GAS CHROMATOGRAPHY

Gas Chromatography (GC) is based on the separation of compounds by their boiling point. The compounds are loaded at the top of a column which has some solid support with some bonded polymer serving as a “liquid” phase which the compound dissolves in (Figure 1).

Compounds with a higher boiling point spend more time in the bonded polymer phase. As the temperature is increased compounds exit beginning with the lowest boiling point compound and moving onto the higher. This is illustrated in Figure 1. A sample and unknown (left hand side) are analyzed by GC/MS by injection through an injection port onto a heated

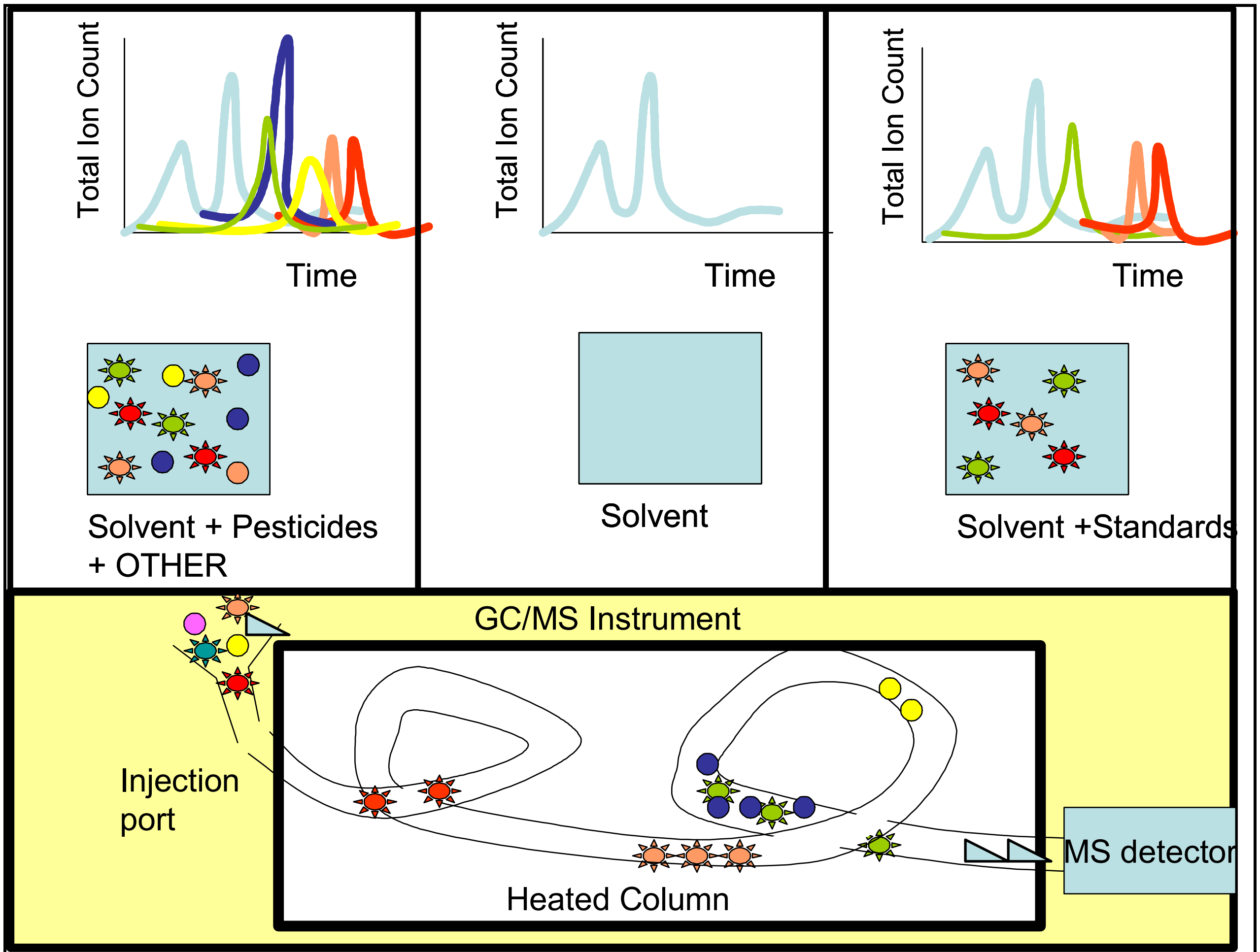

Figure 1: A sample with unknowns (circles) and standards (stars) (left hand side) are analyzed by GC/MS by injection through an injection port onto a heated column. Compounds with low boiling point spend more time in the gas phase and move through the column faster (blue solvent triangle) while compounds with high boiling points spend more time in the liquid (bonded phase) and elute later in time (red stars). The identity of peaks in a complex chromatogram (left hand side, top) can be identified by comparison with a pure solvent (center panel) and standards (right hand panel).

