Journal of Chromatography, 242 (1982) 77–96
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 14,811

HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY–MASS SPECTROMETRY OF TRIAZINE HERBICIDES

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(First received November 26th, 1981; revised manuscript received February 12th, 1982)

SUMMARY

Five classes of triazine herbicides were studied by combined high-performance liquid chromatography–mass spectrometry (HPLC–MS). Separations were done on a reversed-phase C_8 column, using acetonitrile–water as the mobile phase, followed by in-line UV and mass spectral analysis. Positive and negative ion mass spectra were recorded. For most of the triazines both positive and negative ion spectra obtained with the direct liquid introduction HPLC–MS probe interface give molecular ion information. Most of the triazine studies were more sensitive in the positive ion mode than in the negative ion mode.

INTRODUCTION

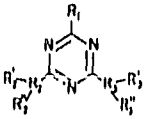
Since their introduction around 1960, triazines have become widely used for weed control in food crops. Methods for the analysis of triazines and their metabolites is important both from agricultural and environmental points of view. Persistence of these compounds in the soil has been found to affect susceptible crops in the next growing season[1,2]. Contamination of wells and streams due to spills, spraying or runoff has been found in Europe[3] and Canada[4–6]. It has been estimated that an average of 1 % of applied atrazine, for example, ends up in streams, with higher losses (about 60 %) occurring due to storm runoff[6]. Atrazine and procyazine have also been detected in human urine, following exposure while spraying these compounds[7].

Most of the triazine herbicides used in agriculture are 1,3,5-triazines, substituted in positions 2, 4 and 6. Nomenclature is primarily determined by the substituent in the 2 position, usually chlorine (-azine), methoxy or ethoxy (-ton) or methylthio or ethylthio (-tryn). In this study, five classes of triazines were examined, including eighteen, 1,3,5-triazines, two 1,2,3-triazines and one 1,2,4-triazine (Table I).

0021-9673/82/0000–0000/$02.75

TABLE I

COMPOUNDS STUDIED



t_R = Retention time. Et = Ethyl; iPr = isopropyl; tBu = *tert.*-butyl; cyPr = cyclopropyl.

Name	*Mol. wt.*	t_R *(min)*	R_1	R_2	R_2'	R_2''	R_3	R_3'	R_3''
2-Chloro-1,3,5-triazines									
Anilazine	274	4.51	Cl	Cl	–	–	N	H	C_6H_4Cl
Simazine	201	2.66	Cl	N	H	Et	N	H	Et
Atrazine	215	3.35	Cl	N	H	Et	N	H	iPr
Propazine	229	3.96	Cl	N	H	iPr	N	H	iPr
Trietazine	229	5.47	Cl	N	H	Et	N	Et	Et
Cyprazine	227	3.08	Cl	N	H	cyPr	N	H	iPr
Terbutylazine	229	4.30	Cl	N	H	tBu	N	H	tBu
Cyanizine	240	2.46	Cl	N	H	Et	N	H	$CCN(CH_3)_2$
Procyazine	252	2.67	Cl	N	H	cyPr	N	H	$CCN(CH_3)_2$
2-Methoxy-1,3,5-triazines									
Atraton	211	2.87	OCH_3	N	H	Et	N	H	iPr
Prometon	225	3.48	OCH_3	N	H	iPr	N	H	iPr
2-Methylthio and 2-ethylthio-1,3,5-triazines									
Ametryn	227	4.03	SCH_3	N	H	Et	N	H	iPr
Terbutryn	241	5.19	SCH_3	N	H	Et	N	H	tBu
Prometryn	241	5.06	SCH_3	N	H	iPr	N	H	iPr
Dimethametryn	255	6.42	SCH_3	N	H	Et	N	H	$CHCH_3CH(CH_3)_2$
Dipropetryn	255	6.08	SC_2H_5	N	H	iPr	N	H	iPr
Other 1,3,5-triazines									
Menazon	281	1.91	$CH_2SPS(OCH_3)_2$	N	H	H	N	H	H
Velpar	252	2.32	CH_3	C_6H_{11}	–	–	N	CH_3	CH_3
*1,2,3-Triazines**									
Azinphos methyl	317	4.30	$CH_2SPS(OCH_3)_2$	–	–	–	–	–	–
Azinphos ethyl	345	6.36	$CH_2SPS(OC_2H_5)_2$	–	–	–	–	–	–
*1,2,4-Triazines**									
Metribuzin	214	2.87	SCH_3	N	H	H	$C(CH_3)_3$	–	–

* For structures, see Table VI.

Analytical methods presently used for the separation of these compounds include gas chromatography (GC)[1–15] and high-performance liquid chromatography (HPLC)[14–22]. Advantages claimed for the HPLC method are its suitability for higher-molecular-weight herbicides, polar herbicides or metabolites, and thermally labile compounds[13,17], and extraction procedures have been developed for the extraction of triazines and their metabolites from water[1–6,15,23,24], plant materials[8,9,16,23,24], soil[4,10,23,24], urine[7] and animal tissue[17].

The HPLC method, with subsequent direct probe electron impact (EI) mass spectrometric (MS) analysis, has been successfully used for the determination of azinphos methyl and its metabolite in tissue samples[17]. Other studies have been done to combine the specificity of mass spectral analysis with the separating ability of the GC by using combined GC–MS in the EI ionization mode[11–13], and in both the methane (MPCI)[12] and isobutane (iBPCI)[12,13] positive ion chemical ionization modes. This paper explores the applicability of a directly coupled HPLC–MS system to the analysis of triazine herbicides.

EXPERIMENTAL

Equipment

The HPLC system consisted of two Waters 600A pumps (Waters Assoc., Milford, MA, U.S.A.), a Waters 660 solvent programmer and a Perkin-Elmer LC-55 variable-wavelength UV detector (Perkin-Elmer, Norwalk, CT, U.S.A.). The LC column used was a RP-8 (C_8) reversed-phase column, particle size 10 μm, 10 cm × 4.6 mm I.D. (Brownlee Labs., Santa Clara, CA, U.S.A.). The mobile phase used was acetonitrile–water (45:55), and the flow-rate was 1 ml/min. The UV detector wavelength was 254 nm.

The HPLC–MS interface was an unmodified Hewlett-Packard direct liquid introduction (DLI) probe[25] (Hewlett-Packard, Palo-Alto, CA, U.S.A.), which is a variable split-type interface. The usual splitting ratio of the mass spectrometer to the fraction collector is 1:99. This means that with an HPLC flow-rate of 1 ml/min, approximately 10 μl/min of mobile phase enters the mass spectrometer source.

The mass spectrometer used for most of this research was a Finnigan 3300 chemical ionization mass spectrometer (Finnigan-MAT, Sunnyvale, CA, U.S.A.), previously modified for negative ion chemical ionization operation[26] and HPLC–MS[27,28]. The mass spectrometer was interfaced to a Finnigan/Incos 2300 data system. Modifications for HPLC–MS involved replacing the standard Finnigan 3300 1/4 in. I.D. direct probe inlet system with a 1/2 in. I.D. inlet system, and adding a desolvation chamber which was mounted on the source. No modification of the mass spectrometer pumping system was found to be necessary[27,28]. The mass spectrometer was scanned at 4 sec per scan from 50 to 500 a.m.u. in the negative ion mode, and from 100 to 500 a.m.u. in the positive ion mode. Source temperature was held at approximately 185°C.

