFICATION FOR BOTH POSITIVE AND NEGATIVE ION DETECTION FOR ACID PESTICIDES

Compound	*Structure*	*Mol.wt.*	*Positive ion*			*Negative ion*		
			m/z	*RA (%)*	*Proposed identification*	*m/z*	*RA (%)*	*Proposed identification*
Dicamba		220	151	14	$[M+H-Cl_2]^+$	150	32	$[M-2Cl]^-$
			155	35	$[M+H-HCl-H_2CO]^+$	182	12	
			154	10		184	100	$[M-HCl]^-$
			169	21	$[M+H-HCl-CH_4]^+$	185	28	$[M-Cl]^-$
			177	17	$[M+H-CO_2]^+$	186	49	
			187	36	$[M+H-H_2O-CH_4]^+$	187	10	
			203	36	$[M+H-H_2O]^+$	202	9	$[M-H_2O]^-$
			205	24		218	13	
			221	100	$[M-H]^+$	219	6	$[M-H]^-$
			222	9		220	22	$[M]^-$
			223	69		221	7	
			224	8		222	12	
			225	12		223	4	
			226	15				
			228	54				
			230	17				
			244	33				
			246	21				
			262	58	$[M+H+CH_3CN]^+$			
			264	28				
Silvex		268	No signal detected			161	12	
						195	10	$[M-CH(CH_3)COOH]^-$
						196	85	$[M-2HCl]^-$
						197	100	$[M-HCl-Cl]^-$
						198	98	$[M-2Cl]^-$
						199	85	
						200	37	
						201	29	
						202	5	
						222	18	$[M-COOH_2]^-$
						224	14	

						232	11	$[M-HCl]^-$
						234	8	
						268	<1	$[M]^-$
						270	<1	
Chloramben		205	No signal detected			169	100	$[M-HCl]^-$
						170	10	
						171	32	
						181	2	
						186	2	$[M-H-H_2O]^-$
						189	2	$[M-NH_2]^-$
						204	2	$[M-H]^-$
2,4,5-T		254	154	35		174	19	$[M-ClCO_2H]^-$
			155	76		176	16	
			156	20		195	8	$[M-CH_2CO_2H]^-$
			157	100		196	37	$[M-CH_2CO_2]^-$
			162	36		197	44	
			166	11		198	42	
			169	27		199	40	
			170	15		200	13	
			182	25		201	11	
			198	12		208	100	$[M-CO_2H_2]^-$
			216	22		209	8	
						210	91	
						211	7	
			254	7	$[M]^+$	212	29	
			296	9	$[M+H+CH_3CN]^+$	218	18	$[M-HCl]^-$
						220	13	
						254	<1	$[M]^-$
2,4-D		220	157	46		161	8	$[M-CH_2CO_2H]^-$
			177	21	$[M+H-CO_2]^+$	162	9	
			178	12		163	18	
			182	69		165	11	
			184	12		174	100	$[M-CO_2H_2]^-$
						175	10	
						176	92	
			219	11	$[M-H]^+$	178	26	
			220	11	$[M]^+$	187	4	
			228	20	$[M-H_2O]^+$			
			262	89	$[M+H-CH_3CN]^+$			
			263	12				
			264	84				

(Continued on p. 228)

TABLE II (*continued*)

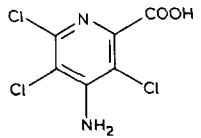
Compound	*Structure*	*Mol.wt.*	*Positive ion*			*Negative ion*		
			m/z	*RA (%)*	*Proposed identification*	*m/z*	*RA (%)*	*Proposed identification*
Picloram		240	163	55	$[M+H-HCl-CO_2]^+$	196	18	$[M-CO_2]^-$
			165	25		197	16	
			167	13		198	20	
			169	12		199	15	
			179	12	$[M+H-NH_3-CO_2H]^+$	200	15	
			197	43	$[M+H-CO_2]^+$	204	26	$[M-HCl]^-$
			199	46		206	50	
			201	12		208	29	
			207	27	$[M+H+H-Cl]^+$	224	16	$[M-NH_2]^-$
			209	25		226	16	
			225	12		240	99	$[M]^-$
			241	100	$[M+H]^+$	241	11	
			242	11		242	100	
			243	97		243	12	
			244	9		244	33	
			245	36				
			280	2				
			282	1	$[M+H+CH_3CN]^+$			

TABLE III

STRUCTURE, MOLECULAR WEIGHT, MASS AND RELATIVE INTENSITY, AND PROPOSED ION IDENTIFICATION FOR BOTH POSITIVE AND NEGATIVE ION DETECTION OF METHYL UREA PESTICIDES

RA = Relative abundance.

