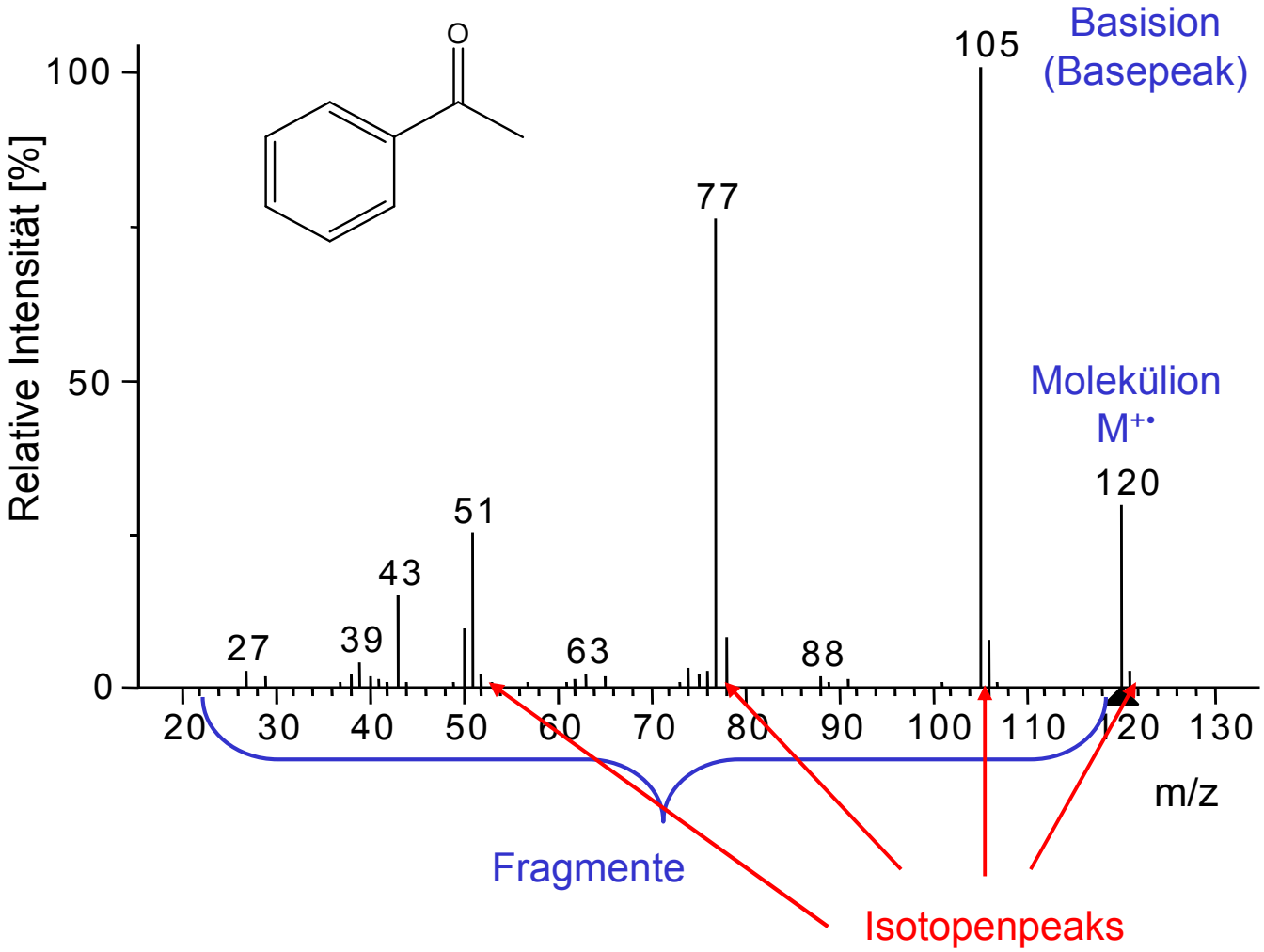
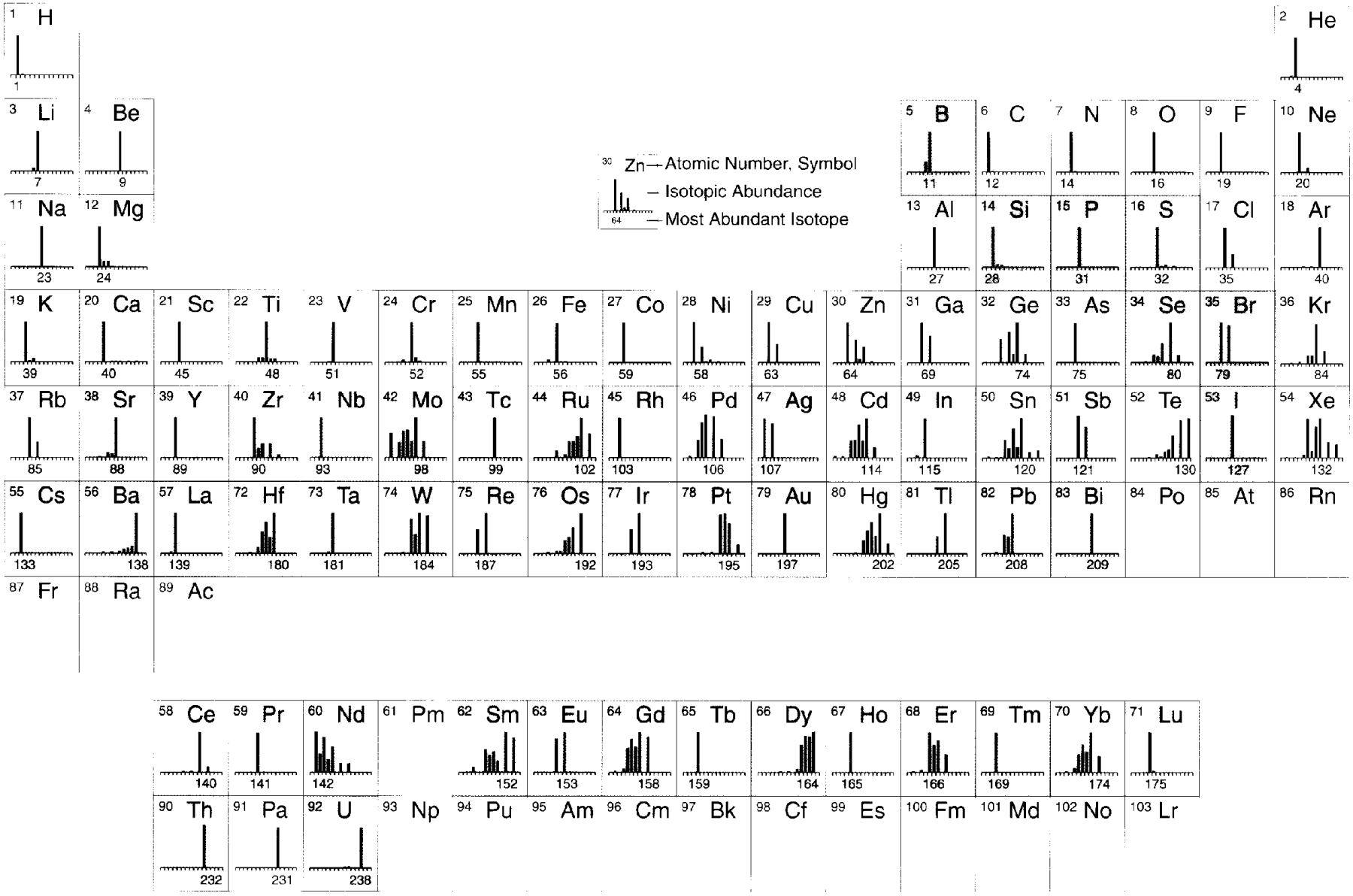
Interpretation von Massenspektren

1. Isotopie und Präzisionsmasse
2. Erkennung/Eigenschaften des Molekülions
3. Fragmentierung (ungeradelektronischer Ionen)

EI-Massenspektrum (Acetophenon, M = 120):



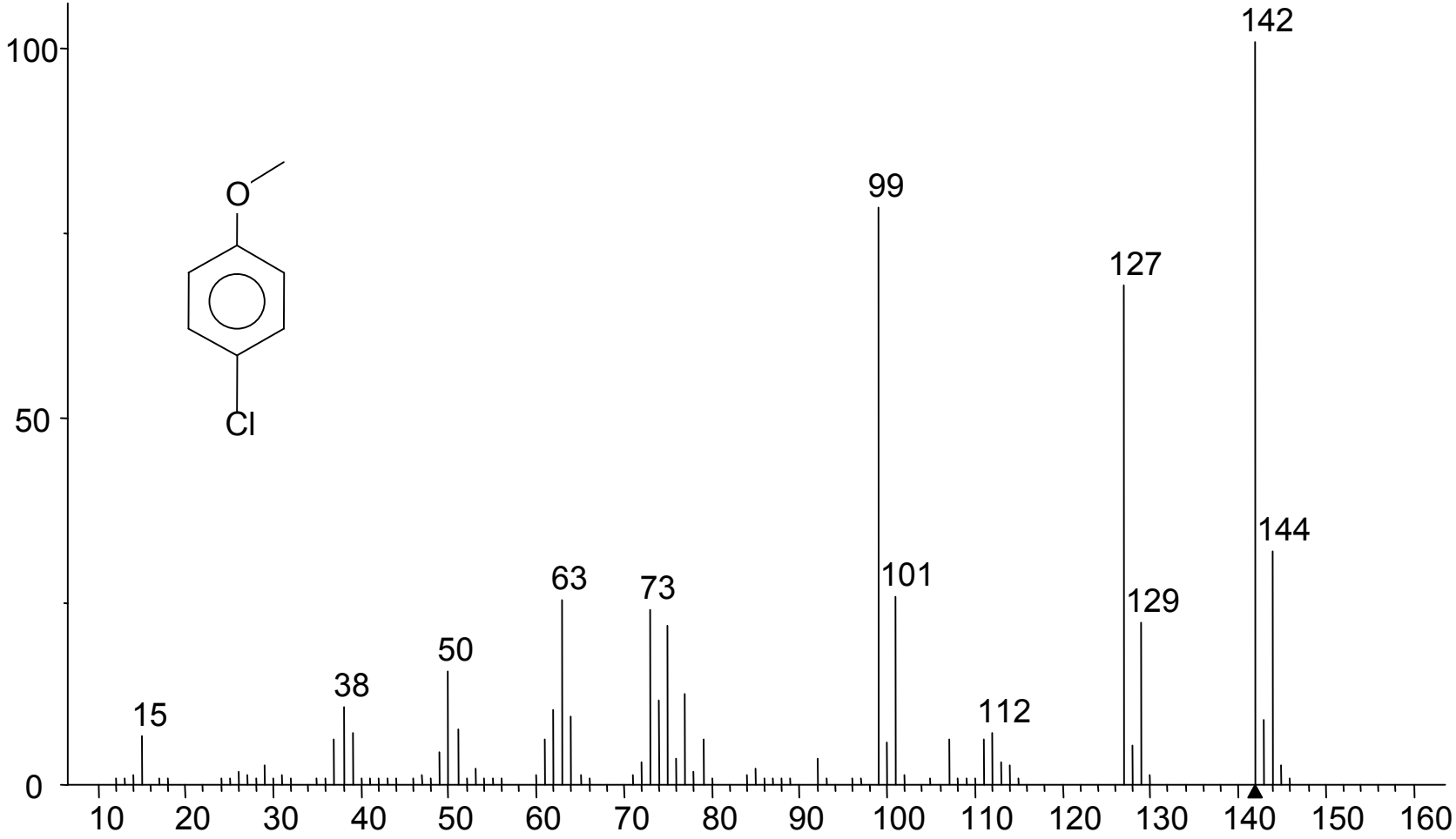
Periodensystem und Isotopie der Elemente



