

Appendix

A.1 Units, Physical Quantities, and Physical Constants

The *International System of Units* (SI) provides the advantage of establishing uniformity and consistency of units for physical quantities – a prerequisite for communication in science.

Table A.1 SI base units

Physical base quantity	SI unit	Symbol
Length/distance	Meter ^a	m
Mass	Kilogram ^b	kg
Time	Second	s
Electric current	Ampere	A
Thermodynamic temperature	Kelvin ^c	K
Amount of substance	Mole	mol
Luminous intensity	Candela	cd

^a1 m = 3.2808 ft. = 39.3701 in. 1 in = 2.54 cm; 1 ft. = 0.3048 m

^b1 kg = 2.2046 lb.; 1 lb. = 0.4536 kg

^cT[°C] = T[K] – 273.15; T[°F] = 1.8 × T[°C] + 32

Table A.2 Derived SI units with special names

Quantity	Name	Symbol	Expression in terms of base units	Expression in terms of other SI units
Frequency	Hertz	Hz	s ⁻¹	
Force	Newton	N	m kg s ⁻²	J m ⁻¹
Pressure	Pascal ^a	Pa	kg m ⁻¹ s ⁻²	N m ⁻²
Volume	Liter	l	10 ⁻³ m ³	
Energy	Joule ^b	J	m ² kg s ⁻²	N m
Power	Watt	W	m ² kg s ⁻³	J s ⁻¹
Electric charge	Coulomb	C	A s	
Electric potential	Volt	V	m ² kg A ⁻¹ s ⁻³	W A ⁻¹
Magnetic flux density	Tesla	T	kg A ⁻¹ s ⁻²	

^a1 bar = 1000 mbar = 10⁵ Pa; 1 Torr = 133 Pa; 1 psi = 6895 Pa = 68.95 mbar

^b1 cal = 4.1868 J; 1 eV = 1.60219 × 10⁻¹⁹ J = 96.485 kJ mol⁻¹

Table A.3 Physical constants and frequently used quantities (from NIST)

Physical constant/quantity	Symbol	Quantity
Charge of the electron	e	$1.60217648 \times 10^{-19}$ C
Mass of the electron	m_e	$9.1093822 \times 10^{-31}$ kg
Mass of the proton	m_p	$1.67262164 \times 10^{-27}$ kg
Mass of the neutron	m_n	$1.67492721 \times 10^{-27}$ kg
Unified atomic mass	u	$1.66053878 \times 10^{-27}$ kg
Speed of light in vacuum	c	2.99792458×10^8 m s ⁻¹
Planck's constant	h	$6.62607004 \times 10^{-34}$ J s or $4.13566766 \times 10^{-15}$ eV s
Avogadro's constant	N_A	$6.02214179 \times 10^{23}$ mol ⁻¹
Boltzmann constant	k_B	$1.38065042 \times 10^{-23}$ J K ⁻¹
Universal gas constant	R	8.314459 J mol ⁻¹ K ⁻¹

Table A.4 SI number prefixes

a	f	p	n	μ	m	c	d	k	M	G	T
Atto	Femto	Pico	Nano	Micro	Milli	Centi	Deci	Kilo	Mega	Giga	Tera
10^{-18}	10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}	10^3	10^6	10^9	10^{12}

A.2 Isotopic Composition of the Elements

Table A.5 comprises the stable elements from hydrogen to bismuth with the radioactive elements technetium and promethium omitted. Natural variations in isotopic composition of some elements such as carbon or lead do not allow for more accurate values, a fact also reflected in the accuracy of their relative atomic mass. However, exact masses of the isotopes are not affected by varying abundances. The isotopic masses listed may differ up to some 10^{-6} u in other publications.

Table A.5 Isotopic mass, isotopic composition, and relative atomic mass [u] of non-radioactive elements. © IUPAC 2001

Atomic symbol	Name	Atomic No.	Mass No.	Isotopic mass	Isotopic comp.	Relative atomic mass
H	Hydrogen	1	1	1.007825	100	1.00795
			2	2.014101	0.0115	
He	Helium	2	3	3.016029	0.000137	4.002602
			4	4.002603	100	
Li	Lithium	3	6	6.015122	8.21	6.941
			7	7.016004	100	
Be	Beryllium	4	9	9.012182	100	9.012182
B	Boron	5	10	10.012937	24.8	10.812
			11	11.009306	100	
C	Carbon	6	12	12.000000	100	12.0108
			13	13.003355	1.08	
N	Nitrogen	7	14	14.003074	100	14.00675
			15	15.000109	0.369	
O	Oxygen	8	16	15.994915	100	15.9994
			17	16.999132	0.038	
			18	17.999161	0.205	
F	Fluorine	9	19	18.998403	100	18.998403
Ne	Neon	10	20	19.992402	100	20.1798
			21	20.993847	0.30	
			22	21.991386	10.22	
Na	Sodium	11	23	22.989769	100	22.989769
Mg	Magnesium	12	24	23.985042	100	24.3051
			25	24.985837	12.66	
			26	25.982593	13.94	
Al	Aluminium	13	27	26.981538	100	26.981538
Si	Silicon	14	28	27.976927	100	28.0855
			29	28.976495	5.0778	
			30	29.973770	3.3473	
P	Phosphorus	15	31	30.973762	100	30.973762
S	Sulfur	16	32	31.972071	100	32.067
			33	32.971459	0.80	
			34	33.967867	4.52	
			36	35.967081	0.02	
Cl	Chlorine	17	35	34.968853	100	35.4528
			37	36.965903	31.96	
Ar	Argon	18	36	35.967546	0.3379	39.948
			38	37.962776	0.0635	
			40	39.962383	100	
K	Potassium	19	39	38.963706	100	39.0983
			40	39.963999	0.0125	
			41	40.961826	7.2167	

(continued)

Table A.5 (continued)

Atomic symbol	Name	Atomic No.	Mass No.	Isotopic mass	Isotopic comp.	Relative atomic mass
Ca	Calcium	20	40	39.962591	100	40.078
			42	41.958618	0.667	
			43	42.958769	0.139	
			44	43.955481	2.152	
			46	45.953693	0.004	
			48	47.952534	0.193	
Sc	Scandium	21	45	44.955910	100	44.955910
Ti	Titanium	22	46	45.952629	11.19	47.867
			47	46.951764	10.09	
			48	47.947947	100	
			49	48.947871	7.34	
			50	49.944792	7.03	
V	Vanadium	23	50	49.947163	0.250	50.9415
			51	50.943964	100	
Cr	Chromium	24	50	49.946050	5.187	51.9962
			52	51.940512	100	
			53	52.940654	11.339	
			54	53.938885	2.823	
Mn	Manganese	25	55	54.938050	100	54.938050
Fe	Iron	26	54	53.939615	6.37	55.845
			56	55.934942	100	
			57	56.935399	2.309	
			58	57.933280	0.307	
Co	Cobalt	27	59	58.933200	100	58.933200
Ni	Nickel	28	58	57.935348	100	58.6934
			60	59.930791	38.5198	
			61	60.931060	1.6744	
			62	61.928349	5.3388	
			64	63.927970	1.3596	
Cu	Copper	29	63	62.929601	100	63.546
			65	64.927794	44.57	
Zn	Zinc	30	64	63.929147	100	65.39
			66	65.926037	57.37	
			67	66.927131	8.43	
			68	67.924848	38.56	
			70	69.925325	1.27	
Ga	Gallium	31	69	68.925581	100	69.723
			71	70.924705	66.367	
Ge	Germanium	32	70	69.924250	56.44	72.61
			72	71.922076	75.91	
			73	72.923459	21.31	
			74	73.921178	100	
			76	75.921403	20.98	

(continued)

Table A.5 (continued)

Atomic symbol	Name	Atomic No.	Mass No.	Isotopic mass	Isotopic comp.	Relative atomic mass
As	Arsenic	33	75	74.921596	100	74.921596
Se	Selenium	34	74	73.922477	1.79	78.96
			76	75.919214	18.89	
			77	76.919915	15.38	
			78	77.917310	47.91	
			80	79.916522	100	
			82	81.916700	17.60	
Br	Bromine	35	79	78.918338	100	79.904
			81	80.916291	97.28	
Kr	Krypton	36	78	77.920387	0.61	83.80
			80	79.916378	4.00	
			82	81.913485	20.32	
			83	82.914136	20.16	
			84	83.911507	100	
			86	85.910610	30.35	
Rb	Rubidium	37	85	84.911789	100	85.4678
			87	86.909183	38.56	
Sr	Strontium	38	84	83.913425	0.68	87.62
			86	85.909262	11.94	
			87	86.908879	8.48	
			88	87.905614	100	
Y	Yttrium	39	89	88.905848	100	88.905848
Zr	Zirconium	40	90	89.904704	100	91.224
			91	90.905645	21.81	
			92	91.905040	33.33	
			94	93.906316	33.78	
			96	95.908276	5.44	
Nb	Niobium	41	93	92.906378	100	92.906378
Mo	Molybdenum	42	92	91.906810	61.50	95.94
			94	93.905088	38.33	
			95	94.905841	65.98	
			96	95.904679	69.13	
			97	96.906021	39.58	
			98	97.905408	100	
			100	99.907478	39.91	
Ru	Ruthenium	44	96	95.907599	17.56	101.07
			98	97.905288	5.93	
			99	98.905939	40.44	
			100	99.904229	39.94	
			101	100.905582	54.07	
			102	101.904350	100	
			104	103.905430	59.02	

(continued)

Table A.5 (continued)

Atomic symbol	Name	Atomic No.	Mass No.	Isotopic mass	Isotopic comp.	Relative atomic mass
Rh	Rhodium	45	103	102.905504	100	102.905504
Pd	Palladium	46	102	101.905608	3.73	106.42
			104	103.904036	40.76	
			105	104.905084	81.71	
			106	105.903484	100	
			108	107.903894	96.82	
			110	109.905151	42.88	
Ag	Silver	47	107	106.905094	100	107.8682
			109	108.904756	92.90	
Cd	Cadmium	48	106	105.906459	4.35	112.412
			108	107.904184	3.10	
			110	109.903006	43.47	
			111	110.904182	44.55	
			112	111.902757	83.99	
			113	112.904401	42.53	
			114	113.903358	100	
			116	115.904755	26.07	
In	Indium	49	113	112.904061	4.48	114.818
			115	114.903879	100	
Sn	Tin	50	112	111.904822	2.98	118.711
			114	113.902782	2.03	
			115	114.903346	1.04	
			116	115.901744	44.63	
			117	116.902954	23.57	
			118	117.901606	74.34	
			119	118.903309	26.37	
			120	119.902197	100	
			122	121.903440	14.21	
			124	123.905275	17.77	
Sb	Antimony	51	121	120.903818	100	121.760
			123	122.904216	74.79	
Te	Tellurium	52	120	119.904021	0.26	127.60
			122	121.903047	7.48	
			123	122.904273	2.61	
			124	123.902819	13.91	
			125	124.904425	20.75	
			126	125.903306	55.28	
			128	127.904461	93.13	
			130	129.906223	100	
I	Iodine	53	127	126.904468	100	126.904468

(continued)

Table A.5 (continued)

Atomic symbol	Name	Atomic No.	Mass No.	Isotopic mass	Isotopic comp.	Relative atomic mass
Xe	Xenon	54	124	123.905896	0.33	131.29
			126	125.904270	0.33	
			128	127.903530	7.14	
			129	128.904779	98.33	
			130	129.903508	15.17	
			131	130.905082	78.77	
			132	131.904154	100	
			134	133.905395	38.82	
			136	135.907221	32.99	
Cs	Cesium	55	133	132.905447	100	132.905447
Ba	Barium	56	130	129.906311	0.148	137.328
			132	131.905056	0.141	
			134	133.904503	3.371	
			135	134.905683	9.194	
			136	135.904570	10.954	
			137	136.905821	15.666	
			138	137.905241	100	
La	Lanthanum	57	138	137.907107	0.090	138.9055
			139	138.906348	100	
Ce	Cerium	58	136	135.907145	0.209	140.116
			138	137.905991	0.284	
			140	139.905434	100	
			142	141.909240	12.565	
Pr	Praseodymium	59	141	140.907648	100	140.907648
Nd	Neodymium	60	142	141.907719	100	144.24
			143	142.909810	44.9	
			144	143.910083	87.5	
			145	144.912569	30.5	
			146	145.913112	63.2	
			148	147.916889	21.0	
			150	149.920887	20.6	
Sm	Samarium	62	144	143.911995	11.48	150.36
			147	146.914893	56.04	
			148	147.914818	42.02	
			149	148.917180	51.66	
			150	149.917271	27.59	
			152	151.919728	100	
			154	153.922205	85.05	
Eu	Europium	63	151	150.919846	91.61	151.964
			153	152.921226	100	