Exact mass measurements were made with a VG Micromass ZAB-2F mass spectrometer and a Finnigan/Incos data system. Methane was used as a reagent gas at a gauge pressure of $4 \cdot 10^{-5}$ Torr (approximately 0.1–0.3 Torr in the source). Perfluorokerosene was used as an internal reference at a mass resolution of 7000. Typical source conditions were: accelerating voltage 8 kV; source temperature 200°C; electron energy 100 eV; emission current 1 mA.

Samples and solvents

Samples of the 21 organophosphorus pesticides were obtained from the Environmental Protection Agency. Standard solutions were prepared in HPLC-grade acetonitrile and/or acetone. Stated purities of these compounds ranged from 85% to 100%. Solvents used in this study were HPLC-grade acetonitrile and acetone (Fisher Scientific, Fair Lawn, NJ, U.S.A.), and HPLC-grade water (J. T. Baker, Phillipsburg, NJ, U.S.A.). The acetonitrile was filtered through a 0.5-μm filter; the water was filtered through a 0.45-μm filter (Millipore, Bedford, MA, U.S.A.).

RESULTS AND DISCUSSION

Retention times on the C_8 column, with acetonitrile–water (45:55) at a flow-rate of 1 ml/min, for the triazine herbicides studied are given in Table I. Mass spectral data for positive and negative ionization modes is given in Tables II–VII.

HPLC–UV and HPLC–TIC Traces

HPLC–UV, HPLC–total ion current (TIC) and HPLC–reconstructed ion chromatogram (RIC) traces are shown in Figs. 1 and 2 for two mixtures of triazines. Fig. 1 shows a separation of simazine, atrazine, propazine and trietazine. Fig. 2 shows the separation of prometryn, ametryn and dimethametryn. Mass spectral data from these mixtures, and from other triazines, is discussed below.

Mass spectral data

In general, HPLC–PCI mass spectra for alkylamino-1,3,5-triazines obtained with this acetonitrile–water "reagent gas" are similar to the reported isobutane PCI spectra[12], source temperature 150°C, in that $(M + 1)^+$ ions are usually the base peaks in the spectra. Literature MPCI spectra[12], source temperature 250°C, for 2-chloro compounds have intense $(M + 1)^+$ ions, but the base peaks corresponded to $[M + 1 - HCl]^+$. This fragment was not seen in the HPLC–PCI mass spectra of these compounds, where the base peaks were $(M + 1)^+$ ions. This may be due to the different source temperature used. Fragment ions seen in the HPLC–PCI mass spectra usually correspond to fragments found in the reported MPCI mass spectra[12]. Fragmentation of the two 1,2,3-triazines studied was predominantly influenced by the side chains, and could not be readily compared with that of the other compounds studied.

HPLC–NCI mass spectra of 2-chloro- and 2,4-dichloro-1,3,5-triazines show more intense $(M - 1)^-$ peaks, and less fragmentation, than do the reported methane negative chemical ionization (MNCI) spectra[29]. Fragmentation of menazon, velpar and the particular 1,2,3- and 1,2,4-triazines studied was greatly affected by the side chains, and was not analogous to fragmentation of the other 1,3,5-triazines studied.

A more detailed description of the mass spectral fragmentation of the various classes of triazines studied is given below. Spectra are shown in Tables II–VI.

2-Chloro- and 2,4-dichloro-1,3,5-triazines (Table II)

Positive ion spectra. The predominant ions from this class of compounds correspond to the $(M + 1)^+$ ions. In the case of the dialkylamino compounds, these ions carried almost all of the ion current, with only a small amount of M^+ being detected.

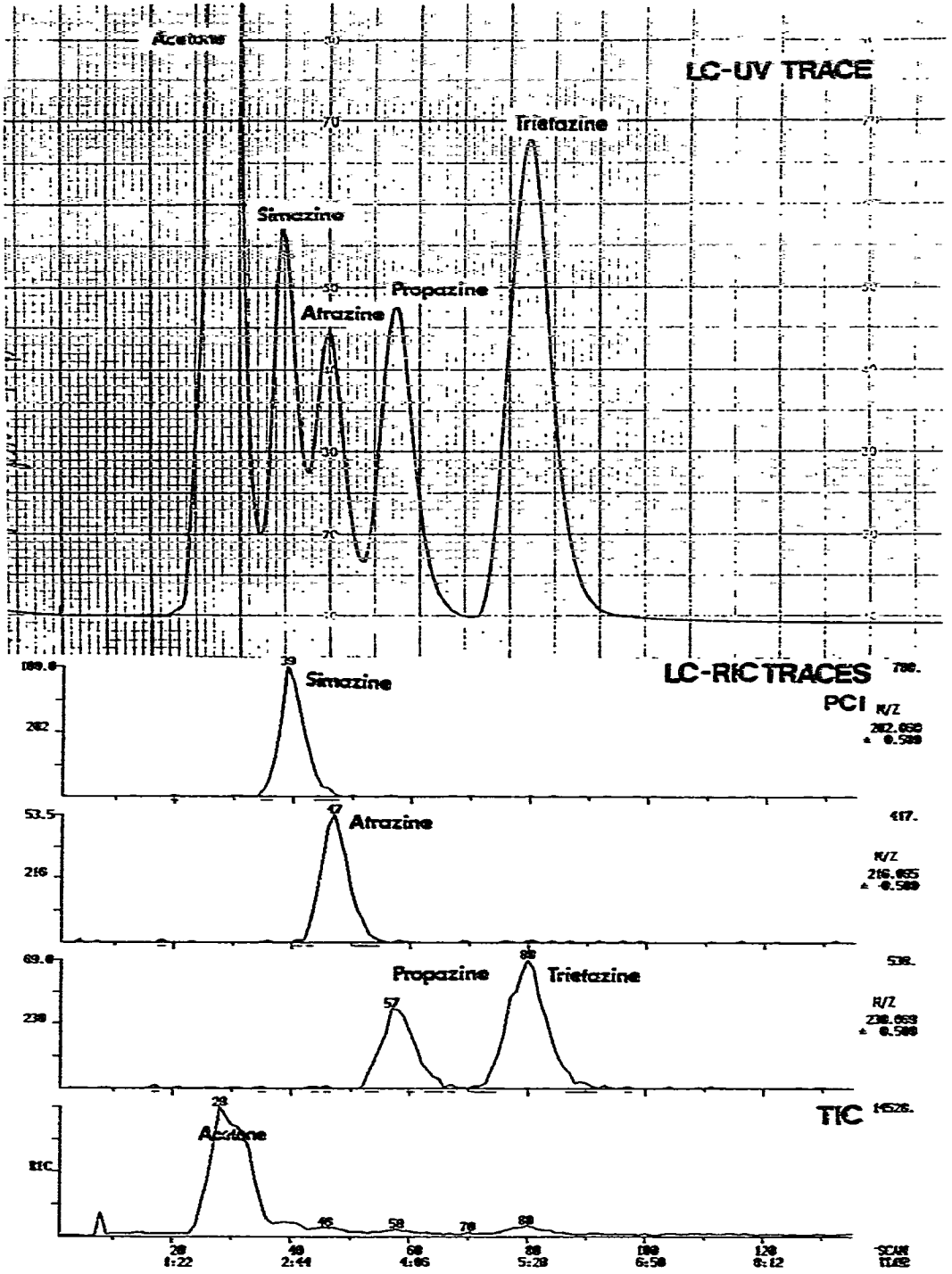


Fig. 1. HPLC–UV trace and HPLC–TIC trace (PCI mode) for a mixture of simazine, atrazine, propazine and trietazine.

