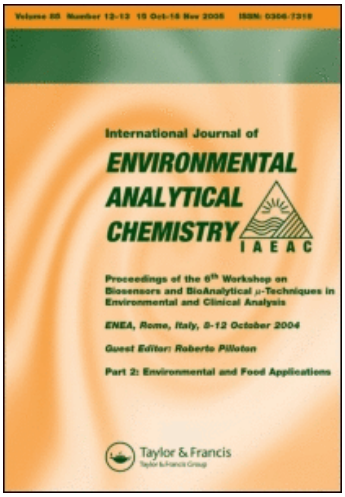

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Signal losses in pesticide analysis using the broadband isolation waveform in a commercial quadrupole ion trap to accomplish precursor ion isolation in tandem mass spectrometry

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Signal losses in pesticide analysis using the broadband isolation waveform in a commercial quadrupole ion trap to accomplish precursor ion isolation in tandem mass spectrometry

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Signal losses due to precursor ion isolation in a quadrupole-ion-trap mass spectrometer were studied using selected pesticides as model compounds. These signal losses originate from isolations of ion populations employing the broadband isolation (bbiso) waveform used in the Varian quadrupole ion-trap precursor ion isolation protocol. Signal losses were found to be 'precursor ion structure' dependent upon isolation using the bbiso. The effect of the bbiso waveform on the ionic structure and nature of substituents on the precursor ion was investigated. Isolation of old electron radical molecular ions of the type $[M^{+\bullet}]$ showed remarkable signal losses compared with isolation of fragment ions derived from the same compounds. The impact of the bbiso waveform on the response of the instrument using mass spectrometry/mass spectrometry and the bbiso waveform was also examined. The response of the instrument as related to the calculated Instrument Detection Limits was observed to parallel ion population losses.

Keywords: Varian; Precursor ion; Broadband; MS/MS; Isolation

1. Introduction

A quadrupole ion trap's sensitivity is largely determined by its ion flux, i.e. the ion throughput from the time of creation to the time of detection. Tandem mass spectrometry has been used widely for analysing complex environmental matrices used as assessment end-points for ecosystem evaluation. This is because it is used as a means of increasing the selectivity of a particular analysis. The efficiency and sensitivity of tandem mass spectrometry have been recognized and documented [1]. Despite its attractiveness, a full scan mass analysis of a sample may be more attractive than tandem mass spectrometry. This is because, in a tandem experiment, isolation of only one precursor ion means that all other ions are ejected. This is signal loss and can lead to

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reduced sensitivity for analytes that are not found in complex matrices. If elimination of chemical noise arising from a complex sample matrix is the goal, the reduction in noise leading to high signal-to-noise (S/N) ratios surpasses signal loss in many instances. Tandem mass spectrometry in this case becomes a method of choice due to enhanced selectivity and sensitivity. The simplest tandem experiment in a quadrupole ion trap involves three stages. Isolation of the precursor ion after ionization is the first step. The second step is collision-induced dissociation (CID), and the third step is mass analysis of product and/or the remainder of precursor ions. Excitation of the isolated precursor ions can be done in two broadly classified categories, i.e. the resonant and the non-resonant modes. In the resonant excitation mode [2], a high-frequency supplemental single or multi-frequency alternating current (a.c.) voltage is applied to the endcaps in either a dipolar or quadrupolar fashion. When the secular frequency of the ion matches that of the applied waveform, resonance occurs, and the ion's translational energy increases, causing it to collide with the helium buffer gas. The ion's translational energy is converted into internal vibrational energy. If the internal energy exceeds the critical energy necessary to cause fragmentation, the ion fragments to give product ions. In the non-resonant mode [3] of excitation, a low-frequency supplemental field is applied to the end caps in a dipolar fashion and out of phase. The potential energy of the ions in the trapping field changes instantly because of the change in field strength. This potential energy is converted into translational energy by the restoring force of the trapping field and subsequently into internal energy. The same process as in the resonant mode follows thereafter.

