

PARENT OR BASE MOLECULAR ION SPECTRA

Source for this module: R. Martin Smith, Understanding Mass Spectra, A Basic Approach, 2nd Ed., Wiley, 2004

Once we have separated our compounds via GC we want to unambiguously identify each peak. Retention times, obtained under some set of standard condition can be used, but retention times are not helpful when several compounds elute simultaneously, or when we do not have a matching standard. In the past one way to eliminate co-eluting samples required a sample purification step between concentration of the sample and the GC measurement. With the advent of the GCMS we are capable of making identifications based on the retention time and on the mass spectra associated with the peak(s) eluting at that retention time. Because mass spectra of any two compounds are very unlikely to be identical we can also identify compounds that were not suspected of being in the sample, providing that we have access to a library of standard mass spectra.

In this module we introduce the method of mass spectral interpretation. In another module we examine the standard mass spectra of our target pesticides.

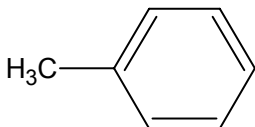
We will examine three compounds to get a introduction to mass spectra. The **parent molecule** is the entire molecule, minus one electron before fragmentation. The calculation of masses depends upon the relative abundances of the isotopes for C, H, and Cl <http://www.carlton.paschools.pa.sk.ca/chemical/molemass/isotopes.htm>

Table 1: Abundances of C, H, and Cl Isotopes

Carbon	12C	13C
Atomic Mass (amu)	12.00000	13.00335
% Natural Abundance	98.89	1.11
% Abundance Relative to Most Abundant	100	1.12
Hydrogen	1H	2H
amu	1.0078250035	2.014101779
% Natural Abundance	99.985	0.015
% Abundance Relative to Most Abundant	100	0.015
Chlorine	35Cl	37Cl
Exact Mass	34.9689	36.9659
% Natural Abundance	75.77	24.23
% Abundance Relative to Most Abundant	100	31.97

The three compounds are the two solvents used in our experiment, toluene and hexane, and one of the pesticides with a relatively simple pattern, DDE.

TOLUENE



m.w. 92; C₇H₈

For toluene we expect a parent molecular ion, M, at "92". The exact mass is

$$7(12) + 8(1.0078250035) = 92.0626 \quad [1]$$

There is only one possible way to obtain this molecule: all 7 carbons must be of the lower mass form. We will ignore the contribution of protons since the natural abundance of the heavier isotope is so low (see Table 1). Let us refer to the low mass form of toluene as:



The intensity of the molecular ion peak, P_{Mn} , is related to the probability of obtaining molecule M with n carbons of mass 12. P_{Mn} is the product of the probability of each carbon of mass 12, P_{12C} , where the probability is the natural abundance

$$P_{Mn} = \left(P_{12C_1}\right)\left(P_{12C_1}\right)\left(P_{12C_2}\right)\left(P_{12C_3}\right)\cdots\left(P_{12C_n}\right) = \left(P_{12C}\right)^n \quad [3]$$

For toluene with 7 carbons the intensity of the molecular ion peak is:

$$P_{Mn} = \left(P_{12C}\right)^n = (0.9889)^7 = 0.92484 \quad [4]$$

In addition to this peak there should be higher mass peaks corresponding to the presence of ¹³C .

Let us first consider the peak "M+1". To predict the intensity of the peak of mass 92+1 let us first consider all of the ways in which we might obtain a peak of mass 92+1 from ¹³C. We find 7 possible permutations

"A" 12C,12C,12C,12C,12C,12C,13C
 "B" 12C,12C,12C,12C,12C,13C,12C
 "C" 12C,12C,12C,12C,13C,12C,12C
 "D" 12C,12C,12C,13C,12C,12C,12C
 "E" 12C,12C,13C,12C,12C,12C,12C
 "F" 12C,13C,12C,12C,12C,12C,12C
 "G" 13C,12C,12C,12C,12C,12C,12C

The mass of the compounds "A" through "G" would be

$$6(C_{12}) + 1(C_{13}) + 8(H_1) = 93.06595 \quad [5]$$

$$6(12) + 1(13.00335) + 8(1.0078250035) = 93.06595 \quad [6]$$

Each of these compounds has a probability of existing based on the relative abundances of the 12C and 13C isotopes. The probabilities are calculated below based on the probability of finding each specified isotope (e.g. fractional natural abundance, Table 1):

$$P_A = (P_{12C})^{n-1} (P_{13C})^1 = (0.9889)^6 (0.011)^1 = 0.010287 \quad [7]$$

Since we have 7 different molecules with the same mass and same probability, the total intensity of the "M+1" peak is seven times greater.

$$[M + 1] = n \left[(P_{12C})^{n-1} (P_{13C}) \right] = 7[0.010287] = 0.0714 \quad [8]$$

The relative intensity of the [M+1] to [M] peak is

$$\frac{[M + 1]}{[M]} = \frac{n \left[(P_{12C})^{n-1} (P_{13C}) \right]}{\left[(P_{12C}) \right]} = \frac{n \left[(P_{13C}) \right]}{\left[(P_{12C}) \right]} = n \frac{0.0111}{0.9889} = n(0.0112) \quad [9]$$

For toluene, C₇H₈, this becomes

$$\frac{[M + 1]}{[M]} = n(0.0112) = 7(0.0112) = 0.0784 \quad [10]$$

This is a useful way of determining the number of carbons in an unknown compound.