Isotopenmassen und -verteilungen häufig vorkommender Elemente

Element	Massenzahl	Rel. Häufigkeit in %	Exakte Masse [amu]	Chemisches Atomgewicht [g/mol]
H	1	99,99	1,007825	1,0079
D	2	0,01	2,014102	
C	12	98,93	12,000000	12,0107
	13	1,07	13,003355	
N	14	99,63	14,003074	14,0067
	15	0,37	15,000109	
O	16	99,76	15,994915	15,9994
	17	0,04	16,999132	
	18	0,21	17,999160	
F	19	100,00	18,998403	18,9984
Si	28	92,23	27,976927	28,0855
	29	4,68	28,976495	
	30	3,09	29,973770	
P	31	100,00	30,973762	30,9738
S	32	94,93	31,972071	32,0660
	33	0,76	32,971459	
	34	4,29	33,967867	
	36	0,02	35,967081	
Cl	35	75,78	34,968853	35,4527
	37	24,22	36,965903	
Br	79	50,69	78,918338	79,9040
	81	49,31	80,916291	
I	127	100,00	126,904468	126,9045

EI-Massenspektrum von p-Chloranisol



(mainlib) Benzene, 1-chloro-4-methoxy-

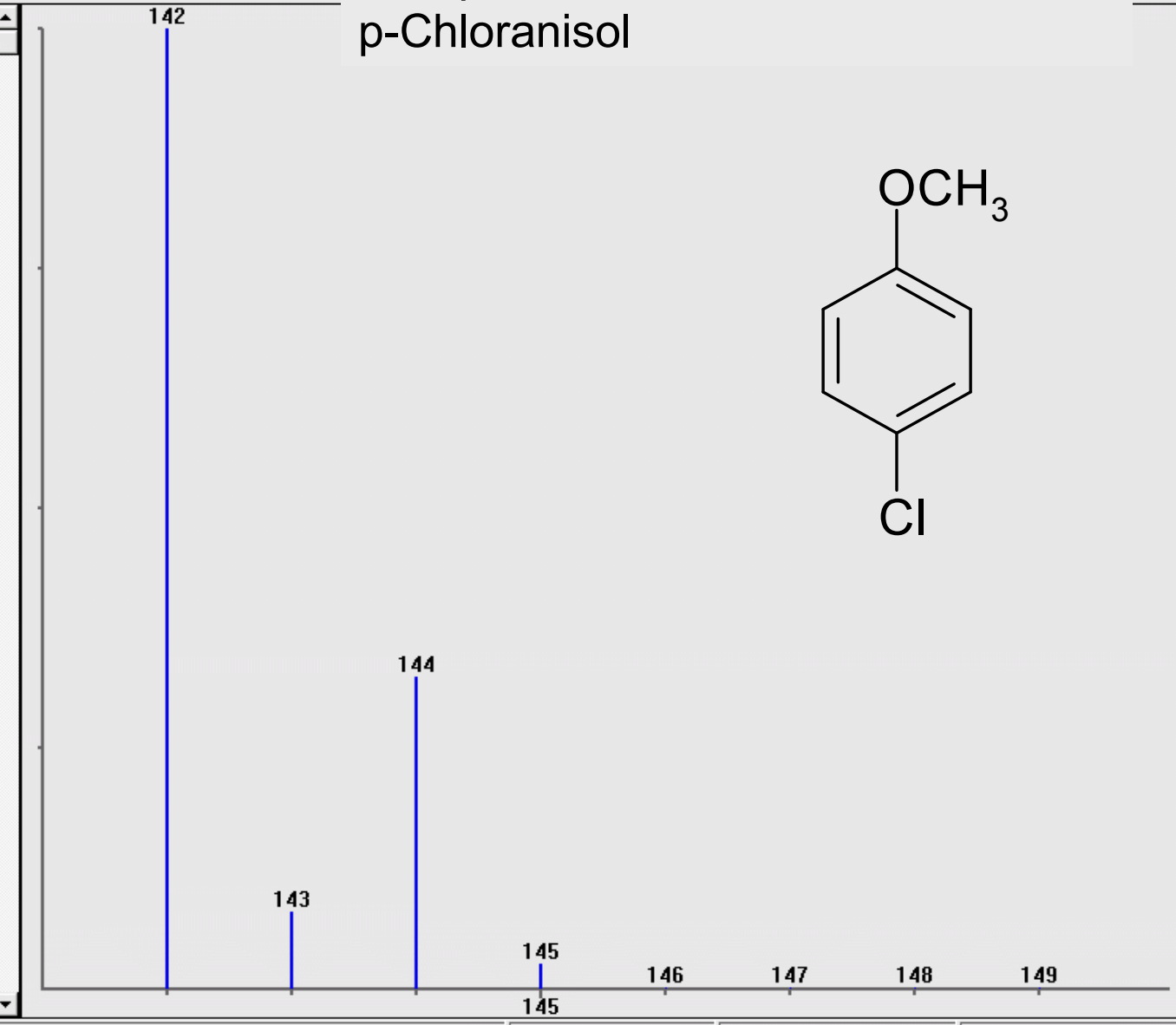
Isotopenmuster des Molekülions von p-Chloranisol

Isotope Calculator

File View Options Help

Max: 100 Formula: C7H7ClO

Mass	Abundance	*Max
142	100.00000	100.00
143	7.91409	7.91
144	32.45051	32.45
145	2.55188	2.55
146	0.15106	0.15
147	0.00671	0.01
148	0.00019	0.00
149	0.00000	0.00

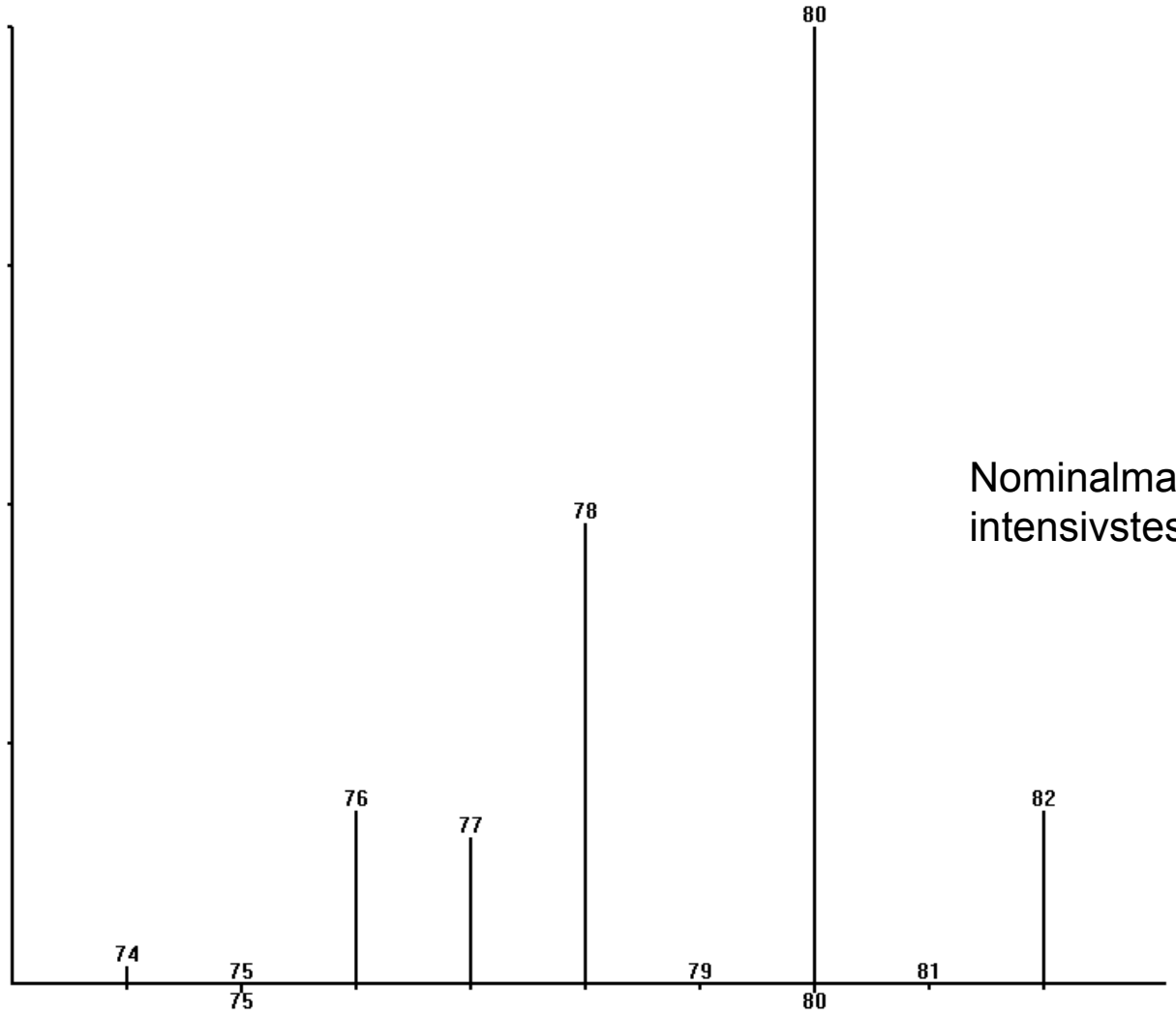


Nominal MW = 142 Exact MW = 142.01854 Average MW = 142.59

SCAN TEXT.
Sorted on M/z (ascending). Entries=54. "All peaks uniquely resolved".