Although there are several parameters that govern the efficiency of a tandem experiment in a quadrupole ion trap [4, 5], precursor-ion isolation before its excitation is a critical step in achieving good ion population recovery. Ions have also been observed to exhibit chemical mass shifts [6] because they are 'fragile' and are capable of fragmenting on application of resonance ejection during mass analysis. These mass shifts are compound-dependent [7, 8]. These types of ions can also fragment during application of an isolation waveform while selecting a precursor ion for tandem experiments, thus making it impossible to achieve unit isolation.

In order to understand the mechanism of internal energy depositions into precursor ions during the resonant excitation in tandem experiments and the parameters governing the experiment, several investigations have been performed on the molecular ion m/z 134 of *n*-butylbenzene [9–11]. Lynn and co-workers [12] discovered that the exclusive production of m/z 91 *versus* 92 from the molecular ion m/z 134 of *n*-butylbenzene is dependent on the isolation procedure employed before ion activation. They attempted to perform a tandem experiment on m/z 134 from *n*-butylbenzene using the Varian Saturn quadrupole ion-trap mass spectrometer and observed an unexpected base peak at m/z 119. They attributed this to a rearrangement reaction that is induced because of using a bbiso waveform which is invoked during the isolation stage and prior to ion activation in the tandem mass spectrometry scan function used by Varian. The exact mechanism through which the rearrangement occurs was not evaluated, but it was assumed that excitation of one of the many secondary motions that the ion exhibits occurs. The bbiso waveform is composed of frequencies that span from 20 to 400 kHz spaced at 500 Hz with an amplitude of 30 V_{p-p}. In a precursor-ion isolation procedure, the bbiso waveform is used to eject higher-mass ions than the precursor whose secular frequency at the time of its application would be above 400 kHz. This means that the bbiso waveform should have no impact on the precursor ion if its

secular frequency lies above 400 kHz. When they reduced the amplitude of the bbiso waveform from the default 30 to 20 V, the isomerization reaction to produce m/z 119 did not occur.

In a quadrupole ion trap, any factors that lead to a reduction in the intensity of the precursor ion during its isolation can cause a significant reduction in the sensitivity of a tandem experiment. This article explores and relates the consequences of the above findings [12] on trace-pesticide analysis in environmental analyses employing the bbiso waveform isolation method in a commercial quadrupole ion trap.

2. Experimental

2.1 *Standards*

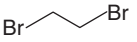
Standards were donated by the Mississippi State Chemical Laboratory (MSCL). All the standards were prepared using acetone from Burdick and Jackson (B & J high-purity solvent grade). Dilutions and preparation of the pesticide mixture were carried out using the same acetone. The cocktail solution containing the pesticide mixture contained the following concentrations in ($\mu g\,mL^{-1}$): endosulphan (1.2), atrazine (5.0), malathion (5.0), hexachlorobenzene (5.1), *pp*′-DDT (5.0), diazinon (5.2), lindane (5.0), heptachlor epoxide (5.0), ethylene dibromide, i.e. EDB (6.0), 1,2-dibromo-3-chloropropane, i.e. DBCP (6.0), piperonyl butoxide (5.0), dieldrin (5.3), and chlorpyrifos (5.7). The aforementioned pesticides are shown in figure 1.

2.2 *Gas chromatography (GC)*

GC separations were done using a Varian Star 3400 CX. A DB-5 capillary column (J & W Scientific) 30 m × 0.25 mm i.d. × 0.25 μm thickness was used for all separations. Automatic injections were performed using the Varian 8200 auto-sampler on a 1077 injector in splitless mode. One microlitre of standard or pesticide mixture was injected throughout. All injections were done isothermally at 220°C. Helium was used as the carrier gas at a flow rate of $1\,mL\,min^{-1}$. The following GC programme was used throughout the experiments. The column was held at 80°C for 1 min and ramped to 240°C at $15°C\,min^{-1}$, then held at that point for 5 min. Following this, the column was ramped to 290°C at $5°C\,min^{-1}$ and held at that point for 14.34 min. The transfer line temperature was set at 290°C.

