

Definitions of terms relating to mass spectrometry (IUPAC Recommendations 2013)*

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Abstract: This document contains recommendations for terminology in mass spectrometry. Development of standard terms dates back to 1974 when the IUPAC Commission on Analytical Nomenclature issued recommendations on mass spectrometry terms and definitions. In 1978, the IUPAC Commission on Molecular Structure and Spectroscopy updated and extended the recommendations and made further recommendations regarding symbols, acronyms, and abbreviations. The IUPAC Physical Chemistry Division Commission on Molecular Structure and Spectroscopy's Subcommittee on Mass Spectroscopy revised the recommended terms in 1991 and appended terms relating to vacuum technology. Some additional terms related to tandem mass spectrometry were added in 1993 and accelerator mass spectrometry in 1994. Owing to the rapid expansion of the field in the intervening years, particularly in mass spectrometry of biomolecules, a further revision of the recommendations has become necessary. This document contains a comprehensive revision of mass spectrometry terminology that represents the current consensus of the mass spectrometry community.

Keywords: definitions; glossary; IUPAC Analytical Chemistry Division; mass spectrometry; terms.

INTRODUCTION

Mass spectrometry is the study of matter through the formation of gas-phase ions that are detected and characterized by their mass and charge. The recommendations in this document pertain to fundamental, technical, and experimental aspects of ion formation, mass selection, detection, and analysis of mass spectra.

In 1991, the Subcommittee on Mass Spectroscopy of the IUPAC Physical Chemistry Division Commission on Molecular Structure issued recommendations on mass spectrometry terminology [1,2]. These recommendations were supplemented by terms, prepared for the Analytical Chemistry Division, related to tandem mass spectrometry of organic molecules (IUPAC Commission on Microchemical

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Techniques and Trace Analysis and the Working Group on Organic Trace Analysis [3]) and accelerator mass spectrometry (IUPAC Commission on Radiochemistry and Nuclear Techniques [4]) and were included as a chapter in the *Compendium of Analytical Nomenclature*, known as the “Orange Book” [5]. Many of these terms are included in the *Compendium of Chemical Terminology*, known as the “Gold Book” [6]. Values for the physical constants and their symbols appearing in the Orange and Gold Books are taken from *Quantities, Units and Symbols in Physical Chemistry*, also known as the “Green Book” [7].

Over the years, IUPAC and the American Society for Mass Spectrometry (ASMS) have both worked in developing mass spectrometry terminology. The ASMS Measurements and Standards Committee published its Standard Definitions of Terms Related to Mass Spectrometry in 1991 [8]; the document represented the compilation of terms and definitions assembled between 1984 and 1990 by the Measurements and Standards Committee and closely paralleled the IUPAC terminology effort. A list of terms was presented at the ASMS Conference in Palm Springs, California in June of 1997 by the Measurements and Standards Committee and was available on the ASMS website between 1998 and 2000 [9]. There have been several other notable efforts at developing mass spectrometry terminology. A book that includes an extensive critical assessment of mass spectrometry terminology, *Mass Spectrometry Desk Reference*, was published in 2000 with a second edition in 2006 [10]. Another book, entitled *A Dictionary of Mass Spectrometry*, was published in 2010 [11]. The most recent peer-reviewed document is a glossary of terms for separations coupled to mass spectrometry that was published in the *Journal of Chromatography A* in 2010 [12].

During the nearly two decades since the last recommendations of IUPAC and ASMS, the field of mass spectrometry has changed radically. The introduction of soft ionization methods for the analysis of biological molecules has expanded the scope of mass spectrometry from its early roots in the analysis of inorganic and organic species into other fields such as biology and medicine. The expansion in scope has led to a growth in the number of terms and also in the use of those terms by those outside the field of mass spectrometry. As a result, this compilation of terms and definitions represents an extensive revision and expansion of the previous compilation. All defined terms recommended here are referenced to peer-reviewed literature.

CONTROVERSIAL TERMS

In the nearly two decades since the last recommendations on mass spectrometry terminology, there has been tremendous growth and expansion and, in some cases, divergence in opinion on correct usage. Below is a discussion of the rationale for the recommendations made for some of the more controversial terms.

Labeling of mass spectra

The labeling of the x -axis of a mass spectrum engendered the most discussion during the creation of this document; however, in spite of a general desire for a better way to label the x -axis of mass spectra, there was no broad consensus for any of the proposed changes. Therefore, this document continues the use of the definitions of the Gold Book [6] and the similar definitions in the Orange Book [5]. The Gold Book recommendation is for the use of m/z as an abbreviation for *mass-to-charge ratio*, a dimensionless quantity obtained by dividing the *mass number* of an ion by its *charge number* [6].

The thomson unit, defined as the quotient of mass in units of u and the number of charges (z), was proposed nearly two decades ago [13], but has not been widely adopted and is therefore not recommended. Labeling the x -axis of a mass spectrum with any unit of mass such as dalton (Da), atomic mass unit (amu), or unified atomic mass unit (u) is strongly discouraged due to the confusion that would result when reporting spectra of multiply charged ions. The quantity plotted on the x -axis of a mass spectrum is a function of both the mass and charge of the ion. Furthermore, the use of amu in place of

u is strongly discouraged in all cases; it has been used to denote atomic masses measured relative to the mass of a single atom of ^{16}O , or to the isotope-averaged mass of an oxygen atom, or to the mass of a single atom of ^{12}C .

Resolution and resolving power

The IUPAC definition of *resolution in mass spectrometry* expresses this value as $m/\Delta m$, where m is the mass of the ion of interest and Δm is the peak width (peak width definition) or the spacing between two equal intensity peaks with a valley between them no more than 10 % of their height (10 % valley definition) [6]. *Resolving power in mass spectrometry* is defined as the ability of an instrument or measurement procedure to distinguish between two peaks at m/z values differing by a small amount and expressed as the peak width in mass units [6]. *Mass resolving power* is defined separately as $m/\Delta m$ in a manner similar to that given above for mass resolution [6]. These definitions of *mass resolving power* and *resolving power in mass spectrometry* are contradictory, the former is expressed as a dimensionless ratio and the latter as a mass. The definitions for *resolution in mass spectrometry* and *resolving power in mass spectrometry* come from Todd's 1991 recommendations [1], and the definition for *mass resolving power* comes from Beynon's 1978 recommendations [14]. Beynon's work contains no definition for *mass resolution*.

Alternative definitions for *resolution* and *resolving power in mass spectrometry* have been proposed [10,15]. It has been suggested that *resolution* be given by Δm and *resolving power* by $m/\Delta m$; however, these definitions are not widely used.

The majority of the mass spectrometry community uses resolution as defined by IUPAC. The term *resolving power* is not widely used as a synonym for *resolution*. In this document, the IUPAC definition of *resolution in mass spectrometry* remains in place. The definition of *resolving power* has been adapted from the current IUPAC definition of *mass resolving power*.

Collision-induced dissociation (CID) and collisionally activated dissociation (CAD)

The terms *collision-induced dissociation (CID)* and *collisionally activated dissociation (CAD)* are both recommended by IUPAC [6] and are used interchangeably in recent literature. They are listed as synonyms in this document.

Neutral species

Although the word "neutral" is commonly used as an adjective, it is often used in *mass spectrometry* as a noun to indicate an atom or molecule as in the reaction of an ion with a neutral. The terms "neutral" and "neutral species" are used interchangeably in this document. This recommendation differs from the current recommendation for *ion/neutral species reaction* that recommends against using "neutral" as a noun [6].

Ions in fragmentation reactions

The anthropomorphic terms for *ions* involved in fragmentation reactions, for example, "*daughter ion*", have fallen into disuse after strong sentiments against the use of the term were voiced two decades ago [16,17]. The term *product ion* is recommended in place of *daughter ion* and *precursor ion* in place of *parent ion*. The use of n^{th} -*generation product ion* is recommended in place of *granddaughter ion* and similar terms.

Abbreviations of combined methods

The hyphen, or alternatively the slash (forward stroke), can be used to indicate combined methods such as gas chromatography separation combined with *mass spectrometry* detection. Thus, the above combination can be written as *gas chromatography-mass spectrometry* or alternatively as *gas chromatography/mass spectrometry*. The corresponding abbreviations are GC-MS or GC/MS. The first use of a hyphen to indicate the combination of a separation method with mass spectrometry was in the early 1960s [18], and the use of a slash separator was in the 1970s [19]. The term “*hyphenated techniques*” was coined in 1980 [20]. Currently, hyphens and slashes are used interchangeably [12]. The journal *Rapid Communications in Mass Spectrometry* has in the past recommended that the combination of two analytical techniques be designated by a slash [21]. A recent *Journal of Chromatography* glossary also favors this usage [12]. IUPAC recommends that hyphens be used to describe variants of separation techniques, for example, gas-liquid chromatography and pyrolysis-gas chromatography [6]. The authors of this document are evenly split in their preference for hyphen or slash. For consistency with the prior recommendations, we use the hyphen for combined techniques but note that the slash can be used interchangeably.

Ionization method terminology

There have been recent rapid developments in ionization methods such as ambient mass spectrometry and laser desorption ionization. This has led to a proliferation of names and acronyms, not all of which have widespread use. We have limited the terminology related to ionization techniques that have been in existence for more than 5 years and have been reported in over 100 publications from multiple research groups.

Isotope delta

The *relative difference of isotope values*, also known as the *isotope delta*, is the subject of some controversy regarding acceptable units. It is often expressed as parts per thousand (ppt) or parts per million (ppm), both of which are deprecated [7].

A NOTE REGARDING NEW AND REVISED TERMS

Terms that can be found in the Orange Book [5] and the Gold Book [6] are indicated by “from [5]” and “from [6]”, respectively. Terms that have been revised are indicated by “revised from [5]” or “revised from [6]”. Rewording and additional cross-referencing are not considered as revision in this document. New terms are not identified other than by lack of such notation. Deprecated terms and synonyms are included as separate entries with a note directing the reader to the appropriate term. Terms appearing elsewhere in the document are indicated by italic type when first mentioned in a definition, and related terms are indicated where appropriate.

DOCUMENT ORGANIZATION

Previous compilations of mass spectrometry terms have been organized alphabetically within sections. This document is organized in glossary format: alphabetically with no sections. It is not intended to be encyclopedic, but rather a list of terms with brief definitions supported by references to publications in the peer-reviewed literature.

1. absolute quantitation of proteins (AQUA)

Method for absolute quantitation of proteins via measurements on constituent proteolytic peptides using chemically synthesized isotope-labeled peptides as *surrogate internal standards* for *mass spectrometry*. From [22].

2. abundance sensitivity

Ratio of the maximum *ion* current recorded at a specified *m/z* value to the maximum *ion* current arising from the same species recorded at a neighboring *m/z* value.

Note: The *abundance sensitivity* is a measure of the contribution of the peak “tail” of a major isotope (with a certain *m/z* value) to an adjacent *m/z* value which in some cases might more than 1 *m/z* removed. Its value is dependent on the *resolving power* of the *mass spectrometer*.

Revised from [5,6] using additional information from [23].

3. accelerating potential

Electrical potential difference used to impart translational energy to *ions*.