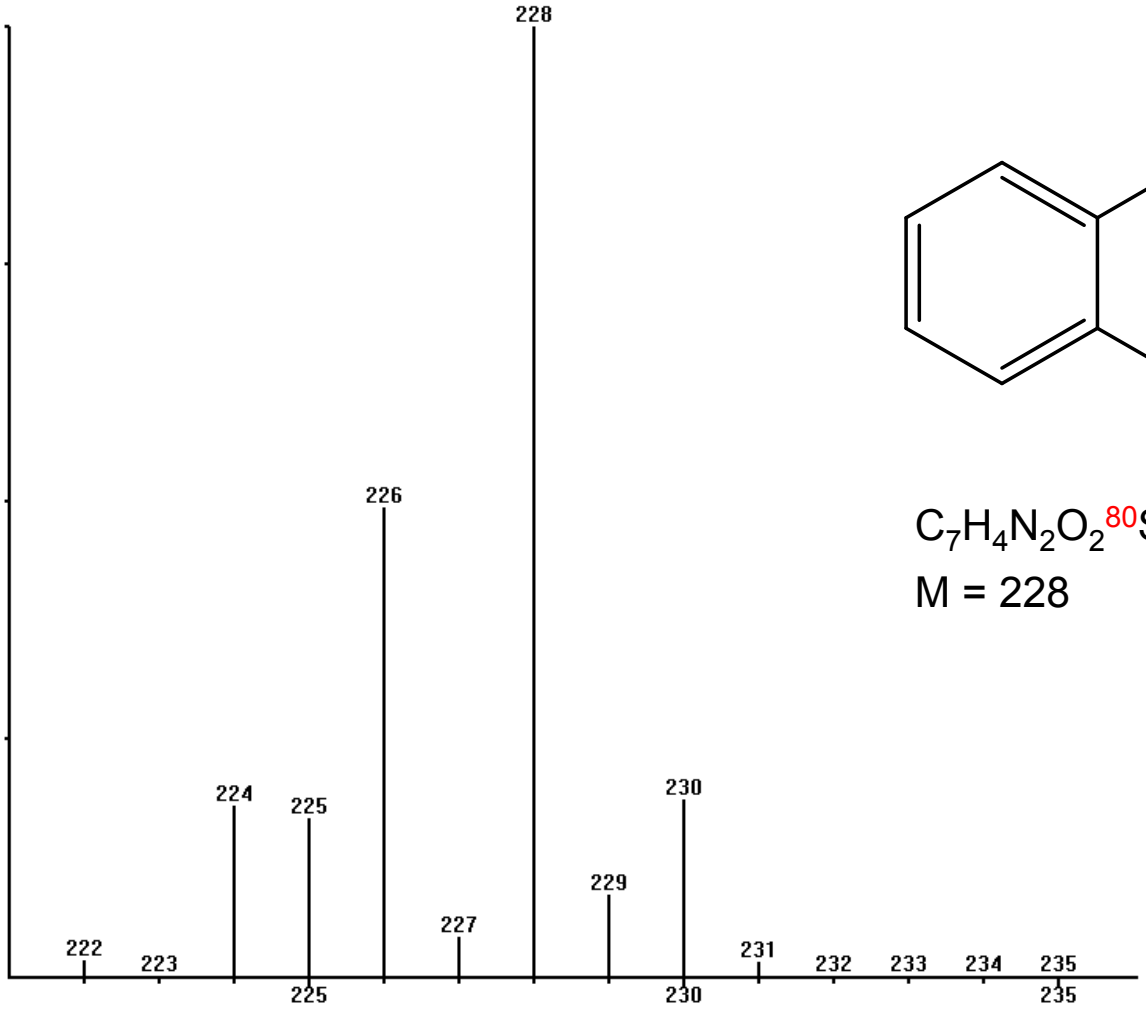
----M/z---	---Int.---	---------Name---------	---%age---
142.01854	695017133	C7.H7.35Cl.O	100.00000
143.02190	54509494	C6.13C.H7.35Cl.O	7.84290
143.02277	257778	C7.H7.35Cl.17O	0.03709
143.02483	729877	C7.H6.2H.35Cl.O	0.10502
144.01559	226756253	C7.H7.37Cl.O	32.62599
144.02278	1421260	C7.H7.35Cl.18O	0.20449
144.02525	1832196	C5.13C2.H7.35Cl.O	0.26362
144.02612	20217	C6.13C.H7.35Cl.17O	0.00291
144.02818	57244	C6.13C.H6.2H.35Cl.O	0.00824
144.02904	271	C7.H6.2H.35Cl.17O	0.00004
144.03110	328	C7.H5.2H2.35Cl.O	0.00005
145.01895	17784265	C6.13C.H7.37Cl.O	2.55882
145.01981	84103	C7.H7.37Cl.17O	0.01210
145.02187	238130	C7.H6.2H.37Cl.O	0.03426
145.02614	111468	C6.13C.H7.35Cl.18O	0.01604
145.02861	34214	C4.13C3.H7.35Cl.O	0.00492
145.02907	1493	C7.H6.2H.35Cl.18O	0.00021
145.02946	680	C5.13C2.H7.35Cl.17O	0.00010
145.03152	1924	C5.13C2.H6.2H.35Cl.O	0.00028
145.03239	21	C6.13C.H6.2H.35Cl.17O	0.00000
145.03445	26	C6.13C.H5.2H2.35Cl.O	0.00000
146.01984	463700	C7.H7.37Cl.18O	0.06672
146.02231	597772	C5.13C2.H7.37Cl.O	0.08601
146.02316	6596	C6.13C.H7.37Cl.17O	0.00095
146.02522	18676	C6.13C.H6.2H.37Cl.O	0.00269
146.02609	88	C7.H6.2H.37Cl.17O	0.00001
146.02815	107	C7.H5.2H2.37Cl.O	0.00002
146.02950	3747	C5.13C2.H7.35Cl.18O	0.00054
146.03197	383	C3.13C4.H7.35Cl.O	0.00006
146.03242	117	C6.13C.H6.2H.35Cl.18O	0.00002
146.03282	13	C4.13C3.H7.35Cl.17O	0.00000
146.03488	36	C4.13C3.H6.2H.35Cl.O	0.00001

Isotopenmuster von Selen:



Nominalmasse: 74 u
intensivstes Isotop: 80 u

Isotopenmuster eines Seleno-organyls:

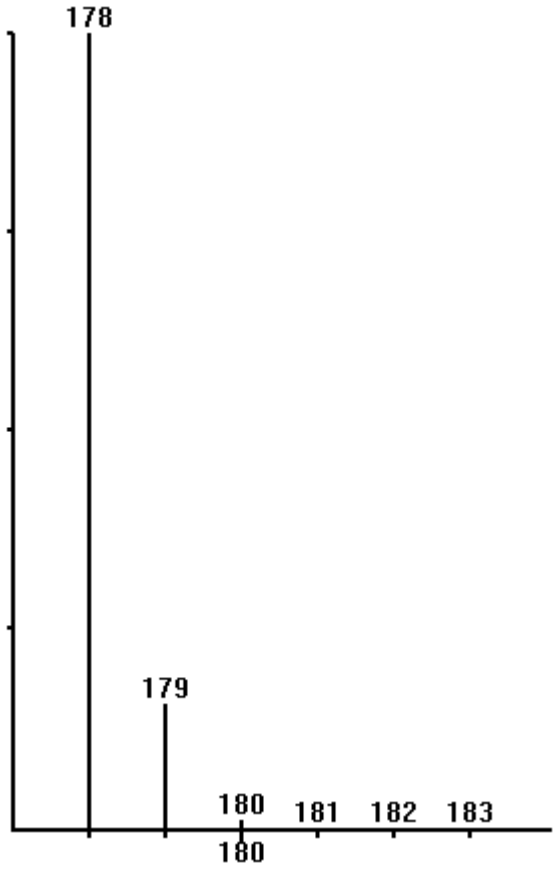


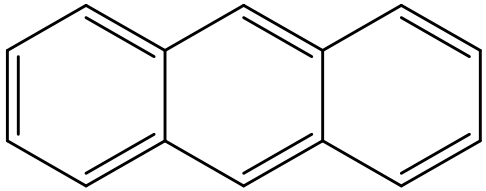
$C_7H_4N_2O_2{}^{80}Se$

M = 228

⇒ Angabe des zur Berechnung verwendeten Isotops notwendig!

Isotopenmuster von Anthracen

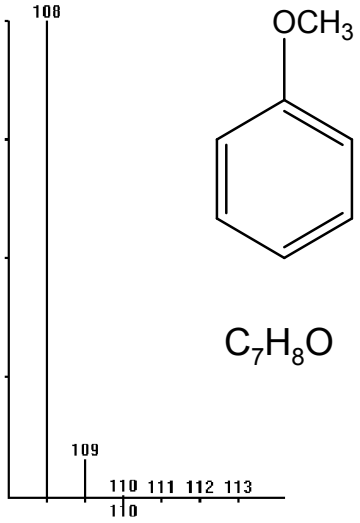




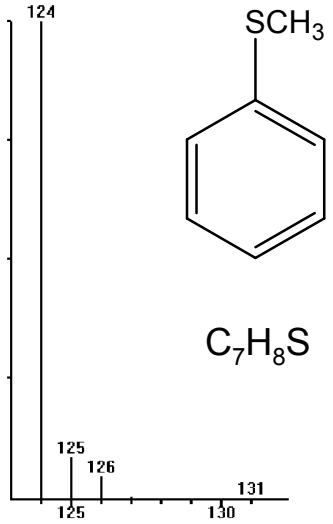
$C_{14}H_{10}$, M = 178

Mass	Abundance
178	100.00000
179	15.69000
180	1.14462
181	0.05148
182	0.00160
183	0.00004

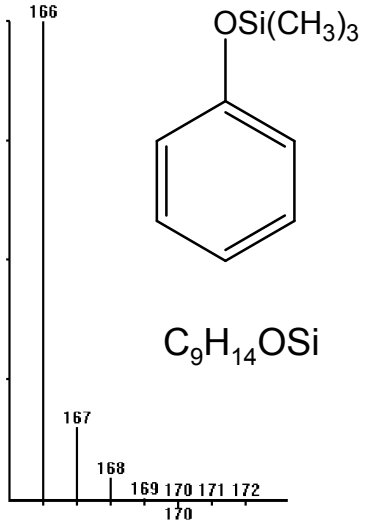
Isotopenmuster verschiedener Anisol-Derivate