For example, if we calculate the peak ratio of "M+1" to "M" as 0.0784 we would know that the number of carbons in the compound is

$$\frac{[M+1]}{[M]} = n(0.0112) \quad [11]$$

$$n = \frac{\left(\frac{[M+1]}{[M]}\right)}{0.0112} = \frac{0.0784}{0.0112} = 7 \quad [12]$$

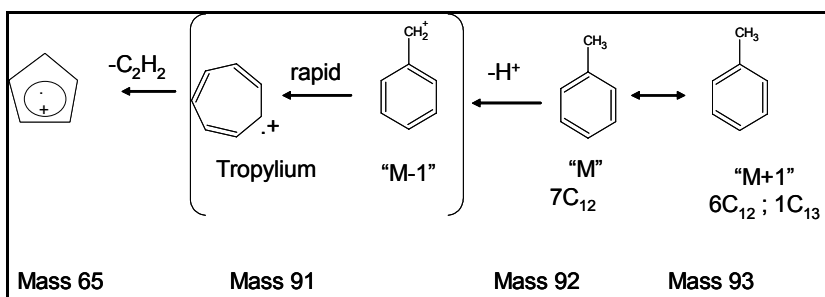
We can confirm the validity of equation [11] by first calculating the **relative** peak intensities (%) of "M" and "M+1" using an online calculator (<http://www2.sisweb.com/mstools/isotope.htm>) and then converting to **fractional** relative peak intensities. If equation [11] holds we should find that fractional peak intensity of the "M+1" peak (Peak at 93) should be 0.0784 as compared to "M" at mass 92.

Online Calculator result:

Peak (mass)	Relative Intensity
92.062600	100.0
93.065960	7.5
93.068879	0.1
94.069310	0.2

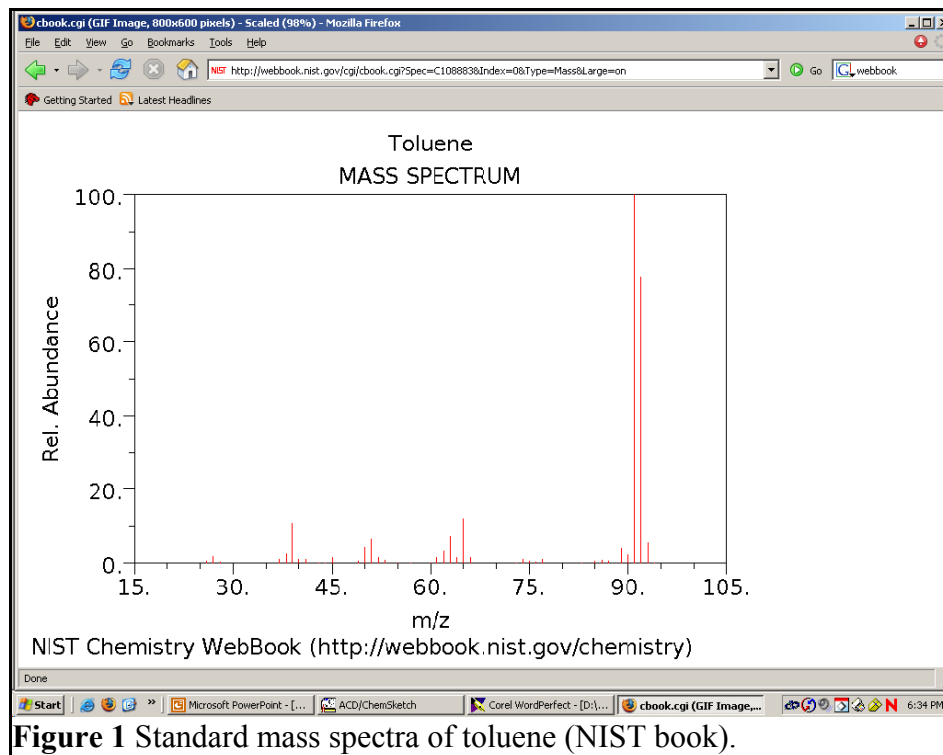
The peaks at 93.065 is accounted for primarily by C₁₃ and the peaks at 93.0688 and 94 are based on considering various isotopes of hydrogen in addition to C₁₃. Together the three peaks account for all the permutations possible in substituting one C₁₂ by one C₁₃. Summing their relative % intensity leads to 7.8. The fractional relative peak intensity for "M+1" attributed to C₁₃ is therefore 7.8/100 or 0.078, predicted by the presence of the 7 carbons via equation [11].