(continued)

Table A.5 (continued)

Atomic symbol	Name	Atomic No.	Mass No.	Isotopic mass	Isotopic comp.	Relative atomic mass
Gd	Gadolinium	64	152	151.919788	0.81	157.25
			154	153.920862	8.78	
			155	154.922619	59.58	
			156	155.922120	82.41	
			157	156.923957	63.00	
			158	157.924101	100	
			160	159.927051	88.00	
Tb	Terbium	65	159	158.925343	100	158.925343
Dy	Dysprosium	66	156	155.924279	0.21	162.50
			158	157.924405	0.35	
			160	159.925194	8.30	
			161	160.926930	67.10	
			162	161.926795	90.53	
			163	162.928728	88.36	
			164	163.929171	100	
Ho	Holmium	67	165	164.930319	100	164.930319
Er	Erbium	68	162	161.928775	0.42	167.26
			164	163.929197	4.79	
			166	165.930290	100	
			167	166.932045	68.22	
			168	167.932368	79.69	
			170	169.935460	44.42	
Tm	Thulium	69	169	168.934211	100	168.934211
Yb	Ytterbium	70	168	167.933894	0.41	173.04
			170	169.934759	9.55	
			171	170.936322	44.86	
			172	171.936378	68.58	
			173	172.938207	50.68	
			174	173.938858	100	
			176	175.942568	40.09	
Lu	Lutetium	71	175	174.940768	100	174.967
			176	175.942682	2.66	
Hf	Hafnium	72	174	173.940040	0.46	178.49
			176	175.941402	14.99	
			177	176.943220	53.02	
			178	177.943698	77.77	
			179	178.944815	38.83	
			180	179.946549	100	
Ta	Tantalum	73	180	179.947466	0.012	180.9479
			181	180.947996	100	

(continued)

Table A.5 (continued)

Atomic symbol	Name	Atomic No.	Mass No.	Isotopic mass	Isotopic comp.	Relative atomic mass
W	Tungsten	74	180	179.946707	0.40	183.84
			182	181.948206	86.49	
			183	182.950224	46.70	
			184	183.950933	100	
			186	185.954362	93.79	
Re	Rhenium	75	185	184.952956	59.74	186.207
			187	186.955751	100	
Os	Osmium	76	184	183.952491	0.05	190.23
			186	185.953838	3.90	
			187	186.955748	4.81	
			188	187.955836	32.47	
			189	188.958145	39.60	
			190	189.958445	64.39	
Ir	Iridium	77	191	190.960591	59.49	192.217
			193	192.962924	100	
Pt	Platinum	78	190	189.959931	0.041	195.078
			192	191.961035	2.311	
			194	193.962664	97.443	
			195	194.964774	100	
			196	195.964935	74.610	
			198	197.967876	21.172	
Au	Gold	79	197	196.966552	100	196.966552
Hg	Mercury	80	196	195.965815	0.50	200.59
			198	197.966752	33.39	
			199	198.968262	56.50	
			200	199.968309	77.36	
			201	200.970285	44.14	
			202	201.970626	100	
			204	203.973476	23.00	
Tl	Thallium	81	203	202.972329	41.892	204.3833
			205	204.974412	100	
Pb	Lead	82	204	203.973029	2.7	207.2
			206	205.974449	46.0	
			207	206.975881	42.2	
			208	207.976636	100	
Bi	Bismuth	83	209	208.980383	100	208.980383
Th	Thorium*	90	232	232.038050	100	232.038050
U	Uranium*	92	234	234.040946	0.0055	238.0289
			235	235.043923	0.73	
			238	238.050783	100	

A.3 Carbon Isotopic Patterns

Provided no other element contributing to $M + 1$ is present, reading out the P_{M+1}/P_M ratio from a mass spectrum yields the approximate number of carbon atoms, n_C , from $n_C \approx (P_{M+1}/P_M) \times 91$. If $M + 1$ has an intensity of 24% of that of M , for example, we can calculate the presence of $(24/100) \times 91 \approx 22$ carbons.

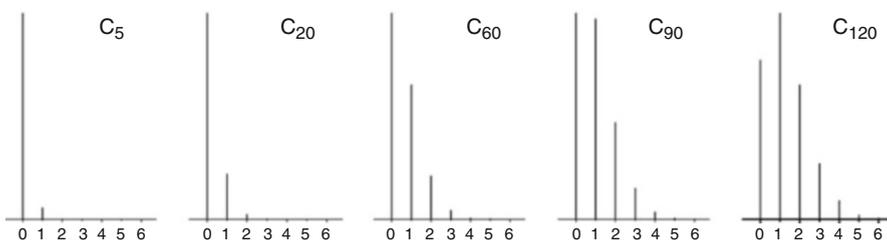


Fig. A.1 Calculated isotopic patterns for carbon. Note the steadily expanding width of the pattern as $X + 2$, $X + 3$, $X + 4$,... become visible. At about C_{90} the $X + 1$ peak reaches the same intensity as the X peak. At higher carbon number it becomes the base peak of the pattern

Table A.6 Calculated isotopic distributions for carbon

Number of carbons	X + 1	X + 2	X + 3	X + 4	X + 5
1	1.1	0.00			
2	2.2	0.01			
3	3.3	0.04			
4	4.3	0.06			
5	5.4	0.10			
6	6.5	0.16			
7	7.6	0.23			
8	8.7	0.33			
9	9.7	0.42			
10	10.8	0.5			
12	13.0	0.8			
15	16.1	1.1			
20	21.6	2.2	0.1		
25	27.0	3.5	0.2		
30	32.3	5.0	0.5		
40	43.2	9.0	1.3	0.1	
50	54.1	14.5	2.5	0.2	0.1
60	65.0	20.6	4.2	0.6	0.2
90	97.2	46.8	14.9	3.5	0.6
120 ^a	100.0	64.4	27.3	8.6	2.2

^aThe X peak has an intensity of 77.0% in that case

A.4 Chlorine and Bromine Isotopic Patterns

For halogens the isotopic peaks are separated by 2 u.

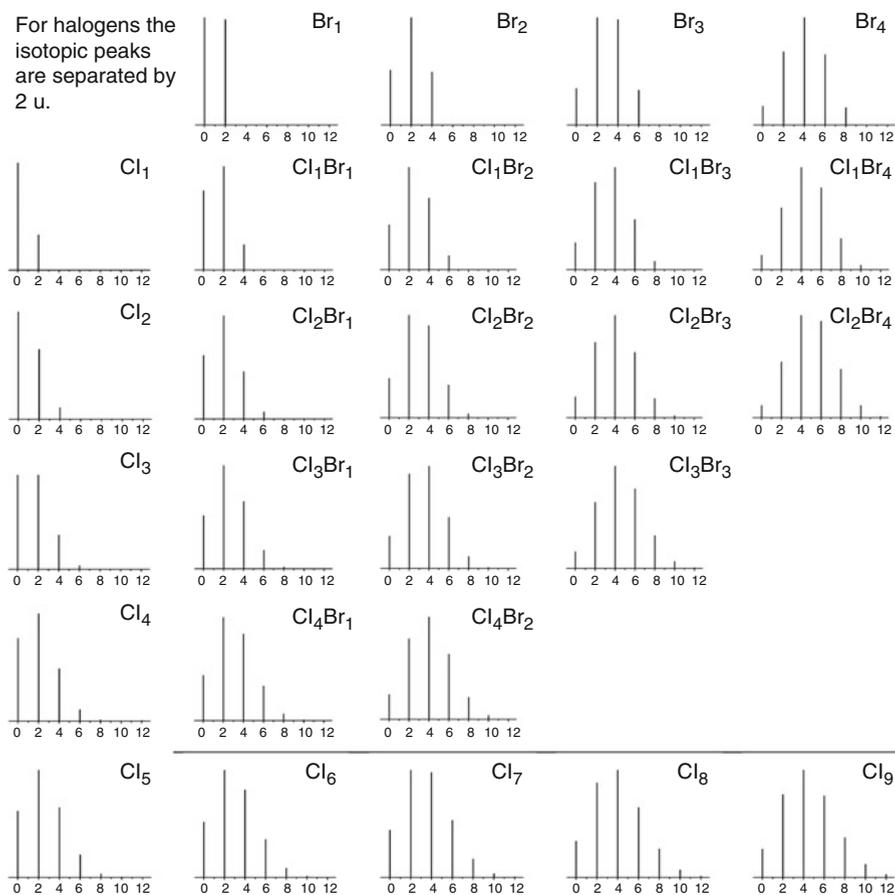


Fig. A.2 Calculated isotopic patterns for combinations of bromine and chlorine. The peak shown at zero position corresponds to the monoisotopic ion at m/z X. The isotopic peaks are then located at $m/z = X + 2, 4, 6, \dots$. The numeric value of X is given by the mass number of the monoisotopic combination, e.g., 70 u for Cl_2

A.5 Silicon and Sulfur Isotopic Patterns

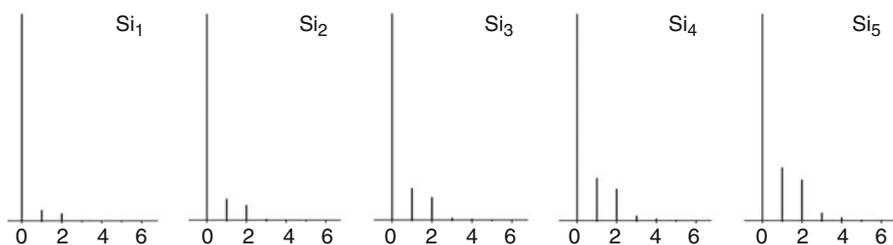


Fig. A.3 Isotopic patterns for silicon. The peak at zero position corresponds to the monoisotopic ion at m/z X. The isotopic peaks are then located at $m/z = X + 1, 2, 3, \dots$

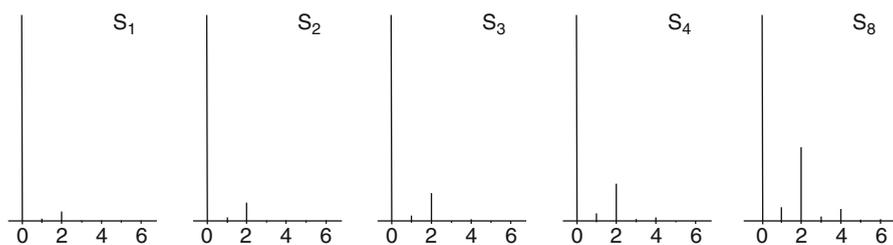


Fig. A.4 Isotopic patterns for sulfur. The peak at zero position corresponds to the monoisotopic ion at m/z X. The isotopic peaks are then located at $m/z = X + 1, 2, 3, \dots$

A.6 Reading Isotopic Patterns

This flow chart can be used as a guideline on how to read and interpret isotopic patterns. The procedure is relevant irrespective of the ionization method employed.

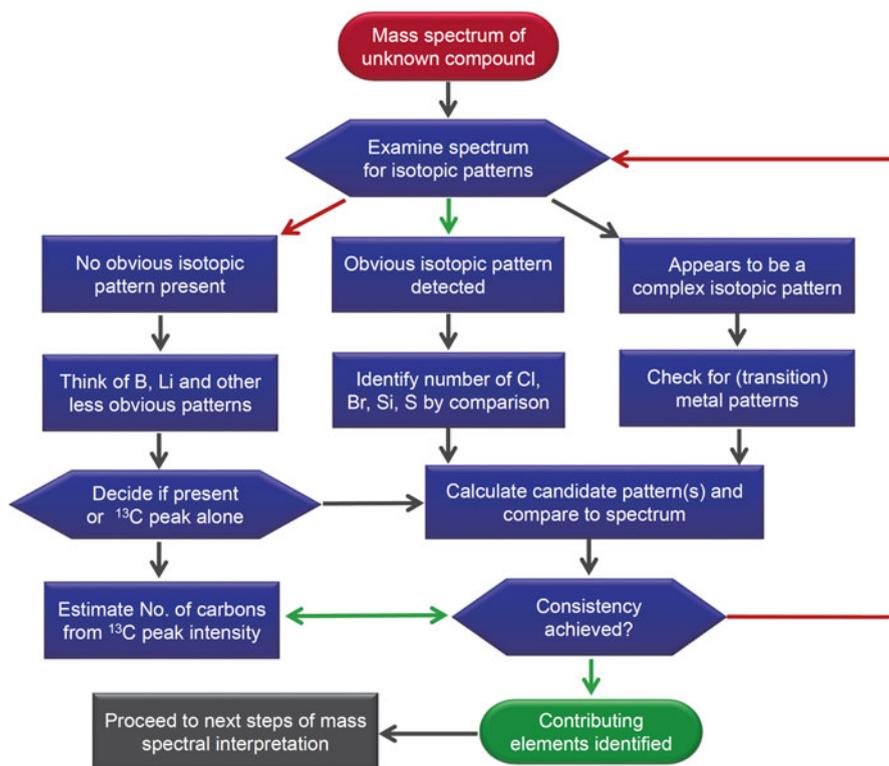


Fig. A.5 Guideline for the identification of contributing elements based on isotopic pattern analysis

A.7 Isotopologs and Accurate Mass

If isotopolog ions are resolved and sufficient mass accuracy is available, the distance between isotopic peaks can yield a new type of analytical information: the differences between isotopic masses are characteristic for certain elements.