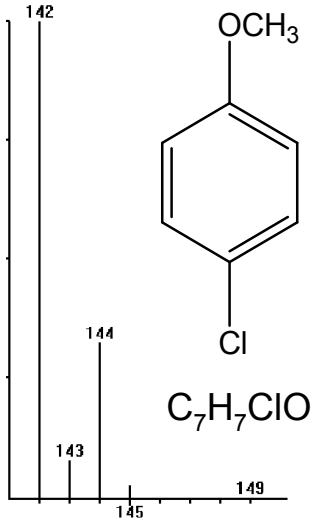
C_7H_8O



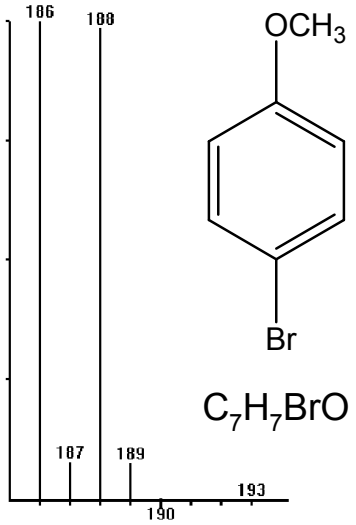
C_7H_8S



$C_9H_{14}OSi$

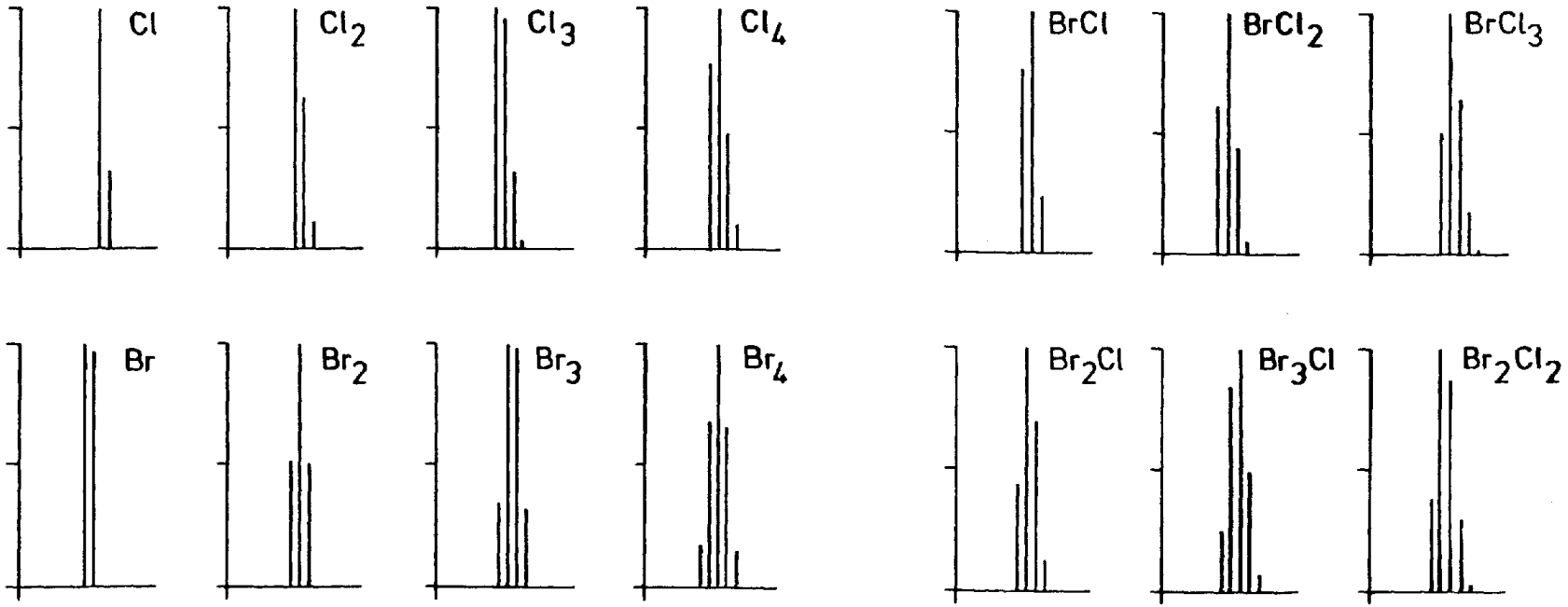


C_7H_7ClO



C_7H_7BrO

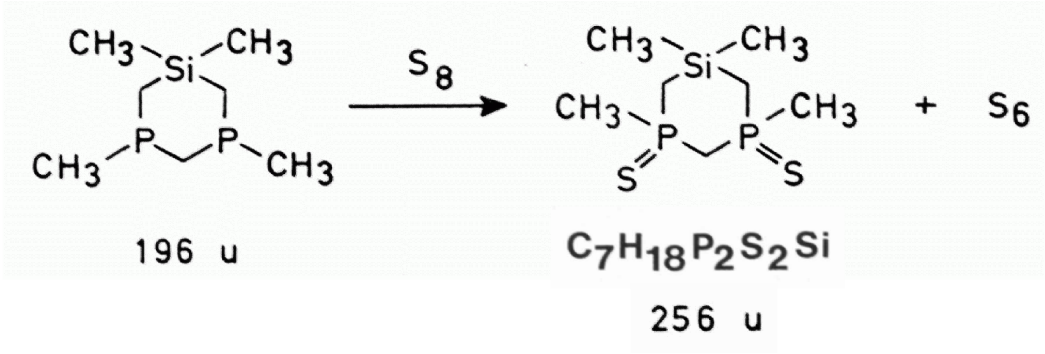
Isotopenmuster verschiedener Kombinationen von Chlor und Brom



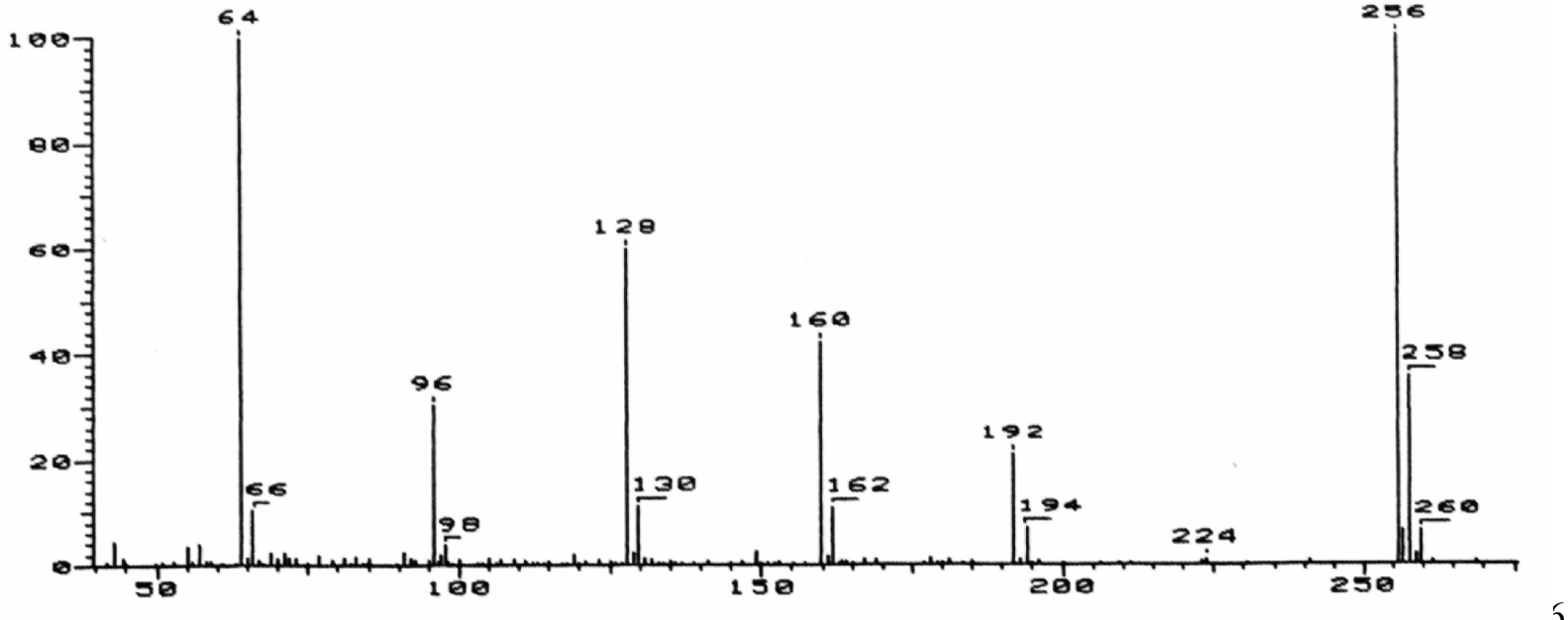
Die Signale liegen jeweils zwei Masseneinheiten auseinander.

Substanzidentifikation anhand des Isotopenmusters des Molekülions

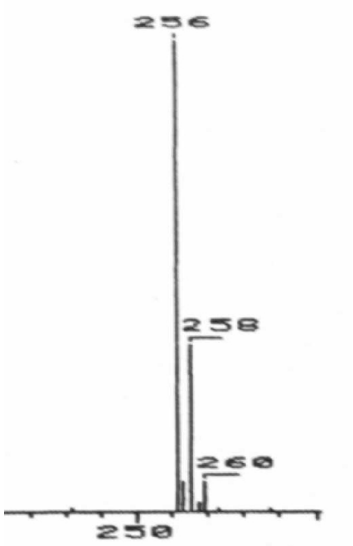
Folgende Reaktion sollte durchgeführt werden:



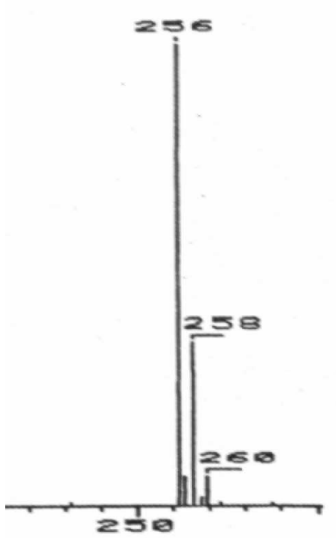
EI-Massenspektrum des Reaktionsprodukts:

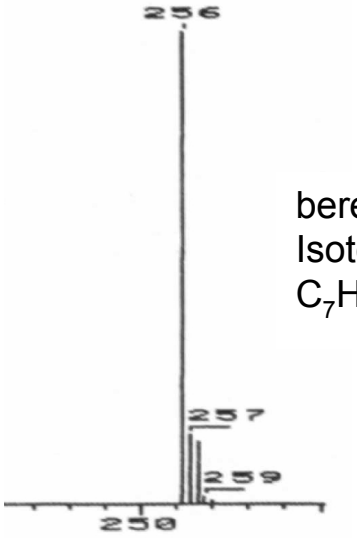


Substanzidentifikation anhand des Isotopenmusters des Molekülions

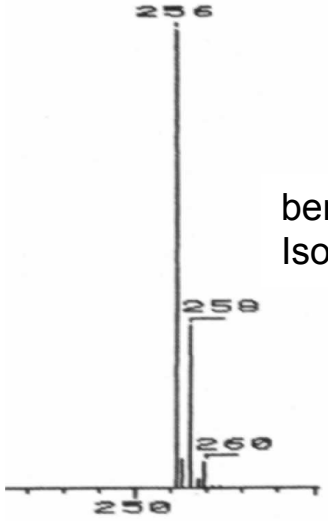


experimentelles
Molekülionenmuster



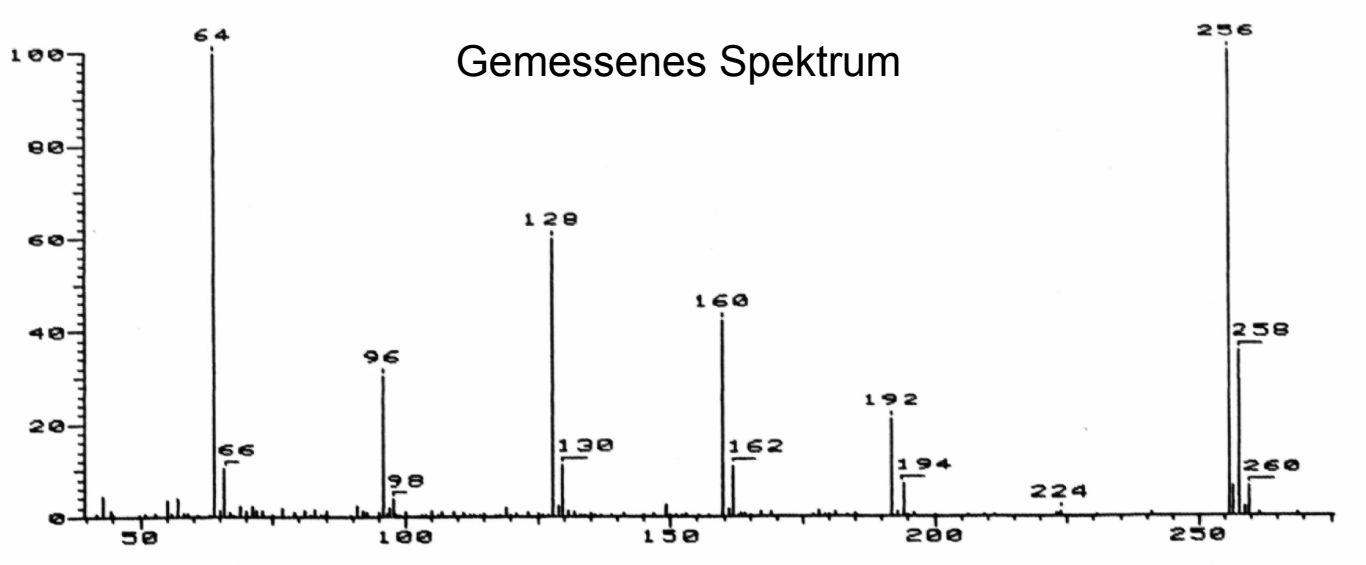


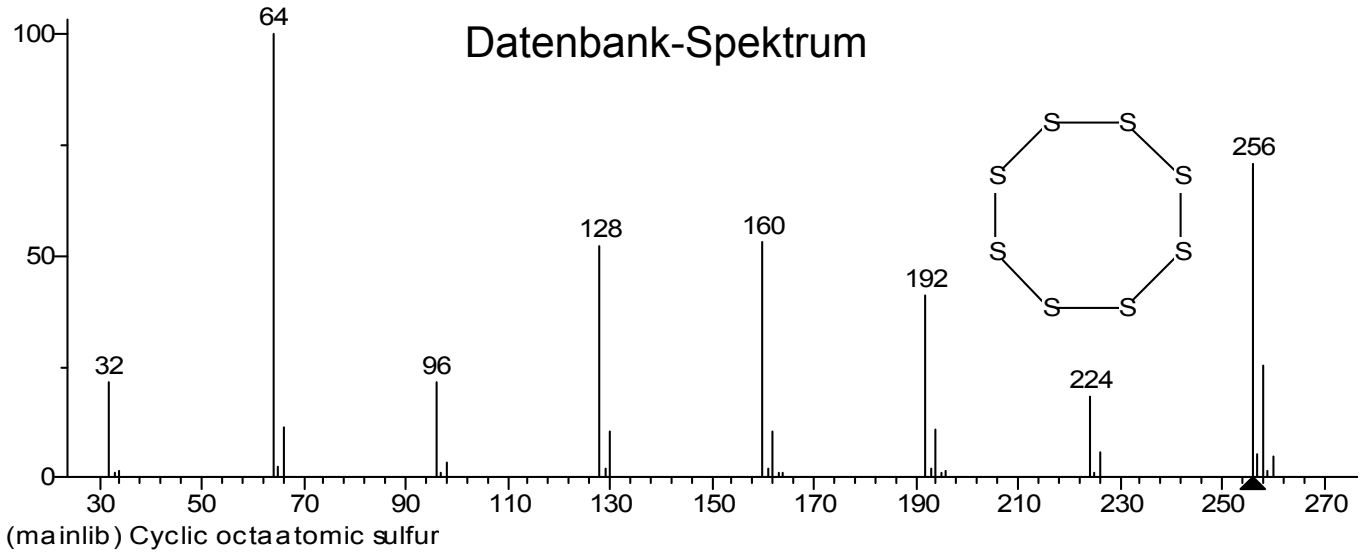
berechnetes
Isotopenmuster für
$C_7H_{18}P_2S_2Si$



berechnetes
Isotopenmuster für **S_8**

Substanzidentifikation anhand des Isotopenmusters des Molekülions





Isotopenmassen und -verteilungen häufig vorkommender Elemente

Element	Massenzahl	Rel. Häufigkeit in %	Exakte Masse [amu]	Chemisches Atomgewicht [g/mol]
H	1	99,99	1,007825	1,0079
D	2	0,01	2,014102	
C	12	98,93	12,000000	12,0107
	13	1,07	13,003355	
N	14	99,63	14,003074	14,0067
	15	0,37	15,000109	
O	16	99,76	15,994915	15,9994
	17	0,04	16,999132	
	18	0,21	17,999160	
F	19	100,00	18,998403	18,9984
Si	28	92,23	27,976927	28,0855
	29	4,68	28,976495	
	30	3,09	29,973770	
P	31	100,00	30,973762	30,9738
S	32	94,93	31,972071	32,0660
	33	0,76	32,971459	
	34	4,29	33,967867	
	36	0,02	35,967081	
Cl	35	75,78	34,968853	35,4527
	37	24,22	36,965903	
Br	79	50,69	78,918338	79,9040
	81	49,31	80,916291	
I	127	100,00	126,904468	126,9045

Genaue Massen einiger Ionen gleicher Massenzahl

Summenformel	Massenzahl	Exakte Masse [amu]
CO_2	44	43,9898
C_2H_4O	44	44,0262
C_2H_6N	44	44,0500
C_3H_8	44	44,0626
$C_2{}^{13}CH_7$	44	44,0581

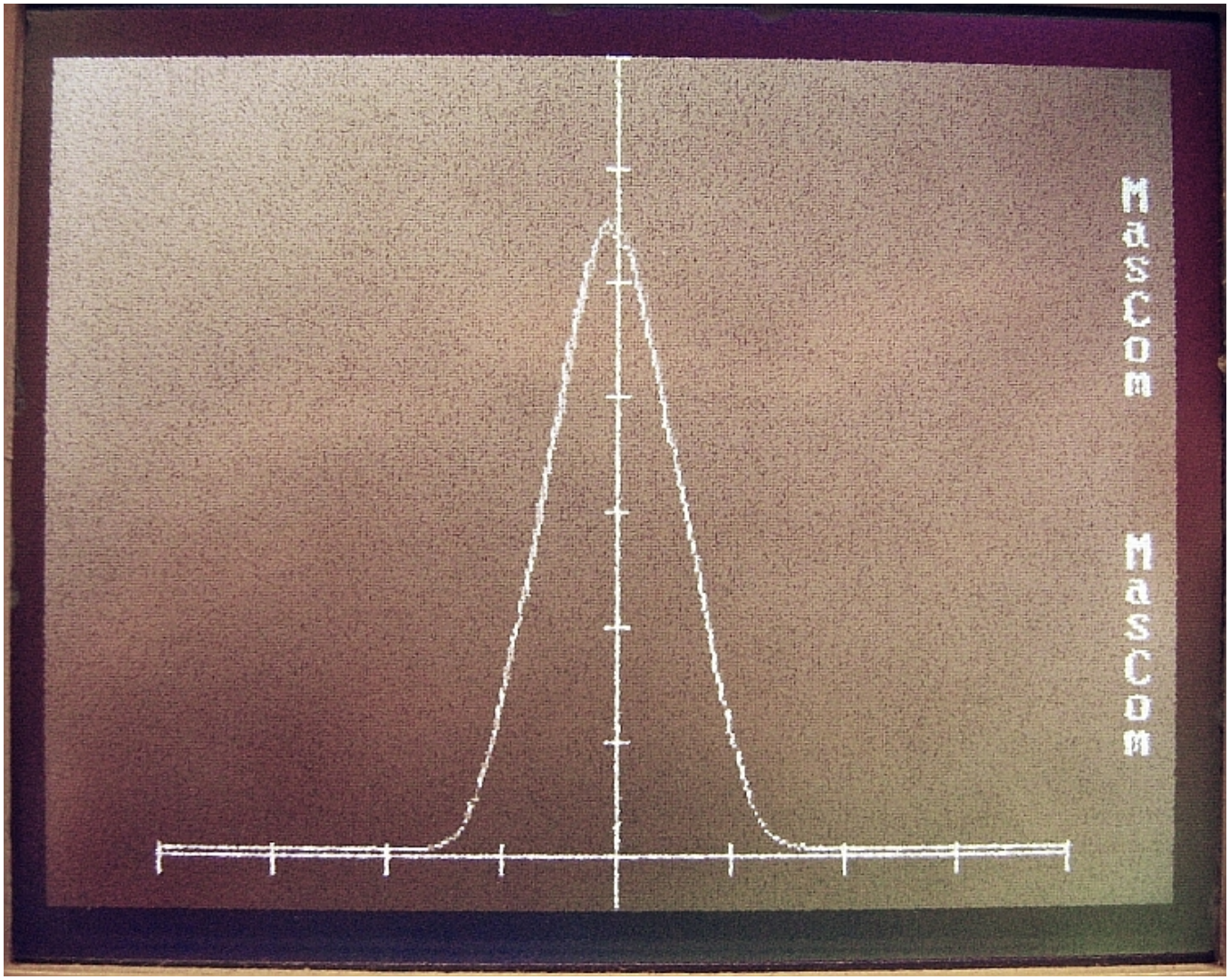
Mehrdeutige Massendifferenzen:

$\Delta m = 43$: C_3H_7- oder $CH_3\overset{|}{C}{=}O$? (43,04578 oder 43,01839)

$\Delta m = 45$: CH_3-CH_2-O- oder -COOH? (45,03404 oder 44,99765)

$\Delta m = 28$: -CH_2-CH_2- oder $>C{=}O$? (28,03130 oder 27,99492)