If we now look at a standard mass spectra we expect to find a peak at 92 and a peak at 93 with the relative peak height 1 to 0.078 (Figure 1). Figure 1 does, indeed, show a peak at 92 and at 93 with the appropriate relative peak heights. However, it shows the largest peak, to which all other peaks are scaled

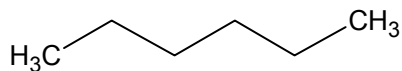


(100%), at 91. This peak is obtained by the loss of a proton from toluene in the electron ionization process. The resulting rearrangement of the ring to incorporate the 7th carbon to form the stable tropylium ion is rapid and gives rise to the larger peak observed at 91.

Subsequent loss of two carbons (C_2H_2) to form the stable five member ring is observed by the presence of the peak at 65. For more information on this please go to http://www.ivv.fhg.de/ms/ms-ion_fragmentation.html



The second solvent is hexane.



The parent molecular ion calculated from the lowest monoisotope is

$$6(12) + 14(1.007825) = 86.10955 \quad [13]$$

We predict from our analysis of toluene that there should be a M+1 peak at

$$5(12) + 1(13.00335) + 14(1.007825) = 87.1129 \quad [14]$$

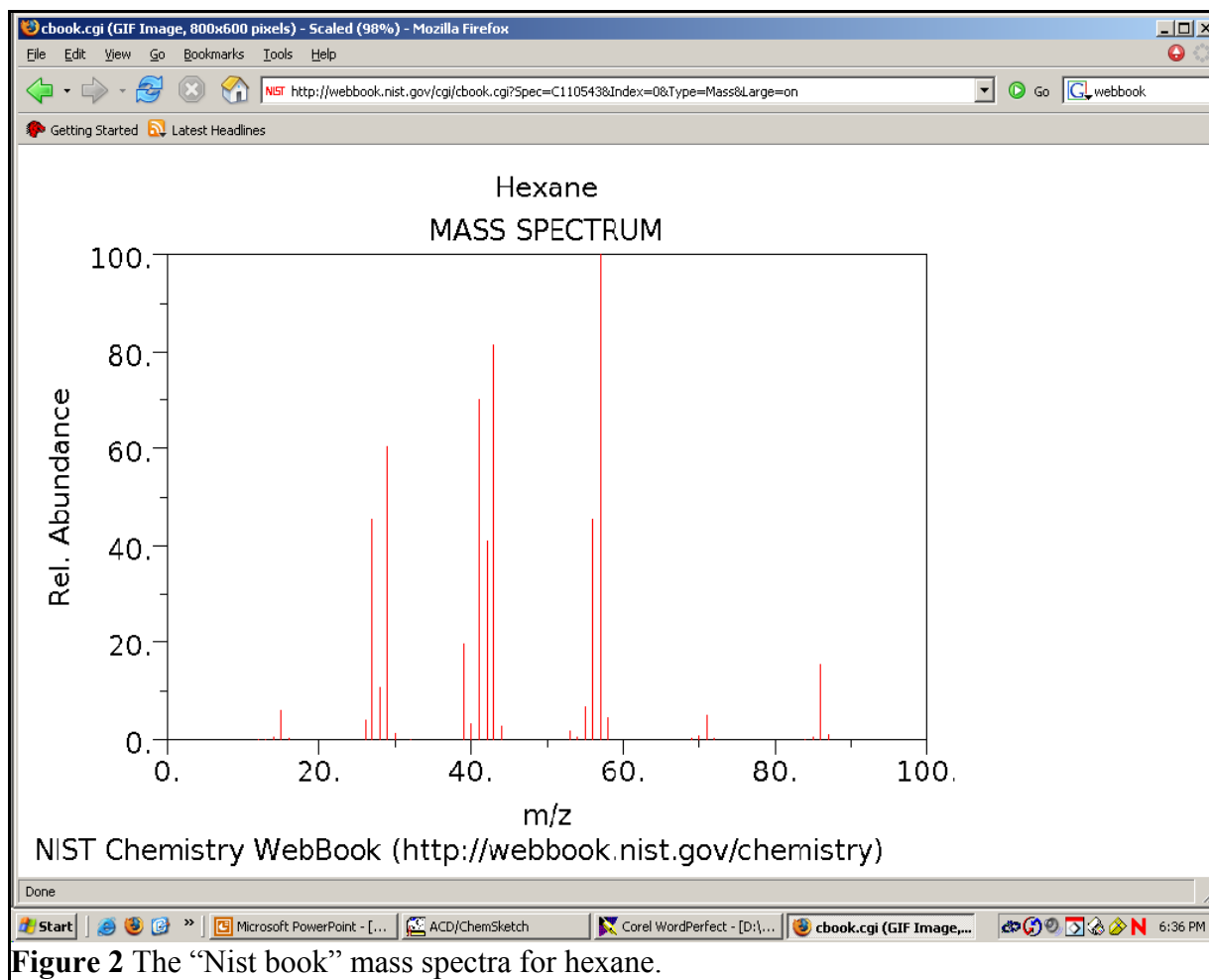
whose intensity relative to M should be:

$$\frac{[M + 1]}{[M]} = n(0.0112) = 6(0.0112) = 0.0672 \quad [15]$$

Table: Web Calculator Results for Hexane Mass Peaks

<u>Peak</u>	<u>Mass</u>	<u>% Relative Intensity</u>
M	86.109549	100.0
M+1(13C)	87.112909	6.5
M+1(2H)	87.115830	0.2
M+2	88.116259	0.2

The predicted relative intensity of the M+1 peak from isotopes matches that from the web based calculator and of the relative peak intensities shown from the NIST webbook spectra (Figure 2).



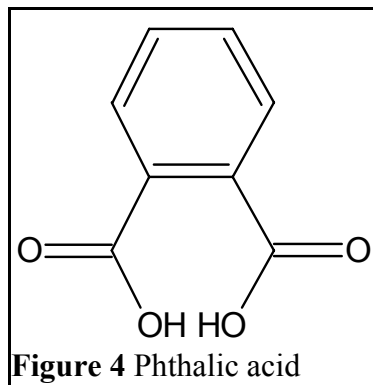
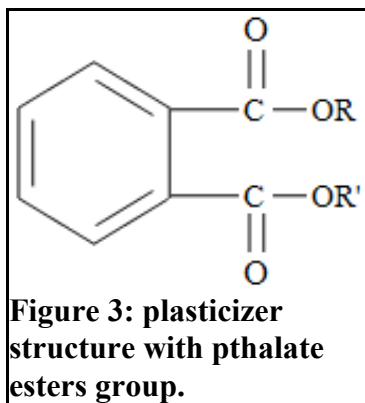
In addition to the parent peak "M" at mass 86, there are a several clusters of peaks of lower mass which correspond to shorter alkanes obtained by fragmentation of hexane (CH_3 at mass 15; CH_3CH_2 at mass 29; $\text{CH}_3\text{CH}_2\text{CH}_2$ at mass 43; $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$ at mass 57; and $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$ at mass 71).

http://www.chem.arizona.edu/massspec/example_html/examples.html

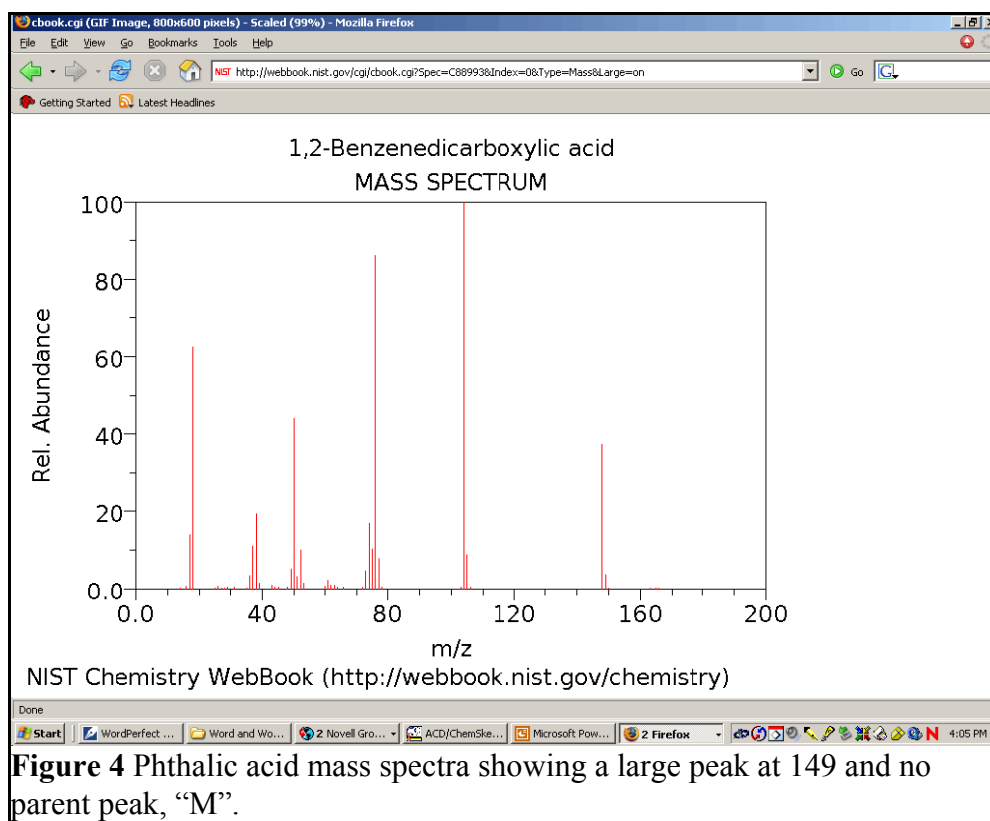
For more information on fragmentation patterns see:
<http://www.chemistry.ccsu.edu/glagovich/teaching/472/ms/ms.html>