Note: *Accelerating voltage* is often used as a synonym, but the terms are equivalent only in the case of a static *accelerating potential*.

From [24].

4. accelerating voltage

This term is deprecated.

See *accelerating potential*.

5. accelerator mass spectrometry (AMS)

Mass spectrometry technique in which atoms and molecules from a sample are ionized, accelerated to MeV energies and separated according to their momentum, charge, and energy, allowing high discrimination for measurement of isotope abundances.

From [4].

6. accurate mass

Experimentally determined mass of an *ion* of known charge.

Note 1: Can be used to determine elemental composition to within limits defined by both the accuracy and precision of the measurement.

Note 2: *Accurate mass* and *exact mass* are not synonymous. *Accurate mass* refers to a measured mass, and *exact mass* refers to a calculated mass.

See also *exact mass*.

From [10,25].

7. accurate mass tag

Value of the mass of a peptide from a protein that has been chemically or enzymatically cleaved into fragments. The mass is recorded with sufficiently high accuracy and precision that it can be used in identification of the protein.

See also *peptide mass fingerprinting (PMF)*.

From [26,27].

8. acyl cation

See *acylium ion*.

**9. acylium ion
acyl cation**

Even-electron ion of general formula $RC O^+$ (or its resonance form $R-C^+=O$).

From [6].

10. adiabatic ionization

Removal of an electron from an atom, radical, or molecule in its lowest energy state, thus producing an *ion* in its lowest energy state.

From [5,6].

11. adduct ion

Ion formed by the interaction of a *precursor ion* with one or more atoms or molecules to form an ion containing all the constituent atoms of the precursor ion as well as the additional atoms from the associated atoms or molecules.

Note: For example, a Na^+ adduct of a molecule (M) that is represented as $[M + Na]^+$.

See also *anionized molecule, cationized molecule, protonated molecule*.

From [5,6].

12. after mass analysis

This term is obsolete.

Term used to describe the *total ion current* measured as the sum of all the separate *ion* currents carried by the different ions of the same sign contributing to the *mass spectrum*.

See also *before mass analysis*.

From [5,6].

13. a-ion

Fragment ion containing the peptide N-terminus formed upon dissociation of a peptide *ion* at the peptide backbone C–C bond.

From [28].

14. α -cleavage

Homolytic cleavage where the bond fission occurs between the atom adjacent to the atom at the apparent charge site and an atom removed from the apparent charge site by two bonds.

Note: In the case of a *distonic ion*, it is important to distinguish between fragmentation adjacent to the charge site and fragmentation adjacent to the radical site.

See also *β -cleavage*.

From [5,6].

15. alkylideneaminylum ion

See *iminylum ion*.

16. alkyl cation

Even-electron positively charged saturated hydrocarbon *ion* containing no aromatic groups, a special case of *carbenium ions*.

From [29,30].

17. all-glass heated inlet system (AGHIS)

All-glass inlet system for *ion sources* operating under vacuum that can be heated to about 500 °C and allows low vapor pressure materials to be introduced into the *mass spectrometer* without breaking vacuum.

From [31].

18. allyl cation

Even-electron ion formulated as $R^1R^2C=CR^3C^+R^4R^5$ and its resonance forms.

From [32,33].

19. ambient ionization

Desorption of molecules and formation of *ions* outside the *mass spectrometer* directly from samples in their native environment with no or minimal sample preparation. Examples are *desorption electrospray ionization (DESI)* and direct analysis in real time (DART).

Note: “Direct analysis in real time” is a proprietary term indicating the formation of *ions* from a solid or liquid sample at atmospheric pressure through the interaction of a gas stream containing internally excited atoms or molecules with the surface. The excited-state species are typically formed in a glow discharge in helium or nitrogen. The term should only be used to describe the commercial product.

From [34].

20. ambient mass spectrometry

Mass spectrometry analysis performed using an *ambient ionization* technique.

From [34].

21. analyte

Component of a sample being analyzed; typically a specific chemical compound.

Revised from [5,6] using additional information from [35,36].

22. angle resolved mass spectrometry

Technique used to investigate details of the collisional excitation process by studying trends relating scattering angle of the *precursor ion*, internal energy transferred, and the masses of the ion and its collision partner.

From [37].

23. anionized molecule

Ion formed by the association of an anion with a molecule, M.

Note 1: For example, $[M + Cl]^-$.

Note 2: The terms *quasi-molecular ion* and *pseudo-molecular ion* are deprecated and should not be used in place of *anionized molecule*.

See also *adduct ion*.

From [38].

24. appearance energy (AE)

Deprecated: appearance potential.

Minimum energy that must be imparted to an atom or molecule to produce a detectable amount of a specified *ion*. In *electron ionization mass spectrometry*, minimum electron energy necessary for the detection of a given *fragment ion*.

Note: This experimental quantity can vary with the detection sensitivity of the instrument used, reflecting different *kinetic shifts*.

Revised from [5,6].

25. appearance potential

This term is deprecated.

See *appearance energy*.

26. array detector

Detector comprising several *ion* collection elements, arranged in a line or grid where each element is an individual detector.

From [39,40].

**27. association reaction
associative ion/molecule reaction**

Reaction of a (slow-moving) *ion* with a neutral in which the reactants combine to form a single ionized species with no further dissociation.

Revised from [5,6] using additional information from [41].

28. associative ionization

Ionization process in which two atoms or molecules, one or both of which is in an excited state, react to form a single positive *ion* and an electron.

See also *dissociative ionization*, *Penning ionization*.

From [5,6].

29. associative ion/molecule reaction

See *association reaction*.

30. atmospheric pressure ionization (API)

Ionization process in which *ions* are formed from atoms or molecules at atmospheric pressure.

Note: Atmospheric pressure ionization is not a synonym for *atmospheric pressure chemical ionization*.

Revised from [6] using additional information from [42,43].

31. atmospheric pressure chemical ionization (APCI)

Chemical ionization of a sample that is a gas or nebulized liquid, using an atmospheric pressure *corona discharge* or beta emitter such as ^{63}Ni .

From [43].

32. atmospheric pressure matrix-assisted laser desorption/ionization (AP MALDI)

Matrix-assisted laser desorption/ionization in which the sample target is at atmospheric pressure.

From [44].

33. atmospheric pressure photoionization (APPI)

Direct ionization of molecules at atmospheric pressure by electron detachment induced by photons forming $\text{M}^{+\bullet}$, or *atmospheric pressure chemical ionization* in which the reactant *ions* are generated by *photoionization* of suitable dopant species and subsequent *ion/molecule reactions* of their *molecular ions*.

From [45].

34. atomic mass unit, amu

See *unified atomic mass unit*.

Revised from [6] using additional information from [46].

35. autodetachment

Process whereby a negative *ion* in a discrete state with energy greater than the detachment threshold loses an electron spontaneously without further interaction with an energy source.

See also *autoionization*.

From [47].

36. autoionization

Formation of an *ion* when an atom or molecule in a discrete state with an internal energy greater than the ionization threshold loses an electron spontaneously without further interaction with an energy source.

See also *autodetachment*.

Revised from [5] using additional information from [48].

37. auxiliary gas

Gas used in a spray *ion source* in addition to the *nebulizing gas* to aid in solvent removal.

From [49,50].

38. average mass

Mass of an *ion* or molecule weighted for its isotopic composition.

See also *monoisotopic mass*, *nominal mass*.

Revised from [5] using additional information from [51].

39. axial ejection

Ejection of an *ion* from an *ion trap* in a direction parallel to the longitudinal axis of the trap.

From [52].

40. axialization

Technique used in *Fourier-transform ion cyclotron resonance mass spectrometers* to limit the translational motion of the trapped *ions* so that they occupy a small volume near the trap center, thus optimizing performance criteria including *resolving power*.

From [53,54].

41. background mass spectrum

Mass spectrum observed when no analyte is introduced into the *mass spectrometer*.

See also *residual spectrum*.

Revised from [5,6] using additional information from [11].

42. base peak (BP)

Peak in a *mass spectrum* that has the greatest intensity.

Note: This term may be applied to the *mass spectra* of pure substances or mixtures.

From [5,6].

**43. base peak chromatogram (BPC)
base peak ion chromatogram**

Chromatogram obtained by plotting the signal of the *ions* represented by the *base peak* detected in each of a series of *mass spectra* recorded as a function of retention time.

Note: This term should be used for samples introduced following a chromatographic separation.

From [55].

44. base peak ion chromatogram

See *base peak chromatogram (BPC)*.

45. bath gas

See *buffer gas*.

46. beam mass spectrometer

Mass spectrometer in which an *ion beam* accelerated from the *ion source* is transmitted through a *m/z* analyzer, or analyzers, to the detector.

From [56].

47. before mass analysis

This term is obsolete.

Total ion current measured as the sum of all the separate *ion* currents for ions of the same sign prior to mass analysis.

See also *after mass analysis*.

From [5,6].

48. benzyl ion

Even-electron ion $C_7H_7^+$ with the same carbon skeleton as toluene that has lost a hydrogen atom from the methyl side-chain that carries the positive charge.

See also *tropylium ion*, *tolyl ion*.

From [57].

49. β -cleavage

Homolytic cleavage where the bond fission occurs between an atom removed from the apparent charge site atom by two bonds and an atom adjacent to that atom and removed from the apparent charge site by three bonds.

See also *α -cleavage*.

From [5,6].

50. b-ion

Fragment ion containing the peptide N-terminus formed upon dissociation of a peptide *ion* at the peptide backbone C–N bond.

From [28].

51. blackbody infrared radiative dissociation (BIRD)

Special case of *infrared multiphoton dissociation* wherein excitation of the reactant *ion* is caused by absorption of infrared photons radiating from heated blackbody surroundings, which are usually the walls of a vacuum chamber.

See also *infrared multiphoton dissociation (IRMPD)*.

From [58].

52. bottom-up proteomics

Method of protein identification that uses proteolytic digestion before analysis by liquid chromatography and *mass spectrometry*. Proteins can be isolated by gel electrophoresis prior to digestion or, in *shot-gun proteomics*, the protein mixture is digested and the resulting peptides are separated by liquid chromatography.

See also *top-down proteomics*.

From [59,60].

**53. Brubaker lens
Brubaker pre-filter**

Additional set of four short, cylindrical electrodes, mounted co-linearly with a *transmission quadrupole mass spectrometer* that is excited with some fraction of the AC potential but not the DC potential applied to the main quadrupole. The Brubaker lens thus acts as a high-pass filter for *ion m/z*, but the resulting delay in application of the DC potential component also results in a reduction in defocusing by *fringe fields* and thus significantly improves overall ion *transmission efficiency* at a given *mass resolution*.

From [61].

54. Brubaker pre-filter

See *Brubaker lens*.

**55. buffer gas
bath gas**

Inert gas used for collisional reduction of the internal or translational energy of *ions*, such as in *ion traps*.

See also *collision gas*.

From [62].

56. capillary exit fragmentation

This term is deprecated.

See *in-source collision-induced dissociation*.

57. carbanion

Even-electron anion with a significant portion of the excess negative charge located on a carbon atom that usually has three substituent groups and an unshared pair of electrons for a total of eight valence electrons, with general formula $R^1R^2R^3C^-$ where the R groups are any organic structure.