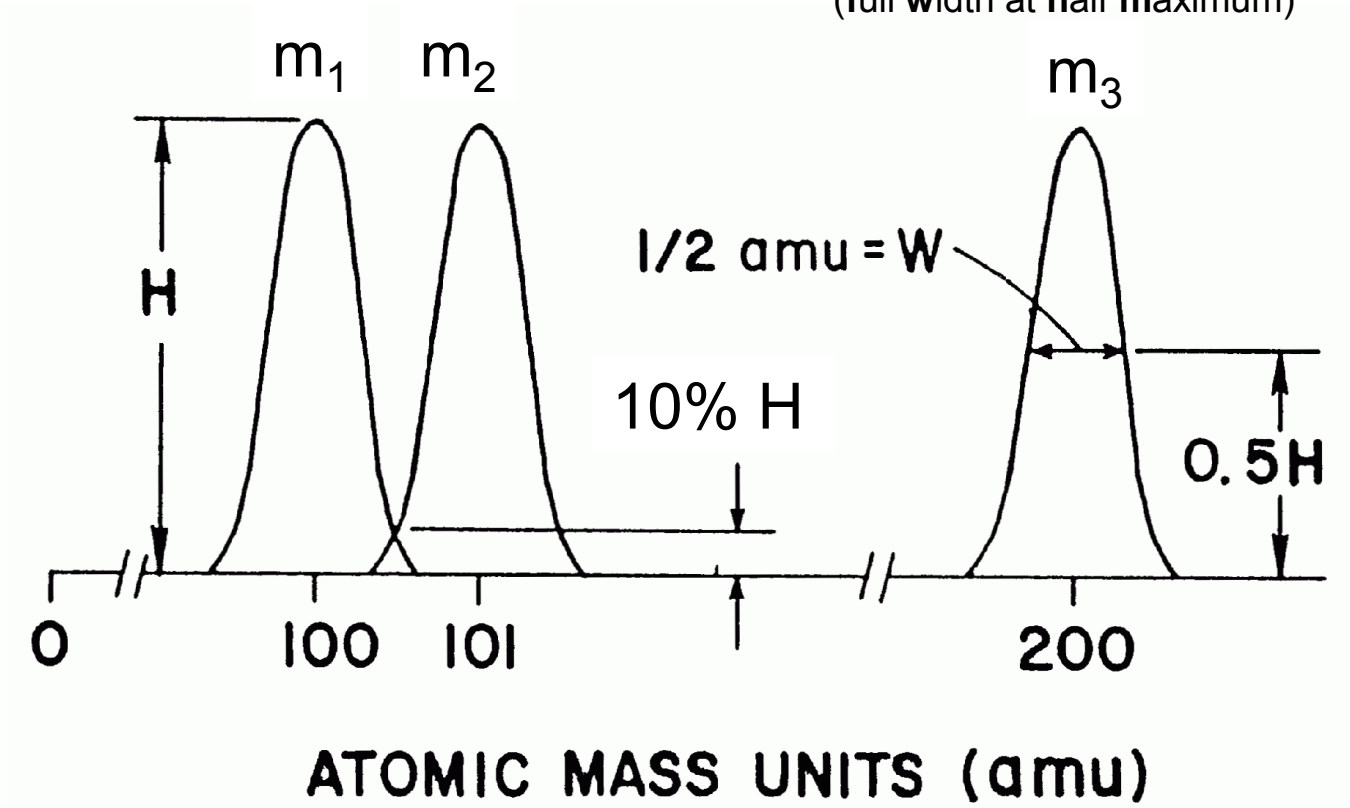
Aussehen eines massenspektrometrischen Peaks



Auflösungsvermögen

10%-Tal-Definition:

FWHM-Definition:
(**f**ull **w**idth at **h**alf **m**aximum)



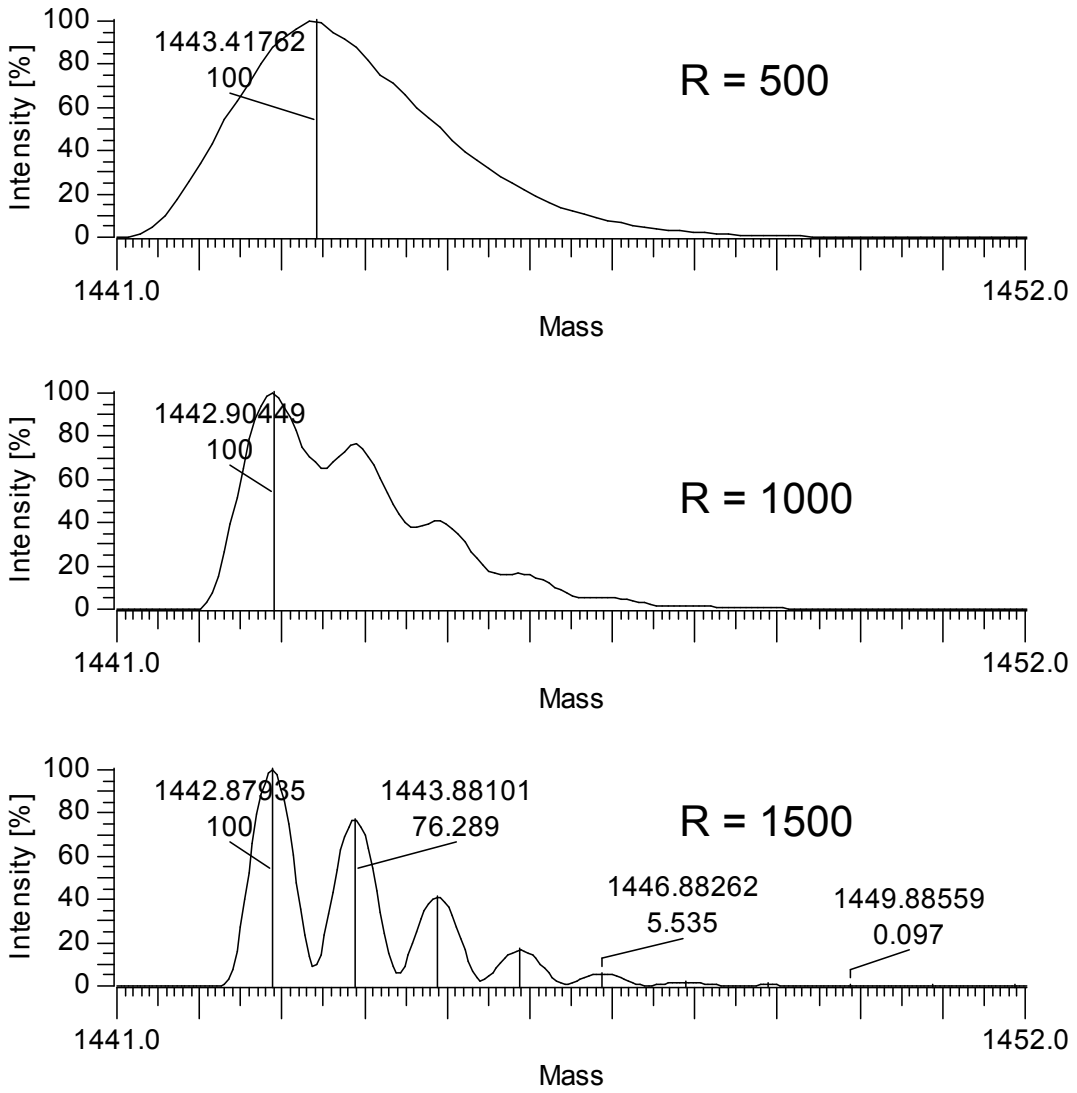
$R = m_1/(m_2-m_1)$
$= m/\Delta m$

$R = m_3/W$

Auflösungsvermögen

Summenformel: $C_{60}H_{122}N_{20}O_{16}S_2$

Nominalmasse: 1442
Exakte Masse: 1441.8788 u
Chemisches Molekulargewicht: 1443.9 g/mol



Magnetisches Sektorfeld-MS

Massentrennung und Richtungsfokussierung

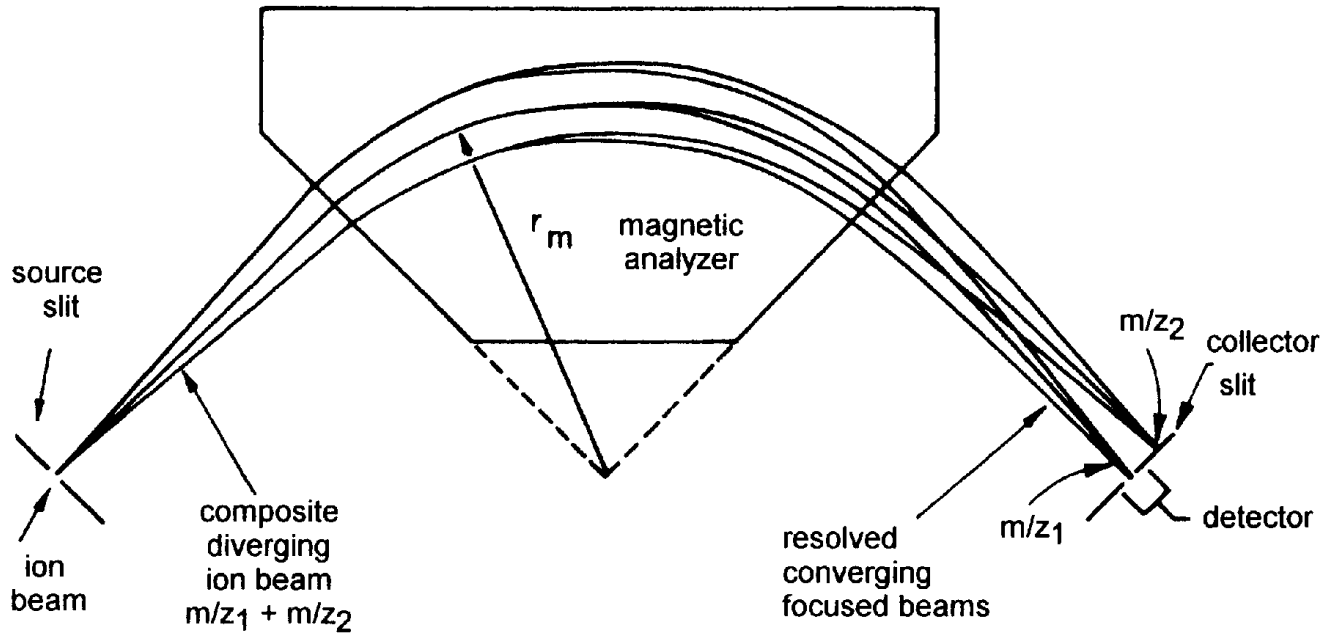
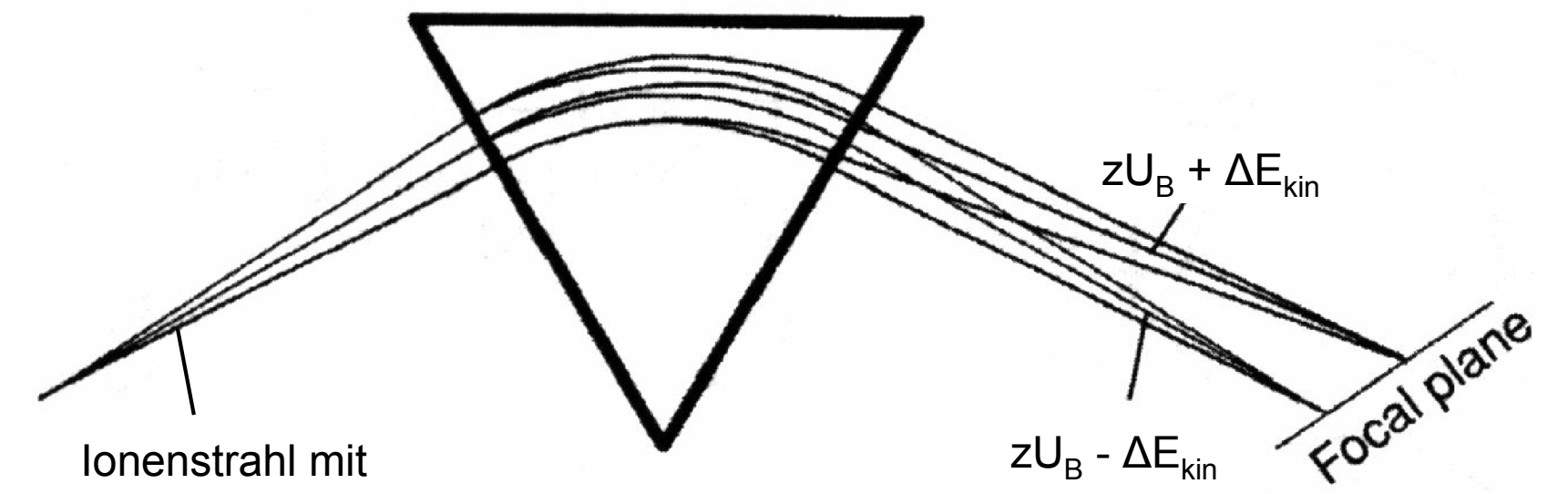


Fig. 4.19. A 90° magnetic sector illustrating *m/z* separation and direction focusing in a plane (angles are shown exaggerated). Reprinted from Ref. [1] with permission. © American Association for the Advancement of Science, 1979.