Table A.7 Characteristic mass differences to identify the presence of elements

Pair of isotopes or modification	Δm [u]
${}^6\text{Li}$ vs. ${}^7\text{Li}$	1.0009
${}^{10}\text{B}$ vs. ${}^{11}\text{B}$	0.9964
${}^{12}\text{C}$ vs. ${}^{13}\text{C}$	1.0033
${}^{32}\text{S}$ vs. ${}^{34}\text{S}$	1.9958
${}^{35}\text{Cl}$ vs. ${}^{37}\text{Cl}$	1.9970
${}^{58}\text{Ni}$ vs. ${}^{60}\text{Ni}$	1.9955
${}^{63}\text{Cu}$ vs. ${}^{65}\text{Cu}$	1.9982
${}^{79}\text{Br}$ vs. ${}^{81}\text{Br}$	1.9980
${}^{191}\text{Ir}$ vs. ${}^{193}\text{Ir}$	2.0023
gain or loss of H	1.0078
gain or loss of H_2	2.0156

A.8 Characteristic Ions and Losses

Care should be taken when using tables of characteristic ions and neutral losses as the values listed represent only a minor fraction of the fragmentations possible.

Table A.8 Characteristic ion series and neutral losses

Ion series	m/z and $[M-X]^+$ ions	Remarks
Carbenium ions	15, 29, 43, 57, 71, 85, 99, 113, 127, 141, ...	Any alkyl group
Acylium ions	29, 43, 57, 71, 85, 99, 113, 127, 141, 155, ...	Aliphatic aldehydes, ketones, carboxylic acids and their derivatives
Immonium ions	30, 44, 58, 72, 86, 100, 114, 128, 142, 156, ...	Aliphatic amines
Oxonium ions	31, 45, 59, 73, 87, 101, 115, 129, 143, 157, ...	Aliphatic alcohols and ethers
Sulfonium ions	47, 61, 75, 89, 103, 117, 131, 145, 159, ...	Aliphatic thiols and thioethers
From benzyl	39, 51, 65, 77, 91	Phenylalkanes
From benzoyl	51, 77, 105	Aromatic aldehydes, ketones, carboxylic acids and derivatives
	$[M-16]^{++}$, $[M-30]^+$, $[M-46]^{++}$	Nitroarenes
	45, 60, 73, $[M-17]^+$, $[M-45]^+$	Carboxylic acids
	59, 74, 87, $[M-31]^+$, $[M-59]^+$	Methyl carboxylates
	73, 88, 101, $[M-45]^+$, $[M-73]^+$	Ethyl carboxylates
By McL	44	McL of aldehydes
	58	McL of methyl ketones
	60	McL of carboxylic acids
	59	McL of carboxylic acid amides
	74	McL of methyl carboxylates
	88	McL of ethyl carboxylates
Halogens	$[M-19]^+$, $[M-20]^{++}$	Fluorine compounds
	35, $[M-35]^+$, $[M-36]^{++}$	Chlorine compounds (Cl pattern)
	79, $[M-79]^+$, $[M-80]^{++}$	Bromine compounds (Br pattern)
	127, $[M-127]^+$, $[M-128]^{++}$	Iodine compounds
General losses	$[M-1]^+$	Loss of H^+ (strong $\rightarrow \alpha$ -cleavage)
	$[M-2]^{++}$	Loss of H_2
	$[M-3]^+$	Loss of H^+ and H_2
	$[M-15]^+$	Loss of methyl
	$[M-16]^{++}$	loss of O from nitroarenes
	$[M-17]^{++}$, $[M-17]^+$	Loss of ammonia from amines, loss of OH^+ from (<i>tert</i>)alcohols
	$[M-18]^{++}$	Loss of water from alcohols
$[M-19]^+$	Loss of F^+	

(continued)

Table A.8 (continued)

Ion series	m/z and $[M-X]^+$ ions	Remarks
	$[M-20]^{++}$	Loss of HF
	$[M-27]^{++}$	Loss of HCN from heterocycles or HNC from aromatic amines
	$[M-28]^{++}$	Loss of CO, C ₂ H ₄ or N ₂
	$[M-29]^+$	Loss of CHO [•] or C ₂ H ₅ [•]
	$[M-30]^{++}$	Loss of H ₂ CO from aromatic methyl ethers etc.; check for nitroarenes
	$[M-31]^+$	Loss of MeO [•]
	$[M-32]^{++}$	Loss of MeOH, O ₂ , (S)
	$[M-34]^{++}$	Loss of H ₂ S
	$[M-35/37]^+$	Loss of Cl [•]
	$[M-36/38]^{++}$	Loss of HCl
	$[M-42]^{++}$	Loss of CH ₂ CO or C ₃ H ₆
	$[M-43]^+$	Loss of CH ₃ CHO [•] or C ₃ H ₇ [•]
	$[M-44]^{++}$	Loss of CO ₂
	$[M-45]^+$	Loss of COOH [•] , EtO [•]
	$[M-46]^{++}$	Loss of HCOOH, EtOH or NO ₂
	$[M-48]^{++}$	Loss of SO from sulfoxides
	$[M-56]^{++}$	Loss of CH ₃ CHCO or C ₄ H ₈
	$[M-57]^+$	Loss of EtCHO [•] or C ₄ H ₉ [•]
	$[M-59]^+$	Loss of COOMe [•] or CH ₂ COOH [•]
	$[M-64]^{++}$	loss of SO ₂ from sulfolanones
	$[M-77]^+$	Loss of phenyl
	$[M-78]^+$	Loss of pyridyl
	$[M-79/81]^+$	Loss of Br [•]
	$[M-80/82]^{++}$	Loss of HBr
	$[M-91]^+$	Loss of benzyl or other C ₇ H ₇ [•]
	$[M-127]^+$	Loss of I [•] , rarely C ₁₀ H ₇ [•] (naphthyl)
	$[M-128]^{++}$	Loss of HI

A.9 Common Impurities

Table A.9 Recognizing common impurities by m/z

m/z	Source
18, 28, 32, 40, 44	Residual air and moisture
149, 167, 279	Phthalic acid esters (plasticizers)
149, 177, 222	Diethyl phthalate (plasticizers)
73, 147, 207, 281, 355, 429	Silicon grease or GC column bleed (Si_x isotopic pattern)
27, 29, 41, 43, 55, 57, 69, 71, 83, 85, 97, 99, 109, 111, 113, 125, 127, ..., up to m/z 500	Hydrocarbons from grease or from suspensions in paraffin
32, 64, 96, 128, 160, 192, 224, 256	Sulfur (S_x isotopic pattern)
51, 69, 119, 131, 169, 181, 219, 231, 243, 281, 317, 331, ...	Background from PFK

A.10 Identification of the Molecular Ion Peak

- The molecular ion must be the ion of highest m/z in the mass spectrum (besides the corresponding isotopic peaks).
- It has to be an odd-electron ion, $\text{M}^{+\bullet}$.
- Peaks at the next lower m/z must be explainable in terms of reasonable losses, i.e., of common radicals or molecules. Signals at $\text{M}-5$ to $\text{M}-14$ and at $\text{M}-21$ to $\text{M}-25$ point towards a different origin of the presumed $\text{M}^{+\bullet}$ (Table 6.11).
- Fragment ions may not show isotopic patterns due to elements that are not present in the presumed molecular ion.
- No fragment ion may contain a larger number of atoms of any particular element than the molecular ion does.

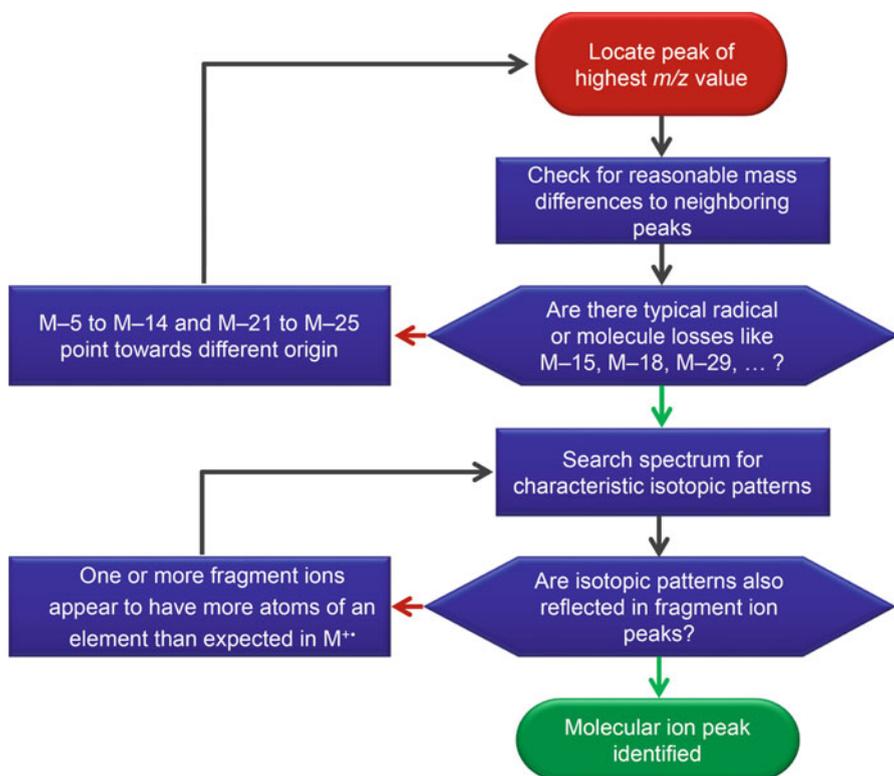


Fig. A.6 Flow chart showing decisions and criteria for the identification of the molecular ion peak

A.11 Rules for the Interpretation of Mass Spectra

- Identify the molecular ion! This is an important initial step, because it should derive the molecular composition (Sect. 6.7). If the EI spectrum does not allow for the identification of the molecular ion, soft ionization methods should be employed in addition.
- The mass differences between the presumed molecular ion and primary fragments must correspond to realistic chemical compositions (Sect. 6.7, Table 6.11).
- The calculated and experimental isotopic patterns have to agree with the molecular formula postulated (Sect. 3.2).
- The derived molecular formula must obey the nitrogen rule (Sect. 6.2.7). An odd-numbered m/z value of the molecular ion requires 1, 3, 5, ... nitrogen atoms to be contained, whereas an even m/z value belongs to 0, 2, 4, ... nitrogen atoms.
- Homolytic cleavages cause odd-numbered mass differences between fragment and molecular ion (Sect. 6.2.7). Rearrangement fragmentations cause even-

numbered mass differences. This rule toggles if odd numbers of nitrogen are contained in the neutral loss.

- In general, fragmentations obey the even-electron rule (Sect. 6.1.3). Odd-electron fragments from rearrangement fragmentations behave as if they were molecular ions of the respective smaller molecule.
- The competition of homolytic cleavages is governed by Stevenson's rule (Sect. 6.2.2). Thermodynamic stability of the pairs of products formed is decisive in selecting the preferred fragmentation route.
- Calculate $r + d$ to check formula proposals and to derive some structural characteristics (Sect. 6.4.4).
- Write down a fragmentation scheme, thereby carefully tracking the origin of primary fragment ions and of characteristic ions used for structure assignment. From the purely analytical point of view this is very useful. However, one should keep in mind that any proposed fragmentation scheme remains a working hypothesis unless experimental confirmation is available.
- Employ additional techniques, such as measurement of accurate mass (Sect. 3.5), tandem mass spectrometry, or other spectroscopic methods to crosscheck and to refine your assignments.