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In GC compounds are identified by their retention time under standard or repetitive experimental conditions. The retention time is measured as the time associated with the solute peak, t_R, which is related to the column length, L, the mobile phase velocity, u, (depends on gas pressure), the distribution of the compound between the stationary phase and the mobile phase, K_D, and the volumes of the stationary and mobile phases, V_L and V_G

$$t_R = \frac{L}{u}\left(1 + K_D\left[\frac{V_G}{V_L}\right]\right) \qquad [1]$$

Equation 1 tells us that we can manipulate the time it takes for a compound to exit the heated column in several ways. The most easy method is to manipulate the distribution coefficient, K_D, which describes the distribution of the compound between the gas and liquid phase by changing the temperature. An increase in temperature allows compounds with higher boiling points to be removed from the liquid phase of the column.

Generally, but not always, the boiling point is related to molecular weight. The larger the molecular weight the larger the number of van der Waals and induced dipole interactions an aliphatic compound can have with near neighbors. These interactions increase the energy necessary to release the compound from the liquid and allow it to enter the vapor phase.

In the table below are listed pesticides in a standard Supelco mix and their molecular weights and boiling points.

Supelco standards

http://www.ars.usda.gov/Services/docs.htm?docid=6433
USDA Agricultural Research Services Pesticide Database

Table 1: Chemical Data Affecting GC of Standard Pesticides

			Melting Point	Boiling Point	
Compound	**formula**	**mw**	**M.P.°C**	**B.P.°C**	**Decomposes °C**
Lindane	$C_6H_6Cl_6$	290.85	112-113	180	
Heptachlor	$C_{10}H_5Cl_7$	373.3	95-96	135-145 at 1-2 mmHg	
Aldrin	$C_{12}H_8C_{16}$	364.9	104	145 at 2mmHg	
Heptachlor epoxide	$C_{10}H_5Cl_7O$	389.32			
Endosulfan I	$C_9H_6C_{16}O_3S$	406.9	70-100		>250
4,4'-DDE	$C_{14}H_8Cl_4$	318	88-90		
Dieldrin	$C_{12}H_8C_{16}O$	380.9	175-176		
Endrin	$C_{12}H_8C_{16}O$	380.9	200	245	>245
4,'4-DDD	$C_{14}H_{10}C_{14}$	320	88-90; 109-112	193	
Endosulfan II	$C_9H_6C_{16}O_3S$	406.9			
4,4'DDT	$C_{14}H_9Cl_5$	354.5	108-109	260	
Endrin aldehyde	$C_{12}H_8Cl_6O$	380.1			
Endosulfan sulfate	$C_9H_6Cl_6O_4S$	422.92		181	
Methoxychlor	$C_{16}H_{15}C_{13}O_2$	345.65	78	346	

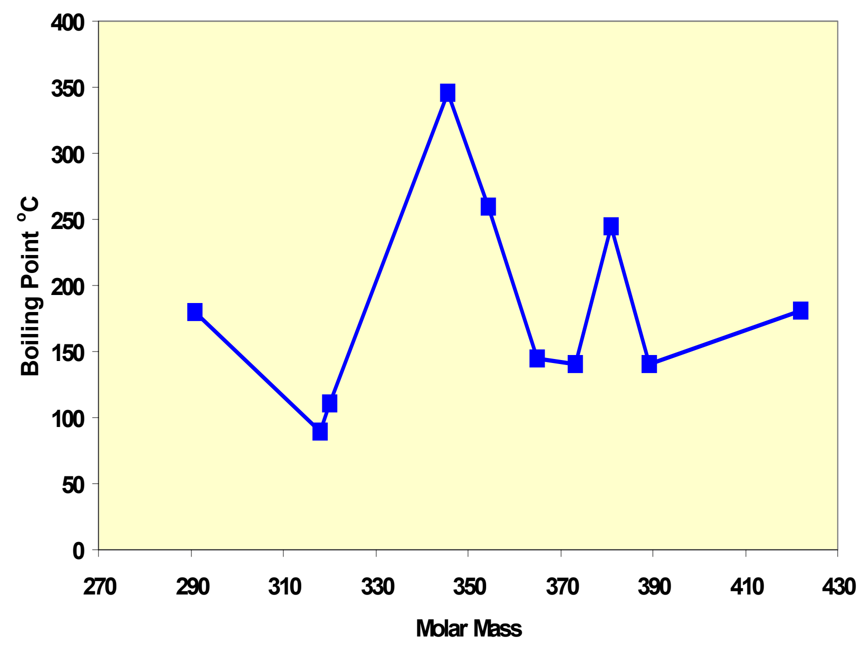
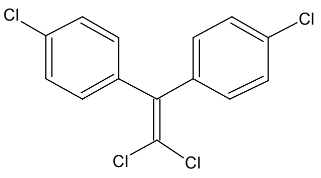