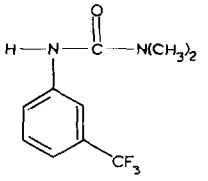
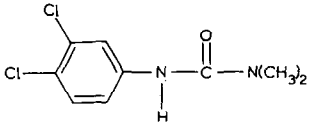
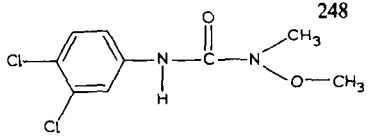
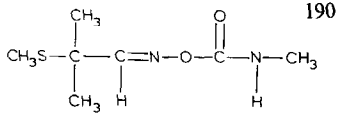
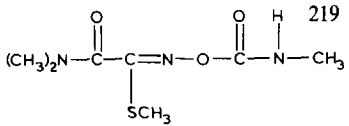
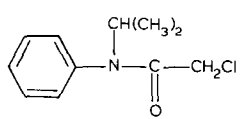
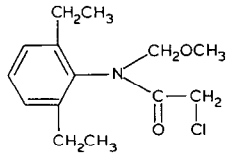
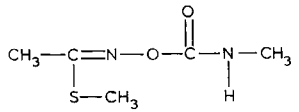
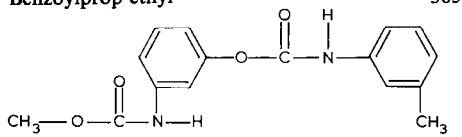
Compound	*Structure*	*Mol.wt.*	*Positive ion*			*Negative ion*		
			m/z	*RA (%)*	*Proposed identification*	*m/z*	*RA (%)*	*Proposed identification*
Fluometuron		232	233	100	$[M+H]^+$	164	2	$[M+H-CF_3]^-$
			234	12		231	100	$[M-H]^-$
			274	14	$[M+H+CH_3CN]^+$	232	13	$[M]^-$
						257	2	$[M-H+CN]^-$
Diuron		232	199	2		218	5	$[M-CH_2]^-$
			233	100	$[M+H]^+$	231	32	$[M-H]^-$
			234	12		232	100	$[M]^-$
			235	73		234	72	
			236	7		235	20	
			237	12		236	13	
			274	17	$[M+H+CH_3CN]^+$	267	4	$[M+Cl]^-$
			276	12				
		t	278	2				
Linuron		248	249	100	$[M+H]^+$	216	10	
			250	11		217	16	$[M-OCH_3]^-$
			251	61		218	100	$[M-CH_2O]^-$
			252	7		219	27	
			253	11		220	65	
			290	31	$[M+H+CH_3CN]^+$	221	14	
			291	5		222	11	
			292	21		247	44	$[M-H]^-$
			293	3		248	64	$[M]^-$
						249	41	
						250	44	
						251	13	
						252	8	
						283	4	$[M+Cl]^-$

TABLE IV

STRUCTURE, MOLECULAR WEIGHT, MASS AND INTENSITY, AND PROPOSED IDENTIFICATION FOR BOTH POSITIVE AND NEGATIVE CHEMICAL IONIZATION OF OXIMINE, ACETANILIDE TYPE PESTICIDES

RA = Relative abundance.