A.12 Systematic Approach to Mass Spectra

- Collect background information such as origin of the sample, presumed compound class, solubility, thermal stability, or other spectroscopic information.
- Write m/z labels for all relevant peaks and calculate mass differences between prominent peaks. Do you recognize characteristic ion series or mass differences that point to common neutral losses?
- Check which ionization method was used and examine the general appearance of the mass spectrum. Is the molecular ion peak intense (as with aromatic, heterocyclic, polycyclic compounds) or weak (as with aliphatic and multifunctional compounds)? Are there typical impurities (solvent, grease, plasticizers) or background signals (residual air, column bleed in GC-MS)?
- Is accurate mass data available for some of the peaks?
- Now, follow the above rules to proceed.
- Derive information on the presence/absence of functional groups.
- Be careful when using collections of common neutral losses and m/z -to-structure relationship tables – they're never comprehensive. Even worse, one tends to get stuck on the first assumption.
- Put together the known structural features and try to assign the structure to the unknown sample. Sometimes, only partial structures of the analyte can be derived or isomers cannot be distinguished.
- Crosscheck proposed molecular structure and mass spectral data. This is also recommended between the single steps of mass spectral interpretation.

- Are there reference spectra available (at least of similar compounds) either from the literature or from mass spectral databases (Sect. 5.9)?
- Never rigidly follow this scheme! Sometimes, a step back or forth may accelerate the process or help to avoid pitfalls (Fig. A.7).

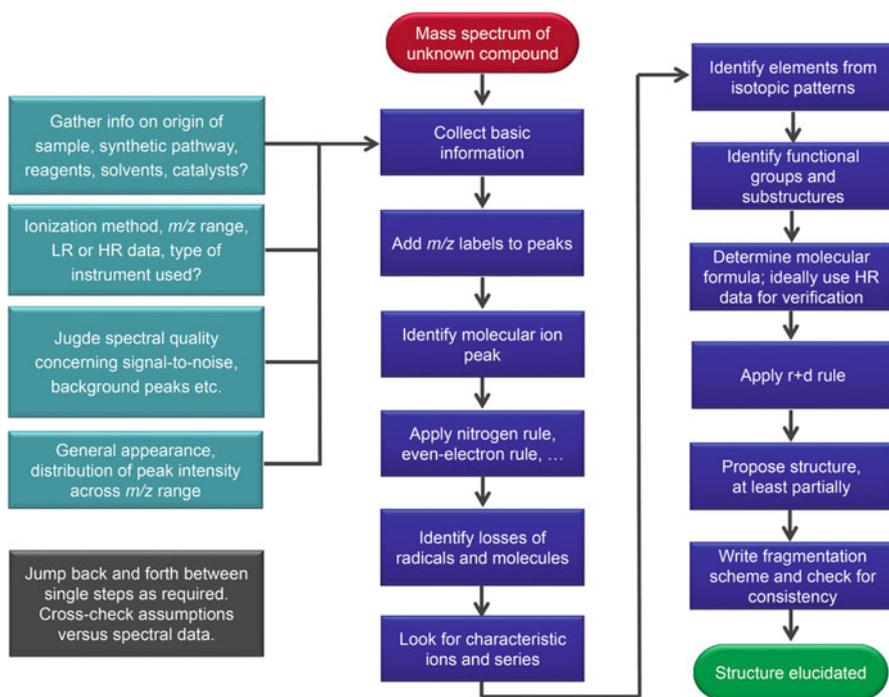


Fig. A.7 Guide to mass spectral structure elucidation

A.13 Method Selection Guide

This diagram (Fig. A.8) may help in selecting the right ionization method for analysis of a sample by MS. Often, there are several reasonable choices and it is advisable to make the best use possible of what is available at your local facility. MS results also depend on user input. Discuss your options with the MS staff at your facility.

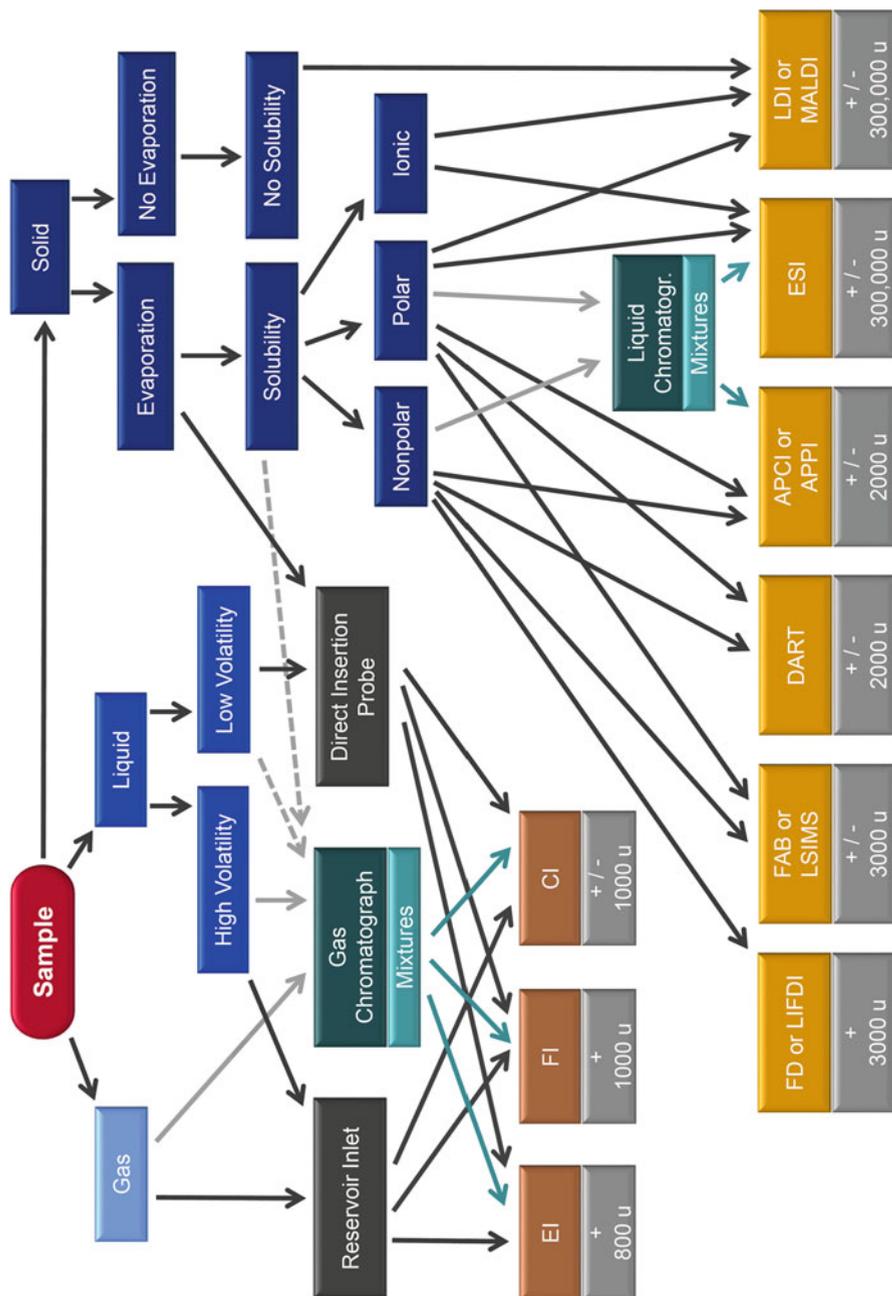


Fig. A.8 Method selection guide. Ionization methods with *bronze-colored* boxes require sample evaporation prior to ionization while methods with *orange* boxes accomplish transfer from the condensed phase along with ionization. The mass ranges are meant as guidelines and in no way define strict limits

A.14 How to Recognize Cationization

Soft ionization methods like FAB, FD, ESI, and MALDI often cause cationization by Na^+ , K^+ , Cs^+ , and Ag^+ . Especially Na^+ , K^+ adducts are almost omnipresent. Other techniques like APCI and DART often yield NH_4^+ adducts in addition or competition to molecular ions and/or protonated molecules (Fig. A.9). Searching a spectrum for those characteristic $\Delta(m/z)$ values reveals the true molecular mass. It is particularly useful to identify adducts by their accurate mass differences (Table A.10).

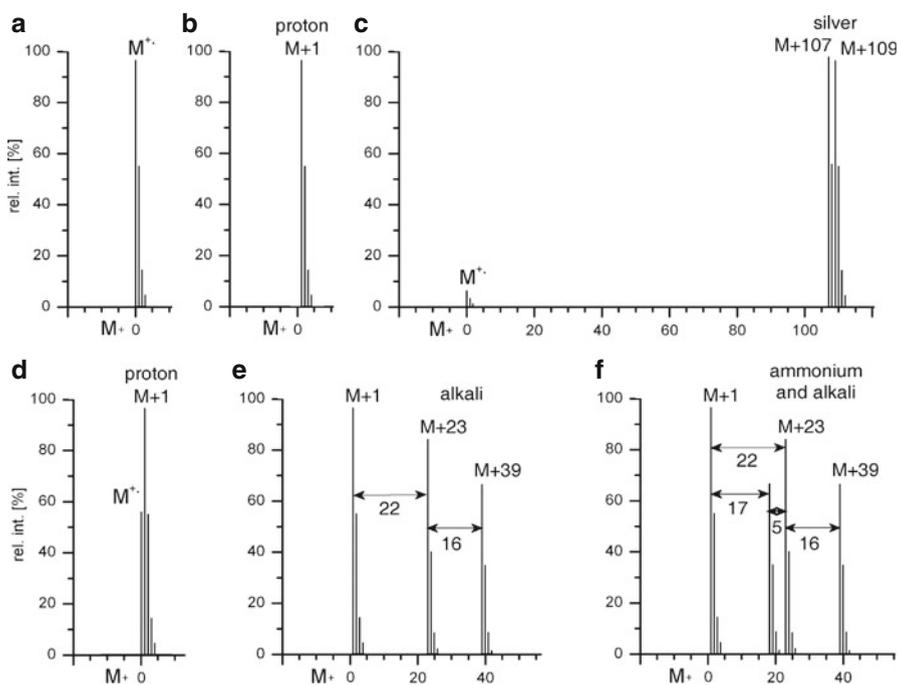


Fig. A.9 Signals representing the intact molecular mass in case of (a) molecular ion formation, (b) protonation, (c) silver cationization, (d) molecular ion and protonation, (e) protonation plus alkali cationization, and (f) protonation, ammonium plus alkali adduct formation. The relative abundances of the respective contributions are subject to wide variations. The abscissa gives the corresponding $M + X$ nominal mass value; artificial isotopic patterns are added for more realistic appearance

Table A.10 Characteristic mass differences to identify frequent cation and anion adducts

Pair of ions	Δm [u]
$M^{+\bullet}$ vs. $^{13}\text{C} - M^{+\bullet}$	1.0033
$M^{+\bullet}$ vs. $[M + \text{H}]^+$	1.0078
$[M + \text{H}]^+$ vs. $[M + \text{NH}_4]^+$	17.0265
$[M + \text{H}]^+$ vs. $[M + \text{Na}]^+$	21.9819
$[M + \text{H}]^+$ vs. $[M + \text{K}]^+$	37.9559
$[M + \text{Na}]^+$ vs. $[M + \text{K}]^+$	15.9739
<hr/>	
$M^{-\bullet}$ vs. $^{13}\text{C} - M^{-\bullet}$	1.0033
$[M - \text{H}]^-$ vs. $M^{-\bullet}$	1.0078
$[M - \text{H}]^-$ vs. $[M + \text{OH}]^-$	18.0106
$[M - \text{H}]^-$ vs. $[M + ^{35}\text{Cl}]^-$	35.9767
$[M - \text{H}]^-$ vs. $[M + \text{COOH}]^-$	46.0055
$[M - \text{H}]^-$ vs. $[M + ^{79}\text{Br}]^-$	79.9261
$[M - \text{H}]^-$ vs. $[M + \text{CF}_3\text{COO}]^-$	113.9928

A.15 Amino Acids

Table A.11 Amino acids (by order of residue mass)