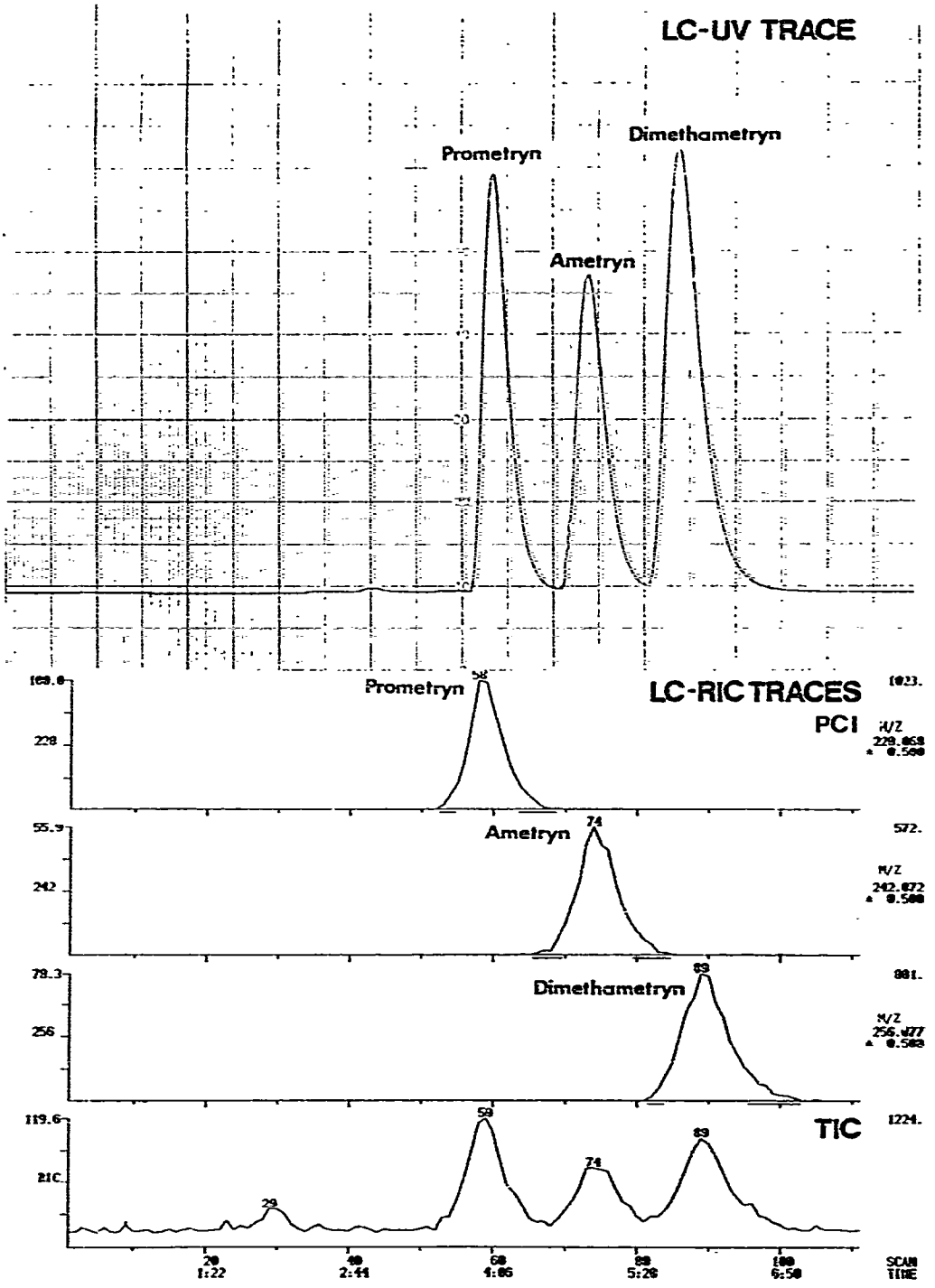


Fig. 2. HPLC–UV trace and HPLC–TIC trace (PCI mode) for a mixture of prometryn, ametryn and dimethametryn.

Other ions of interest include the $[M + 1 - HCN)^+$ ion from cyanizine and procyazine. Cyanizine gives a small $[M + 1 - CH_3]^+$ ion, and terbutylazine gives a fragment corresponding to $[M + 1 - C_4H_8]^+$, or $[M + 1 - (R_3 - 1)]^+$ following the nomenclature of LeClercq and Pacáková[12], at a relative abundance (RA) of 15%. This ion has been reported at 81% RA in the MPCI mass spectrum, with a source temperature of 250°C, and at 4% RA in the 150°C iBPCI mass spectrum[12]. The analogous ion $[M^+ - C_4H_8]$ has been observed in the EI mass spectra of these compounds[11–13,30], and has been attributed to a McLafferty rearrangement of the side chain[30].

Negative ion mass spectra. The base peak for anilazine corresponds to $[M - 1 - HCl]^-$, with additional peaks from $[M - 1 - Cl_2]^-$ and $[M - Cl_2]^-$. The small peak at *m/z* 219 may correspond to $[M - 1 + O - Cl_2]^-$. All of the peaks in the HPLC–NCI mass spectrum were observed in the reported MNCI spectrum[11], but the base peak in the MNCI spectrum, $[M - Cl]^-$, was not found in the HPLC–NCI-MS spectrum.

All of the monochloro alkylamino-1,3,5-triazines studied show only $[M - 1]^-$ ions, with the exception of cyanizine and procyazine, where the base peak corresponds to $[M - 1 - HCN]^-$. Other fragments of interest include $[M - CCN(CH_3)_2]^-$ and $[M - CCN(CH_3)_2 - HCl]^-$, and small peaks are found which correspond to $[M - HCl]^-$.

2-Methoxy 1,3,5-triazines (Table III)

Positive ions. Positive ion spectra for these compounds show predominantly $(M + 1)^+$ ions, with a small relative abundance of M^+ ions.

Negative ions. Negative ion mass spectra show only $(M - 1)^-$ ions.