2.3 *Mass spectrometry*

A Varian Saturn 4D-quadrupole ion-trap mass spectrometer was used in all experiments. All experiments were done using electron ionization (EI). The instrument was equipped with the built in mass spectrometry/mass spectrometry (MS/MS) and toolkit software. The toolkit software allowed for additional MS/MS capabilities such as Selected Ion Storage (SIS), Multiple Reaction Monitoring (MRM), etc. Isolation of ions of interest were done at a q_z value of 0.4 of the stability diagram, which is the default setting used by Varian for carrying out



Ethylene dibromide
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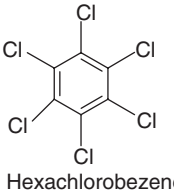

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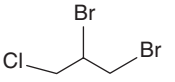
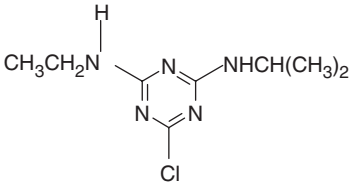
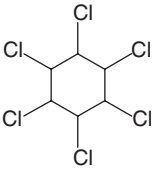


1,2-dibromo-3-chloropropane
3



Atrazine
4



Lindane
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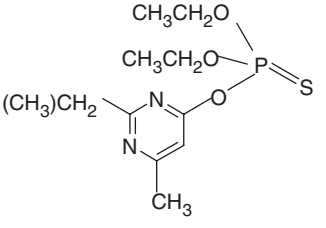

Diazinon
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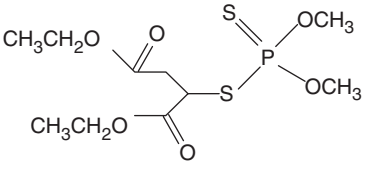

Malathion
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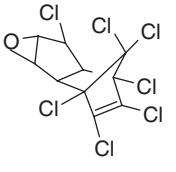
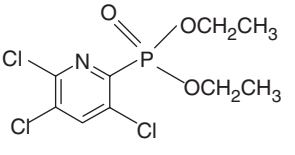


Heptachlor epoxide
8



Chlorpyrifos
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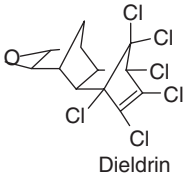

Dieldrin
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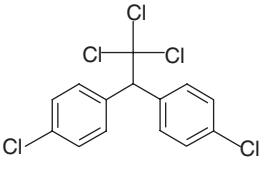
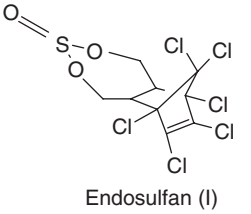
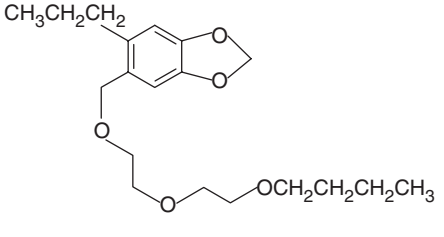


pp'-DDT
11



Endosulfan (I)
12



Piperonyl butoxide
13

Figure 1. Pesticides of environmental interest evaluated in this study.

MS/MS experiments. It has also been demonstrated [13] that at this q_z value, no black canyons that would cause ion population losses exist on the stability diagram. The manifold temperature was held at 220°C throughout the experiments. The tune parameters for the instrument were kept constant throughout the experiment and were typically 1600 V for the multiplier voltage and 60 μA for the emission current, and a default of 4.0 V was set as the axial modulation amplitude. The default bbiso waveform parameters pre-set by Varian, i.e. a frequency range of 20–400 kHz spaced at 500 Hz, irradiated for 5.756 ms was used throughout ion isolations. This step falls within 10 temporal isolated steps built in the Varian isolation protocol and takes a total of 29.7 ms to execute [12]. The Varian Saturn ion-trap mass spectrometer utilizes Automatic Gain Control (AGC) [14] scan function to control ionization in the trap. The AGC was used throughout in order to minimize the impact of signal degradation as a result of space charge effects. Table 1 shows compounds, their molecular weights, and the precursor ions that were isolated in each case. The toolkit software that allows adjustment of the bbiso waveform amplitude as well as MRM was used in all experiments.