Amino acid	Codes	Polarity	Charge ^a	Formula of residue	Residue nominal mass [u]	Residue accurate mass [u]
Glycine	Gly, G	nonpolar	O	C ₂ H ₃ NO	57	57.0520
Alanine	Ala, A	nonpolar	O	C ₃ H ₅ NO	71	71.0371
Serine	Ser, S	polar	O	C ₃ H ₅ NO ₂	87	87.0320
Proline	Pro, P	nonpolar	O	C ₅ H ₇ NO	97	97.0528
Valine	Val, V	nonpolar	O	C ₅ H ₉ NO	99	99.0684
Threonine	Thr, T	polar	O	C ₄ H ₇ NO ₂	101	101.0477
Cysteine	Cyc, C	nonpolar	O	C ₂ H ₅ NOS	103	103.0092
Leucine	Leu, L	nonpolar	O	C ₆ H ₁₁ NO	113	113.0841
Isoleucine	Ile, I	nonpolar	O	C ₆ H ₁₁ NO	113	113.0841
Asparagine	Asn, N	polar	O	C ₄ H ₆ N ₂ O ₂	114	114.0429
Aspartic acid	Asp, D	polar	–	C ₄ H ₅ NO ₃	115	115.0269
Glutamine	Gln, Q	polar	O	C ₅ H ₈ N ₂ O ₂	128	128.0586
Lysine	Lys, K	polar	+	C ₆ H ₁₂ N ₂ O	128	128.0950
Glutamic acid	Glu, E	polar	–	C ₅ H ₇ NO ₃	129	129.0426
Methionine	Met, M	nonp.	O	C ₅ H ₉ NOS	131	131.0405
Histidine	His, H	polar	(+)	C ₆ H ₇ N ₃ O	137	137.0589
Phenylalanine	Phe, F	nonpolar	O	C ₉ H ₉ NO	147	147.0684
Arginine	Arg, R	polar	+	C ₆ H ₁₂ N ₄ O	156	156.1011
Tyrosine	Tyr, Y	polar	O	C ₉ H ₉ NO ₂	163	163.0633
Tryptophan	Trp, W	nonpolar	O	C ₁₁ H ₁₀ N ₂ O	186	186.0793

^aNeutral amino acids are marked by O, basic AAs (+) tend to assume positive charge from protonation, acidic AAs (–) tend to be negative by dissociation of the acidic group

A.16 Nobel Prizes for Mass Spectrometry

Table A.12 Nobel laureates highly regarded in mass spectrometry

Laureate	Category and year	Prize motivation
Joseph John Thomson	Physics 1906	In recognition of the great merits of his theoretical and experimental investigations on the conduction of electricity by gases
Francis William Aston	Chemistry 1922	For his discovery, by means of his mass spectrograph, of isotopes in a large number of nonradioactive elements, and for his enunciation of the whole-number rule
Wolfgang Paul and Hans G. Dehmelt	Physics 1989	For the development of the ion trap technique
John B. Fenn jointly with Koichi Tanaka	Chemistry 2002	For their development of soft desorption ionization methods for mass spectrometric analyses of biological macromolecules

A.17 One Hundred Common Acronyms

ADC	Analog-to-digital converter
AE	Appearance energy
AMS	Accelerator mass spectrometry
APCI	Atmospheric pressure chemical ionization
API	Atmospheric pressure ionization
AP-MALDI	Atmospheric pressure matrix-assisted laser desorption/ionization
APPI	Atmospheric pressure photoionization
ASAP	Atmospheric solids analysis probe
B	Magnetic sector (as part of an instrument configuration)
CE	Capillary electrophoresis
CE	Charge exchange (equivalent to CT)
CI	Chemical ionization
CID	Collision-induced dissociation
CT	Charge transfer (formerly CE)
DART	Direct analysis in real time
DCI	Desorption (or direct) chemical ionization
DEI	Desorption (or direct) electron ionization
DE	Delayed extraction
DESI	Desorption electrospray/ionization
DIP	Direct insertion probe
E	Electrostatic sector (as part of an instrument configuration, cf. ESA)
EA	Electron affinity
EC	Electron capture
ECD	Electron capture dissociation

EDD	Electron detachment dissociation
EI	Electron ionization
ESA	Electrostatic analyzer (cf. E)
ESI	Electrospray ionization
ETD	Electron transfer dissociation
FAB	Fast-atom bombardment
FD	Field desorption
FI	Field ionization
FT-ICR	Fourier-transform ion cyclotron resonance
GB	Gas phase basicity
GC	Gas chromatography
GC-MS	Gas chromatography-mass spectrometry
GD	Glow discharge
HDX	Hydrogen–deuterium exchange
HR	High resolution
HV	High vacuum
HV	High voltage
ICP	Inductively coupled plasma
ICR	Ion cyclotron resonance
IE	Ionization energy
IMS	Ion mobility spectrometry
IR-MS	Isotope-ratio mass spectrometry
IR-MALDI	Infrared matrix-assisted laser desorption/ionization
IRMPD	Infrared multiphoton dissociation
KER	Kinetic energy release
LA	Laser ablation
LC	Liquid chromatography
LC-MS	Liquid chromatography-mass spectrometry (includes HPLC and UHPLC)
LDI	Laser desorption/ionization
LIFDI	Liquid injection field desorption/ionization
LIT	Linear quadrupole ion trap
LOD	Limit of detection
LR	Low resolution
LSIMS	Liquid secondary ion-mass spectrometry
MALDI	Matrix-assisted laser desorption/ionization
MCP	Microchannel plate
MID	Multiple ion detection
MIKES	Mass-analyzed ion kinetic energy spectroscopy
MS	Mass spectrometry (not to be used for ‘mass spectrometer’ or ‘mass spectrum’)
MS/MS	Mass spectrometry/mass spectrometry or tandem mass spectrometry
MRM	Multiple reaction monitoring
MUPI	Multiphoton ionization

nanoESI	Nano electrospray ionization
NCI	Negative-ion chemical ionization.
NICI	Negative-ion chemical ionization.
PA	Proton affinity
PCI	Positive-ion chemical ionization
PICI	Positive-ion chemical ionization
PIE	Pulsed ion extraction
PTR-MS	Proton transfer reaction-mass spectrometry
Py	Pyrolysis
Q	Linear quadrupole (as part of an instrument configuration)
q	RF-only linear quadrupole (as part of an instrument configuration)
QET	Quasi equilibrium theory
QIT	Quadrupole ion trap
RE	Recombination energy
REMPI	Resonance-enhanced multiphoton ionization
RF	Radio frequency
RIC	Reconstructed ion chromatogram
SEC	Size exclusion chromatography
SEM	Secondary electron multiplier
SIM	Selected ion monitoring
SIMS	Secondary-ion mass spectrometry
SRM	Selected reaction monitoring
SSMS	Spark source mass spectrometry
TI	Thermal ionization
TIC	Total ion chromatogram
TIMS	Thermal ionization mass spectrometry
TMP	Turbomolecular pump
TOF	Time-of-flight (analyzer)
TWIG	Traveling wave ion guide
UHR	Ultrahigh resolution
UHV	Ultrahigh vacuum
UV-MALDI	Ultraviolet matrix-assisted laser desorption/ionization.
YIKES	Well, after reading all that
ZEKE	Zero kinetic energy electron

Index

A

- Accumulation, of spectra, 849
- Accurate mass measurement, 116
- Activation energy of the reverse reaction, 57
- Acylium ions, 338
- ADC. *See* Analog-to-digital converter (ADC)
- ADI. *See* Ambient desorption/ionization (ADI)
- Adiabatic ionization, 38
- AE. *See* Appearance energy (AE)
- Alkali adduct ions, of carbohydrates, 686
- Allylic bond cleavage
- of alkenes, 360
 - isomerization prior to, 360
- α -cleavage
- of acetone, 332
 - of amines, ethers, and alcohols, 339
 - of halogenated hydrocarbons, 347
 - of ketones, 336
 - of thioethers, 346
- Ambient desorption/ionization (ADI), 780
- Ambient mass spectrometry, 780. *See also* Ambient desorption/ionization
- Ammonium adducts
- in APCI, 474
 - in DART, 811
- amu. *See* Atomic mass unit (amu)
- Analog-to-digital converter (ADC), 266
- Analysis of complex mixtures, 831
- Anion abstraction, 441
- APCI. *See* Atmospheric pressure chemical ionization (APCI)
- API. *See* Atmospheric pressure ionization (API)
- AP-MALDI. *See* Atmospheric pressure MALDI (AP-MALDI)
- Appearance energy (AE)
- definition, 42
 - determination, 70
- Appearance potential (AP). *See* Appearance energy (AE)
- APPI. *See* Atmospheric pressure photoionization (APPI)
- Array detector, 272
- ASAP. *See* Atmospheric pressure solids analysis probe (ASAP)
- Aspirin, analyzed by DESI, 788
- Aston, F.W., 3
- Atmospheric pressure chemical ionization (APCI), 471
- ion source, 471
 - negative ion formation, 475
 - positive ion formation, 472
 - spectra, 477
 - switching between methods, 480
 - on the way leading to ESI, 723
- Atmospheric pressure, comparison to vacuum ionization, 474
- Atmospheric pressure ionization (API), 470
- as collective term, 472, 723
 - interface for AP-MALDI, 703
- Atmospheric pressure ionization methods, 721
- Atmospheric pressure MALDI (AP-MALDI), 703
- Atmospheric pressure photoionization (APPI), 479
- relationship to ESI, 723
 - spectra, 482
 - switching between methods, 480
- Atmospheric pressure solids analysis probe (ASAP), 806
- applications, 806
 - polystyrene analysis, 807
 - setup of source, 806
- Atomic mass unit (amu), 90
- Atomic number, 86
- Atomic weight. *See* Relative atomic mass
- Atropa belladonna*, analyzed by DESI, 789
- Autoprotonation, 443
- Averaging, of spectra, 849

B

- Background subtraction, from spectra, 849
- Bar graph, representation of spectra, 14
- Base peak chromatogram (BPC), 16
- Base peak, definition, 11
- Benzylic bond cleavage, 354
 - phenylalkanes, 354
- Benzyl/tropylium isomerization, 356
- BEqQ, 255
- Bimolecular reactions
 - in APCI, 472
 - in DART, 810
- Blackbody infrared radiative dissociation (BIRD), 588
- Block copolymer, by MALDI-TOF-MS, 692
- Born-Oppenheimer approximation, 36
- Bottom-up protein analysis, 681
- BPC. *See* Base peak chromatogram (BPC)
- Bradbury-Nielsen gate, 556
- Breakdown graph, 71–72

C

- CA. *See* Collision-induced dissociation
- Calibration file, 123
- ²⁵²Californium plasma desorption (²⁵²Cf-PD), 638
- Capillary columns, in gas chromatography, 837
- Capillary zone electrophoresis (CZE), 728
- Capillary zone electrophoresis-mass spectrometry (CZE-MS), 831
- Carbenium ions, 338
 - stability of isomers, 365
- Carrier gas, for gas chromatography, 837
- CE. *See* Charge exchange
- CEM. *See* Detectors
- Center-of-mass collision energy, 547
- ²⁵²Cf-PD. *See* ²⁵²Californium plasma desorption (²⁵²Cf-PD)
- Characteristic ions, 338
- Charge deconvolution
 - display of spectra, 753
 - in ESI, 751
 - ESI of transferrin, 752
 - by high resolution, 754
- Charge deconvolution software, 752
- Charged-residue model, in ESI, 745
- Charge exchange. *See* Charge transfer
- Charge exchange chemical ionization
 - regio- and stereoselectivity, 459
 - selective ionization, 458
- Charge localization, 34
- Charge reduction electrospray, 756
- Charge retention, 333
- Charge transfer chemical ionization, 441, 486
 - energetics, 456
 - reagent gases, 457
- Charge transfer ionization, 455
- Chemical ionization (CI), 439
 - ion formation, 440
 - ion source, 441
 - reagent gas, 441
- Chemi-ionization, 444
- Chevron plate, 271
- Chirp excitation. *See* Fourier transform ion cyclotron resonance (FT-ICR)
- Chromatogram, 836
- Chromatographic column, 832
- Chromatographic resolution, 835
- Chromatography, origin of term, 832
- CI. *See* Chemical ionization (CI)
- CID. *See* Collision-induced dissociation (CID)
- CIT. *See* Cylindrical ion trap (CIT)
- Closed-shell ion. *See* Even-electron ion (EE)
- Cluster ions
 - in FAB-MS, 622
 - for mass calibration, 622
- Collisional activation. *See* Collision-induced dissociation
- Collisional cooling, 198
- Collisional focusing, 199
- Collisionally activated dissociation. *See* Collision-induced dissociation
- Collisional quenching, in APPI, 481
- Collision cell, 197, 546
- Collision gases, for CID, 549
- Collision-induced dissociation (CID), 545
 - in API interfaces, 735
- CO loss, 386
 - of arylmethylethers, 390
 - of carbonyl compounds, 393
 - differentiation from N₂, C₂H₄, 394
 - of phenols, 386
 - of quinones, 388–389
 - of transition metal carbonyl complexes, 393
- Column bleed, in GC-MS, 862
- Composite metastable peak, 391
- Comprehensive gas chromatography, 838
- Constant neutral loss scan (CNL), 563, 567
- Consumption of analyte, by MS in general, 10
- Conversion dynode, 271–272
- Cryopump, 274
- C-trap, 250
 - ion injection into Orbitrap, 250
- Curved-field reflectron, 557
- Cylindrical ion trap (CIT), 221