From [6].

58. carbenium ion

Carbocation that has at least one important contributing structure containing a trivalent carbon atom with a vacant p-orbital. Common examples are even-electron hypovalent ions with the charge formally localized on a carbon atom, with general formula $R^1R^2R^3C^+$ where the R groups are any monovalent organic structure.

Note: In earlier literature, such *ions* were referred to as *carbonium ions*. Both types are collectively referred to as carbocations.

Revised from [6].

59. carbocation

Cation containing an even number of electrons with the excess positive charge formally located on a carbon atom. This is a general term embracing *carbenium ions*, *carbonium ions*, and cations derived from corresponding carbon-centred free radicals by removal of the unpaired electron.

Note: Such carbocations may be named by adding the word “cation” to the name of the corresponding radical, but such names do not imply structure (e.g., whether three- or five-coordinated carbon atoms are present).

From [5,6].

60. carbonium ion

Even-electron hypervalent *carbocation* in which the charge is located on a carbon atom that carries a fifth covalent bond (e.g., H_5C^+), the most abundant *reagent ion* formed in *chemical ionization* using methane as *reagent gas*.

Note: This term was formerly used to describe *ions* of the type now referred to as *carbenium ions*.

From [6].

61. cationized molecule

Ion formed by the association of a cation with a molecule M.

Note 1: For example, $[M + Na]^+$, $[M + K]^+$, and $[M + NH_4]^+$.

Note 2: The terms *quasi-molecular ion* and *pseudo-molecular ion* are deprecated and should not be used in place of cationized molecule.

See also *adduct ion*.

From [62].

62. centroid acquisition

Procedure of recording *mass spectra* in which an automated computer-based system detects peaks, calculates the centroid based on the average m/z value weighted by the intensity, and assigns m/z values based on a calibration file. Only the centroid m/z value and the peak magnitude are stored.

See also *profile mode*.

From [63].

63. channel electron multiplier (CEM)

See *continuous dynode particle multiplier*.

64. channel electron multiplier array (CEMA)

See *microchannel plate*.

65. charged residue model

Theoretical model for production of highly charged macromolecules by *electrospray ionization* in which the excess charges on electrosprayed droplets are transferred to and remain on molecules enclosed within the droplets after solvent evaporation.

See also *ion evaporation model*.

From [64].

66. charge exchange ionization (CEI)

Interaction of an *ion* with an atom or molecule in which the charge on the ion is transferred to the neutral species without the dissociation of either species.

From [5,6].

67. charge exchange reaction

See *charge-transfer reaction (in mass spectrometry)*.

68. charge inversion mass spectrum

Plot of the relative abundances of *ions* that result from a *charge inversion reaction* as a function of m/z .

From [5,6].

69. charge inversion reaction

Reaction of an *ion* with a neutral, surface, or ion of opposite polarity, in which the charge on the *product ion* is reversed in sign with respect to the reactant ion.

See also *charge inversion mass spectrum*.

Revised from [5] using additional information from [65].

**70. charge-mediated fragmentation
heterolytic fragmentation; inductive cleavage**

Fragmentation of an *ion* in which the cleavage of one of its bonds is induced by the charge site. The cleaved bond is adjacent to the apparent charge site, and its cleavage involves movement of the electron pair forming that bond to the original charge site and thus migration of the charge to the released fragment.

See also *charge remote fragmentation (CRF)*.

From [66].

71. charge number, z

Absolute value of charge of an *ion* divided by the value of the elementary charge (e) rounded to the nearest integer.

See also m/z .

Revised from [5,6].

72. charge permutation reaction

Reaction of an *ion* with a neutral with a resulting change in the magnitude or sign of the charge on the reactant ion.

See also *charge stripping reaction*.

From [5,6].

73. charge remote fragmentation (CRF)

Fragmentation of an *ion* in which the cleaved bond is isolated from the apparent charge site by a distance of several bond lengths.

See also *charge-mediated fragmentation*.

From [67,68].

74. charge site derivatization

Chemical derivatization of molecules to introduce a fixed charge site, thus improving *ionization efficiency* by *electrospray ionization* or *matrix-assisted laser desorption/ionization* and directing subsequent *ion* fragmentation in a manner that facilitates structure identification.

Note: Examples are quaternary ammonium or phosphonium derivatization.

From [69].

75. charge stripping reaction (CSR)

Reaction of an *ion* with a neutral or collision partner ion in which a free electron is stripped from the ion, resulting in the charge on the product ion being more positive than that of the reactant ion.

Note: A particular example of an *ionizing collision*.

See also *charge permutation reaction*, *ionizing collision*.

Revised from [5,6] using additional information from [70].

76. charge-transfer reaction (in mass spectrometry)
charge exchange reaction

Reaction of an *ion* with a neutral or collision partner ion in which some or all of the charge on the reactant ion is transferred to the neutral or collision partner ion.

Revised from [5,6] using additional information from [71].

77. chemical ionization (CI)

Formation of a new *ion* in the gas phase by the reaction of a neutral with an ion. The process may involve transfer of an electron, a proton, or other charged species between the reactants.

Note 1: When a positive ion results from *chemical ionization*, the term may be used without qualification. When a negative ion results, the term *negative ion chemical ionization* should be used.

Note 2: This term is not synonymous with *chemi-ionization*.

See also *atmospheric pressure chemical ionization*.

From [5,6].

78. chemi-ionization

Ionization of an atom or molecule by interaction with another internally excited atom or molecule.

Note 1: This term is not synonymous with *chemical ionization*.

Note 2: *Chemi-ionization* differs from *Penning ionization* in that chemical change is not excluded.

Revised from [5,6] using additional information from [72].

79. c-ion

Fragment ion containing the peptide N-terminus formed upon dissociation of a peptide *ion* at the peptide backbone N–C bond.

From [28].

80. cluster ion

Ion formed by the combination via noncovalent forces of two or more atoms or molecules of one or more chemical species with an ion.

Note: For example, $[(\text{H}_2\text{O})_n\text{H}]^+$, $[(\text{H}_2\text{O})_n(\text{CH}_3\text{OH})_m\text{H}]^+$, $[(\text{NaCl})_n\text{Na}]^+$, Au_{10}^- , or $[\text{M} + \text{Na} + \text{CH}_3\text{OH}]^+$ where M represents a molecule.

Revised from [5,6].

81. coaxial reflectron

Reflectron that is arranged such that its main axis is coaxial with the *ion source* and first stage of the *time-of-flight analyzer*.

From [73].

82. collector slit

Slit installed in a *magnetic sector mass spectrometer* to allow only those *m/z* separated ions with a specific *m/z* into the detector system.

From [74,75].

83. collisional activation (CA)

See *collisional excitation*.

**84. collisional excitation
collisional activation**

Interaction of an *ion* with another gas-phase species in which part of the relative translational energy of the collision partners is converted into internal energy.

From [5,6].

85. collisional focusing

Effect where collisions with a *buffer gas* in a radio-frequency *ion trap* or *transmission quadrupole* causes *ions* to lose translational energy and concentrate at the center of the trap or axis of the linear quadrupole. The effect increases with gas pressure up to a point where ion scattering becomes the dominant process.

From [76].

86. collisionally activated dissociation (CAD)

See *collision-induced dissociation (CID)*.

87. collision cell

Chamber in the *ion* path between *m/z* separation elements, or between *ion source* acceleration region and the first analyzer, in *tandem mass spectrometry in space* configurations.

See also *collision reaction cell*.

From [77].

88. collision gas

Deprecated: target gas.

Inert gas used for *collisional excitation* or a reactive gas used for *ion/molecule reactions*.

See also *buffer gas*.

From [78].

**89. collision-induced dissociation (CID)
collisionally activated dissociation**

Dissociation of an *ion* after *collisional excitation*.

Note: The terms *collision-induced dissociation (CID)* and *collisionally activated dissociation (CAD)* can be used interchangeably.

From [5,6].

90. collision quadrupole

Transmission quadrupole to which an oscillating radio frequency potential is applied so as to focus a beam of *ions* through a *collision gas* or *buffer gas* with no *m/z* separation other than low *m/z* cut-off.

Note: Higher-order multipoles can also be used in this manner.

See also *RF-only quadrupole*.

From [79,80].

91. collision reaction cell (CRC)

Collision cell for removal of interfering *ions* by *ion/neutral reactions* in *inductively coupled plasma-mass spectrometry*.

From [81].

92. concentric nebulizer

Pneumatic nebulizer in which the liquid flows through a central capillary and dispersion gas flows through a surrounding outer tube.

From [82].

93. cone voltage dissociation

This term is deprecated.

See *in-source collision-induced dissociation*.

94. consecutive reaction monitoring (CRM)

Multiple-stage mass spectrometry experiment with three or more stages of *m/z* separation in which products of sequential fragmentation or bimolecular reactions are selected for detection.

See also *multiple reaction monitoring*.

From [83].

95. constant neutral mass gain spectrum

fixed neutral gain spectrum

fixed neutral mass gain spectrum

Spectrum formed of all *precursor ions* that have undergone a selected *m/z* increase corresponding to the mass of a particular neutral species divided by the *charge number* of the precursor. The *ions* detected are the *product ions* produced by gain of a preselected neutral species mass following *ion/molecule reactions* of the precursor ions with a reactant gas in a *collision cell*.

See also *constant neutral mass loss spectrum*.

From [5,6].

96. constant neutral mass loss spectrum

fixed neutral loss spectrum

fixed neutral mass loss spectrum

Spectrum of all *precursor ions* that have undergone a selected *m/z* decrement corresponding to the mass of a particular neutral divided by the *charge number* of the precursor. The *ions* detected are the *product*

ions produced by loss of a preselected neutral mass following *collision-induced dissociation* of the precursor ions in a *collision cell*.

See also *constant neutral mass gain spectrum*.

From [5,6].

**97. continuous dynode particle multiplier
channel electron multiplier**

Ion-to-electron detector in which the *ion* strikes the inner surface of a continuous tube device and induces the production of *secondary electrons* that, in turn, impinge on the inner surfaces of the device to produce more secondary electrons. This avalanche effect produces an increase in the final measured current pulse.

See also *discrete dynode particle multiplier*.

From [84].

98. continuous-flow fast atom bombardment (CF-FAB)

Variation of *fast atom bombardment* in which the mixture of analyte and liquid matrix is continuously supplied to the sample probe tip.

From [85,86].

99. continuous-flow matrix-assisted laser desorption/ionization (CF-MALDI)

Variation of *matrix-assisted laser desorption/ionization* in which the analyte is dissolved in a liquid matrix that is continuously supplied to the sample probe tip.

From [87].

100. conversion dynode

Surface that is held at high potential so that *ions* striking the surface produce secondary charged particles that are subsequently detected.

Note: For positive ions, the potential is negative and the secondary particles are electrons and negative ions. For negative ions, the potential is positive and the secondary particles are positive ions.

From [88–90].

101. corona discharge

Electric discharge generated in a gas, usually at atmospheric pressure, surrounding a conductor carrying a sufficiently high potential that the electric field around it ionizes the gas so as to form a *plasma* in the immediate vicinity of the conductor without causing complete electric breakdown or arcing.