Compound	*Structure*	*Mol.wt.*	*Positive ion*			*Negative ion*		
			m/z	*RA (%)*	*Proposed identification*	*m/z*	*RA (%)*	*Proposed identification*
Allicarb		190	157	100	$[M+H-H_2S]^+$	155	31	
			158	11		156	11	
			159	22	$[M+H-CH_3CH]^+$	207	9	$[M+OH]^-$
			191	73	$[M+H]^+$	216	22	$[M+CN]^-$
			192	7		264	100	$[M+74]^-$
			232	43	$[M+H+CH_3CN]^+$	265	11	
Oxamyl		219	157	8		156	30	$[M-H-CH_3SCH_3]^-$
			163	21	$[M+H-OCNCH_3]^+$	161	100	$[M-CONHCH_3]^-$
			172	15	$[M+H-HSCH_3]^+$	172	18	$[M-SCH_3]^-$
			177	20	$[M+H-CH_3NCH_3]^+$	218	<1	$[M-H]^-$
			204	29	$[M+H-CH_4]^+$	293	41	$[M+74]^-$
			220	60	$[M+H]^+$			
			238	53	$[M+H+H_2O]^+$			
			261	100	$[M+H+CH_3CN]^+$			
			262	12				
			279	9	$[M+CH_3CNH+H_2O]^+$			
			314	8	$[M+H+CH_2CHCNNCCH_3]^+$			
Propachlor		211	176	1	$[M+H-HCl]^+$	174	5	$[M-H-HCl]^-$
			212	100	$[M+H]^+$	210	100	$[M-H]^-$
			213	12		211	13	
			214	30		212	34	
			253	33	$[M+H+CH_3CN]^+$			
			255	11				

Alachlor		269	236	3		202	9	$[M-CH_3CHCO_2C_2H_5]^-$
			238	5	$[M+H-CH_3OH]^+$	249	3	
			270	100	$[M+H]^+$	268	100	$[M-H]^-$
			271	15		269	24	
			272	33		270	33	
			273	5		271	9	
			311	18	$[M+H-CH_3CN]^+$	294	2	$[M-H+CN]^-$
			313	5		304	4	$[M+Cl]^-$
Methomyl		162	163	100	$[M+H]^+$	161	29	$[M-H]^-$
			164	8		188	11	$[M+CN]^-$
			204	80		236	100	$[M+74]^-$
			205	88	$[M+H+CH_3CN]^+$			
Benzoylprop ethyl		365	266	5	$[M+H-CH_2CHCO_2C_2H_5]^+$	264	100	$[M-CH_3CHCO_2C_2H_5]^-$
			332	4	$[M+2H-Cl]^+$	265	27	
			366	100	$[M+H]^+$	266	83	
			367	22		267	18	
			368	71		268	15	
			369	13		364	1	$[M-H]^-$
			370	12				

displayed a $[M-1]^-$ ion with occasional $[M+CN]^-$ clusters. Again, cleavages of R_1 and R_2 account for the fragment ions. Little sample–solvent clustering was observed in negative ion detection mode.

Chlorinated carboxylic acids

The chlorinated carboxylic acid class of pesticides analyzed usually produced $[M+H]^+$ ions and exhibited clustering to form $[M+H+CH_3CN]^+$ ions and losses of H_2O, Cl and HCO_2 from the protonated molecular ion (Table II). For example, the $[M+H]^+$ ion of dicamba was the base peak with fragments due to the loss of H_2O (*m/z* 203), H_2O and CH_4 (*m/z* 187), CO_2 (*m/z* 177), and HCl and CH_4 (*m/z* 169). Negative ion detection provided molecular weight information on all samples. The negative ion spectra for these compounds usually yielded $[M-H]^-$ and $[M]^-$ anions, again with losses of CO_2, H_2O and HCl. For example, dicamba exhibited $[M]^-$, $[M-H]^-$ and $[M-2]^-$ anions with losses of H_2O (*m/z* 202) and HCl (*m/z* 184). In general the acids were difficult to analyze in positive ion mode because of the lack of sensitivity. Silvex and chloramben produced no positive ion signal.

Methylureas

The methylureas (Table III) exhibited relatively simple spectra in the positive ion detection mode, with the $[M+H]^+$ ion being the base peak and a solvent–sample cluster $[M+H+CH_3CN]^+$ as the only other signal detected. With negative ion detection, the $[M-H]^-$ anion was the base peak for diuron and fluometuron. These samples exhibited weak fragment ions and in the case of linuron and diuron, an $[M+Cl]^-$ anion due to chloride attachment was detected.