2-Methylthio- and 2-ethylthio-1,3,5-triazines (Table IV)

Positive ions. HPLC–PCI mass spectra show mainly $(M + 1)^+$ ions, with traces of M^+ ions. The $[M + 1 - (R_3 - 1)]^+$ ion was present, but at very low intensity for all but terbutryne, where it had approximately 15% relative abundance. This is approximately the same relative abundance found for the corresponding ion in terbutylazine, the other 1,3,5-triazine where R_3 = *tert.*-butyl. This ion has been reported as the base peak in the MPCI mass spectrum of terbutryn[2].

Negative ions. HPLC–NCI mass spectra show only $(M - 1)^-$ ions.

Other 1,3,5-triazines (Table V)

Positive ions. Menazon and velpar have $(M + 1)^+$ ions as the base peaks in the positive ion spectra. Menazon shows a small peak for the $(CH_3O)_2PS_2^+$ fragment at *m/z* 157, as well as for the loss of this fragment from the $(M + 1)^+$ ion, at *m/z* 125. Velpar shows an abundant fragment for the loss of the cyclohexyl group minus one hydrogen from the $(M + 1)^+$ ion, the equivalent of the $[M + 1 - (R_3 - 1)]^+$ ions found in methylthio- and ethylthio-1,3,5-triazines. Also present is a trace of $[M + 1 - CO]^+$ or $[M + 1 - C_2H_4]^+$, and $[M + 1 - C_4H_8]^+$.

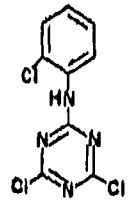
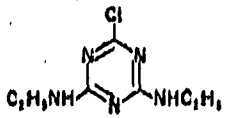
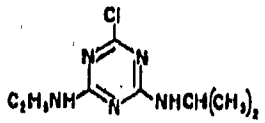
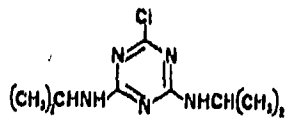
Fragmentation of velpar was unlike that of the other triazines studied, and some of the ions produced were difficult to explain based only on nominal mass data. High-resolution MS was used to determine the elemental compositions of some of these ions.

Since these high resolution studies were done on a different mass spectrometer —one not interfaced to an HPLC— the individual compounds were introduced by direct probe. Ionization techniques used were MPCI and MNCI, which were assumed to be approximations for acetonitrile–water HPLC–PCI-MS and HPLC–NCI-MS. Differences in source geometries, source temperature, source pressures and reagent gas compositions led to differences in the observed mass spectra, but ions of the same

TABLE II

POSITIVE AND NEGATIVE ION MASS SPECTRA OF 2-CHLORO- AND 2,4-DICHLORO-1,3,5-TRIAZINES

RA = Relative abundance; ID = Identity.

Compound	*Mol. wt.*	*HPLC-PCI MS*			*HPLC-NCI-MS*		
		m/z	*% RA*	*Proposed ID*	*m/z*	*% RA*	*Proposed ID*
Anilazine 	274	108	171.3		203	79.7	$[M - 1 - Cl_2]^-$
		109	5.6		204	7.2	
		275	100.0		205	18.1	$[M - Cl_2]^-$
		277	92.6		206	1.1	
		278	7.4	$[M + 1]^+$	219	4.6	$[M - 1 + O - Cl_2]^-$
		279	9.3		221	1.2	
					237	81.5	
					239	100.0	
					240	21.4	$[M - 1 - HCl]^-$
					241	8.4	
					242	2.4	
					273	3.6	
					275	3.9	$[M - 1]^-$
					277	0.4	
Simazine 	201	201	2.1	M^+	200	100.0	$[M - 1]^-$
		202	100.0		202	34.5	
		204	26.0	$[M + 1]^+$			
		205	2.8				
Atrazine 	215	215	2.2	M^+	214	100.0	$[M - 1]^-$
		216	100.0		216	32.2	
		217	11.1	$[M + 1]^+$			
		218	43.0				
Propazine 	229	229	4.6	M^+	228	100.0	$[M - 1]^-$
		230	100.0		230	23.5	
		231	17.1	$[M + 1]^+$			
		232	29.3				

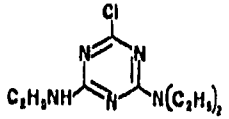
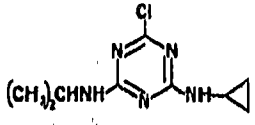
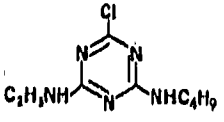
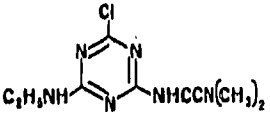
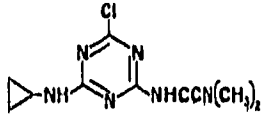
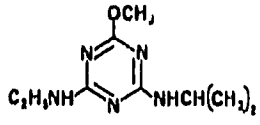
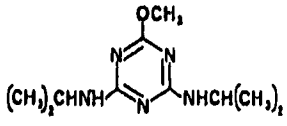
Trietazine 	229	229	3.5	M^+	228	100.0	$[M - 1]^-$
		230	100.0	$[M + 1]^+$	230	23.2	
		232	37.0				
		233	0.7				
Cyprazine 	227	228	100.0	$[M + 1]^+$	226	100.0	$[M - 1]^-$
		229	9.4		227	6.9	
		230	30.9		228	26.0	
		231	1.6				
Terbutylazine 	229	174	17.6	$[M + 1 - C_4H_8]^+$	228	100.0	$[M - 1]^-$
		229	22.6	M^+	230	25,8	
		230	100.0	$[M + 1]^+$			
		232	40.9				
Cyanizine 	240	214	13.8		136	25.2	$[M - CCN(CH_3)_2 - HCl]^-$
		215	1.7	$[M + 1 - HCN]^+$	172	9.1	
		216	3.4		174	2.0	$[M - CCN(CH_3)_2]^-$
		226	0.3	$[M + 1 - CH_3]^+$	184	1.3	
		239	1.1	M^+	198	7.1	$[M - 1 - CH_3CN]^-$
		241	100.0		204	2.3	$[M - HCl]^-$
		243	20.8		212	100.0	
		244	2.4		213	4.4	$[M - 1 - HCN]^-$
		267	0.4	$[M + HCN]^+$	214	32.4	
					239	9.4	
					241	1.4	$[M - 1]^-$
Procyazine 	252	226	18.7	$[M + 1 - HCN]^+$	148	48.2	$[M - CCN(CH_3)_2 - HCl]^-$
		228	2.5		184	23.8	
		253	100.0		186	7.6	$[M - CCN(CH_3)_2]^-$
		254	14.1		188	3.6	
		255	26.0	$[M + 1]^+$	216	3.3	$[M - HCl]^-$
		256	1.2		223	6.5	
					224	100.0	
					225	9.2	$[M - 1 - HCN]^-$
					226	22.6	
					251	17.0	$[M - 1]^-$

TABLE III

POSITIVE AND NEGATIVE ION MASS SPECTRA OF 2-METHOXY-1,3,5-TRIAZINES

Compound	*Mol. wt.*	*HPLC–PCI-MS*			*HPLC–NCI-MS*		
		m/z	*% RA*	*Proposed ID*	*m/z*	*% RA*	*Proposed ID*
Atraton 	211	211	1.6	M^+	210	100.0	$[M - 1]^-$
		212	100.0	$[M + 1]^+$	211	2.0	
		214	0.8				
		215	0.3				
Prometon 	225	225	2.4	M^+	224	100.0	$[M - 1]^-$
		226	100.0	$[M + 1]^+$	225	2.2	

nominal mass which appeared in both spectra were assumed to have the same elemental composition. High-resolution data for this compound are shown in Table VII.