Note: A *corona discharge* can also be sustained in a liquid.

See also *glow discharge ionization*.

From [91].

102. corona discharge ionization

Formation of *ions* in a *corona discharge*.

From [92].

103. counter-current gas

Stream of inert gas, often heated, that is used in an *electrospray* or other *spray ionization* source to aid in the evaporation of solvent from the sprayed particles. The flow of the gas is in the direction opposite to that of the spray.

Note: Curtain gas is a proprietary term used to indicate a flow of counter-current gas emanating from between two closely spaced plates each with a central orifice along the axis of a spray ionization source. The term should only be used to describe the commercial device.

See also *drying gas*.
From [82,93,94].

104. counter electrode

Counter electrode in an *electrospray ionization ion source* is one of two electrodes between which the high electric potential is applied, the other electrode being the *electrospray needle*.
From [95].

105. crossed electric and magnetic fields

Electric and magnetic fields with the electric field direction at right angles to the magnetic field direction.

See also *Wien filter*.
From [5,6].

106. cross-flow nebulizer

Pneumatic nebulizer in which the dispersion gas flows at an angle, usually 90°, with respect to the column of liquid emerging from a capillary.
From [95,96].

107. curved field reflectron

Reflectron designed to provide a decelerating field strength that varies with depth of *ion* penetration and thus with ion translational energy, permitting energy focusing of ions with a range of translational energies such as those formed as *product ions* from *post-source decay* of *metastable ions*.
From [97].

108. cycloidal mass spectrometer

This term is deprecated.
See *prolate trochoidal mass spectrometer*.

109. cyclotron motion

Circular motion of a charged particle moving perpendicularly to the direction of a magnetic field that results from the Lorentz force.
From [15].

110. dalton, Da

See *unified atomic mass unit*.

111. Daly detector

Detector consisting of an off-axis *conversion dynode*, scintillator, and photomultiplier. The dynode at high potential emits *secondary electrons* when *ions* impinge on the surface. The secondary electrons are accelerated onto the scintillator that produces light that is then detected by the photomultiplier detector, which can be outside the vacuum system.

See also *ion-to-photon detector*.

From [98].

112. data-dependent acquisition

Mode of data collection in *tandem mass spectrometry* in which a fixed number of *precursor ions* whose *m/z* values were recorded in a survey scan are selected using predetermined rules and are subjected to a second stage of mass selection in an *MS/MS* analysis.

From [99].

113. daughter ion

This term is deprecated.

See *product ion*.

114. daughter ion analysis

This term is deprecated.

See *product ion analysis*.

115. deconvoluted mass spectrum

Mass spectrum processed with an algorithm designed to extract a desired signal or signals from raw experimental data in which the desired signals have been complicated (convolved) by some interferences or in some other way.

Note: Examples of *deconvoluted mass spectra* include *mass spectra* corrected for instrumental mass bias, or extraction of spectra for pure components from the spectrum of a mixture, or a mass (not *m/z*) spectrum of a biopolymer from an *electrospray ionization* spectrum containing peaks corresponding to several charge states.

From [100,101].

116. delayed extraction (DE)

Application of the *accelerating voltage* pulse after a time delay in *desorption ionization* from a surface.

Note: The extraction delay can produce energy focusing in a *time-of-flight mass spectrometer*. See also *time-lag focusing*.

From [102,103].

117. delta notation

See *relative isotope-ratio difference*.

118. deprotonated molecule

Deprecated: pseudo-molecular ion, quasi-molecular ion.

Ion formed by the removal of a proton from a molecule M to produce an anion represented as $[M - H]^-$.

See also *protonated molecule*.

From [104].

119. desorption chemical ionization (DCI)

Formation of gas-phase *ions* by *chemical ionization* of gaseous molecules produced by the rapid heating and desorption of a solid or low vapour pressure liquid.

From [105,106].

120. desorption electrospray ionization (DESI)

Formation of gas-phase *ions* from a solid or liquid sample at atmospheric pressure through the interaction of *electrosprayed* droplets with the sample surface.

See also *ambient ionization*.

From [107].

121. desorption ionization

Formation of gas phase *ions* from a solid or liquid sample surface upon activation by heat, strong electric field, particles, droplets, or photon bombardment.

From [108].

122. desorption ionization on silicon (DIOS)

Soft ionization alternative to *matrix-assisted desorption/ionization* involving *laser desorption ionization* of a sample deposited on a porous silicon surface.

See also *matrix-assisted laser desorption/ionization*.

From [109].

123. detection limit

See *relative detection limit*.

124. diagnostic ion

Product ion whose formation reveals structural or compositional information about its *precursor ion*.

Note: For example, the phenyl cation in an *electron ionization mass spectrum* is a diagnostic *ion* for benzene and derivatives.

From [110].

125. dielectric barrier discharge ionization

Atmospheric pressure chemical ionization in which the low-temperature *plasma* is not generated by a *corona discharge* but by a device consisting of two electrodes with at least one dielectric layer that separates the electrode from the plasma.

From [111].

126. dimeric ion

Ion formed by ionization of a dimer or by the association of an ion such as $[M]^+$, $[M + H]^+$, or $[M - H]^-$ with its neutral counterpart M.

See also *adduct ion*.

From [5,6].

127. d-ion

High-energy fragment *ion* of a protonated peptide, formally equivalent to a *fragment ion* formed by homolytic cleavage of a peptide C–N bond together with the part of the C-terminal side-chain starting at the γ -carbon (if any).

From [112].

128. direct analysis of daughter ions (DADI)

This term is deprecated.

See *mass-analyzed ion kinetic energy spectrometry (MIKES)*.

129. direct exposure probe (DEP)

Device based on a modification of a *direct insertion probe* for exposing an involatile sample directly to the electron beam (in an *electron ionization source*) or to a *chemical ionization plasma* as in *desorption chemical ionization*.

Note: The sample can be deposited on an inert surface or on a heater filament for rapid heating.

From [105,113].

130. direct infusion

Method of liquid sample introduction in which the sample is continuously flowed into a *mass spectrometer ion source*.

From [114].

131. direct insertion probe (DIP)

Device for introducing a single sample of a solid or liquid, usually contained in a quartz or other non-reactive sample holder, into a *mass spectrometer ion source*.

See also *direct exposure probe*.

From [115].

132. direct liquid introduction (DLI)

Direct delivery of a liquid sample at a low solvent flow rate into the *chemical ionization ion source* of a *mass spectrometer*. The solvent vapour can act as the *reagent gas*.

From [116].

133. discrete dynode particle multiplier

Ion-to-electron detector in which the ion strikes the surface of an electrode and induces the production of *secondary electrons*. In turn, these impinge in sequence on dynodes at a more positive electric potential to produce more secondary electrons. This avalanche effect produces an amplification of several orders of magnitude in the final measured current pulse.

See also *continuous dynode particle multiplier*.

From [117].

134. dissociative electron capture

Ionization mechanism in which capture of a low-energy electron by a molecule leads directly to a dissociative state of the nascent anion, an example of *dissociative ionization*.

From [118].

135. dissociative ionization

Reaction of a gas-phase molecule that results in its decomposition to form products, one of which is an *ion*.

See also *associative ionization*.

From [5,6].

136. distonic ion

Radical ion whose charge and radical sites are neither at the same atom nor in conjugation with each other.

Note 1: For example, $\cdot\text{CH}_2\text{-OH}_2^+$ is a distonic *ion*, whereas the *molecular ion* of methanol, $\text{CH}_3\text{OH}^{+\bullet}$ is a conventional radical cation.

Note 2: In a valence bond description, α -distonic ions have the charge and radical sites on adjacent atoms, β -distonic ions are separated by one atom, γ -distonic ions by two atoms, and so forth.

From [119,120].

137. double-focusing mass spectrometer

Mass spectrometer that incorporates a *magnetic sector* and an *electric sector* connected in series in such a way that *ions* with the same m/z but with distributions in both the direction and the translational energy of their motion are brought to a focus.

From [5,6].

138. drift tube

Cylindrical chamber containing a *buffer gas*. *Ions* introduced at one end are caused to move to the other end by either a flow of the buffer gas or by a uniform longitudinal electric field.

From [121].

139. drying gas

Inert gas that is used to promote the removal of solvent from aerosol particles in *spray ionization*.

See also *counter-current gas*.

From [122].

140. dynamic exclusion

Software method used to minimize repeat selections of identical *precursor ions* for *collision-induced dissociation* in replicate chromatography-*tandem mass spectrometry* analyses of complex mixtures.

See also *data-dependent acquisition*.

From [123].

141. dynamic field mass spectrometer

Mass spectrometer in which *m/z* separation is achieved using one or more electric fields that vary with time.

From [5,6].

142. dynamic secondary ion mass spectrometry (DSIMS)

Secondary ion mass spectrometry analysis with primary *ion* current density sufficiently high for use in analysis of sample surface layers in the depth direction.

From [124].

143. einzel lens

Three-element charged particle lens in which the first and third elements are maintained at the same electric potential. Such a lens produces focusing without changing the translational energy of the particle.

From [125].

144. elastic scattering

Interaction between two particles (atom, molecule, or *ion*) wherein there is an exchange of translational energy between the collision partners but no conversion of translational energy into internal energy. Both the magnitudes and directions of the particle speeds can change.

See also *inelastic scattering*.

Revised from [5,6].

145. electric sector

See *electrostatic energy analyzer*.

146. electrohydrodynamic ionization

Ionization process that produces charged droplets and gas-phase *ions* from a liquid under vacuum with the application of an electric field.

Note: The process is formally equivalent to sub-ambient pressure *electrospray ionization*.
From [126–128].

147. electron affinity, E_{EA}

Minimum energy required for a species M to be formed in the process $M^{-\bullet} \rightarrow M + e^{-}$ where $M^{-\bullet}$ and M are in their ground rotational, vibrational, and electronic states and the electron has zero translational energy.

From [5,6].

148. electron attachment ionization

This term is deprecated.

See *electron capture ionization*.

149. electron capture dissociation (ECD)

Process in which multiply *protonated molecules* interact with low-energy electrons followed by fragmentation. The capture of an electron by the even-electron cation $[M + nH]^{n+}$ liberates energy and reduces its charge state, thus producing the corresponding $[M + nH]^{(n-1)+\bullet}$ *odd-electron ion*, which readily fragments.

From [129].

**150. electron capture ionization (ECI)
electron capture negative ionization**

Deprecated: electron attachment ionization.

Ionization of a gas-phase atom or molecule by attachment of a free electron to form *molecular ions* of the $M^{-\bullet}$ type.

From [130].

151. electron capture negative ionization (ECNI)

See *electron capture ionization (ECI)*.

152. electron energy

Translational energy that electrons acquire when accelerated in an electric field.

From [5,6].

153. electron impact ionization

This term is deprecated.

See *electron ionization (EI)*.

154. electron ionization (EI)

Deprecated: electron impact ionization.

Ionization that removes one or more electrons from an atom or molecule through interactions with electrons that are typically accelerated to energies between 10 and 150 eV.

From [5,6].