Oxime, oxamimidate, acetamidate, and acetonilide pesticides

The positive ion spectra for the remaining pesticides consisted primarily of $[M+H]^+$ and $[M+H+CH_3CN]^+$ ions with little fragmentation or other clustering (Table IV). For example, propachlor exhibited an $[M+H+CH_3CN]^+$ cluster ion and a small $[M+H-HCl]^+$ fragment ion. The negative ion spectra exhibited $[M-H]^-$ ions and clustering to form $[M+CN]^-$ and $[M+Cl]^-$. The few fragments observed were formed from simple cleavages. For example, propachlor exhibited an $[M-1]^-$ anion and one other fragment due to the loss of HCl from the $[M-1]^-$ anion.

Detection limits

The approximate detection limits for the majority of the pesticides analyzed were determined for both positive and negative ion detection (Table V). Mass spectrometry using the 1:100 probe split was unable to offer lower detection limit for most pesticides over UV, electron-capture and fluorescence HPLC detection methods for these pesticides. HPLC–MS did offer detection limits comparable to HPLC–UV for propoxur and carbofuran[7]. Without the 1:100 split, (*e.g.* micro HPLC–MS) the absolute detection limits can be lowered, but due to reduced load ability of the microcolumns, the actual matrix concentration sensitivity might remain unchanged[23,24]. However, the main advantage in the use of MS is the added specificity in the analysis.

Detection limits were obtained by using ions in the molecular weight region

TABLE V

DETECTION LIMITS FOR SELECTED PESTICIDES ANALYZED USING BOTH POSITIVE AND NEGATIVE ION DETECTION WITH DLI PROBE AND APPROXIMATELY 1/100 SPLIT

– = Not detected.

Class	*Compound*	*Detection limits**			
		Positive ion (μg)	*Ion monitored*	*Negative ion (μg)*	*Ion monitored*
Carbamates	Carbaryl	0.04	202	0.6	161
	BPMC	0.02	208	0.2	173
	Propoxor	0.05	210	0.04	151
	Chlorpropham	0.15	214	0.005	212
	Carbofuran	0.05	222	0.03	163
	Phenmedipham	40.0	301	0.5	299
	Desmedipham	12.0	301	0.5	180
	Asulam	30	231	0.6	155
	Benomyl	0.5	159	0.5	190
Acids	Dicamba	50	221	10	220
	Silvex	–	–	5	197
	Chloramben	–	–	10	169
	2,4,5-T	75	296	5	208
	2,4-D	60	262	15	174
	Picloram	75	241	60	240
Oxime	Oxamyl	2	220	5	293
	Methomyl	1	163	5	161

* Amounts listed are quantities actually injected on column; only about 1–3% enters the mass spectrometer.

if available; otherwise, the most significant fragment ion was used. The instrument was operated in full scan mode and the selected ions were mapped with respect to the various amounts injected on-column. The detection limit for a compound was determined as the area response of the analyte at approximately three times noise. Selected ion monitoring, which would greatly improve detection limits, was not performed because the HPLC–MS technique would be used to search for a variety of pesticides. The full scan detection limits would be more appropriate for evaluating the HPLC–MS technique for environmental analysis.

Carbamates

The carbamate pesticides displayed a range of sensitivity in positive ion mode. Detection limits ranged from 40 μg to 0.02 μg injected on-column. The broad range of detection limits for these pesticides can be accounted by the variability in structure of the carbamates analyzed. The pesticides asulam, phenmedipham and desmedipham exhibited high detection limits, near 40 μg, while the other carbamates analyzed have detection limits near 0.1–0.02 μg. Such variability in detection limits are common in chemical ionization processes. The selected ion current (Fig. 2) for a number of carbamates is shown for three different quantities injected on-column. With positive ion detection, detection limits were determined by monitoring $[M + H]^+$ or other structurally significant ions. Negative ion detection involved using low mass fragment