Magnetisches Sektorfeld-MS

Energiedispersion

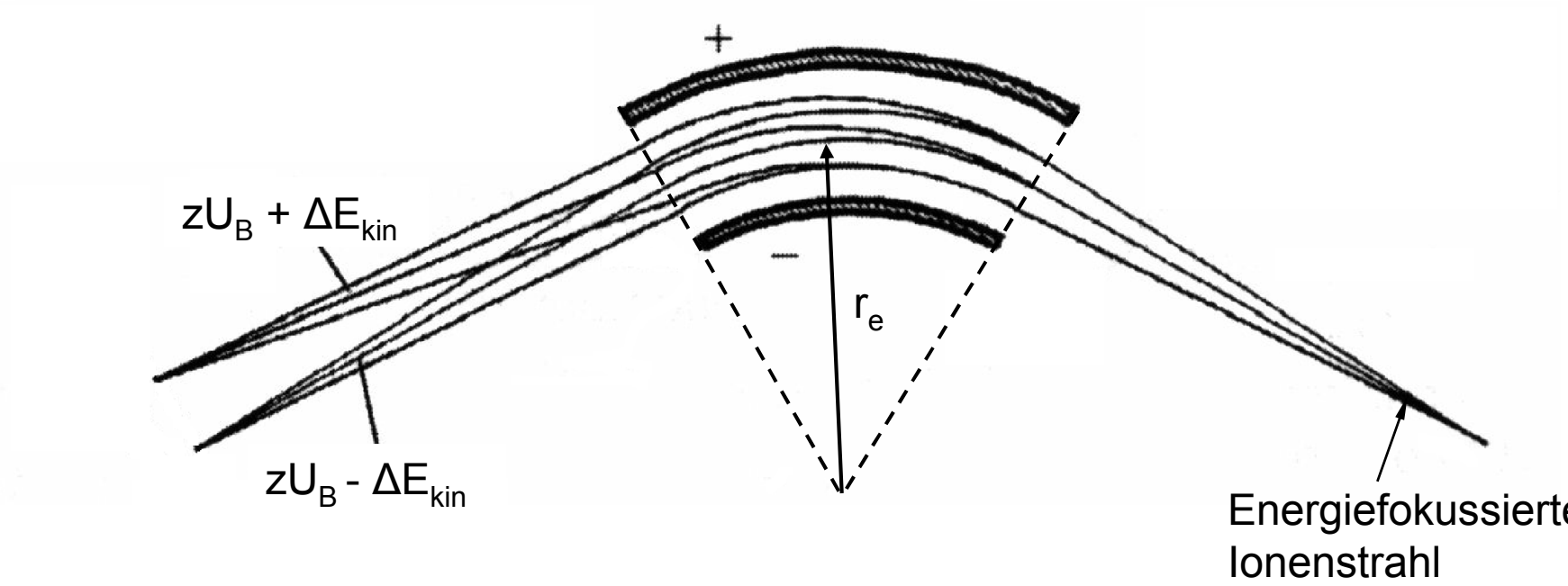


Ionenstrahl mit
m = const., aber
$zU_B \pm \Delta E_{kin}$

$$r_m = \sqrt{\frac{m}{z} \cdot \frac{2U_B}{B^2}}$$

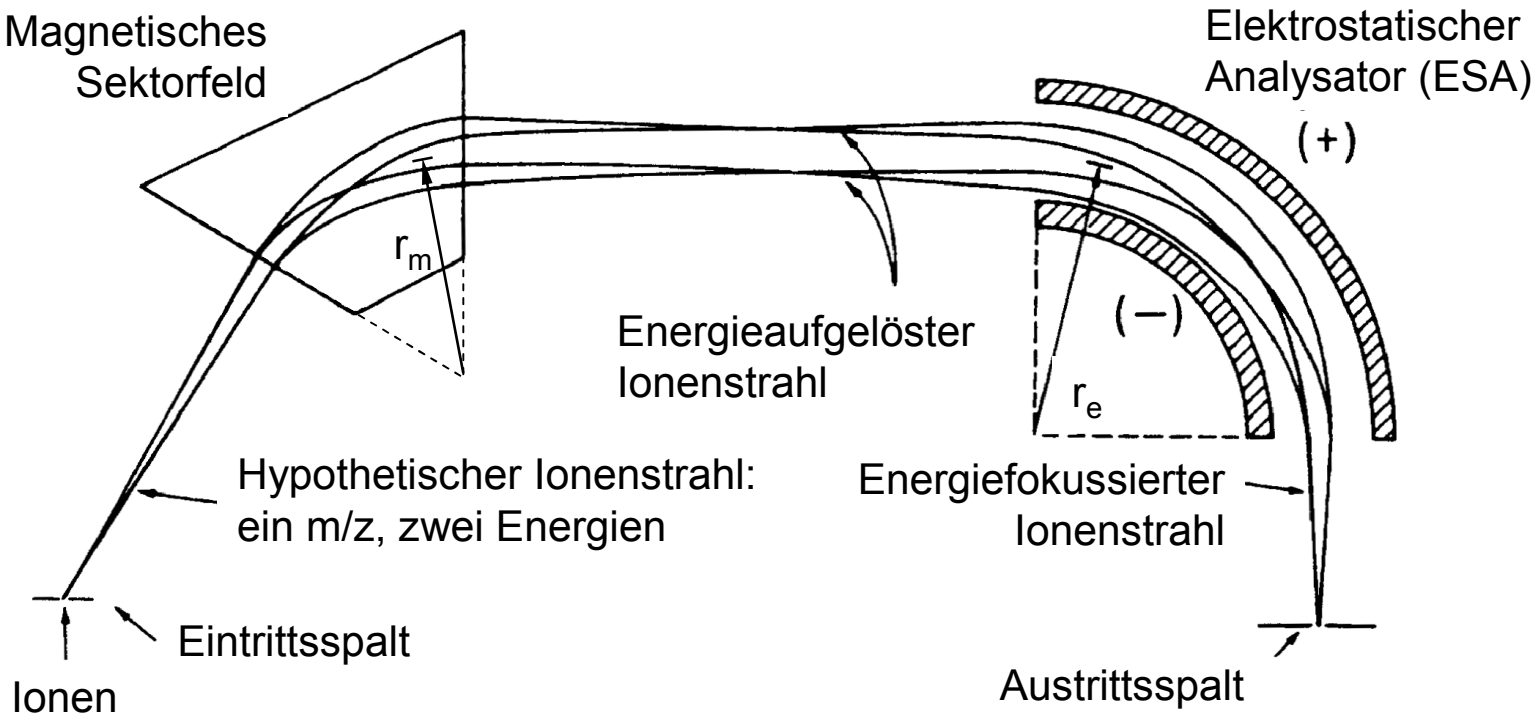
Ursache von ΔE_{kin}: thermische Energieverteilung der Ionen

Elektrostatischer Sektor (electrostatic analyzer, ESA)



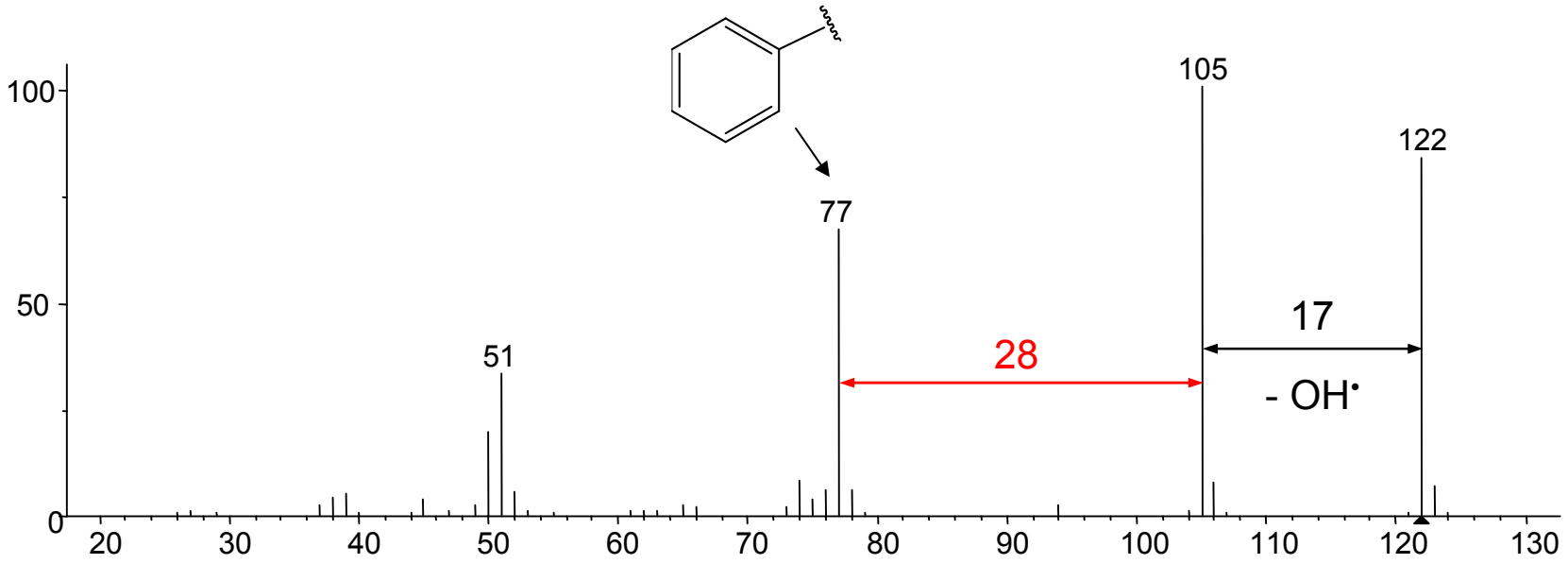
Energiedispersion: $r_e = \frac{2U_B}{E_e}$ Keine Massenabhängigkeit!