A full-scan mass spectrum of a mixture of the pesticides was performed after auto-tuning the instrument. This was followed by isolation of the precursor ion for all pesticides while incrementing the bbiso waveform amplitude in units of 5 V from 10 V to the instrument's default value of 30 V. Excitation of the isolated ions was disabled by setting the CID voltage to 0 V to establish the ion populations of the precursor ions relative to the ion populations in the full-scan mode. Peak areas for all precursor ions of the pesticides were calculated in the full scan and MS/MS isolation modes after reconstructing ion-trace chromatograms for a particular precursor ion. Percentage signal losses were calculated using equation (1) as follows:

$$\% \text{ signal loss} = 100 - (A_i/A_f)100, \quad (1)$$

where A_i is the peak area of precursor ion reconstructed chromatographic peak after isolation at a given bbiso amplitude and A_f is the peak area of the precursor ion reconstructed chromatogram in the full scan mode, i.e. equivalent to the total ion current (TIC).

Table 1. Compounds, their molecular weights, and precursor ions isolated.

No.	Compound	Molecular weight	Precursor ion
1	Ethylenedibromide	186	107
2	Hexachlorobenzene	284	284
3	1,2-Dibromo-3-chloropropane	236	157
4	Atrazine	215	215
5	Lindane (γ-BHC)	288	219
6	Diazinon	304	304
7	Malathion	330	173
8	Heptachlor epoxide	388	353
9	Chlorpyrifos	333	314
10	Dieldrin	378	277
11	*pp*-DDT	352	235
12	Endosulphan (I)	404	207
13	Piperonyl butoxide	338	176
14	Naphthalene	128	128

3. Results and discussion

3.1 *Ion population losses caused by the bbiso waveform*

Table 2 shows a comparison of peak areas (PAs) in the full-scan mode, i.e. equivalent to the TIC and the PAs after isolation at particular bbiso voltages for selected precursor ions.

Table 3 shows the calculated percentage losses based on equation (1). These values were calculated using data given in table 2. From table 3, the following average percentage losses (in parentheses) in signals were calculated: hexachlorobenzene (0), heptachlor epoxide (12), dieldrin (5), *pp*-DDT (3), and endosulphan (I) (4). These compounds did not produce significant signal losses within the range of broadband isolation waveform amplitudes that were employed.

It was assumed that, the precursor ions from these compounds are very stable and not perturbed by the bbiso waveform during isolation. The molecular radical cation m/z 284 from hexachlorobenzene, the fragment ions m/z 353 from heptachlor epoxide, m/z 277 from dieldrin, m/z 235, and from *pp*′-DDT are unique, since they contain rigid aromatic and polycyclic ring systems. From table 3, signal losses exhibited by the isolation of precursor ions devoid of rigid aromatic or polycyclic rings such as m/z 157 from 1,2-dibromo-3-chloropropane and m/z 173 from malathion were the largest ranging from 65 to 86% and from 46 to 79%, respectively.

In order to investigate the interaction between the bbiso waveform and the structure including the type of substituent on the precursor ions, structurally related compounds shown in figure 2 were probed, i.e. with concentrations ($ng\,\mu L^{-1}$) in parentheses: (a) atrazine (5.0), terbuthylazine (4.8) (b) atraton (5.1), (c) terbumeton (5.0), (d) terbutryn (5.0).

3.2 *Effect of the bbiso on ionic structure and nature of substituents*

The impact of the bbiso waveform on ionic structure was investigated using triazines. Table 4 shows the impact of the bbiso waveform on the isolation of molecular ions and fragment ions of the type $[M-CH_3]^+$ for the compounds shown in figure 2. A comparison of PAs for these ions in the full-scan mode and PAs upon isolation across the 10–30 V range in bbiso voltages was done.