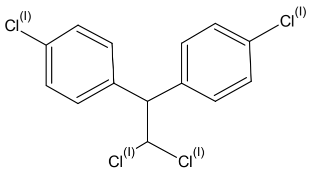
Figure 2: The boiling point does not vary uniformly with molar mass when considering all of the standard pesticides together.

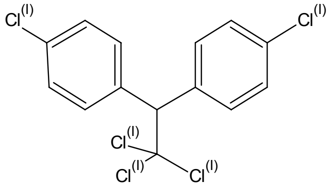
Figure 2 indicates no clear trend in our pesticides as a function of boiling point. This is because the boiling point is influenced not only by the molar mass but by the functional groups and their arrangement leading to the possibility of hydrogen bonds and dipole moment interactions.

If we sort the compounds out by structure we can see that there are, indeed, general trends within a class of compounds, with respect to the boiling point.

DDE, DDD, and DDT



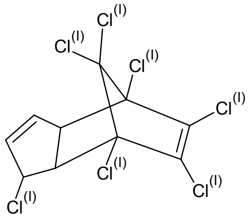
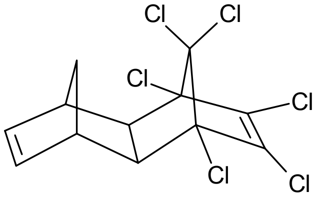
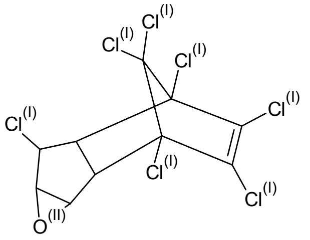




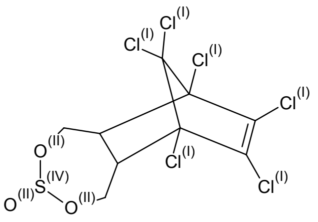
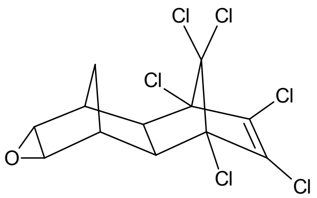
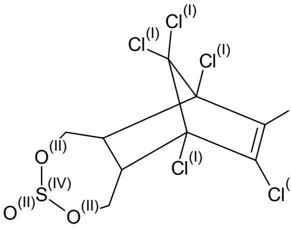
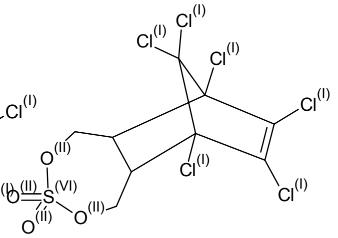
	DDE	DDD	DDT
m.w.	318	320	354.5
M.p.	88-90 °C	88-90 °C;	109-112 °C
Chromatographic Peak Number	9	12	14

DDE, DDD, and DDT have the same basic structure of two aromatic linked rings. The central portion of the molecule has increasing number of atoms from two Cl in DDE, to two Cl and one H in DDD and three Cl in DDT. The addition of a single H in going from DDE to DDT causes only a slight change in molecular weight which accounts for the similar boiling points of the two compounds. The addition of a third Cl in DDT increases the molecular weight substantially which is accompanied by a large change in the boiling point.