- CZE. *See* Capillary zone electrophoresis (CZE)
CZE-MS. *See* Capillary zone electrophoresis-mass spectrometry (CZE-MS)
- D**
- DAD. *See* Diode array detectors (DAD)
Dalton (Da), 11
DAPCI. *See* Desorption atmospheric pressure chemical ionization (DAPCI)
DAPPI. *See* Desorption atmospheric pressure photoionization (DAPPI)
DART. *See* Direct analysis in real time (DART)
Data reduction, 14, 15, 845
DBE. *See* Double bond equivalents (DBE)
DCI. *See* Desorption chemical ionization (DCI)
DE. *See* Delayed extraction (DE)
Deadly nightshade, analyzed by DESI, 788
Dead time, of a chromatographic column, 833
Dead volume, of a chromatographic column, 833
Degrees of freedom
 external, 40
 internal, 40
Degrees of freedom effect (DOF), 60
Delayed extraction (DE), 166
Deltamass, 142
Dendrimers, by MALDI-TOF-MS, 694
DEP. *See* Direct exposure probe
Deprotonation, in NICI, 461
DESI. *See* Desorption electrospray ionization (DESI)
Desorption atmospheric pressure chemical ionization (DAPCI), 780, 791
Desorption atmospheric pressure photoionization (DAPPI), 780, 792
Desorption chemical ionization (DCI), 311, 468
Desorption electron ionization (DEI), 468. *See also* Direct electron ionization (DEI)
Desorption electrospray ionization (DESI), 779, 782
 applications, 787
 ion formation, 786
 parameters, 783
 sources, 783
Desorption/ionization on silicon (DIOS), 694
Desorption sonic spray ionization (DeSSI), 780, 795
Detection limit, 18
Detectors, 266
 channel electron multiplier (CEM), 269
 channeltrons, 269
 in chromatography, 836
 conversion dynode, 271–272
 Faraday cup, 266
 focal plane detector (FPD), 272
 microchannel plate (MCP), 270
 post-acceleration, 271
 secondary electron multiplier (SEM), 268
Differential pumping, 545
Digital object identifiers (DOIs), in references, 5–6
Digitization, data points per peak, 693
Di-isotopic element, definition, 86
Diode array detectors (DAD), 836
DIOS. *See* Desorption/ionization on silicon (DIOS)
DIP. *See* Direct insertion probe (DIP)
Direct analysis in real time (DART), 779, 808
 applications, 815
 articles of daily use, 818
 color of discharge, 808
 configurations, 813
 detection of explosives, 817
 fruit flies, 817
 need for additional pumping stage, 813
 negative ion formation, 812
 operating conditions, 809
 polydimethylsiloxanes, 818
 positive ion formation, 810
 related ionization techniques, 813
 source, 808
 Vapor Interface, 813
 volatiles from garlic, 815
Direct electron ionization (DEI), 311
Direct exposure probe (DEP), 311, 468
Direct insertion probe (DIP), 302
 applications, 305
 AUDEVAP, 307
 automated, 307
 SIM automated probe, 307
Dissolved organic matter (DOM), 877
Distonic ions, 351
 formation, 352
Distribution coefficient, in chromatography, 833
DOF. *See* Degrees of freedom effect (DOF)
DOIs. *See* Digital object identifiers (DOIs)
DOM. *See* Dissolved organic matter (DOM)
Double α -cleavage
 of alicyclic compounds, 349
 identification of regioisomers, 350
Double bond equivalents (DBE), 359
Double-focusing. *See* Magnetic sector analyzer

- Doubly charged ion, in EI, 31
Drift tube ion mobility (DT-IMS), 265
Droplet jet fission, in ESI, 744
DT-IMS. *See* Drift tube ion mobility (DT-IMS)
Dual-target FAB probe (DTP), 632
Duoplasmatron source, 908
Duty cycle, 169
Dynamically harmonized ICR cell, 242
Dynamic range, 266
- E**
- EA. *See* Electron affinity (EA)
Easy ambient sonic-spray ionization. *See*
Desorption sonic spray ionization
Easy sonic spray ionization (EASI), 780
EBqQ, 255
EC. *See* Electron capture (EC)
ECNI. *See* Electron capture negative ionization
(ECNI)
EDD. *See* Electron detachment dissociation
(EDD)
EESI. *See* Extractive electrospray ionization
(EESI)
EHI. *See* Electrohydrodynamic ionization
(EHI)
EI. *See* Electron ionization (EI)
EIC. *See* Extracted ion chromatogram (EIC)
ELDI. *See* Electrospray-assisted laser
desorption/ionization (ELDI)
Electrohydrodynamic ionization (EHI),
724–725
Electron affinity (EA), 464
Electron attachment. *See* Electron capture (EC)
Electron capture (EC), 32, 462
creating thermal electrons, 465
cross section, 583
energetics, 463
ionization process, 463
spectra, 468
Electron capture detector (ECD), 836
Electron capture dissociation (ECD), 583
in ICR cells, 589
peptide cleavage, 584
posttranslational peptide modifications, 589
Electron capture negative ionization (ECNI),
462
versus NICI, 462
Electron detachment dissociation (EDD), 592
Electron impact. *See* Electron ionization (EI)
Electron ionization (EI), 30, 293
doubly charged ions, 30
fragmentation pathways, 56
fragment ions, 31
interpretation, 325
ionization process, 30
ion source, 294
contamination, 295
efficiency, 297
emission-controlled filament, 296
filament, 296
ionization chamber, 294
repeller, 294
low-energy, low-temperature, 314
mass spectral libraries, 316
measuring EI with DIP, 305
primary electrons, 296
rearrangement ions, 31
timescale, 52
Electron mass, in calculation of exact mass, 93
Electron monochromator, 66
Electron transfer dissociation (ETD), 591
Electrophilic addition, in PICI, 440, 486
Electrospray-assisted laser desorption/
ionization (ELDI), 797
Electrospray ionization (ESI), 71
analytes for ESI, 766
charge deconvolution, 751
charge reduction, 756
compared to APCI and APPI, 768
conventional *vs.* nanoESI, 737
design of sprayers, 727
disintegration of droplets, 744
formation of a spray, 741
high-mass up to 1 μ , 764
interface designs, 727
ion formation, 745
ionic metal complexes, 758
ion source/interface, 726
milestones leading to, 723
oligonucleotides and DNA, 759
oligosaccharides, 762
principle, 725
for protein complexes, 765
for pseudo-rotaxanes, 762
sample consumption, 768
small molecules, 757
surfactants, 759
switching between methods, 479
Taylor cone, 741
types of ions, 767
versatile interface, 471
Electrostatic analyzer (ESA), 181
energy dispersion, 182
Electrostatic sector. *See* Electrostatic analyzer
Elimination of carbon monoxide. *See* CO loss

- Elution, in chromatography, 834
Emitter heating current (EHC), 518
End cap electrodes. *See* Quadrupole ion trap (QIT)
Endgroup of polymer, determination, 691
Energy-sudden methods. *See* MALDI, FAB
ESI interface. *See* Electrospray ionization
ETD. *See* Electron-transfer dissociation (ETD)
70 eV EI, 39
Even-electron ion (EE), 31, 326
Even-electron rule, 329
Exact mass, definition, 93
External ion sources
 in FT-ICR-MS, 243
 for quadrupole ion trap, 222
External mass calibration, 124
Extracted ion chromatogram (EIC), 15
Extractive electrospray ionization (EESI), 780, 796
- F**
FAB. *See* Fast atom bombardment (FAB)
Faraday cup. *See* Detectors
FAST. *See* Fragment analysis and structural TOF (FAST)
Fast atom bombardment (FAB), 614, 625, 640
 accurate mass, 632
 criteria for the liquid matrix, 625
 gas, 617
 gun, 616
 high-mass analytes, 631
 ion formation, 621, 623
 ionic analytes, 629
 ion source, 616
 low-temperature (LT) FAB, 633
 low-to medium polarity analytes, 627
 matrix, 624
 matrix spectra, 626
 peptide sequencing, 635
 role of the liquid matrix, 624
 side-reactions, 626
 target, 620
 types of ions, 636
Fast GC-MS, 863
FD. *See* Field desorption (FD)
FFR. *See* Field-free region (FFR)
FI. *See* Field ionization (FI)
FID. *See* Flame ionization detector (FID)
Field anode/emitter. *See* FI/FD ion source
Field asymmetric ion mobility (FAIMS), 265
Field desorption (FD), 497
 best anode temperature (BAT), 518
 cationization, 511
 cluster ions, 514
 emitter activation, 502
 emitter handling, 504
 emitter heating current (EHC), 503
 field-induced desolvation, 512
 ion evaporation, 512
 ionic analytes, 515
 liquid injection field desorption ionization (LIFDI), 522
 protonation, 511
 spectra, 509
 surface mobility, 509
 wire emitters, 501
Field-free region (FFR), 542, 545, 559
Field ionization (FI), 497
 electric field strength, 498
 emitter activation, 502
 field emitter/field anode, 499
 field-induced dissociation, 507
 mass spectra, 505
 [M+H]⁺ ions, 506
 multiply charged ions, 506
 post-ionization, 506
 process, 498
 wire emitters, 501
FI/FD ion source, 499
 counter electrode, 499
 field emitter, 499
Flame ionization detector (FID), 836
Fourier transformation. *See* Fourier transform
 ion cyclotron resonance (FT-ICR)
Fourier transform ion cyclotron resonance (FT-ICR), 225
 axial trapping, 237
 cyclotron frequency, 226
 cyclotron motion, 227
 Fourier transformation, 239
 free induction decay, 239
 frequency domain, 239
 frequency sweep (chirp), 236
 image current detection, 240
 infrared multiphoton dissociation (IRMPD), 584
 principle, 226
 stored waveform inverse Fourier transform (SWIFT), 236
 sustained off-resonance irradiation (SORI), 581
 time domain, 239
FPD. *See* Detectors
Fragment analysis and structural TOF (FAST), 557

- Fragmentation pathways of peptide ions,
peptide sequencing, 681
- Fragment ion peaks, definition, 11
- Fragment ions, definition, 11
- Franck-Condon factor, 36–37
- Franck-Condon principle, 36
- FT-ICR. *See* Fourier transform ion cyclotron
resonance (FT-ICR)
- FT-MS, 245
- Full width at half maximum (FWHM), 113
- G**
- γ -H shift with β -cleavage. *See* McLafferty
rearrangement (McL)
- Gas chromatography (GC), 832, 837
chromatograms, 14
columns
fused silica capillaries, 860
narrow bore capillaries, 864
- Gas chromatography-mass spectrometry
(GC-MS), 831
- Gas chromatography-mass spectrometry
coupling, 833
derivatization, 861
fast GC-MS, 864
narrow-bore columns, 864
- Gas-liquid chromatography. *See* Gas
chromatography
- Gas phase basicity (GB), 73
- GC. *See* Gas chromatography (GC)
- GC \times GC. *See* Comprehensive gas
chromatography
- GC-MS. *See* Gas chromatography-mass
spectrometry (GC-MS)
- Gradient, solvent composition in LC, 842
- Gummy bears, by MALDI-TOF-MS, 686
- H**
- HCN loss, 421, 423
- HDX. *See* Hydrogen-deuterium exchange
(HDX)
- Height equivalent of a theoretical plate
(HETP), 835
- Helicobacter pylori*, proteins by ESI, 764
- Heterocyclic compounds, 416
aromatic heterocycles, 423
aromatic *N*-heterocycles, 421
HCN loss, 421
saturated heterocycles, 416
- Heterolytic bond dissociation, 43
- HETP. *See* Height equivalent of a theoretical
plate (HETP)
- High energy collisions, 549
- High-performance liquid chromatography
(HPLC), 840
- High-pressure liquid chromatography (HPLC),
840
- High-resolution, 115
- High-resolution SIM (HR-SIM), 850, 858
- Histogram. *See* Bar graph
- H₂O loss, of alkanols, 95
- Homolytic bond cleavage, *k*(E) functions, 52
- Homolytic bond dissociation, 43
- Hot hydrogen atom model, peptide cleavage by
ECD, 586
- HR-MS, in FAB/LSIMS, 632
- Hybrid instruments, 254, 265
- Hydrogen-deuterium exchange (HDX), 596
- Hypenated methods, 831
- I**
- IE. *See* Ionization energy (IE)
- IEM. *See* Ion evaporation model (IEM)
- Image current detection, in ICR-MS, 230
- Imaging mass spectrometry. *See* Mass spectral
imaging (MSI)
- Immonium ions, 339, 342
- IM-MS. *See* Ion mobility-mass spectrometry
(IM-MS)
- IM-TOF-MS hybrid, 261
- INC. *See* Ion-neutral complexes (INC)
- Infrared matrix-assisted laser desorption/
ionization (IR-MALDI), 663
- Infrared multiphoton dissociation (IRMPD),
582, 584
of deprotonated ganglioside, 587
in FT-ICR cells, 587
in quadrupole ion traps, 584
- Infrared photodissociation spectroscopy
(IRPD), 588
- Injector, in gas chromatography, 837
- Inlet. *See* Inlet system
- Inlet system, 300
direct exposure probe (DEP), 310
direct insertion probe (DIP), 302
liquid introduction system, 301
reservoir inlet, 301
sample vials for DIP, 303
- In-source decay (ISD), 557, 688
- Intermolecular reactions, 74
- Internal energy, 38
consequences, 56
influence on rate constants, 48
randomization, 45
- Internal mass calibration, 128
- Interpretation of EI mass spectra, 325
- Ion beam, 154