In the positive ion spectrum of velpar, high resolution was used to confirm the elemental compositions of the ions at *m/z* 253, 252, 197 and 171 described above. The ion at *m/z* 128 gave an elemental composition consistent with $[M + 1 - C_6H_{11}NCO]^+$.

Negative ions. HPLC–NCI mass spectra for these two compounds are unlike those of the other triazines due to the strong influences of the side chains. Menazon gives $(CH_3O)_2PS_2^-$ as the base peak, with only a trace of the $(M - 1)^-$ ion. This has been previously observed for menazon[28] and for other phosphorodithioates[28,31]. Velpar has a base peak at *m/z* 110, corresponding to $(C_3N_3O_2)^-$. Also present are fairly intense peaks corresponding to $[M - CH_3]^-$ at *m/z* 237, at *m/z* 292, corresponding to the addition of CH_3CN from the solvent–reagent gas to the $(M - 1)^-$ ion, and at *m/z* 235, possibly corresponding to the loss of C_4H_9 from the *m/z* 292 ion. The elemental compositions of the ions at *m/z* 110 and 237 were confirmed by high-resolution MS.

1,2,3-Triazines (Table VI)

The positive ion mass spectra of azinphos methyl and azinphos ethyl are greatly influenced by the side chain, as was the case for menazon, the other organophosphorus compound in this study. The abundant fragments in the HPLC–PCI mass spectra, *m/z* 160 and 132, for both azinphos methyl and azinphos ethyl, are the same as those in the reported 100°C MPCI mass spectrum[32] of azinphos methyl. The elemental compositions of these ions were assigned by high resolution mass spectrometry (Table VII) to $[M - (CH_3O)_2PS_2]^+$ and $[M - (CH_3O)_2PS_2 - N_2]^-$, $(=[C_8H_6NO]^+)$, respectively. The *m/z* 132 ion has been given as $[M - (CH_3O)_2PS_2 - CO]^+$ based on low resolution data, in the MPCI[33] and EI[32] ionization modes. The loss of N_2 from trichloro- and perfluorotin–isopropyl-1,2,4-triazines has previously been reported[34]. Other ions which were examined with high resolution mass spectrometry were *m/z* 120 (C_7H_6NO) and *m/z* 105 (probably C_7H_5O, but could also be $C_5H_3N_3$).

The NPLC–NCI mass spectra of azinphos methyl and azinphos ethyl have been described previously[28], and are very similar to reported MNCI spectra[29]. High resolution studies were done on *m/z* 164, 157 and 132 in azinphos ethyl. As expected, the *m/z* 157 and 185 peaks corresponded to $(RO)_2PS_2^-$ where R = CH_3 and C_2H_5, respectively. The elemental composition of the *m/z* 132 peak was the same in the negative ion mode as it was in the positive ion mode, corresponding to $[CH_2NCOC_6H_4]^{-\text{ or }+}$. The peak at *m/z* 164 also corresponded to a loss of N_2 rather than CO, $[M - (CH_3O)_2PS_2 - N_2]^-$.

1,2,4-Triazines (Table VI)

Positive ions. Metribuzin gives the $[M + 1]^+$ ion as the base peak in the HPLC–PCI mass spectrum, with about 8% relative abundance of the M^+ ion.

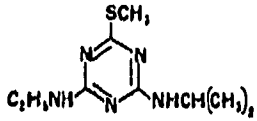
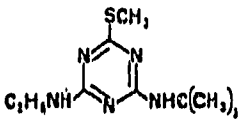
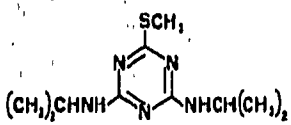
Negative ions. The base peak in the negative ion spectrum corresponds to a loss of CH_3 from the $[M - 1]^-$ ion. Other major peaks correspond to $[M - (CH_3)_2]^-$ and $[M - CH_3]^-$. There also appears to be a small $[M - 1]^-$ peak present, as well as a trace of $[M - SCH_3]^-$.

Sensitivity considerations

In general, sensitivities for this class of compounds were better in the HPLC–PCI-MS mode of operation than in the HPLC–NCI-MS mode, with the exception of menazon, azinphos methyl, azinphos ethyl and metribuzin. The first three of these compounds are also organophosphorus compounds, and their enhanced sensitivity in negative ionization modes has already been reported[26,27]. The marked sensitivity

TABLE IV

POSITIVE AND NEGATIVE ION MASS SPECTRA OF 2-METHYLTHIO- AND 2-ETHYLTHIO-1,3,5-TRIAZINES

Compound	*Mol. wt.*	*HPLC–PCI-MS*			*HPLC–NCI-MS*		
		m/z	*% RA*	*Proposed ID*	*m/z*	*% RA*	*Proposed ID*
Ametryn 	227	186	0.8	$[M + 1 - C_3H_7]^+$	226	100.0	$[M - 1]^-$
		227	1.6	M^+	227	3.1	
		228	100.0	$[M + 1]^+$	228	1.9	
		230	3.9				
Terbutryn 	241	186	14.6	$[M + 1 - C_4H_8]^+$	240	100.0	$[M - 1]^-$
		241	3.1	M^+	241	3.5	
		242	100.0	$[M + 1]^+$			
		243	13.9				
Prometryn 	241	242	100.0	$[M + 1]^\pm$	240	100.0	$[M - 1]^-$
		244	5.1		241	6.0	

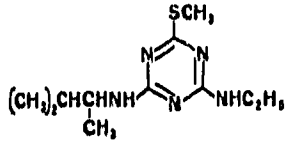
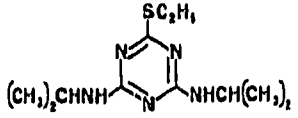
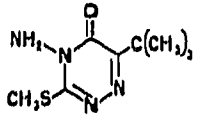
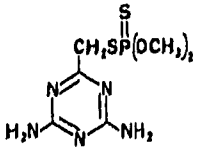
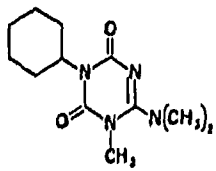
Dimethametryn 	255	255	1.5	M^+	254	100.0	$[M - 1]^-$
		256	100.0		255	7.6	
		258	2.1	$[M + 1]^+$			
		259	0.5				
Dipropetryn 	255	255	1.7	M^+	254	100.0	$[M - 1]^-$
		256	100.0	$[M + 1]^+$	255	7.2	
		257	5.6				
Metribuzin 	214	214	8.2	M^+	168	0.1	$[M - SCH_3]^-$
		215	100.0		184	57.3	
		216	12.5	$[M + 1]^+$	185	3.4	$[M - (CH_3)_2]^-$
		217	1.8		186	1.1	
					198	100.0	$[M - 1 - CH_3]^-$
					199	26.0	
					200	6.2	
					201	0.4	$[M - CH_3]^-$
					213	1.0	$[M - 1]^-$