Two precursor ions, i.e. m/z 215 of atrazine and m/z 229 of terbuthylazine, from two compounds which differ from each other in the homologous series by a $-CH_2$ group, i.e. 14 mass units, were compared. The signal loss by isolation of the molecular ion m/z 229 from terbuthylazine was on average 40% greater than that of isolating the molecular ion m/z 215 from atrazine. This was observed across the 10–30 V range of bbiso waveform amplitudes. The molecular ion m/z 225 from terbumeton lost 50% more than its next-lower member in the homologous series, i.e. the m/z 211 molecular ion from atraton on the same scale of bbiso waveform amplitudes. As observed, these two ions differ structurally by a $-CH_2$ group, i.e. 14 mass units, while they differ significantly from the molecular ion structures of atrazine and terbuthylazine, since they have methoxy in place of chloro substituents in their structures. These data showed that the smaller ion in the same homologous series lost less current when the bbiso waveform was used for isolation. If precursor ions did not belong to the same series but differed in size due to different substituents, the higher-ionic-weight precursor ion lost more

Table 2. Peak areas of precursor ions in the full scan and upon isolation of the ions using the broadband isolation (bbiso) waveform.[a]

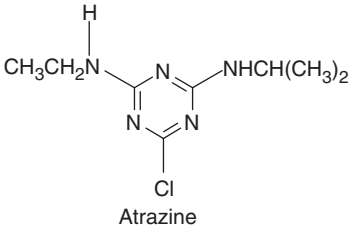
Compound		1	2	3	4	5	6	7	8	9	10	11	12	13
PA before isolation	Full scan ≡ TIC bbiso (V)	6513	7428	5069	4416	3305	4092	692	7134	8525	2369	14 419	2875	485 410
PA after ion isolation	30	4654	7400	692	2491	2351	3174	148	6209	5402	2039	13 183	2637	372 523
	25	4694	7454	961	2510	2243	3290	212	6207	5559	2205	13 914	2704	380 582
	20	5083	7420	1084	2896	2111	3049	358	6300	5552	2249	14 157	2767	383 066
	15	5427	7435	1448	3092	2443	3446	373	6320	6604	2360	14 340	2861	397 670
	10	5509	7422	1775	3183	2363	3350	318	6434	6630	2361	14 400	2870	417 801

[a] 1: Ethylene dibromide (EDB); 2: hexachlorobenzene; 3: 1,2-dibromo propane (DBCP); 4: atrazine; 5: lindane (γ-BHC); 6: diazinon; 7: malathion; 8: heptachlor epoxide; 9: chlorpyrifos; 10: dieldrin; 11: *pp*-DDT; 12: endosulphan; 13: piperonyl butoxide; PA: peak area; TIC: total ion current.

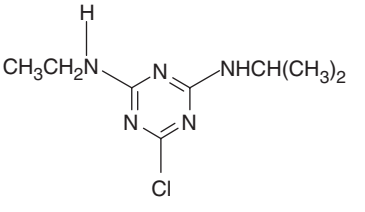
Table 3. Percentage ion signal losses upon isolation of the precursor ions using the broadband isolation (bbiso) waveform.

	Compound and corresponding ion current loss (%)												
bbiso (V)	1	2	3	4	5	6	7	8	9	10	11	12	13
30	29	0	86	44	29	22	79	13	37	14	9	8	23
25	28	0	81	43	32	20	69	13	35	7	4	6	22
20	22	0	79	34	36	25	48	12	35	5	2	4	21
15	17	0	71	30	26	16	46	11	23	0	1	0	18
10	15	0	65	28	29	18	54	10	22	0	0	0	14

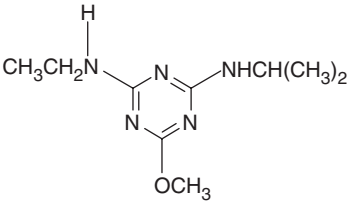
[a] 1: Ethylene dibromide (EDB); 2: hexachlorobenzene; 3: 1,2-dibromo propane (DBCP); 4: atrazine; 5: lindane (γ-BHC); 6: diazinon; 7: malathion; 8: heptachlor epoxide; 9: chlorpyrifos; 10: dieldrin; 11: *pp*-DDT; 12: endosulphan; 13: piperonyl butoxide.