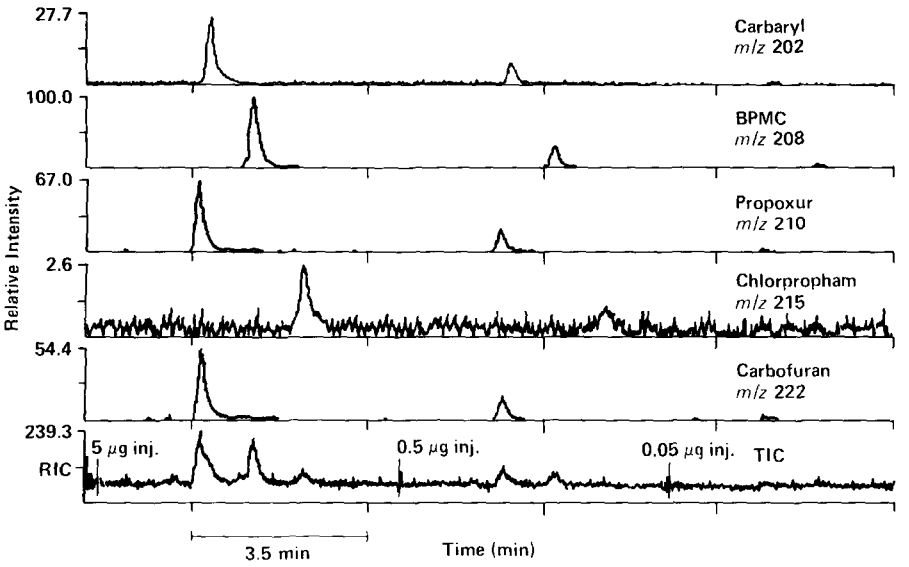


Fig. 2. Selected ion chromatograms and total ion current, using positive ion detection, for three different quantities of carbamates injected on-column.

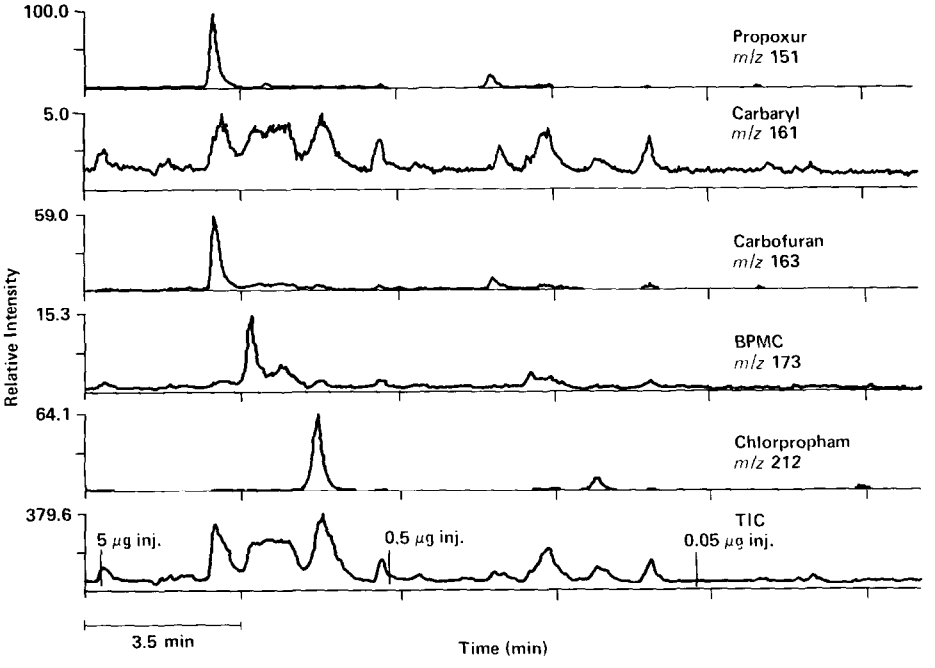


Fig. 3. Selected ion chromatograms and total ion current, using negative ion detection, for three different quantities of carbamates injected on-column.

ions because of the lack of intense high mass fragments. The negative ion detection limits for the carbamates did not differ as greatly as in the positive ion case (0.6–0.005 μg). Fig. 3 displays the negative ion traces for the same pesticides given in Fig. 2 at the same three concentrations. More interferences were detected when using lower mass fragment ions to determine the presence of a particular pesticide. Positive ion detection appeared to offer the best specificity (due to molecular weight information) with reasonable sensitivity and would therefore be the method of choice for the analysis of carbamate pesticides.

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