TABLE V

POSITIVE AND NEGATIVE ION MASS SPECTRA OF OTHER 1,3,5-TRIAZINES

Compound	*Mol. wt.*	*HPLC-PCI-MS*			*HPLC-NCI-MS*		
		m/z	*% RA*	*Proposed ID*	*m/z*	*% RA*	*Proposed ID*
Menazon 	281	125	3.7	$[M + 1 - \{SPS(OCH_3)_2 - 1\}]^+$	138	<0.1	
		126	4.5		154	<0.1	
		156	2.4	$SPS(OCH_3)_2^+$	157	100.0	$(CH_3O)_2PS_2^-$
		157	0.2		159	10.3	
		281	2.5	M^+	171	1.0	
		282	100.0	$[M + 1]^+$	280	<0.1	$[M - 1]^-$
		284	6.9		282	0.2	
		285	0.2				
Velpar 	252	128*	0.7	$[M + 1 - C_6H_{11}NCO]^+$	110*	100.0	$C_3N_3O_2^-$
		170	0.8		235	24.9	$[(M - 1 + CH_3CN) - C_4H_9]^-$
		171*	24.2	$[M + 1 - C_6H_{10}]^+$	237*	9.7	$[M - CH_3]^+$
		172	2.3		292	24.1	$[M - 1 + CH_3CN]^-$
		197*	0.2	$[M + 1 - C_4H_8]^+$			
		226	0.2	$[M + 1 - CO]^+$ or $[M + 1 - C_2H_4]^+$			
		252*	1.6	M^+			
		253*	100.0	$[M + 1]^+$			
		255	0.2				

* Elemental composition confirmed by high-resolution MS.

TABLE VI

POSITIVE AND NEGATIVE ION MASS SPECTRA OF 1,2,3- AND 1,2,4-TRIAZINES

Compound	*Mol. wt.*	*HPLC–PCI-MS*			*HPLC–NCI-MS*		
		m/z	*% RA*	*Proposed ID*	*m/z*	*% RA*	*Proposed ID*
Azinphos methyl	317	105*	4.3	$C_7H_5O^+$ or $C_5H_3N_3^+$	120	0.6	
		120*	5.0	$C_7H_6NO^+$	132*	0.4	$CH_2NCOC_6H_4^-$
		131	0.6		146	0.2	$N_3COC_6H_4$
		132*	100.0	$C_8H_6NO^+$, $[M - (CH_3O)_2PS_2 - N_2]^+$	156	0.3	
		133	11.8		157*	100.0	$(CH_3O)_2PS_2^-$
		150	2.9		159	7.8	
		159	0.6		164*	1.0	$[M - (CH_3O)_2PS_2 - N_2]^-$
		160*	8.5	$C_8H_6N_3O^+$, $[M - (CH_3O)_2PS_2]^{+\cdot}$	166	3.2	
		161	0.8				
		261	2.3	$C_9H_{10}PO_3S_2^+$, $[M - CH_2N_3]^+$ or $C_7H_8N_3O_2PS_2^+$, $[M - C_3H_4O]^+$			
Azinphos ethyl	345	105*	2.4	$C_7H_5O^+$ or $C_5H_3N_3^+$	120	0.4	
		120*	1.8	$C_7H_6NO^+$	132	0.2	$CH_2NCOC_6H_4^-$
		131	0.9		146	0.4	$N_3COC_6H_4$
		132*	100.0	$[M - (C_2H_5O)_2PS_2 - N_2]^+$	153	0.3	$(C_2H_5O)_2PS^-$
		134	2.7		164	0.9	$[M - (C_2H_5O)_2PS_2 - N_2]^-$
		150	3.6		185*	100.0	
		160*	6.0	$[M - (C_2H_5O)_2PS_2]^+$	187	9.9	$(C_2H_5O)_2PS_2^-$
		161	0.5		188	0.1	
		289	0.2				

* Elemental composition confirmed by high-resolution MS.

TABLE VII

HIGH-RESOLUTION MASS SPECTRAL DATA FOR VELPAR, AZINPHOS METHYL AND AZINPHOS ETHYL

Compound	*Nominal mass*	*Calculated*	*Observed*	*Elemental composition*
Velpar (MPCI)	128	128.0824	128.0826	$C_5H_{10}N_3O$
	171	171.0882	171.0890	$C_6H_{11}N_4O_2$
	197	197.1039	197.1056	$C_8H_{13}N_4O_2$
	252	252.1586	252.1533	$C_{12}H_{20}N_4O_2$
	253	253.1665	253.1609	$C_{12}H_{21}N_4O_2$
Velpar (MNCI)	110	109.999	109.998	$C_3N_3O_2$
	237	237.1352	237.1364	$C_{11}H_{17}N_4O_2$
Azinphos methyl (MPCI)	105	105.0340	105.0334	C_7H_5O or
		105.0327	105.0334	$C_5H_3N_3$
	120	120.0449	120.0461	C_7H_6NO
	132	132.0450	132.0425	C_8H_6NO
	160	160.0511	160.0483	$C_8H_6N_3O$
	261	260.9796	260.9812	$C_7H_8N_3O_2PS_2$ $(M - CH_2N_3)$
		or		
		260.9809	260.9812	$C_9H_{10}PO_3S_2$ $(M - C_3H_4O)$
Azinphos methyl (MNCI)	132	132.0450	132.0425	C_8H_6NO
	146	146.0354	146.0338	$C_7H_4N_3O$
	157	156.9548	156.9564	$C_2H_6O_2PS$
	159	158.9506	158.9520	$C_2H_6O_2P^{32}S_1{}^{34}S_1$
	164	164.0169	164.0151	C_8H_6NOS
Azinphos ethyl (MPCI)	105	105.0340	105.0334	C_7H_5O or
		105.0327	105.0334	$C_5H_3N_3$
	120	120.0449	120.0461	C_7H_6NO
	132	132.0450	132.0435	C_8H_6NO
	134	134.0605	134.0598	C_8H_8NO
	160	160.0511	160.0494	$C_8H_6N_3O$
	289	289.0236	289.0214	$C_{10}H_{14}N_3O_2PS_2$
Azinphos ethyl (MNCI)	185	184.9861	184.9895	$C_4H_{10}O_2PS_2$

differences between these and the other compounds can be seen in Figs. 3–5. Fig. 3 shows five approximately 60-μg injections onto the column ($\approx$600 ng to the source), of dipropetryn, atraton, prometon, velpar and metribuzin in the negative ionization mode (leading peaks in the chromatogram correspond to acetone). The greater relative sensitivity of metribuzin in the negative ion mode can be clearly seen. Fig. 4 shows a mixture of ametryn, prometryn and dimethametryn run in both ionization modes, along with RIC traces of abundant ions. As can be seen from this figure, these three compounds are more sensitive in the positive ion mode. Fig. 5 shows a mixture of azinphos methyl and azinphos ethyl. Here, there is clearly greater sensitivity in the negative ion mode. Positive ion and negative ion chromatograms shown in Figs. 1, 2, 4 and 5 were obtained from 50-μg injections ($\approx$500 ng to the source). Numbers in the upper right hand corner of each chromatogram indicate peak heights. Unfortunately, triazines, as a class, do not appear to be particularly sensitive compounds for analysis by HPLC–MS, either by positive chemical ionization or by negative chemical ionization, although sensitivities appear to be better in the positive ion mode than in the negative ion mode.