Doppelfokussierung

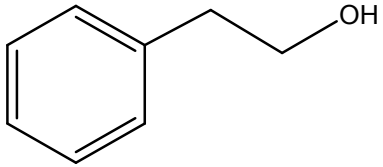


Doppelfokussierung: Energiefokussierung
Richtungsfokussierung (2. Ordnung)
Massendispersion

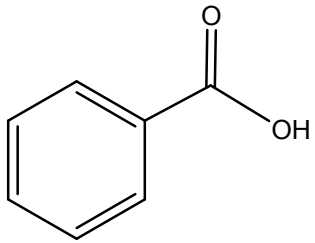
Bestimmung von Strukturelementen über die Präzisionsmasse



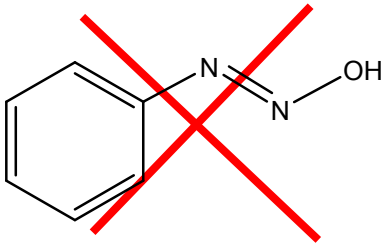
m/z 105 - m/z 77 = 28 ⇒ ? (-CH_2-CH_2-, >C=O, -N=N-)



$C_8H_{10}O$



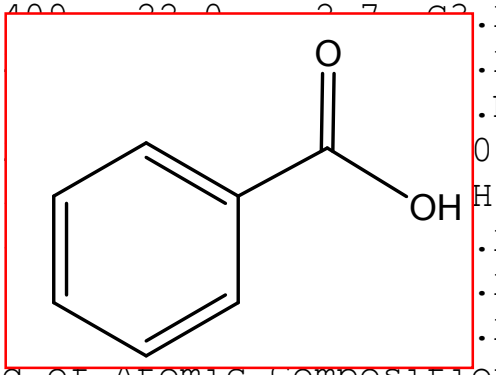
$C_7H_6O_2$



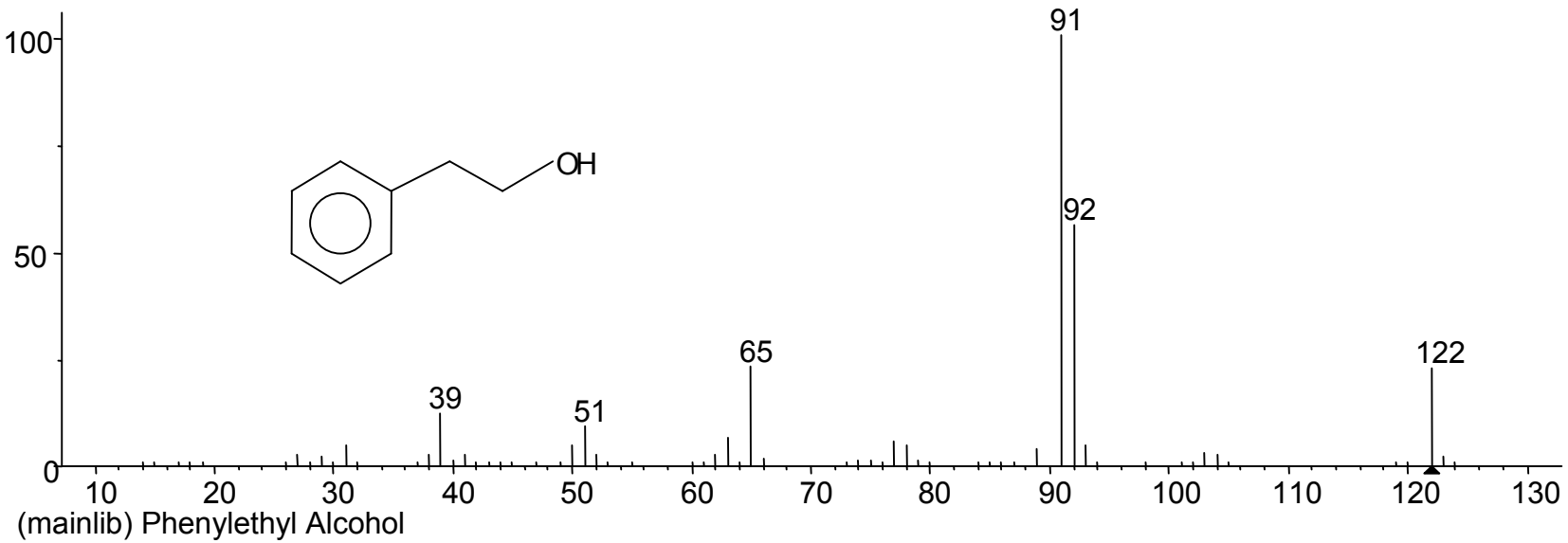
$C_6H_6N_2O$

Präzisionsmasse der Verbindung: 122,03678 u

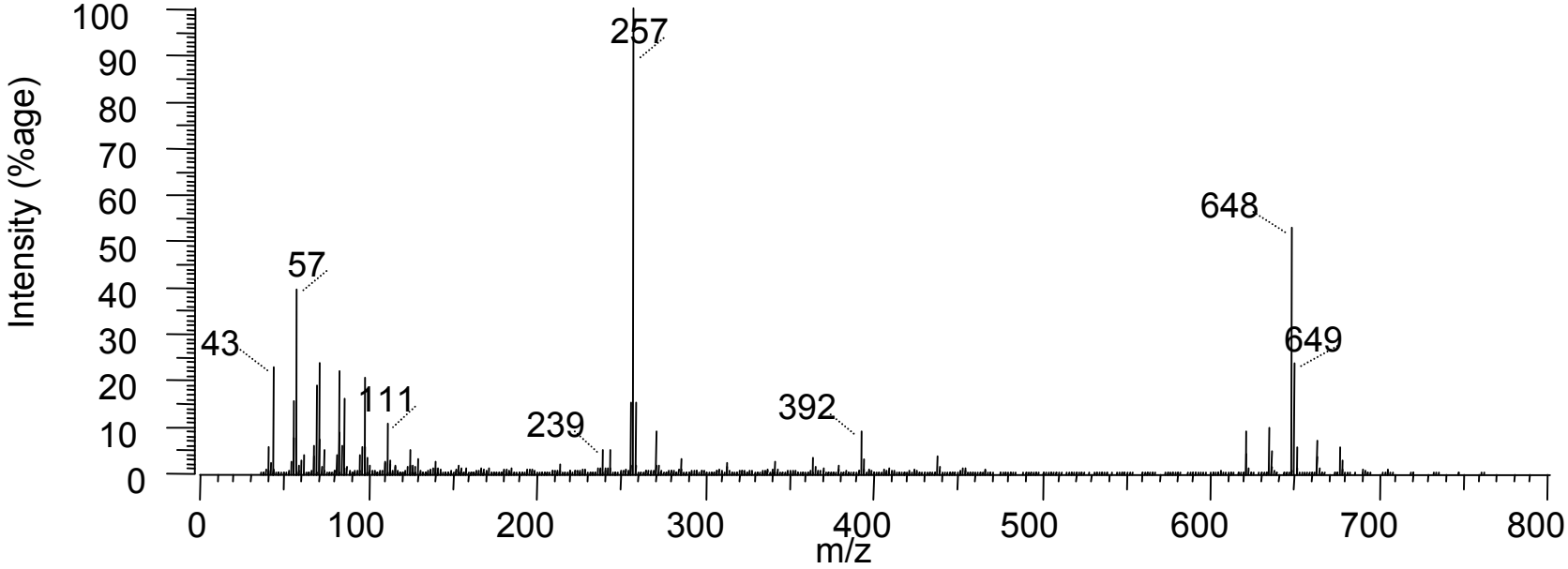
```
 ATOMIC COMPOSITION REPORT (MANUAL)
          ---------------------------------
Selected isotopes:
-------------------------------------------------
  Symbol   Min   Max   V'cy Name
-------------------------------------------------
       C     0 auto    4   Carbon-12
       H     0 auto    1   Hydrogen-1
       N     0 auto    3   Nitrogen-14
       O     0 auto    2   Oxygen-16
-------------------------------------------------
Allowable error = minimum of 100.0 ppm, 100.0 mmu.
-----------------------------------------------------------
       Mass  Calculated    ppm    mmu  Formula
-----------------------------------------------------------
  122.03678   122.03678   -0.0   -0.0  C7.H6.O2
              122.03544  -11.0   -1.3  C5.H4.N3.O
              122.03400  -22.0   -2.7  C3.H2.N6
              122.03                   .H6.N2.O4
              122.03                   .N5.O3
              122.04                   0.O7
              122.04                   H6.N4.O3
              122.04                   .H8.N.O4
              122.04                   .H4.N5
              122.04                   .H6.N2.O
          ***** End of Atomic Composition Report *****
```



Massenspektrum der „falschen“ Verbindung:



Ermittlung der Elementarzusammensetzung aus der Präzisionsmasse



aus NMR bekannt: langkettiger Carbonsäureester

Informationen aus dem Massenspektrum:

- Kohlenwasserstoff-Fragmente im unteren Massenbereich;
- Homologengemisch (Δm = 14), Hauptkomponente M = 648;
- keine auffallende Isotopie, also (außer O) keine Heteroatome;
- Höhe des M+1-Peaks zeigt mindestens 40 C-Atome an;
- Fragment m/z 257 spricht für einen Palmitinsäureester.

Ermittlung der Elementarzusammensetzung aus der Präzisionsmasse

gemessene Präzisionsmasse: 648,67919

Mass	Calculated	ppm	mmu	Formula
648.67919	648.67887	-0.5	-0.3	C18.H223.O13
	648.67843	-1.2	-0.8	C44.H88.O2
	648.68080	2.5	1.6	C19.H100.O20
	648.68090	2.6	1.7	C9.H473.O4
	648.67729	-2.9	-1.9	C.H108.O33
	648.67695	-3.5	-2.2	C17.H346.O6
	648.68238	4.9	3.2	C36.H215
	648.68282	5.6	3.6	C10.H350.O11
	648.67536	-5.9	-3.8	H231.O26
	648.67492	-6.6	-4.3	C26.H96.O15
	648.68431	7.9	5.1	C37.H92.O7
	648.68475	8.6	5.6	C11.H227.O18
	648.68485	8.7	5.7	C.H600.O2
	648.67300	-9.5	-6.2	C25.H219.O8

Bestätigung der Elementarzusammensetzung durch MS

Experimentelle Angaben zur Genauigkeit der Bestimmung

Absoluter Wert	mmu = millimass unit (1 Millimasse = 0.001 Da)
Relativer Wert	ppm = parts per million
Beispiel:	berechnet: 545.2034 Da
	gefunden: 545.2011 Da
	Δm: -0.0023 Da = -2.3 mmu
Fehlerangabe:	in mmu oder in ppm

Umrechnung mmu → ppm:

$\Delta m\ [ppm] = -0.0023/545 = -0.0000042 = -4.2 \cdot 10^{-6} = -4.2$ ppm

→ korrekte Angabe: 545.2011 Da – 2.3 mmu oder
545.2011 Da – 4.2 ppm

Geforderte Genauigkeit für die Bestätigung einer Präzisionsmasse: ± 5 ppm

Berücksichtigung der Ruhemasse eines Elektrons bei hoher Auflösung

Relative Ruhemasse des Elektrons: M_r = 0.000548 Da = 0.548 mmu

Beispiel: $[M - 2H]^{2-}$ von Coenzym A

Ohne Berücksichtigung von 2 Elektronen:	382.54978 Da
Mit Berücksichtigung von 2 Elektronen:	382.55088 Da
Experimenteller Wert:	382.55045 Da

Abweichung ohne Berücksichtigung der Elektronen	1.75 ppm
Abweichung mit Berücksichtigung der Elektronen	-1.12 ppm