155. electron transfer dissociation

Process in which multiply *protonated molecules* accept an electron from an anion with relatively low *electron affinity*. Capture of the electron leads to the liberation of energy and a reduction in charge of the *ion* with the production of the $[M + nH]^{(n-1)+}$ *odd-electron ion*, which is readily fragmented by *collision-induced dissociation*.

See also *electron capture dissociation (ECD)*.

From [131].

156. electronvolt, eV

Non-SI unit of energy (symbol eV) defined as the energy acquired by a particle containing charge equal to elementary charge accelerated through a potential difference of one volt.

Note: An electronvolt is equal to $1.602\,176\,565\,(35) \times 10^{-19}$ J where the digits in parentheses indicate the estimated uncertainty in the final two digits of the value.

Revised from [6] using additional information from [46].

157. electrospray emitter

See *electrospray needle*.

158. electrospray ionization (ESI)

Spray ionization process in which either cations or anions in solution are transferred to the gas phase via formation and desolvation at atmospheric pressure of a stream of highly charged droplets that result from applying a potential difference between the tip of the *electrospray needle* containing the solution and a *counter electrode*.

Note: When a pressurized gas is used to aid in the formation of a stable spray, the term *pneumatically assisted electrospray ionization* is used. The term *ionspray* is deprecated unless describing the commercial product.

From [132,133].

**159. electrospray needle
electrospray emitter**

Narrow bore tube from which highly charged droplets are emitted in *electrospray ionization*.

From [95,133].

**160. electrostatic energy analyzer (ESA)
electric sector**

Device consisting of pairs of parallel conducting plates, concentric cylinders, or concentric spheres that separate charged particles according to their ratio of translational energy to charge by means of a potential difference applied between the pair.

From [134].

161. even-electron ion

Ion containing no unpaired electrons in its ground electronic state.

From [5,6].

162. even-electron rule

Rule that states that *even-electron ions* tend to form even-electron *fragment ions* whereas *odd-electron ions* tend to dissociate to form either odd- or even-electron *ions*.

From [135].

163. exact mass

Calculated mass of an *ion* or molecule with specified isotopic composition.

See also *accurate mass*.

From [136].

**164. extracted ion chromatogram
mass chromatogram
reconstructed ion chromatogram**

Chromatogram created by plotting the intensity of the signal observed at a chosen m/z value or set of values in a series of *mass spectra* recorded as a function of retention time.

From [137,138].

**165. extracted ion electropherogram
extracted ion electrophorogram**

Electropherogram created by plotting the intensity of the signal observed at a chosen m/z value or set of values in a series of *mass spectra* recorded as a function of electrophoresis time.

From [139,140].

166. extracted ion electrophorogram

See *extracted ion electropherogram*.

167. extracted ion profile

Any plot of signal intensity observed at a chosen m/z value or set of values in a series of *mass spectra* recorded as a function of time, including *extracted ion chromatogram*, *extracted ion electropherogram*, or from flow injection analysis or any other time-dependent sampling.

See also *total ion current profile*.

From [141].

168. Faraday cup

Conducting cup or chamber that intercepts a charged particle beam and is electrically connected to a current measuring device.

From [5,6].

169. fast atom bombardment ionization (FAB)

Ionization of molecules initiated by a beam of neutral atoms with translational energies in the keV range. Labile molecules susceptible to dissociation are dissolved in an involatile liquid matrix that absorbs the energy of the bombarding atoms to form a selvedge region above the liquid surface in which ionization of the molecules occurs.

Note: Positive *ions* (e.g., *protonated* or *cationized molecules*) or negative ions (e.g., *deprotonated molecules*) are formed depending on the polarity of ionization.

See also *liquid secondary ionization*.

Revised from [5,6] using additional information from [142].

170. fast ion bombardment (FIB)

Ionization of any species by the interaction of a focused beam of *ions*, with a translational energy of several thousand eV, with a solid or liquid sample.

Note: For a liquid sample, fast ion bombardment is the same as *liquid secondary ionization*.
From [143].

171. field desorption (FD)

Deprecated: field desorption ionization.

Formation of gas-phase *ions* from a material deposited on a solid surface (known as an “emitter”) in the presence of an electric field.

Note: Because this process probably encompasses ionization by *field ionization* in conjunction with other mechanisms of ionization, the term *field desorption ionization*, despite its widespread use, is imprecise and therefore not recommended.

From [5,6].

172. field desorption ionization

This term is deprecated.

See *field ionization*.

173. field-free region (FFR)

Section of a *mass spectrometer* in which there are no electric or magnetic fields.

From [144].

174. field ionization (FI)

Ionization by the removal of electrons from any gas-phase species via the action of a high electric field.

See also *field desorption*.

From [5,6].

175. first stability region

Stability region of a *Mathieu stability diagram* closest to the origin.

Note: Ions within this region can traverse the full length of a *transmission quadrupole* or can be trapped in a *Paul ion trap*.

From [145].

176. fission fragment ionization

See *plasma desorption ionization*.

177. fixed neutral gain spectrum

See *constant neutral mass gain spectrum*.

178. fixed neutral loss spectrum

See *constant neutral mass loss spectrum*.

179. fixed neutral mass gain spectrum

See *constant neutral mass gain spectrum*.

180. fixed neutral mass loss spectrum

See *constant neutral mass loss spectrum*.

181. fixed precursor ion scan

Scan that determines, in a single experiment, the m/z values of *product ions* that are produced by the reaction of a selected *precursor ion* with a user-specified m/z value.

From [5,6].

182. fixed precursor ion spectrum

Spectrum obtained when data are acquired that determine the m/z values of *product ions* produced by the reaction of a selected *precursor ion* with a user-specified m/z value.

From [5,6].

183. fixed product ion scan

Scan that determines, in a single experiment, the m/z values of *precursor ions* that react to produce a *product ion* with a user-selected m/z value.

From [5,6].

184. flow injection analysis mass spectrometry

See *flow injection mass spectrometry*.

**185. flow injection mass spectrometry
flow injection analysis mass spectrometry**

Method of flow injection analysis in which an aliquot of sample is injected, without chromatographic separation, into a liquid carrier stream for on-line *mass spectrometry*.

From [146,147].

186. focal plane detector

Detector for m/z spatially dispersed *ion* beams in which all ions simultaneously impinge on the detector plane to produce spatially defined signals.

From [148].

**187. forward geometry
normal geometry**

Double-focusing mass spectrometer configuration in which the ion beam traverses the *electric sector* before the *magnetic sector*.

See also *reverse geometry*.

From [149].

188. forward library search

Procedure of comparing a *mass spectrum* of an unknown compound with a *mass spectral library* so that the unknown spectrum is compared in turn with the library spectra, considering only the m/z peaks that have intensities greater than a specific threshold in the unknown.

Note: In a *forward library search*, a higher similarity index indicates the extent to which the library spectrum resembles the unknown spectrum.

See also *reverse library search*.

From [150].

189. Fourier transform-ion cyclotron resonance-mass spectrometer (FT-ICR-MS)

Mass spectrometer based on the principle of *ion cyclotron resonance* in which an *ion* in a magnetic field moves in a circular orbit at the cyclotron frequency that is characteristic of its m/z value. Ions are coherently excited to a larger radius orbit using a pulse of radio frequency electric field, and their image charge is detected on receiver plates as a time domain signal. Fourier transformation of the time domain signal results in a frequency domain signal that is converted to a *mass spectrum* based on the inverse relationship between cyclotron frequency and m/z .

See also *ion cyclotron resonance mass spectrometer*.

From [5,6].

190. Fourier transform mass spectrometry

Mass spectrometry technique in which m/z values are represented by frequencies of *ion* motion and *mass spectra* are generated by Fourier transform mathematical operations from time domain transients produced by image current detection.

Note: Fourier transform mass spectrometry is typically carried out using *Fourier transform-ion cyclotron resonance-mass spectrometers* or *Kingdon traps*.

From [151].

191. fragmentation reaction (in mass spectrometry)

Reaction of an *ion* that results in two or more fragments of which at least one is an *ion*.

Revised from [6].

192. fragment ion

Product ion that results from the dissociation of a *precursor ion*.

Revised from [5,6] using additional information from [152,153].

193. fringe field

Electric or magnetic field that extends from the edge of an *electric sector*, *magnetic sector*, lens, or other *ion optics* element.

From [154].

**194. gas chromatography-mass spectrometry (GC-MS)
gas chromatography/mass spectrometry (GC/MS)**

Technique by which a mixture is separated into individual components by gas chromatography, followed by detection with a mass spectrometer.

Note 1: Either a hyphen or slash can be used to indicate combined instruments.

Note 2: The *mass spectrum* is typically obtained on a time scale that allows resolution of the component in a single chromatographic peak.

See also *liquid chromatography-mass spectrometry (LC-MS)*, *supercritical fluid chromatography-mass spectrometry (SFC-MS)*, *thin layer chromatography-mass spectrometry (TLC-MS)*.

From [18,155].

195. glow discharge ionization

Formation of *ions* from gaseous atoms or molecules or from the vapor of a solid sample at the cathode by applying a potential difference between two electrodes immersed in a low-pressure inert gas environment.

From [156,157].

196. granddaughter ion

This term is deprecated.

See n^{th} -generation product ion.

197. gridless reflectron

Reflectron design in which the decelerating/accelerating field is produced without the use of wire-mesh grids.

Note: This design improves *ion* transmission but at the cost of a less homogeneous field and thus reduced *resolution*.

From [158].

198. hard ionization

Formation of gas-phase *ions* accompanied by extensive fragmentation.

See also *soft ionization*.

From [24].

199. high-energy collision-induced dissociation

Collision-induced dissociation process wherein the projectile *ion* has laboratory-frame translational energy greater than a given value, often taken to be 1 keV.

See also *low-energy collision-induced dissociation*.

From [159,160].

200. high-field asymmetric waveform ion mobility spectrometry (FAIMS)**RF-DC ion mobility spectrometry**

Separation of *ions* at atmospheric pressure between two electrodes due to simultaneous application of a high potential asymmetric waveform, whereby ions migrate towards one of the two electrodes depending on the ratio of the high- to low-field mobility of the ion. A variable compensating DC potential is used to selectively transmit ions of interest.

From [161,162].

201. hybrid mass spectrometer

Mass spectrometer that combines *m/z* analyzers of different types to perform *tandem mass spectrometry* or higher-order MS^n experiment.

From [5].

202. hydride ion

See *hydron*.

203. hydrogen/deuterium exchange (HDX)

Exchange of hydrogen atoms with deuterium atoms in a chemical species in solution prior to introduction into a *mass spectrometer*, or by *ion/molecule reaction* with a *neutral gas* inside a *mass spectrometer*.

From [163,164].

204. hydrogen shifts

Sigmatropic reactions of *ions* in which the σ -bonds broken and formed involve hydrogen atoms, and are subject to the Woodward–Hofmann rules resulting from orbital symmetry considerations.

From [165].

**205. hydron
hydride ion**

General name for the cation H^+ .

Note 1: The species H^- is the hydride anion, and H is the hydro group.

Note 2: These are general names to be used without regard to the nuclear mass of the hydrogen entity, either for hydrogen in its *natural isotopic abundance* or where it is not desired to distinguish among the isotopes.