- Ion-dipole interactions, 76
Ion evaporation model (IEM), in ESI, 745
Ion funnel, 731
Ion guides. *See* RF-only quadrupole
Ionization cross section, 39
Ionization efficiency, 39
Ionization energy (IE)
 definition, 34
 determination, 65
Ionization potential (IP). *See* Ionization energy
Ion mobility-mass spectrometry (IM-MS),
 257
Ion mobility Q-TOF, 264
Ion mobility, separation, 259–260
Ion mobility spectrometry (IMS), 257
Ion mobility spectrometry-mass spectrometry,
 applications, 869
Ion-molecule reactions, 76, 595
 role in chemical ionization, 440
 in tandem MS, 541
Ion-neutral complexes (INC), 77, 405
 electrostatic attraction, 406
 evidence, 406
 as intermediate, 77
 intermediates of onium reaction, 403
 of radical ions, 408–409
 reorientation criterion, 408
Ion-pair formation, in NICI, 461
Ion source, simple implementation, 154
Ion spray. *See* Pneumatically assisted ESI
Ion trajectory calculations, 294
IRMPD. *See* Infrared multiphoton dissociation
 (IRMPD)
IR-MS. *See* Isotope ratio mass spectrometry
 (IR-MS)
IRPD. *See* Infrared photodissociation
 spectroscopy (IRPD)
ISD. *See* In-source decay (ISD)
Isobaric ions, 338
Isotope dilution, 857
Isotope effect, 60
 determination, 62
 intermolecular, 60
 intramolecular, 60
 kinetic, 60–61
 primary, 61
 secondary, 64
Isotope pattern. *See* Isotopic pattern
Isotope ratio mass spectrometry (IR-MS), 93,
 890
Isotope ratios, determination, 889
Isotopes, definition, 86
Isotopic abundance, representation, 87
Isotopic compositions. *See* Isotopic abundance
Isotopic distribution. *See* Isotopic pattern
Isotopic enrichment, 110
Isotopic ions, 98
Isotopic labeling, 112
Isotopic mass, definition, 90, 116
Isotopic molecular ion, 98
Isotopic pattern, 88, 95
 average molecular mass, 137
 calculation, 95
 carbon, 95
 effect of charge state, 140
 effect of resolution, 139
 halogens, 98
 linear TOF, 160
 of multiply charged ions, 159
 oxygen, silicon, sulfur, 104
 polyisotopic elements, 102, 106, 109
 at very high resolution, 132
- K**
Kendrick mass scale, 143
KER. *See* Kinetic energy release (KER)
 $k(E)$ function, 50
Kinetic energy release (KER), 58, 561
Kinetic method, for detn. of GB, 597
Kinetic shift, 71
Kingdon trap, 247
- L**
Laboratory frame of reference, 547
Ladder sequencing. *See* Peptide sequencing
Laser ablation electrospray ionization
 (LAESI), 799
Laser desorption/ionization (LDI), 675
 applications, 675
LC. *See* Liquid chromatography (LC)
LC-MS, Liquid chromatography–mass
 spectrometry (LC–MS)
LDI. *See* Laser desorption/ionization (LDI)
Limit of detection (LOD), 18, 857
Limit of quantitation (LOQ), 857
Linear quadrupole analyzer, 193
 hyperbolic vs. cylindrical rods, 196
 principle, 190–191
 properties, 190
 triple quadrupole, 566
 unit resolution, 196
Linear quadrupole ion trap (LIT), 201
Liquid chromatography (LC), 832
 chromatograms, 14

- Liquid chromatography-mass spectrometry (LC-MS), 831
- Liquid chromatography-mass spectrometry coupling, interfaces, 867
- Liquid injection field desorption ionization (LIFDI). *See* Field desorption
- Liquid matrix, in FAB/LSIMS, 614
- Liquid secondary ion mass spectrometry (LSIMS), 614
- ion source, 620
 - primary ions, 620
- LIT. *See* Linear quadrupole ion trap (LIT)
- LIT-ICR, 254, 256
- Localization of double bonds, 362
- Lock mass, in SIM, 850
- LOD. *See* Limit of detection (LOD)
- Loose transition state, 52
- LOQ. *See* Limit of quantitation (LOQ)
- Lorentz force, 178, 226
- Low-energy collisions, 549
- Low-energy EI spectra, 314
- Low-temperature EI spectra, 314
- LSIMS. *See* Liquid secondary ion mass spectrometry (LSIMS)
- M**
- M⁺. *See* Molecular ion (M⁺)
- Magnetic sector analyzer
- Bainbridge-Jordan, 183
 - double-focusing, 183
 - forward geometry, 185
 - four-sector, 564
 - lamination of the yoke, 187
 - linked scans, 562
 - magnet scan, 183
 - Mattauch-Herzog, 183
 - Nier-Johnson, 183
 - principle, 179
 - reversed geometry, 185
 - setting resolution, 186
 - tandem MS, 559
- Magnetic sector instrument. *See* Magnetic sector analyzer
- Magnetic sector-*oa*TOF, 254
- Magnetic sector-QIT, 254
- Magnetic sector-quadrupole hybrid, 254
- Main beam, attenuation in CID, 551
- MALDESI. *See* Matrix-assisted laser desorption electrospray ionization (MALDESI)
- MALDI. *See* Matrix-assisted laser desorption/ionization (MALDI)
- Mass accuracy, 119
- limits, 121
 - specification, 129
- Mass-analyzed ion kinetic energy spectrometry (MIKES), determination of KER, 561–563
- Mass-analyzed ion kinetic energy spectrum (MIKES), 560
- Mass-analyzed threshold ionization (MATI), 68
- Mass analyzer, 151
- ideal, 153
- Mass calibration, 123
- compound, 123
 - reference list, 124
- Mass defect. *See* Mass deficiency
- Mass deficiency, 118
- Mass-energy equivalence, 117
- Massive cluster impact (MCI), 614, 637
- Mass number, 86
- in definition of m/z , 10
- Mass reference compound. *See* Mass calibration, compound
- Mass reference list, 124
- Mass resolving power, minimum for separation of isotopic peaks, 757
- Mass-selective detector (MSD), 836
- Mass spectral imaging (MSI), 697
- Mass spectrograph, 180
- term, 8
- Mass spectrometer, 18
- components of, 9
 - term, 8
- Mass spectrometry
- basic principle, 8
 - relevance and uses, 1
 - term, 8
- Mass spectrometry/mass spectrometry. *See* Tandem mass spectrometry
- Mass spectroscopy. *See* Mass spectrometry
- Mass spectrum, definition, 11
- Mass-to-charge ratio (m/z), definition, 10
- Mathieu equations, 192, 213
- MATI. *See* Mass-analyzed threshold ionization (MATI)
- Matrix-assisted laser desorption electrospray ionization (MALDESI), 798
- Matrix-assisted laser desorption/ionization (MALDI), 652
- biotyping, 678
 - carbohydrates, 686
 - cationization, 670
 - characteristic fingerprint, 678

- delayed extraction, 653
dendrimer analysis, 694
desalting/cation exchange, 672, 689
detection limit, 705
expansion of plume, 657
for gummy bears, 686
imaging, 697
 fingermarks, 700
 instrumentation, 698
 lateral resolution, 698
 tissue, 698
ion formation, 654, 660
ion source, 652
laser fluence, 654
laser irradiance, 654
laser spot size, 655
MALDI target, 667
matrices in IR-MALDI, 663
matrices in UV-MALDI, 663
matrix spectra, 666
oligonucleotides and DNA, 689
oligosaccharide structures, 687
polymer endgroups, 692
role of the matrix, 663
sample holder, 667
sample introduction, 667
sample load, 705
sample preparation, 667
solvent-free preparation, 674
synthetic polymers, 690
thin layer technique, 669
tissuotyping, 700
types of ions in LDI/MALDI, 706
 as vacuum ionization technique, 659
MBSA. *See* Molecular beam solid analysis (MBSA)
MCI. *See* Massive cluster impact (MCI)
McLafferty rearrangement (McL), 370
 of aldehydes and ketones, 371
 of aromatic hydrocarbons, 376
 of carboxylic acids and derivatives, 373–374
 concerted/stepwise, 371
 with double hydrogen transfer, 379
 even-electron analogy, 398
 frequent product ions, 377
 requirements, 371
 role of the γ -hydrogen, 373
MCP. *See* Detectors
Measurement, running EI with DIP, 306
Memory effect, 315
Metastable dissociation, 688
Metastable ions, 53, 557
 in linear TOF, 161
 in tandem MS, 545
Methane, C-H bond activation by Ni ions, 596
Mobile applications, 220
Molecular beam solid analysis (MBSA), 614, 615, 625, 640
Molecular ion (M^{+}), 30, 326
 criteria, 368–369
 definition, 11
 recognition, 368
 writing conventions, 357
Molecular ion peak, definition, 11
Molecular weight. *See* Relative molecular mass
Monoisotopic elements, definition, 86
Monoisotopic mass, definition, 91
Most abundant mass, 98
Mouse liver tissue, analyzed by DESI, 789
MRM. *See* Multiple reaction monitoring (MRM)
MSD. *See* Mass-selective detector (MSD)
MSI. *See* Mass spectral imaging (MSI)
 MS^n , 569
Multiple ion detection (MID). *See* Selected ion monitoring (SIM)
Multiple reaction monitoring (MRM), 852
Multiplexing, 865
Multiply charged ions, isotopic patterns, 140
MULTUM Linear plus, 171
 resolving power, 171
- N**
Nano-assisted laser desorption/ionization, 696
Nano-electrospray (nanoESI), 737
 chip-based, 740
 droplet size, 737
 memory effects, 739
 spray capillaries, 737
Negative-ion chemical ionization (NICI), 442, 461
Neutral, detection in linear TOF, 161
Neutralization-reionization mass spectrometry (NR-MS), 599
NICI. *See* Negative-ion chemical ionization (NICI)
“Nier-type” ion source, 296
NIST/EPA/NIH Mass Spectral Database, 316
Nitroarenes, 415
Nitrogen phosphorus detector (NPD), 836
Nitrogen rule, 343
 effect of autoprotonation, 443

