FRAGMENTATION OF HALOGEN COMPOUND

1. The presence of halogen atom Cl^-, Br^- and $+I^-$ can be identified easily by the mass spectrum

R – Cl	R – Br	R – I
Cl^+	Br^+	$I^+(127)$

CH_3Cl give 2 peak. due to isotope of Cl $\begin{cases} \text{Cl } 35 \\ \text{Cl } 37 \end{cases}$

Cl^{35}	Cl^{37}
3	1

100 mole 75% 25%

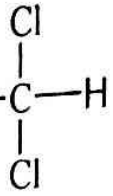
75 $CH_3—Cl^{35}\overset{+\cdot}{}$ = 50 [M] peak hight ratio 3 : 1

25 $CH_3—Cl^{37}\overset{+\cdot}{}$ = 52 [M+2]

Presence of I : The iodine compound shows fragmentation by a loss of I^+ cation at 127 m/z. This peak is characteristic for compounds having iodine atom.

Presence of Cl : Presence of Cl^- can be identify easily by the mass spectrum due to isotopic abundance of 2 isotope Cl^{35} & Cl^{37} in the ratio 3 : 1.
If the fragment has 1 Cl atom then the intensity ratio of M & M + 2 peak will be 3 : 1.
eg : CH_3Cl molecular ion peak 50 & 52 will appear in the intensity ratio 3 : 1

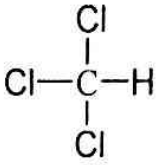
1 Cl ⟶ 2 peak	M : M + 2	3 : 1
2Cl ⟶ 3 peak	M : M + 2 : M + 4	9 : 6 : 1
3Cl ⟶ 4 peak	M : M + 2 : M + 4 : M + 6	27 : 27 : 9 : 1

Example: CH_2Cl_2, 

There are 3 posibilities

35	35 37	37
35	37 35	37
3	3 1	1
×	× + ×	×
3	1 3	1
9	6	1

So, the ratio is 9 : 6 : 1.

$CHCl_3$: 

Chloroform :

3 Cl ⟶ 4 peak M : M + 2 : M + 4 : M + 6

There are 4 possibilities.

M	M+2	M+4	M+6
35	35 35 37	35 37 37	37
35	35 37 35	37 37 35	37
35	37 35 35	37 35 37	37
3	3 3 1	3 1 1	1
×	× × ×	× × ×	×
3	3 + 1 + 3	1 + 1 3	1
×	× × ×	× × ×	×
3	1 3 3	1 3 1	1
27	9 + 9 + 9	3 + 3 + 3	1
27 :	27	: 9	: 1

So the ratio is 27 : 27 : 9 : 1.

Presence of Br : The two isotope of Br are ^{79}Br and ^{81}Br are present in the nature 1 : 1 means 50% + 50% Hence the presence of 1 Br atom in a fragment can be identified easily by the intensity of M and M + 2 peak in the ratio 1 :1.

CH_3Br : $CH_3Br]^{+\bullet}$ ⟶ m/z 94, m/z 96 intensity ratio 1 :1

CH_2Br_2 :

$CH_2Br]^{+\bullet}$

M	M+2	M+4
79	79 81	81
79	81 79	81
1	1 1	1
×	× + ×	×
1	1 1	1
1	2	1

So the ratio is 1 : 2 : 1

CH_3Br_3:

$CH_3Br_3]^{+\bullet}$

M	M + 2			M + 4			M + 6
79	79	79	81	79	81	81	81
79	79	81	79	81	79	81	81
79	81	79	79	81	81	79	81
1	1	1	1	1	1	1	1
×	×	×	×	×	×	×	×
1	1 + 1 + 1			1 + 1 + 1			1
×	×	×	×	×	×	×	×
1	1	1	1	1	1	1	1
1	: 3			: 3			: 1