The lack of mass spectral sensitivity of this class of compounds may not be

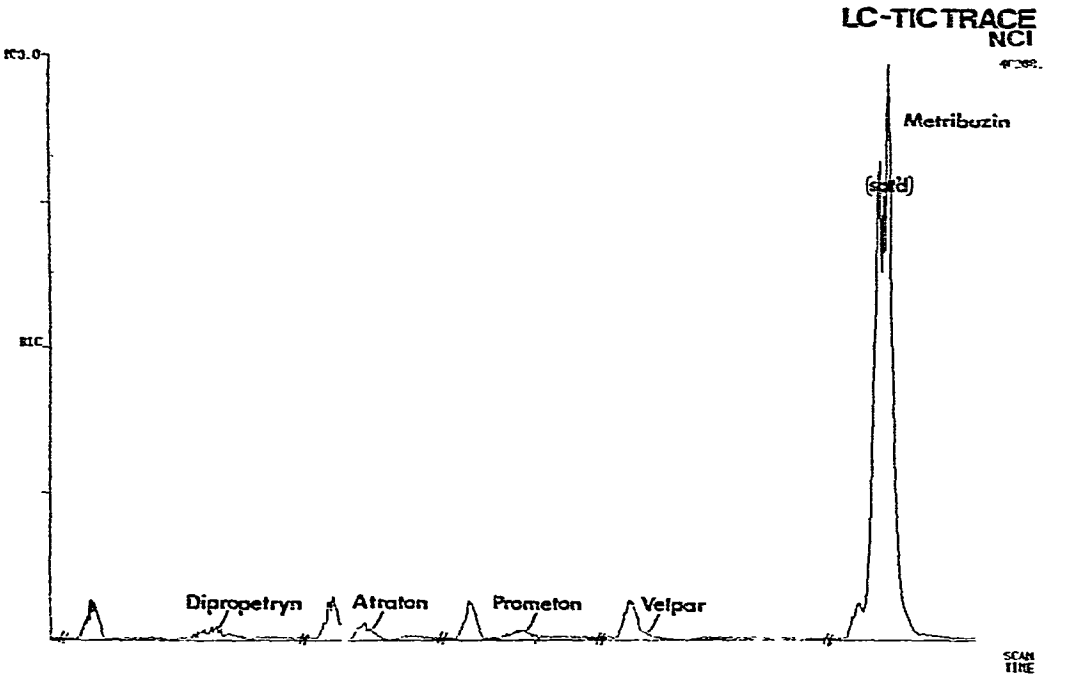


Fig. 3. HPLC–TIC trace from five consecutive injections of approximately equal amounts of different triazines (in acetone).

specific to HPLC–MS, however. A similar sensitivity problem was encountered in negative chemical ionization, with sample introduction by direct probe[35], and Damico[32] reported using 3–5 μg of azinphos methyl to get the EI direct probe mass spectrum.

Overall HPLC–MS system detection limits are, of course, a function of the amount of material entering the source. Using the present HPLC–MS system, only about 1 % of the injected sample reaches the mass spectrometer. Thus, if the need for an effluent split could be eliminated, the amount of sample injected onto the column could be reduced by a factor of about 100, and the same amount of material would reach the source. For example, if a sample containing 100 ng of a particular compound is injected into a standard HPLC–MS all 100 ng go through the UV detector but only 1 ng would enter the MS source. If a sample containing 100 ng is injected into a micro HPLC–MS system all 100 ng go through the UV detector, *and* all 100 ng would go into the MS source. This would give a factor of 100 increase in sensitivity over that of the present HPLC–MS system, and should be achievable with the use of micro HPLC–MS systems such as have been described in the literature[36–39]. Additional sensitivity could be obtained through the use of single ion monitoring techniques, rather than full-scan mass spectra.

CONCLUSIONS

Mass spectra observed for most triazines using the DLI HPLC–MS technique, with acetonitrile–water as the mobile phase, are similar to MNCI spectra in the negative ion mode, and to MPCI and iBPCI spectra in the positive ion mode. Fragmentation of certain of the triazines which were also organophosphorus compounds were so greatly influenced by the side chains as to be unlike that of the other triazines