Pesticide Mass Spectra Background

The background peaks to be expected in the pesticide chromatography derive from toluene (91 and 92), hexane (57, 43, 29) and phthalate esters from non-teflon containers (<http://www.biologydaily.com/biology/Phthalate>).
<http://www.iscpubs.com/articles/al/a9911kum.pdf>



Electron impact ionization breaks at least on CO-OR bond. As an example consider phthalic acid. Loss of OH (mass 17) from the compound (Mass 166.13) results in a peak at 149 seen in the mass spectra for phthalic acid (Figure 5). Similar mass 149 peaks are observed for plasticizer compounds used in plastic and are often present in samples stored in or collected in plastic bottles.



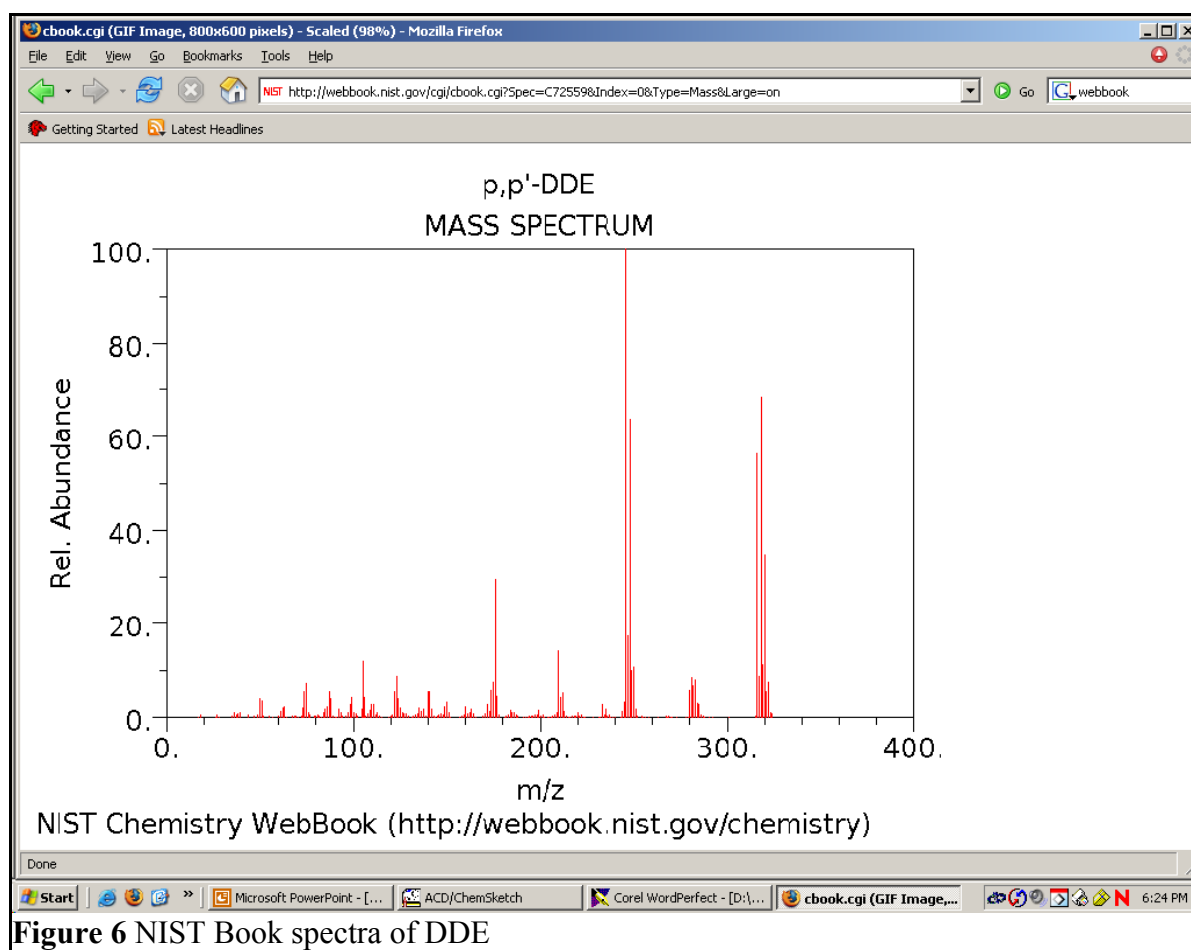
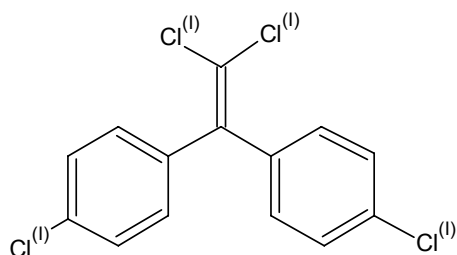
Pesticide patterns