Atrazine
1



Terbuthylazine
2



Atraton
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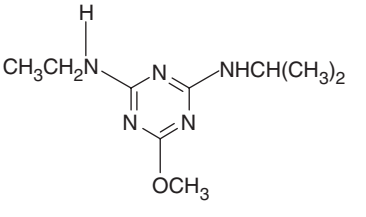
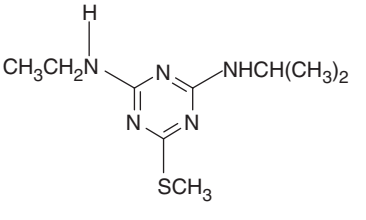


Terbumeton
4



Terbutryn
5

Figure 2. Structures of triazines used to study the effect of the bbiso on ionic structure, nature of substituents, and consequence of isolating molecular ions in comparison with fragment precursor ions.

Table 4. Comparison of molecular and fragment ion peak areas in the full scan mode and upon isolation using the bbiso waveform for selected triazines.

		Molecular ion [$M^{+\bullet}$]	% signal loss	Fragment [M-15]	% signal loss
Atrazine		*m/z* 215		*m/z* 200	
	PA full-scan	4416		11713	
	bbiso (V)				
	30	2491	44	7732	34
	25	2510	43	8466	28
	20	2896	34	8777	25
	15	3092	30	8405	28
	10	3183	28	9197	21
Terbuthylazine		*m/z* 229		*m/z* 214	
	PA full-scan	2850		4703	
	bbiso (V)				
	30	485	83	3948	16
	25	489	83	4371	7
	20	616	78	4418	6
	15	836	71	4667	1
	10	1022	64	4971	−6
Atraton		*m/z* 211		*m/z* 196	
	PA full-scan	1517		4162	
	bbiso (V)				
	30	840	45	3133	25
	25	968	36	3363	19
	20	915	40	3177	24
	15	964	36	3223	23
	10	1080	29	3191	23
Terbumeton		*m/z* 225		*m/z* 210	
	PA full-scan	1340		3125	
	bbiso (V)				
	30	112	92	2481	21
	25	117	91	2609	17
	20	138	90	2482	21
	15	183	86	2230	29
	10	268	80	2808	10
Terbutryn		*m/z* 241		*m/z* 226	
	PA full-scan	3720		2735	
	bbiso (V)				
	30	678	82	2011	26
	25	494	87	2336	15
	20	510	86	2239	18
	15	913	75	2735	0
	10	1073	71	2094	23

signal than the lower-ionic-weight ion. No trend was observed as a result of using the bbiso waveform to isolate precursor ions of different homologous series differing only by the type of substituent. From table 4, isolation of the molecular ion of atrazine *m/z* 215 lost on average the same signal as isolation of *m/z* 211, the molecular ion of atraton. The only difference between the two precursor ions is the presence of a chloro- and a methoxy-substituent on atrazine and atraton, respectively. In addition, the molecular ions *m/z* 229 from terbuthylazine and *m/z* 225 of terbumeton lost, on average, the same current, although they differ by a chloro- and methoxy-substituent, respectively. These observations indicated that the nature of substituents on the bulk of the molecule

has no bearing on signal losses when the bbiso waveform isolation method is used in tandem experiments.

3.3 *Molecular* versus *fragment precursor ions and the bbiso waveform*

The ion population loss due to isolation of the radical molecular $[M^{+\bullet}]$ and fragment precursor ions $[M-R]^{5+}$ of triazines are compared in table 4. For the corresponding fragment ions, i.e. $[M-CH_3]^+$ of the compounds in figure 2, isolation of these ions caused on average 59% at the upper limit and 29% at the lower limit of signal loss less than isolation of molecular ions at 30 and 10 V bbiso amplitude, respectively. According to Lynn and co-workers [12], the bbiso waveform could be responsible for perturbation of a secondary motion of a precursor ion during isolation which greatly diminishes the probability of isolating it without changing its excited state configuration. Molecular radical cations may be more prone to this phenomenon than their corresponding fragment ions, and this was assumed to be the probable cause of signal losses in this experiment involving triazines.