From [6].

206. hyphenated mass spectrometry technique

Analytical technique in which *mass spectrometry* is interfaced with a pretreatment step, most often chromatographic separation but many other combinations are possible.

Note: Despite the use of the term “hyphenated” in the name of the general category, a slash separator as in *gas chromatography/mass spectrometry* may also be used.

From [166,167].

207. image current detection

Method of *ion* detection by measuring the current that results from the image charge induced by a coherent motion of ions passing near a conductor.

Note: In *Fourier transform mass spectrometers* or *Kingdon traps*, the coherent orbital motion of ions between a pair of electrodes induces a radio frequency image charge in the electrodes and an alternating image current in the detection circuit connecting to the electrodes.

From [168,169].

208. imaging mass spectrometry

Procedure used to form chemically selective images of an object based on the *mass spectrometric* detection of *ions* desorbed from its surface.

From [170].

**209. iminium ion
alkylideneaminylium ion**

Deprecated: imonium ion, immonium ion.

Cation with the structure $R_2C=N^+R_2$.

Note: The terms *imonium ion* and *immonium ion* are irregularly formed and should not be used.

From [6].

210. imonium ion

This term is deprecated.

See *iminium ion*.

211. immonium ion

This term is deprecated.

See *iminium ion*.

212. impact parameter

Distance of closest approach of two particles if they had continued in their original directions of motion at their original speeds without the influence of intermolecular forces.

From [5,6].

**213. iminylium ion
alkylideneaminylium ion**

Cation having the structure $R^1R^2C=N^+$.

Note 1: A contraction of *alkaniminylium ion*.

Note 2: A subclass of *nitrenium ions*.

From [6].

214. inductively coupled plasma (ICP)

Gas discharge *ion source* in which the energy is supplied to the *plasma* by electromagnetic induction.

From [171].

215. inductively coupled plasma-mass spectrometry (ICP-MS)

Mass spectrometry technique based on coupling a *mass spectrometer* with an *inductively coupled plasma* as an *ion source* that both atomizes samples into their constituent atoms and ionizes them to form atomic cations.

Note: The technique is highly sensitive for a range of metals and several non-metals, and provides information on isotopic distributions.

From [171,172].

216. inelastic scattering

Interaction between two particles (atom, molecule, or *ion*) wherein there is both an exchange of translational energy between the collision partners and a conversion of translational energy into internal energy. Both the magnitudes and directions of the particle speeds can change.

See also *elastic scattering*.

Revised from [5,6].

217. infrared multiphoton dissociation (IRMPD)

Dissociation of a reactant *ion* as a result of the absorption of multiple infrared photons.

See also *Blackbody infrared radiative dissociation (BIRD)*.

From [173–175].

218. in-source collisionally activated dissociation

See *in-source collision-induced dissociation*.

**219. in-source collision-induced dissociation
in-source collisionally activated dissociation**

Deprecated: capillary exit fragmentation, cone voltage dissociation.

Dissociation of an *ion* as a result of *collisional excitation* during ion transfer from an atmospheric pressure *ion source* to the vacuum chamber of the *mass spectrometer*.

Note 1: This process is similar to *ion desolvation* but uses higher collision energy.

Note 2: Terms such as *cone voltage dissociation* and *capillary exit fragmentation* are design-specific versions of this term, and are deprecated.

From [176].

**220. intensity relative to base peak (in mass spectrometry)
relative intensity (in mass spectrometry)**

Ratio of intensity of a resolved *peak* to the intensity of the resolved peak that has the greatest intensity (*base peak*). This ratio is generally measured as the normalized ratio of the heights of the respective *peaks* in the *mass spectrum*, with the height of the base peak taken as 100.

Note: *Intensity* is a measure of detector response and should not be used to describe the abundance of *ions*.

From [5,6].

221. interaction distance

Farthest distance of approach of two particles at which it is discernable that they will not pass at the *impact parameter*.

From [5,6].

222. interference

Systematic error in the measurement of a signal caused by the presence of contaminants in a sample.

From [5,6].

223. internal fragment

Fragment ion of a peptide *ion* precursor formed by a double backbone cleavage that contains neither the original C- or N-terminal residues. Typically a combination of b- and y-type cleavages or occasionally an a- and y-type combination.

From [177].

224. internal standard

See *surrogate internal standard*.

225. ion

Atomic, molecular, or radical species with a non-zero net electric charge.

From [6].

226. ion collector

Device for the capture of selected *ions* such as a *Faraday cup collector* or an electron multiplier.

From [6].

227. ion cyclotron resonance-mass spectrometer (ICR-MS)

Mass spectrometer in which the *ions* to be detected, with a selected value of m/z , absorb energy through the effect of a high-frequency electric field and a constant magnetic field perpendicular to the electric field. Maximum energy is gained by the ions that satisfy the cyclotron resonance condition and as a result they are separated from ions of different m/z .

See also *Fourier transform-ion cyclotron resonance-mass spectrometer (FT-ICR-MS)*.

From [5,6].

228. ion desolvation (in mass spectrometry)

Removal of solvent molecules clustered around a gas-phase *ion* by means of heating and/or collisions with gas molecules.

From [176].

229. ion energy loss spectrum

Spectrum that shows the loss of translational energy of *ions* involved in *ion/neutral reactions*.

See also *ion kinetic energy spectrometry (IKES)*, *mass-analyzed ion kinetic energy spectrometry (MIKES)*.

From [5,6].

**230. ion enhancement
ionization enhancement**

Phenomenon in which the *ionization efficiency* of a compound is increased by the presence of another compound.

Note: The effect is most significant in *electrospray ionization* but is also observed in *atmospheric pressure chemical ionization* and to a lesser extent in other ionization methods.

See also *ion suppression*, *matrix effects*.

From [178].

231. ion evaporation model

Mechanism for production of gas-phase *ions* from highly charged fine liquid droplets as in *electrospray ionization* that involves direct ejection of the ions from the droplet surface.

Note: This mechanism is thought to be dominant for smaller molecules.
See also *charged residue model*.
From [179,180].

232. ion funnel

Series of stacked ring electrodes with progressively decreasing inner diameter to which a combined radio frequency and fixed potential is applied. The resulting field focuses *ions* travelling along the central axis.
From [181].

233. ion gate

Set of plates or grid of wires in an *ion mobility spectrometer*, *time-of-flight mass spectrometer*, or other *mass spectrometer* that is used to apply a pulsed electric field with the purpose of selectively deflecting charged particles.
See also *mass gate*.
From [182].

234. ionic dissociation

Dissociation of an *ion* into another ion of lower mass and one or more neutral or ions with a lower charge.
From [5,6].

235. ion/ion reaction

Reaction between two *ions*, generally of opposite polarity.

Note: The hyphenated term *ion-ion reaction* is superseded.
From [183].

236. ionization efficiency

Ratio of the number of *ions* generated to the number of molecules consumed in the *ion source* of a *mass spectrometer*.

Note 1: The method for estimating the number of molecules consumed must always be clearly stated.

Note 2: In some older literature the ionization efficiency is defined as the fraction of electrons or photons that ionize a fixed number of molecules. The *ionization efficiency* varies with both the energy and the number of the ionizing entities, and in such cases an *ionization efficiency curve* can provide useful thermochemical information.

Note 3: The ionization efficiency strictly refers to the ionization events in the ion source. The fraction of molecules that are ionized and are subsequently detected also depends on the detection sensitivity of the instrument used.

Revised from [5,6] using additional information from [26,184].

237. ionization efficiency curve

Ionization efficiency as a function of the energy of the electrons or photons used to produce ionization of a fixed number of molecules.

From [5,6].

238. ionization energy, E_i

Deprecated: ionization potential.

Minimum energy required to remove an electron from a neutral atom or molecule in its ground state.

Note 1: *Adiabatic ionization energy* refers to the formation of the *molecular ion* in its ground vibrational state and *vertical ionization energy* applies to the transition to the molecular ion without change in geometry.

Note 2: This quantity was formerly called *ionization potential*.

Note 3: Second ionization energy is the energy required to remove the second electron from the singly charged *ion*.

From [5,6].

239. ionization enhancement

See *ion enhancement*.

240. ionization potential

This term is deprecated.

See *ionization energy*.

241. ionization suppression

See *ion suppression*.

242. ionizing collision (in mass spectrometry)

Reaction of an *ion* with a neutral in which one or more electrons are removed from either the *ion* or neutral to form free electrons.

Note 1: This term has come to be used to describe collisions of fast-moving ions with a neutral in which the neutral is ionized with no change in the number of charges carried by the ion.

Note 2: Care should be taken when this term is used to emphasize whether or not *charge stripping* of the ion has taken place.

See also *charge stripping reaction*.

From [5,6].

243. ion kinetic energy spectrum (IKES)

Spectrum obtained when a beam of *ions* is separated according to the translational energy-to-charge ratios of the ions contained in it.

Note 1: A radial electric field (E) achieves separation of the various ionic species in this way.

Note 2: In this context, kinetic energy is interpreted as translational, rather than vibrational or rotational kinetic energy.

See also *ion energy loss spectrum, mass-analyzed ion kinetic energy spectrometry (MIKES)*.

From [5,6].

244. ion mobility spectrometry (IMS)

Separation of *ions* according to their velocity through a *buffer gas* under the influence of an electric field.

From [185,186].

See also *high-field asymmetric waveform ion mobility spectrometry (FAIMS)*.

245. ion/molecule reaction

Ion/neutral reaction in which the neutral is a molecule.

Note: The hyphenated formulation of this term, *ion-molecule reaction*, is deprecated; the hyphen suggests a reaction of a species that is both an ion and a molecule and is not the intended meaning.

See also *ion/neutral reaction*.

From [5,6].

246. ion/neutral complex

Weakly bound species formed from an *ion* and neutral.

Note 1: In the context of some unimolecular ion dissociations, these complexes are particular types of transition states or local energy minima that lie between *precursor ions* and *product ions* on the reaction coordinate.

Note 2: The hyphenated formulation of this term, *ion-neutral complex*, is deprecated; the hyphen suggests a reaction of a species that is both an ion and a molecule and is not the intended meaning.

See also *adduct ion*.

From [187].

247. ion/neutral reaction

Process wherein an ion interacts with a neutral reactant to produce either chemically different species or changes in the internal energy of one or both of the reactants.

See also *ion/molecule reaction*.

From [5,6].

248. ion/neutral exchange reaction

Reaction of a gas-phase *ion* with a neutral to produce a different neutral and ion as the products.

See also *ion/neutral reaction*.

From [5,6].

249. ion optics

Devices designed to control the formation, focusing, and deflection of charged particle beams in a vacuum under the influence of electric and magnetic fields.

See also *mass spectrometer focusing system*.

From [188].

250. ion pair formation (in mass spectrometry)

Gas-phase reaction of a molecule to form both positive *ion* and negative ion fragments among the products.

From [5,6].

251. ion source

Region in a *mass spectrometer* where gas-phase *ions* are produced.

Revised from [6] using additional information from [189].

**252. ion suppression
ionization suppression**

Phenomenon in which the *ionization efficiency* of a species is lowered by the presence of a different species.