The pesticides we are looking for contain chlorine. Because the relative abundances of the two stable isotopes of Cl are similar the mass patterns observed for the parent molecule ions will be distinctive.

We take as an example the pesticide DDE

4,4'-DDE, C₁₄H₈Cl₄

Mw-318.02



Several major peaks are observed in the standard spectra for DDE. These are listed:

4,4'-DDE 176 210 246 248 316 318 320

The parent molecular ion is calculated from the monoisotope compound:

$$M = 14[(12.0000)] + 8[(1.007825)] + 4[(34.9689)] \quad [16]$$

$$M = 315.9382$$

Our compound has 4 Cl which can be occupied by two isotopes both with a significant probability. The variations in the molecular ions with respect to Cl are shown below where the ³⁷Cl is in bold.

Molecular ion	Arrangement	Number of possibilities
M	35Cl35Cl35Cl35Cl	1
M+2	35Cl35Cl35Cl 37Cl 35Cl35Cl 37Cl 35Cl 35Cl 37Cl 35Cl35Cl 37Cl 35Cl35Cl35Cl	4
M+4	35Cl35Cl 37Cl37Cl 35Cl 37Cl37Cl 35Cl 35Cl 37Cl 35Cl 37Cl 37Cl37Cl 35Cl35Cl 37Cl 35Cl 37Cl 35Cl 37Cl 35Cl35Cl 37Cl	6
M+6	37Cl37Cl37Cl 35Cl 37Cl37Cl 35Cl 37Cl 37Cl 35Cl 37Cl37Cl 35Cl 37Cl37Cl37Cl	4
M+8	37Cl37Cl37Cl37Cl	1

We expect the molecular ions arising from 4 Cl present on DDE composed of 2 different

Cl isotopes (35 and 37) to be M, M+2, M+4, M+6, and M+8 with a relative number of patterns of 1:4:6:4:1.

The intensity of the peaks is calculated from the relative abundance of the two different Cl isotopes (see Table 1):

$$[M] = (P_{35Cl})^n = (0.75)^4 = 0.3296 \quad [17]$$

$$[M + 2] = n \left[(P_{35Cl})^{n-1} (P_{37Cl}) \right] = 4 \left[(0.7577)^3 (0.2433) \right] = 0.421605 \quad [18]$$

$$[M + 4] = n \left[(P_{35Cl})^2 (P_{37Cl})^2 \right] = 6 \left[(0.7577)^2 (0.2433)^2 \right] = 0.202233 \quad [19]$$