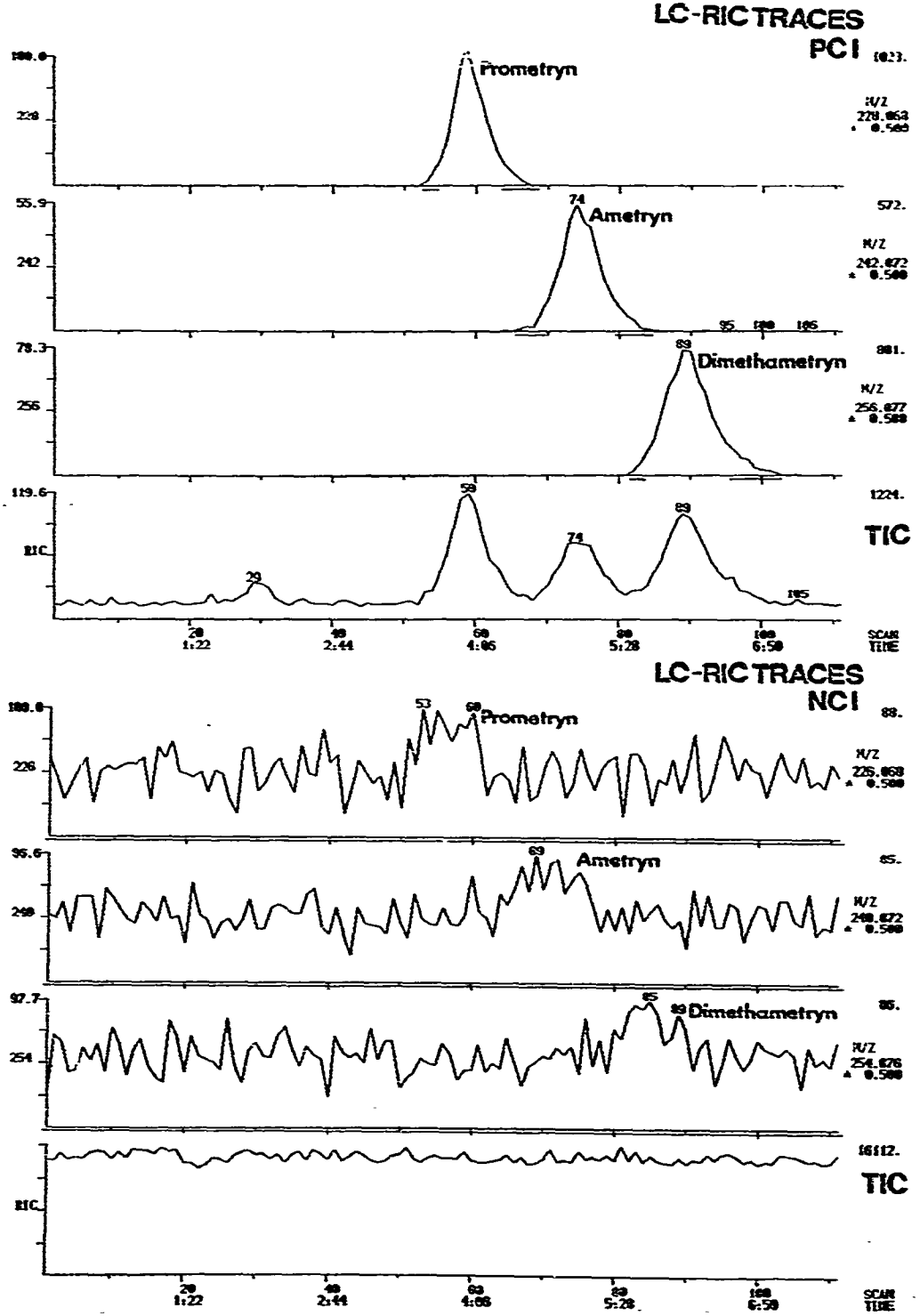


Fig. 4. HPLC–PCI and HPLC–NCI traces from mixture of prometryn, ametryn and dimethametryn.

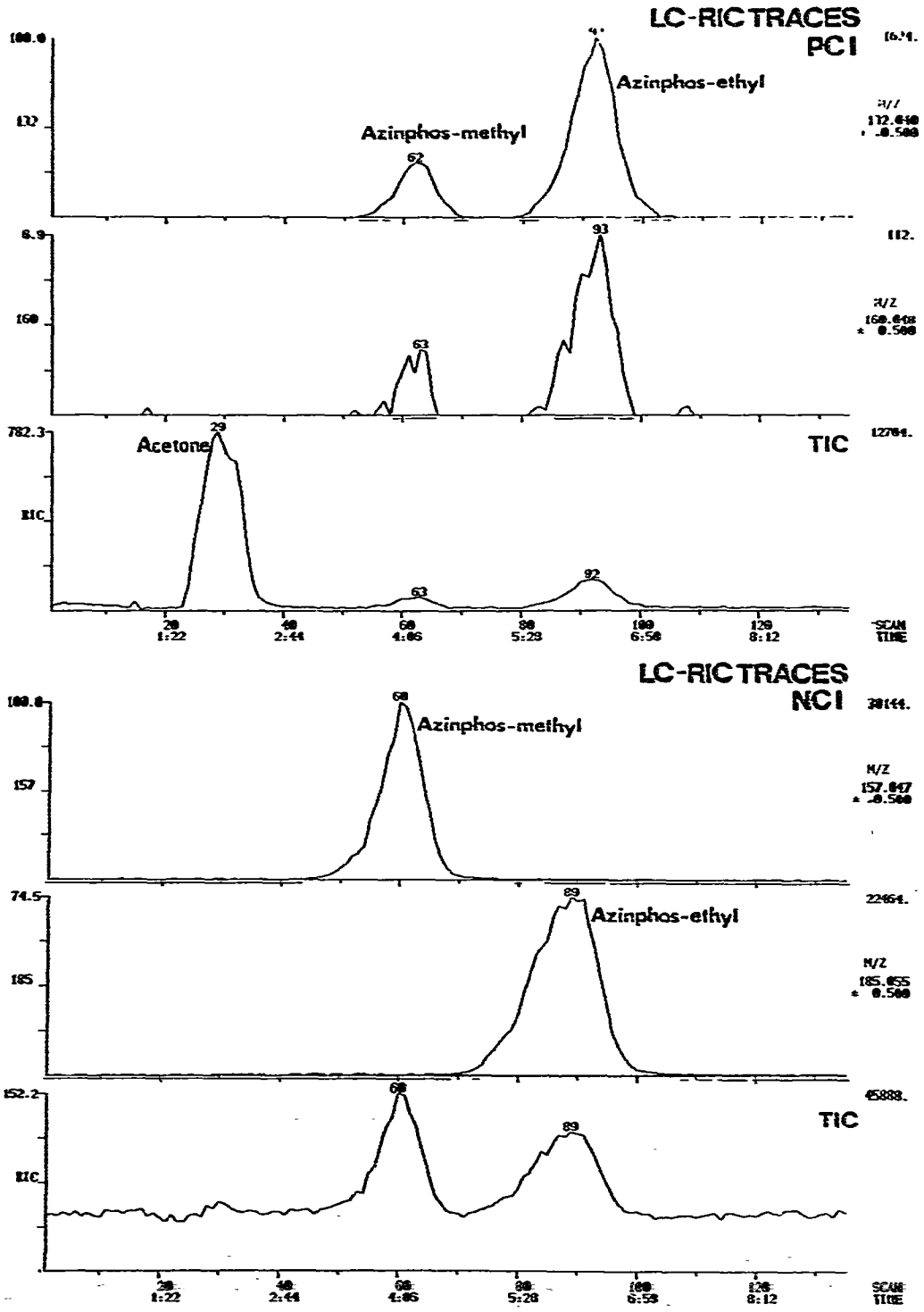


Fig. 5. HPLC–PCI and HPLC–NCI traces for a mixture of azinphos methyl and azinphos ethyl.

studied, but the mass spectra of even these compounds was similar to reported MNCI and MPCI mass spectra.

Most triazines showed pseudomolecular ions, $(M + 1)^+$ or $(M - 1)^-$, in the positive and negative ionization modes, and showed more sensitivity by HPLC–PCI than by HPLC–NCI. Exceptions to this were metribuzin and the three organophosphorus compounds (menazon, azinphos methyl and azinphos ethyl), which were more sensitive in the negative ion mode.

In summary, if the mass spectral sensitivity limitations can be overcome, perhaps by the use of a micro HPLC system, the DLI HPLC–MS method should provide useful information in the analysis of triazine herbicides and their metabolites by providing molecular weight and/or structural information in addition to information obtained from HPLC retention times. The DLI HPLC–MS technique should also allow quantitation of herbicides that cochromatograph or are not completely resolved on the HPLC, by monitoring ions specific to the compounds of interest.

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