Note: The effect is most significant in *electrospray ionization* but is also observed in *atmospheric pressure chemical ionization* and to a lesser extent in other ionization methods.

See also *ion enhancement*, *matrix effects*.

From [178].

253. ion-to-photon detector

Detector in which *ions* strike a *conversion dynode* to produce electrons that in turn strike a phosphor and the resulting photons are detected by a photomultiplier.

See also *Daly detector*.

From [190].

254. ion trap (IT)

Device for spatially confining *ions* using electric and magnetic fields alone or in combination.

Revised from [5,6] using additional information from [15,191].

255. isobar (in mass spectrometry)

Atomic or molecular species with the same *nominal mass* but different *exact masses*.

Note 1: In the case of atoms, this is equivalent to different nuclides of equal *mass number*.

Note 2: *Isobaric ions* are *isobars* that all carry an electric charge.

Note 3: This term is used in meteorology to denote lines connecting points of equal atmospheric pressure.

Revised from [6].

256. isobaric ion

See *isobar* (in mass spectrometry).

257. isobaric tag for relative and absolute quantitation (iTRAQ)

Chemical labeling reagents used for relative or absolute quantitation in proteomics, based on covalent labeling of the N-terminus and side-chain amines of peptides from protein digestions with tags of varying mass.

From [192,193].

258. isotope cluster

Group of peaks representing *ions* of the same elemental composition, but different isotopic compositions.

See also *isotope pattern*.

From [24].

259. isotope coded affinity tag (ICAT)

Chemical labeling reagents used for relative quantitation in proteomics, consisting of a reactive group capable of labeling a defined amino acid side-chain, an isotopically coded linker, and a tag for the affinity isolation of labeled proteins and peptides.

From [194].

260. isotope delta

See *relative isotope-ratio difference*.

261. isotope dilution mass spectrometry (IDMS)

Quantitative *mass spectrometry* technique in which an isotopically enriched compound is used as a *surrogate internal standard*.

From [195].

262. isotope–number ratio

See *isotope ratio*.

263. isotope pattern

Set of peaks related to *ions* with the same chemical formula but containing different isotopes that has a particular pattern associated with the relative abundance of the isotopes.

See also *isotope cluster*.

From [5,6].

**264. isotope ratio, *R*
isotope–number ratio**

Ratio of the number of atoms of one isotope to the number of atoms of another isotope of the same chemical element in the same system.

Note: Usually the minor, less abundant isotope to the major, most abundant isotope, for example, $^{13}\text{C}/^{12}\text{C}$.

From [196,197].

**265. isotope ratio mass spectrometry (IRMS)
stable isotope mass spectrometry**

Measurement and study of the relative abundances of the different isotopes of an element in a material using a *mass spectrometer*.

From [198].

266. isotopically enriched ion

Ion enriched in an isotope in which the abundance of the particular nuclide is increased above the abundance at which it occurs in a reference, usually a naturally occurring sample.

From [5,6].

267. isotopic ion

Any *ion* containing one or more of the less abundant naturally occurring isotopes of the elements that make up its structure.

Note: For example, CH_2D^+ .

From [5,6].

268. isotopic scrambling

Complete random mixing of isotopes between specified positions in an *ion* or neutral to achieve an equilibrium distribution of isotopes.

Note: In *mass spectrometry*, this term usually refers to the random mixing of isotopes in isolated ions that were formed with a fixed isotopic composition.

See also *partial isotopic scrambling*.

From [5,6].

269. isotopolog ions

Ions that differ only in the isotopic composition of one or more of the constituent atoms.

Note 1: For example, $\text{CH}_4^{+\bullet}$ and $\text{CH}_3\text{D}^{+\bullet}$ or $^{10}\text{BF}_3^{+\bullet}$ and $^{11}\text{BF}_3^{+\bullet}$, or the ions forming an *isotope cluster* corresponding to the *natural isotopic abundances* of the constituent atoms.

Note 2: Isotopolog is an abbreviation of isotopic homolog.

From [6,10].

270. isotopomeric ion

Isomeric *ions* having the same numbers of each isotopic atom but differing in their positions within the ion.

Note 1: Examples are $D_2C=CH_2^{+\bullet}$ and $HDC=CHD^{+\bullet}$.

Note 2: Isotopomeric ions can be either configurational isomers in which two atomic isotopes exchange positions or isotopic stereoisomers.

Note 3: Isotopomer is an abbreviation of isotopic isomer.

From [6,10].

271. jet separator

Gas chromatograph-to-*mass spectrometer* interface where the gas chromatography effluent expands into a lower-pressure region and then through a downstream orifice. The low mass carrier gas molecules diffuse from the jet axis, leaving the sample stream enriched in the heavier analyte molecules.

See also *momentum separator*.

From [199,200].

272. kinetic energy release (KER)

Translational energy of fragments resulting from dissociation of a *metastable ion* measured relative to the center-of-mass.

Note: In this context, kinetic energy is interpreted as translational, rather than vibrational or rotational, kinetic energy.

See also *kinetic energy release distribution (KERD)*.

From [201].

273. kinetic energy release distribution (KERD)

Distribution of values of translational energies in the center-of-mass reference for an ensemble of *metastable ions* undergoing a specific dissociation reaction.

Note: In this context, kinetic energy is interpreted as translational, rather than vibrational or rotational, kinetic energy.

See also *mass-analyzed ion kinetic energy spectrometry (MIKES)*.

From [201].

274. kinetic method

Method for the determination of *ion* thermodynamic quantities by a procedure in which the relative probabilities of competing *ionic dissociations* are measured via the relative abundances of the reaction products.

Note: The extended kinetic method takes the associated entropy changes into account.

Revised from [6].

275. kinetic shift

Excess energy above the thermochemical threshold required to observe dissociation of a *precursor ion* within the timeframe of a particular *mass spectrometry* experiment.

Note: Kinetic shifts are important when thermochemical quantities are deduced from *appearance energy* measurements.

From [202].

276. Kingdon trap

Ion trapping device that consists of an outer barrel-like electrode and a coaxial inner spindle-like electrode that form an electrostatic field with a quadro-logarithmic potential distribution.

Note 1: The frequency of harmonic oscillations of the orbitally trapped ions along the axis of the electrostatic field is independent of the ion velocity and is inversely proportional to the square root of m/z so that the trap can be operated as a mass analyzer using *image current detection* and Fourier transformation of the time domain signal.

Note 2: The trademarked term *Orbitrap* has been used to describe a Kingdon trap used as a *mass spectrometer*.

From [203].

277. label-free quantitation

Method for determining the concentration of proteins through a combination of protein digestion and *liquid chromatography-mass spectrometry (LC-MS)* without relying on stable isotope labeling. Protein quantification is achieved by measuring the signal intensity of peptide ions corresponding to a protein or by counting and comparing the number of fragment *mass spectra* identifying peptides of a given protein.

From [204].

278. laser ablation

Removal of material from a solid or liquid sample using energy delivered by a short laser pulse to form gas-phase species and particles.

See also *laser desorption*.

From [205].

279. laser desorption (LD)

Formation of gas-phase species from a solid or liquid sample surface upon activation using a short pulse of photons from a laser.

See also *laser ablation*.

From [206].

280. laser desorption ionization (LDI)

Formation of gas-phase *ions* by the interaction of a laser with a solid or liquid material.

See also *matrix-assisted laser desorption/ionization*.

From [207].

281. laser ionization (LI)

Formation of *ions* through the interaction of photons from a laser with solid or liquid materials or with gas-phase atoms or molecules.

See also *laser desorption ionization (LDI)*, *photoionization*.

From [5,6].

282. laser microprobe mass spectrometry (LMMS)

Laser desorption ionization mass spectrometry, particularly emphasizing spatially resolved composition information.

From [208].

283. linear ion trap (LIT)

Two-dimensional *Paul ion trap* in which *ions* are confined in the axial dimension by means of a static electric potential.

From [209].

284. linked scan

Scan in a *tandem mass spectrometer* with two or more *m/z* analyzers or in a *sector mass spectrometer* that incorporates at least one *magnetic sector* and one *electric sector*. The analyzers and/or other electric fields are scanned simultaneously so as to preserve a predetermined relationship between scan parameters to produce a *product ion spectrum*, *precursor ion spectrum*, *constant neutral loss spectrum*, or *constant neutral mass gain spectrum*.

From [5,6].

285. liquid chromatography-mass spectrometry (LC-MS)**liquid chromatography/mass spectrometry (LC/MS)**

Technique by which a mixture of analytes is separated into individual components by liquid chromatography (typically high-performance liquid chromatography), followed by detection with a *mass spectrometer*.

Note: Either a hyphen or slash can be used to indicate combined instruments.

From [210,211].

286. liquid ion evaporation

Spray ionization interface in which droplets are dispersed from a pneumatic nebulizer toward a high potential electrode that produces a static charge on the droplets leading to *ion* formation after solvent evaporation.

From [94].

287. liquid junction interface

Means of coupling capillary electrophoresis to a *mass spectrometer* in which a liquid reservoir surrounds the separation capillary and transfer capillary to the mass spectrometer and provides electric contact for the capillary electrophoresis.

From [212,213].

288. liquid secondary ionization (LSI)

Ionization of any species by the interaction of a focused beam of *ions* or atoms with a sample that is dissolved in a solvent matrix.

See also *fast atom bombardment ionization (FAB)*.

From [214].

289. liquid sheath

Flow of make-up liquid in a *sheath flow interface*.

From [215–217].

290. lock mass

Mass of an *ion* of known m/z value, derived from a suitable standard compound introduced into an *ion source* together with the sample to be analyzed, which permits real-time recalibration by correction of m/z shifts arising from instrumental drift.

From [218].

291. low-energy collision-induced dissociation

Collision-induced dissociation process wherein the *precursor ion* has laboratory-frame translational energy lower than a given value, often taken to be 1 keV.

Note: This process can be carried out under single collision conditions but typically requires multiple collisions and the *collisional excitation* is cumulative.

See also *high-energy collision-induced dissociation*.

From [219].

292. lyonium ion

Cation produced by addition of a *hydron* to a solvent molecule.

Note: For example, CH_3OH_2^+ and CH_3OHD^+ are both lyonium ions of methanol.

See also *onium compounds*.

From [6].

293. magnetic deflection

Deflection of an *ion* beam as a result of the motion of the ions in a magnetic field.

Note 1: An example is a *magnetic sector*.

Note 2: Generally, the direction of deflection of the ions is perpendicular to both the direction of the magnetic field and to that of the ion beam.

From [5,6].

294. magnetic field scan

Method of producing a mass spectrum from a mono-energetic *ion* beam by varying the strength of the magnetic field in a *sector mass spectrometer*.

Note 1: The magnetic field scan is sometimes called B-scan, but this is a misnomer since the symbol B denotes the magnetic flux density. The magnetic field strength H in a vacuum is defined in SI units as $H = (1/\mu_0) B - M$ where μ_0 is the magnetic constant or permeability of the vacuum and M the magnetization. B is often wrongly referred to as “magnetic field strength.”