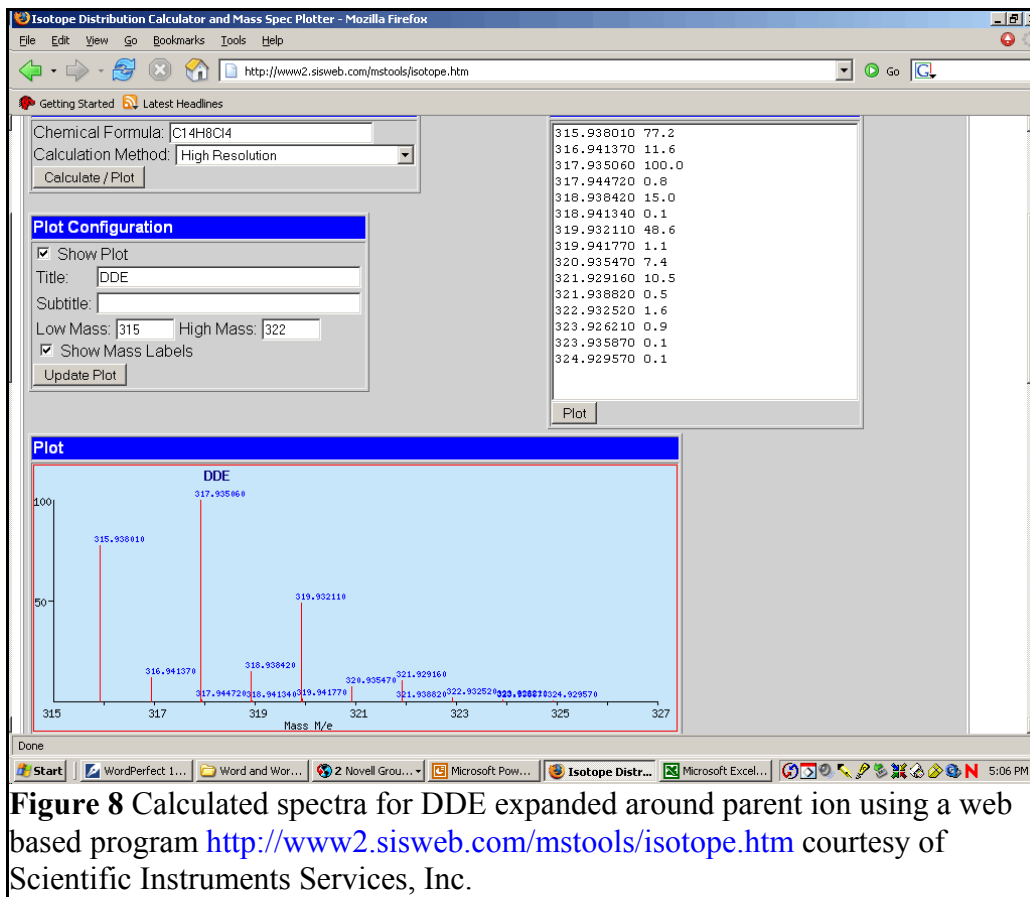
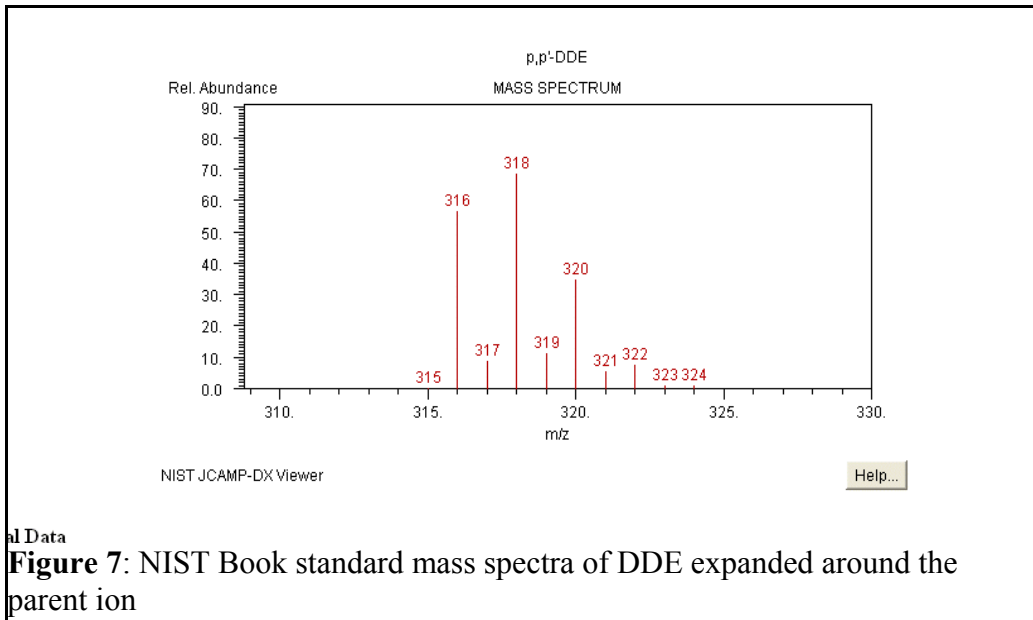
$$[M + 6] = n \left[(P_{35Cl}) (P_{37Cl})^3 \right] = 4 \left[(0.7577) (0.2433)^3 \right] = 0.04331 \quad [20]$$

$$[M + 8] = \left[(P_{37Cl})^4 \right] = \left[(0.2433)^4 \right] = 0.003447 \quad [21]$$

The calculated peak intensities, their relative % intensity scaled to the largest peak at "M+2" and the fractional relative peak intensities are shown in the box below. This is excellent agreement with the data from our web calculator which calculates a wider range of peaks based on the relative abundance of the isotopes of hydrogen and oxygen.