3.4 *Impact of the bbiso waveform on instrument detection limits (IDLs)*

Instrument detection limits (IDLs) from the *t*-test [15] method were used to gauge the response of the instrument in relation to the bbiso waveform towards selected pesticides. The IDLs were determined using standard pesticide solutions and were used as a measure of the response of the instrument at those concentration levels.

Using the bbiso waveform, each precursor ion was isolated seven times by carrying out seven injections of the same standard solution. The concentrations of standard solutions that were injected were approximately 10 times the estimated limits of detection (LODs). The peak areas for the precursor ions were normalized to their corresponding concentrations using the average peak area as the equivalent of the concentration injected. The standard deviations in units of concentrations were calculated from equation (2), in which the IDLs were computed as follows:

$$\mathrm{IDL} = ts, \tag{2}$$

where t is the Student t-value at the 99% confidence level, and 6 degrees of freedom for seven data points, while s is the standard deviation. Table 5 shows the pesticides, precursor ions, their optimum broadband isolation waveform amplitudes, and IDLs in the full scan and after isolation of the precursor ions. Peak area integrations were done after each ion's trace chromatogram was constructed. IDL comparisons were made using the full-scan IDLs as reference values.

The instrument's response improved, remained the same, or deteriorated in comparison with full-scan experiments when precursor ions were isolated and IDLs calculated. As expected, the instrument showed an improvement in response towards the following compounds when isolations were done using the optimized bbiso waveform amplitudes (percentages calculated with respect to full scan IDLs in parentheses): hexachlorobenzene (31%), dieldrin (10%), *pp*-DDT (31%), and endosulphan (34%). All these compounds except ethylene dibromide, lindane, and diazinon did not show significant signal losses upon isolation of the precursor ions

Table 5. Pesticides, precursor ions, their optimum broadband isolation (bbiso) waveform amplitudes, instrument detection limits (IDLs) in the full scan and after isolation of the precursor ions.

Compound	Precursor ion (m/z)	Optimum bbiso amplitude (V)	IDL full scan (ng μL^{-1})	IDL optimum bbiso (ng μL^{-1})
Ethylene dibromide	107	20	0.32	0.24
Hexachlorobenzene	284	30	0.16	0.11
1,2-Dibromo-3-chloropropane	157	10	0.26	0.44
Atrazine	215	10	0.64	1.01
Lindane (γ-BHC)	219	25	0.44	0.32
Diazinon	304	15	0.26	0.15
Malathion	173	15	0.25	0.25
Heptachlor epoxide	353	30	0.17	0.24
Chlorpyrifos	314	25	0.21	0.24
Dieldrin	277	30	0.61	0.55
pp-DDT	235	30	0.13	0.09
Endosulphan	207	30	0.68	0.45
Piperonyl butoxide	176	30	0.01	0.01

(see table 2). In addition, the instrument's response improved towards the following compounds: ethylene dibromide (25%), lindane (27%), and diazinon (42%). Those whose responses decreased included the following: 1,2-dibromo-3-chloropropane, atrazine, heptachlor epoxide, and chlorpyrifos. The response of the instrument with respect to malathion and piperonyl butoxide did not change either in the full scan or when the precursor ions were isolated. The reason for this was not investigated.

4. Conclusions

The bbiso waveform used in the Varian precursor-ion isolation protocol was probed in relation to its impact on ion population losses and with respect to the compounds enumerated in this study. It was observed that the structure of the precursor ion plays a critical role in retaining the ion population before ion activation. Isolation of the m/z 284, the molecular ion of hexachlorobenzene and other rigid cyclic systems confirmed this observation, although this phenomenon needs further investigation to include other compounds of environmental interest. Further, it was observed that isolation of large molecular radical cations of the form $[M^{+\bullet}]$ which have an odd number of electrons using the bbiso waveform induces significant ion population losses compared with isolation of fragment ions of the type $[M-R]^+$ when these ions are created by EI. The instrument's response towards the compounds that were studied closely paralleled the ion population losses that were observed.

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