- Nominal mass
 definition, 88
 deviations, 118
- Nonergodic process, 586
- Non-targeted analysis, 851
- Nozzle/skimmer CID. *See* Skimmer CID
- Nozzle-skimmer system, in ESI source, 727
- NPD. *See* Nitrogen phosphorus detector (NPD)
- NR-MS. *See* Neutralization-reionization mass spectrometry (NR-MS)
- Nucleon number, 86. *See also* Mass number
- Nucleophilic addition, in NICI, 461
- Number-average molecular weight, of polymers, 691
- Number of charges, in definition of m/z , 10
- O**
- oaTOF. *See* Orthogonal acceleration TOF (oaTOF)
- Odd-electron ion (OE), 31, 326
- Oil diffusion pump, 274
- Oligosaccharides, of a gummy bear, 687
- Omegatron, 228
- Onium ions, 398
 immonium ions, 398
 McLafferty rearrangement, 398, 399
 onium reaction, 398, 403
 oxonium ions, 398
 sulfonium ions, 398
- Open-shell ion, 31. *See also* Odd-electron ion (OE)
- Orbitrap, 246
 vs. FT-ICR, 249
 ion injection, 249
 as part of a hybrid, 251–252
 principle of operation, 247
 resolving power, 249
- Orbitrap Fusion, 256
- Organic salts, EI mass spectra, 397
- Ortho effect. *See* Ortho elimination
- Ortho elimination, 410
 of aromatic molecular ions, 411
 of even-electron ions, 413
 of nitroarenes, 416
- Orthogonal acceleration TOF (oaTOF), 167
- Over-the-counter drug, analyzed by DESI, 788
- Oxonium ions, 340, 345
- Paracell, 243
- Parasite cells, MALDI biotyping, 678
- PD. *See* 252 Californium plasma desorption
- PDB standard, 93
- Peak capacity, 835
- Peak shapes, and KER, 562
- Penning cell. *See* Penning trap
- Penning ionization, 32
 in ambient MS, 812
 in DART-MS, 810
 in GD-MS, 899
- Penning trap, for ICR, 241
- Peptide backbone cleavages, 683
- Peptide fragmentation, in tandem MS, 683
- Peptide mass map, 681
- Peptide sequencing, 635
- Perfluorokerosene (PFK), 301
 mass calibration in EI, 124
- Perfluorokerosene, ECNI spectrum, 467
- Perfluorotributylamine (PFTBA), 124, 301
- PES. *See* Photoelectron spectroscopy (PES)
- PFK. *See* Perfluorokerosene
- PFTBA. *See* Perfluorotributylamine (PFTBA)
- Photodissociation, in APPI, 481
- Photoelectron spectroscopy (PES), 68
- Photoexcitation, in APPI, 480
- Photoionization (PI)
 in APPI, 481
 for determination of IEs, 66
 process, 66
- Physical quantities, units for, 21, 927
- PI. *See* Photoionization (PI)
- PICI. *See* Positive-ion chemical ionization (PICI)
- PIE. *See* Pulsed ion extraction (PIE)
- Pneumatically assisted ESI, 727
- Polydispersity, of polymers, 691
- Polyisotopic elements, definition, 87
- Polymer endgroup determination, by MALDI-TOF-MS, 692
- Positive-ion chemical ionization (PICI), 440, 442, 486
 ammonia reagent gas, 450
 isobutane reagent gas, 450
 methane reagent gas, 444, 448
- Post-acceleration detectors. *See* Detectors
- Post-source decay (PSD), 557, 688
- ppb (parts-per-billion), 120
- ppm (parts-per-million), 120
- Precursor ion scans, 563, 567
- Product ion scan, 567
- Profile data, representation of spectra, 14
- Proteomics, 681
- P**
- PA. *See* Proton affinity (PA)
- Parabola spectrograph, 3

- Proton affinity (PA), 73, 446
Protonation
 in CI, 440
 in PICI, 440
Proton transfer, in CI, 440, 486
PSD. *See* Post-source decay (PSD)
Pulsed ion extraction (PIE), 166
Pyrolysis DCI, 468
Pyrolysis mass spectrometry (Py-MS), 312
- Q**
QET. *See* Quasi-equilibrium theory (QET)
Qh-ICR, 256
QIT. *See* Quadrupole ion trap (QIT)
QITTOF, 254
QqICR, 255
QqLIT, 254
Qq-TOF hybrids, 255
Quadrupole analyzer. *See* Linear quadrupole analyzer
Quadrupole ion trap (QIT), 210
 automatic gain control, 217
 axial modulation, 216–217
 mass-selective instability, 215
 mass-selective stability, 214
 MSⁿ, 569
 nonlinear resonances, 217–218
 principle, 211
 resonant ejection, 215
 shape of electrodes, 211
 trajectories, 214
Quadrupole mass filter. *See* Linear quadrupole analyzer
Quantitation, 855
 calibration curve, 856
 external standardization, 856
 internal standardization, 857
 isotope dilution, 857
Quasi-equilibrium theory (QET), 47
 basic assumptions, 48
Quasi-molecular ions, 441
- R**
Radical ion, 30, 326
Radical-site initiated process, 333
Rapid evaporative ionization mass spectrometry (REIMS), 801
 setup, 801
 spectra, 801
 in surgeries, 801
Rate constants, 48
 of bi-and trimolecular reactions, 75
 meaning, 50
Rayleigh limit, 725, 744
RDA. *See* Retro-Diels-Alder reaction (RDA)
Reagent gas, in chemical ionization, 440
Reagent ions, in chemical ionization, 440
Rearrangement fragmentation, *k*(E) functions, 52
Recombination energy, 456
Reconstructed ion chromatogram (RIC), 15, 308, 845
Rectilinear ion trap (RIT), 220
Reduced mobility, in IMS, 259
Reference inlet system. *See* Reservoir inlet system
Reflector, in TOF-MS, 163–164
Reflectron. *See* Reflector
REIMS. *See* Rapid evaporative ionization mass spectrometry (REIMS)
Relative atomic mass
 definition, 91
 variations, 93
Relative intensity, definition, 11
Relative molecular mass, definition, 91
Reservoir inlet system, 301
Residual air, EI spectrum, 113
Resolution
 determination, 113
 full width at half maximum definition, 113
 10 % valley definition, 112
Resolving power, 112
 in FT-ICR-MS, 232
 ultrahigh by FT-ICR, 135
Retention factor, 833
Retention time, in chromatography, 834
Retro-1,4-addition. *See* Ortho elimination
Retro-Diels-Alder reaction (RDA), 381
 of isomeric ions, 385
 of natural products, 384
 requirements, 382–383
Retro-ene reaction, 38
Retrospective analysis, 851
Reversed phase, stationary phase in LC, 841
RF-only quadrupole, 197
 collisional cooling, 198
 collisional focusing, 199
RIC. *See* Reconstructed ion chromatogram (RIC)
Rice-Ramsperger-Marcus-Kassel (RRKM) theory, 47
Ring electrode. *See* Quadrupole ion trap (QIT)
Rings plus double bonds (r + d), 359
RIT. *See* Rectilinear ion trap (RIT)

- ROSETTA space mission, 173
RRKM theory. *See* Rice-Ramsperger-Marcus-Kassel (RRKM) theory
Rules for interpretation, 425, 944
- S**
Saddle field gun, 616
Sample introduction system, 300
Sample vial, 303
 loading of sample, 305
Sampling cone, in ICP source, 903
S/B. *See* Signal-to-background ratio (S/B)
Scrambling, 356
Secondary ion mass spectrometry (SIMS), 613, 640
 dynamic, 908
 static, 908
Selected ion monitoring (SIM), 849
Selected reaction monitoring (SRM), 852
Self-chemical ionization (Self-CI), 443
SEM. *See* Detectors
Sensitivity, 17
Septum bleed, in GC-MS, 862
SFC-MS. *See* Supercritical fluid chromatography-mass spectrometry (SFC-MS)
Sheath flow, ESI sprayers for CZE, 728
SID. *See* Surface-induced dissociation (SID)
 σ -bond cleavage
 of functionalized molecules, 331
 of non-functionalized molecules, 328
 of saturated hydrocarbons, 363
Signal-to-background ratio (S/B), 18
Signal-to-noise ratio (S/N), 18, 849
SIM. *See* Selected ion monitoring (SIM)
SIMION, 297
SIMS. *See* Secondary ion mass spectrometry (SIMS)
Single-crystal silicon nanowires (SiNWs), 695
SI units, 21
Skimmer CID, 35
S/N. *See* Signal-to-noise ratio (S/N)
 S_N2 reaction, in the gasphase, 76
Soft ionization
 chemical ionization, 439
 field desorption, 497
Sonic spray ionization (SSI), 795
SORI. *See* Fourier transform ion cyclotron resonance
SpiralTOF
 design of analyzer, 174
 polymer analysis, 692
 resolving power, 692
Spray capillary, in electrospray ionization, 726
SRIG. *See* Stacked ring ion guide (SRIG)
SRM. *See* Selected reaction monitoring (SRM)
SSI. *See* Sonic spray ionization (SSI)
Stability diagram. *See also* Linear quadrupole analyzer
 of two-dimensional quadrupole field, 192–193
Stable ions, 53
Stacked ring ion guide (SRIG), 261
Stevenson's rule, 334
Sulfonium ions, 346, 347
Supercritical fluid chromatography-mass spectrometry (SFC-MS), 831
Supersonic expansion
 in FAB-MS, 623
 in MALDI, 657
Surface-induced dissociation (SID), 551
 device, 553
 energy uptake, 553
 of protein complexes, 555
 on Synapt G2, 553
SWIFT. *See* Fourier transform ion cyclotron resonance (FT-ICR)
Symbols, in MS, 21
Synapt series, 263
Systematic approach to interpretation, 426, 945
- T**
Tabular listing, representation of spectra, 14
Tandem-in-time, 569, 579
Tandem mass spectrometry, 539
 of an octapeptide, 683
 on a dual-LIT, 572
 on FT-ICR instruments, 579
 in mixture analysis, 831
 on a QIT, 569
 on quadrupole ion traps, 569
 on ReTOF instruments, 557
 in space, 540
 for structure elucidation, 576
 in time, 540
 on TOF instruments, 543
 on triple quadrupole instruments, 567
Target analysis, 849
Target compounds, 849
Taylor cone, in ESI, 741
TCD. *See* Thermal conductivity detector (TCD)
TDC. *See* Time-to-digital converter (TDC)
Termolecular reactions, 75

- in APCI, 472
 - in DART, 810
 - Tetraiodoethene, NICI spectrum, 461
 - Thermal conductivity detector (TCD), 836
 - Thermal degradation
 - decarbonylation, 395
 - decarboxylation, 395
 - elimination of water, 395
 - of organic salts, 397
 - RDA reaction, 395
 - Thermokinetic method, for detn. of GB, 598
 - Thermospray (TSP), 723
 - Thin layer chromatography (TLC), analyzing plates by DESI, 790
 - Thomson, J.J., 3, 11
 - Thomson Medal, 3
 - Three-dimensional quadrupole field. *See* Quadrupole ion trap (QIT)
 - Threshold laser irradiance, in MALDI, 654
 - TIC. *See* Total ion current (TIC)
 - TICC. *See* Total ion current chromatogram (TICC)
 - Tight transition state, 52
 - Time lag focusing (TLF), 166
 - Time-of-flight (TOF) analyzer
 - flight times, 157
 - principle, 155
 - properties, 156
 - reflector TOF, 162–163
 - Time scale
 - of ion-activating events, 551
 - of MS, 53
 - Time-to-digital converter (TDC), 267
 - TIMS. *See* Trapped ion mobility spectrometry (TIMS)
 - TLC. *See* Thin layer chromatography (TLC)
 - TLF. *See* Time lag focusing (TLF)
 - TOF analyzer
 - folded flight path, 171
 - LECO Pegasus HRT, 175
 - multi-reflecting, 174
 - zig-zag ion path, 174–175
 - Top-down protein analysis, 681
 - Total ion chromatogram, 15, 845
 - Total ion current (TIC), 15, 845
 - Total ion current chromatogram (TICC), 15
 - Transannular cleavages, 416
 - Trapped ion mobility, 264
 - Trapped ion mobility spectrometry (TIMS), 871
 - Traveling wave, 261
 - ion guide, 261
 - Travelling-wave ion mobility (TW-IMS), 265
 - Tribrid, 256
 - Trimolecular reaction. *See* Termolecular reactions
 - Triple quadrupole analyzer. *See* Linear quadrupole analyzer
 - Tripily charged ion, in EI, 31
 - Trypanosoma cruzi*, MALDI biotyping, 678
 - Tryptic digest
 - peptide sequencing, 694
 - for proteomics, 681
 - TSP. *See* Thermospray (TSP)
 - Tuning, of the instrument, 298
 - Turbomolecular pump, 274
 - TW-IMS. *See* Travelling-wave ion mobility (TW-IMS)
 - Two-dimensional chromatography. *See* Comprehensive gas chromatography
 - Two-stage ion funnels, 733
 - off-axis alignment, 733
- U**
- Ultrafine-metal-plus-liquid-matrix method, 651
 - Ultrahigh-pressure liquid chromatography (UHPLC), 841
 - Ultrahigh resolution, 134
 - applications, 877
 - Ultra-performance liquid chromatography (UPLC), 841
 - Ultrasonic expansion, in ESI, 727
 - Unified atomic mass (u), definition, 11, 90
 - Unimolecular reactions, 74
 - Unit resolution. *See* Linear quadrupole analyzer
 - Units, for physical quantities, 21, 927
 - Unstable ions, 53
 - UPLC. *See* Ultra-performance liquid chromatography (UPLC)
 - UV detector, 836
 - UV-MALDI, 663
- V**
- Vacuum, 273
 - cryopump, 273
 - oil diffusion pump, 273
 - pumping speed, 273
 - rotary vane pump, 273
 - turbomolecular pump, 73
 - Vacuum lock, 302
 - van Deemter equation, 835
 - Velocity of ions, 157
 - Vertical transitions, 36

W

Wastewater analysis, 852
Weight-average molecular weight, of
polymers, 691
Wiley/NBS Mass Spectral Database, 316

Z

Zero kinetic energy photo-electron
spectroscopy (ZEKE-PES), 68
z-spray, 730
z-stack, 270