Another class of compounds are the following seven pesticides**:**

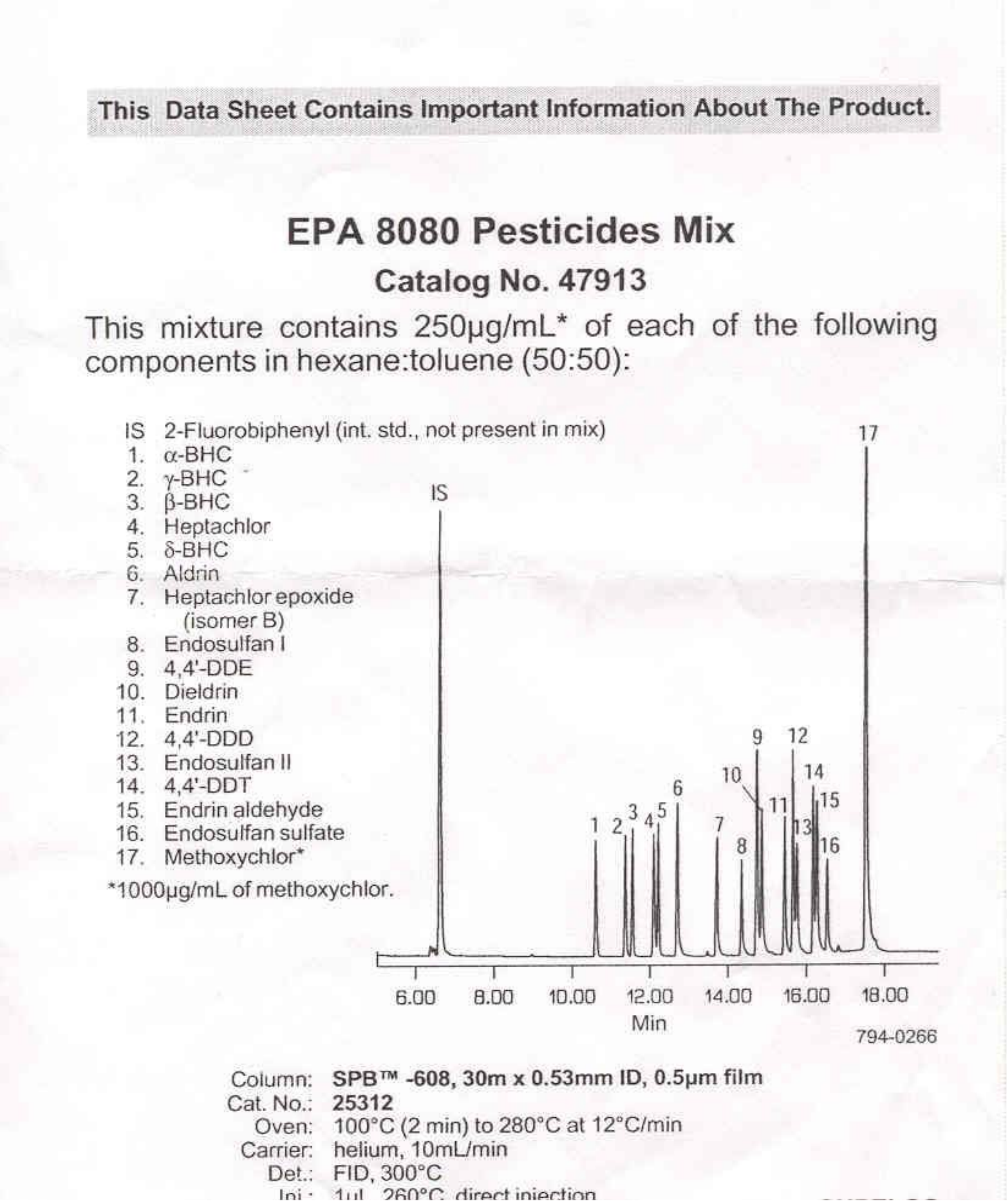




	heptachlor	aldrin	Heptachlor Epoxide
mw:	373.3	364.9	389.32
bp:	135-145	145	
retention	4	6	7

	Endosulfan I	Endrin	Endosulfan II	Endosulfan Sulfate
mw	406.9	380.9	406.9	422.92
Bp	132-217	245 dec.		
retention	8	11	13	16

Each of these compounds has the same chlorinated structure but differs in the attached ring. Because they have somewhat similar structure, the mechanism of localization to the column bonded phase is somewhat similar and the main driving force for the boiling point is the extra mass of the attached ring and the variations in the functional group to the left of the molecule.



This Data Sheet Contains Important Information About The Product.

EPA 8080 Pesticides Mix

Catalog No. 47913

This mixture contains 250µg/mL* of each of the following components in hexane:toluene (50:50):

IS 2-Fluorobiphenyl (int. std., not present in mix)
1. α-BHC
2. γ-BHC
3. β-BHC
4. Heptachlor
5. δ-BHC
6. Aldrin
7. Heptachlor epoxide (isomer B)
8. Endosulfan I
9. 4,4'-DDE
10. Dieldrin
11. Endrin
12. 4,4'-DDD
13. Endosulfan II
14. 4,4'-DDT
15. Endrin aldehyde
16. Endosulfan sulfate
17. Methoxychlor*

*1000µg/mL of methoxychlor.

Column: **SPB™ -608, 30m x 0.53mm ID, 0.5µm film**
Cat. No.: **25312**
Oven: 100°C (2 min) to 280°C at 12°C/min
Carrier: helium, 10mL/min
Det.: FID, 300°C
Inj.: 1µL, 260°C, direct injection

PA 8080 Pesticides Mix