Calculated Relative Peak Intensities for DDE

Peak	Mass	(Our Calc.) Intensity	(Our Calc.) Fractional Relative Intensity	(Our-Calc) Relative Intensity	(Web Calc.) Relative Intensity
[M]	315.9380	0.3296	0.78	78.2%	77.2
[M+1]	316.9413				11.6
[M+2]	317.9350	0.4216	1	100	100
[M+2']	317.9447				0.8
[M+3]	318.9384				15.0
[M+3']	318.94134				0.1
[M+4]	319.9321	0.2022	0.479	47.96	48.6
[M+4']	319.941770				1.1
[M+5]	320.935470				7.4
[M+6]	321.929160	0.0433	0.102	10.2	10.5
[M+6']	321.938820				0.5
[M+7]	322.932520				1.6
[M+8]	323.926210	0.003447	0.00817	0.817	0.9
[M+8']	323.935870				0.1



Cluster of peaks at 280

11-Parent Molecular Ion Spectra

In addition to these parent ions we expect specific ions related to fragmentation of the compound in the highly energetic ion source (70 eV). When the compound enters the ionization source it fragments into component parts. The most likely bond breaking site is the C-Cl bond so we expect that the mass that we observe comes from the loss of 1 chlorine of mass 34.9689 or mass 36.9659.

Expected Mass Peaks from loss of Cl from DDE

Ion	Intensity	Mass	Expected Mass on Loss of:				
			1 35Cl	1 37Cl	2 35Cl	1 35Cl 137Cl	2 37Cl
M	77.2	315.938	280.9691	278.9721	246.0002	244.0032	242.0062
M+1	11.6	316.9414	281.9725	279.9755	247.0036	245.00657	243.0096
M+2	100	317.935	282.9661	280.9691	247.9972	246.0002	244.0032
M+3	15	318.938	283.9691	281.9721	249.0002	247.0032	245.0062
M+4	48.6	319.932	284.9631	282.9661	249.9942	247.9972	246.0002
M+5	7.4	320.935	285.9661	283.9691	250.9972	249.0002	247.0032
M+6	10.5	321.9291	286.9602	284.9632	251.9913	249.9943	247.9973

We expect a cluster of peaks between 279 and 284 associated with the loss of 35Cl and 37Cl from the most intense peaks "M", "M+2", and "M+3". We also expect a second cluster of peaks between 242 and 249 associated with the loss of a second Cl. Loss of a third Cl should result in a cluster of peaks at 210. The peaks are shown in Figure 9.

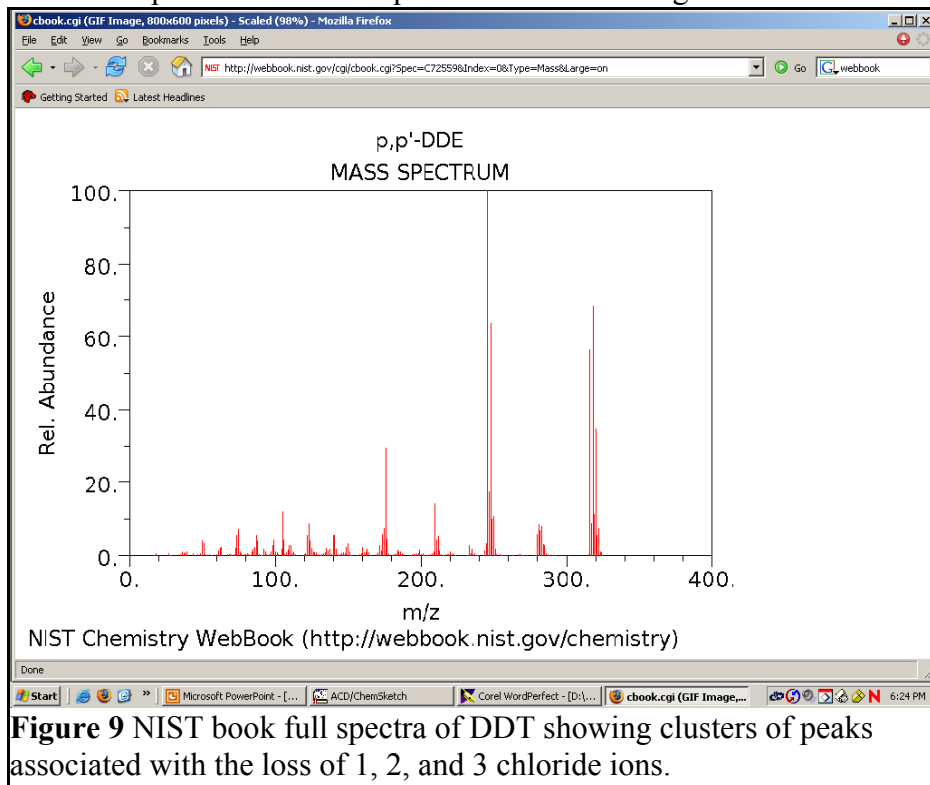


Figure 9 NIST book full spectra of DDT showing clusters of peaks associated with the loss of 1, 2, and 3 chloride ions.