Note 2: A sector magnetic field produces a momentum/charge spectrum of an ion beam, but if all ions have the same translational energy this is equivalent to a mass spectrum. The force F on a particle with charge q and velocity v is $F = q(v \times B)$.

From [5,6].

295. magnetic sector

Device that produces a magnetic field perpendicular to a charged particle beam that deflects the beam to an extent that is proportional to the ratio of particle momentum and charge.

Note: For a mono-energetic beam, the deflection is proportional to m/z .

From [5].

296. magnetron motion

Slow rotation of the center of *cyclotron motion* around the central axis of a *Penning ion trap* that results from a drift of the cyclotron centre along the electric equipotential lines perpendicular to the magnetic field direction.

Note: The characteristic frequency of this motion is called the magnetron frequency.

From [220,221].

297. make-up liquid

Solvent that is mixed with the sample flow in a liquid introduction *mass spectrometry* interface in order to adjust the flow rate or solvent characteristics of the system, for example, to promote *ionization efficiency*.

From [217].

298. mass analysis

Process by which a mixture of ionic or neutral species is identified according to their m/z values (*ions*), or their aggregate atomic masses (neutrals), and their relative abundances. The analysis may be qualitative and/or quantitative.

From [5,6].

299. mass-analyzed ion kinetic energy spectrometry (MIKES)

Deprecated: direct analysis of daughter ions (DADI).

Procedure by which translational energy spectra are obtained from a *sector mass spectrometer* that incorporates at least one *magnetic sector* plus one *electric sector* in *reverse geometry* (a magnetic sector followed by an electric sector).

Note 1: In this context, kinetic energy is interpreted as translational rather than vibrational or rotational kinetic energy.

Note 2: The *accelerating potential*, V , and the magnetic flux density, B , are set at fixed values to m/z select the precursor *ions*, which are then allowed to dissociate or to react in a *field-free region* between the two sectors. The translational energy-to-charge ratios of the various *product ions* are analyzed by scanning the electric sector field E . The width of a product ion spectral peak is related to the *kinetic energy release distribution* for the dissociation process.

From [222].

300. mass calibration

Means of determining m/z values of *ions* from experimentally detected signals using a theoretical or empirical relational equation.

Note: Most commonly this is accomplished using a computer-based data system and a calibration file obtained from a *mass spectrum* of a compound that produces ions of known m/z values.

From [223].

301. mass chromatogram

See *extracted ion chromatogram*.

302. mass defect (in mass spectrometry)

Deprecated: mass excess.

Difference between the nominal *mass* and the *monoisotopic mass* of an atom, molecule, or *ion*.

Note: *Mass defect* can be a positive or negative value dependent upon the elemental composition.

From [224].

303. mass discrimination

Differences in overall detection sensitivities for ions of different m/z values in a mass spectrum, caused by variations in *ionization efficiency*, *transmission efficiency* through the interface between the ion source and the analyzer vacuum system, analyzer, and detector response.

From [225].

304. mass excess

This term is deprecated.

See *mass defect*.

305. mass fragmentography

This term is deprecated.

See *selected ion monitoring*.

306. mass gate

Ion gate used to transmit *ions* in a given m/z range.

See also *ion gate*.
From [226].

307. mass limit

Value of m/z above or below which *ions* cannot be detected in a *mass spectrometer*.
From [227].

308. mass mapping

See *peptide mass fingerprinting*.

309. mass number, A

Sum of the numbers of protons and neutrons in an atom, molecule, or *ion*.

Note: When expressed as a mass in *daltons*, *mass number* is equivalent to *nominal mass*.
From [5,6].

310. mass peak

peak (in mass spectrometry)

Localized region of relatively intense detector response in a *mass spectrum* when *ions* of a specified m/z are detected. If *resolving power* is insufficient two or more components of similar m/z may contribute to one unresolved mass peak.

Note 1: Although mass peaks are often associated with particular *ions*, the terms *peak* and *ion* should not be used interchangeably.

Note 2: Care should be used to distinguish *mass spectrum peaks* from chromatographic peaks in *GC-MS* and *LC-MS*.

Revised from [5,6].

311. mass range

Range of mass over which a *mass spectrometer* can detect *ions* or is operated to record a *mass spectrum*.

Note: When indicating a range of m/z instead of mass, this should be specified explicitly.
From [6].

312. mass resolution

See *resolution (in mass spectrometry)*.

313. mass resolving power

See *resolving power (in mass spectrometry)*.

314. mass selective axial ejection

Use of *mass selective instability* to eject *ions* of selected m/z values from an *ion trap* along the trap axis.
From [228].

315. mass selective instability (MSI)

Unstable trajectories in an ion trap for *ions* within a particular range of m/z values caused by an appropriate combination of oscillating electric fields.

See also *mass selective axial ejection*.

From [229].

316. mass spectral library

Collection of *mass spectra* of different compounds, usually represented as arrays of signal intensity vs. the m/z values.

From [230].

317. mass spectrograph

Mass spectrometer in which the *ions* are directed onto a *focal plane detector* such as a photographic plate.

From [5,6].

318. mass spectrometer

Instrument that measures the m/z values and abundances of gas-phase *ions*.

From [5,6].

319. mass spectrometer focusing system (deflection system)

This term is obsolete.

Assembly in a *sector mass spectrometer* permitting the separation of *ions* according to their ratios of mass-to-charge.

See also *ion optics*.

From [6].

320. mass spectrometry

Obsolete: mass spectroscopy

Study of matter through the formation of gas-phase *ions* that are characterized using *mass spectrometers* by their mass, charge, structure, and/or physico-chemical properties.

Note 1: The term is a misnomer because it is m/z rather than mass that is the independent variable in a *mass spectrum*.

Note 2: *Mass spectroscopy* is an obsolete synonym for *mass spectrometry* that should not be used to avoid confusion with spectroscopies in which the measured quantity is the absorption or emission of electromagnetic radiation.

From [5,6].

**321. mass spectrometry/mass spectrometry (MS/MS)
tandem mass spectrometry**

Acquisition and study of the spectra of the *product ions* or *precursor ions* of m/z selected *ions*, or of precursor ions of a selected neutral mass loss.

Note: MS/MS can be accomplished using instruments incorporating more than one analyzer (*tandem mass spectrometry in space*) or in trap instruments (*tandem mass spectrometry in time*).

From [5].

322. mass spectroscopy

This term is obsolete.

See *mass spectrometry*.

323. mass spectrum

Plot of the relative abundances of *ions* forming a beam or other collection as a function of their m/z values.

Note: The term is a misnomer because it is m/z rather than mass that is the independent variable in a *mass spectrum*.

From [5,6].

324. mass-to-charge ratio

This term is deprecated. The term “ratio of mass to charge” should be used for the quantity expressed in kg C^{-1} in SI units.

See m/z .

**325. Mathieu stability diagram
stability diagram**

Graphical representation expressed in terms of dimensionless reduced coordinates that describes the stability or instability of charged particle motion in a *transmission quadrupole mass spectrometer* or *Paul ion trap*, based on an appropriate form of the Mathieu differential equation.

From [231].

326. matrix-assisted laser desorption/ionization (MALDI)

Formation of gas-phase *ions* from molecules present in a solid or liquid matrix that is irradiated with a laser. The matrix is a material that absorbs the laser energy and promotes ionization.

From [232].

327. matrix effects

In quantitative analysis, especially with *atmospheric pressure ionization* techniques, matrix components co-extracted and co-eluting with the analytes can alter the *ionization efficiency* resulting in poor ana-

lytical accuracy, linearity, and reproducibility. These effects can be either *ionization suppression* or *ionization enhancement*.

From [233].

328. Mattauch–Herzog geometry

Arrangement for a *double-focusing mass spectrograph* in which a deflection of $\pi/(4\sqrt{2})$ rad in a radial *electrostatic energy analyzer* is followed by a magnetic deflection of $\pi/2$ rad.

See also *Nier–Johnson geometry*.

From [5,6].

329. McLafferty rearrangement

Rearrangement reaction involving transfer of a hydrogen atom via a six-member transition state to the formal radical/charge site from a carbon atom four atoms distant from the charge/radical site (the γ -carbon); subsequent rearrangement of electron density can lead to expulsion of an olefin molecule.

Note: Originally applied to ketone molecular *ions* where the charge/radical site is the carbonyl oxygen, but is now more widely applied.

Revised from [5,6].

330. membrane inlet mass spectrometry

See *membrane introduction mass spectrometry (MIMS)*.

331. membrane interface mass spectrometry

See *membrane introduction mass spectrometry (MIMS)*.

332. membrane introduction mass spectrometry (MIMS)

membrane inlet mass spectrometry

membrane interface mass spectrometry

Mass spectrometry measurement that uses a semi-permeable membrane separator that permits the passage of analytes directly from solutions or ambient air to the *mass spectrometer ion* source.

From [234].

333. membrane separator

GC-MS interface with a polymer membrane that selectively passes analyte molecules in preference to the carrier gas thereby enriching the analyte in the gas stream.

From [200].

334. metastable ion

Ion formed with internal energy higher than the threshold for dissociation but with a lifetime great enough to allow it to exit the *ion source* and enter the mass analyzer region where it dissociates before detection.

From [5,6].

**335. microchannel plate (MCP)
channel electron multiplier array**

Thin plate that contains a closely spaced array of channels each of which acts as a *continuous dynode particle multiplier*. A fast charged or neutral particle, or a photon, that strikes the plate causes a cascade of *secondary electrons* that ultimately exits the opposite side of the plate.

See also *continuous dynode particle multiplier*.

From [235].

336. microelectrospray

Electrospray ionization at a low solvent flow rate, typically several microliters per minute or lower, where a pump is used to provide the sample flow.

See also *nanoelectrospray*.

From [236].

337. molar mass, M

Mass of an element or chemical compound divided by its amount of substance.

Note: Amount of substance has historically been referred to as number of moles.

From [6,7].

338. molecular anion

See also *molecular ion*.

From [5,6].

339. molecular beam mass spectrometry

Mass spectrometry measurement in which the sample is introduced into the *ion source* of the *mass spectrometer* as a collimated beam of molecules with a narrow velocity distribution.

From [237].

340. molecular cation

See also *molecular ion*.

From [5,6].

341. molecular effusion separator

GC-MS interface that subjects the *GC* effluent to effusive flow through a porous glass tube. The lighter carrier gas passes out of the tube, leaving the gas within the tube enriched in analyte.

From [200,238].

342. molecular ion

Ion formed by the removal of one or more electrons from a molecule to form a positive ion or the addition of one or more electrons to a molecule to form a negative ion.

Note: *Pseudo-molecular ion* and *quasi-molecular ion* are deprecated; *molecular ion* is reserved for the intact ionized molecule with no component added or removed other than electrons.

From [5,6].

343. momentum separator

Mass spectrometer interface to inlets including chromatography and spray-based *ion sources* that enriches the sample by selecting the central part of the effluent or spray using an orifice or skimmer. Particles with a higher forward momentum diverge less from the spray axis for a given radial momentum.

See also *jet separator*.

From [239,240].

344. monodisperse aerosol generating interface for chromatography (MAGIC)

Particle beam interface that incorporates a monodisperse aerosol generator.

From [96].

345. monoisotopic mass

Exact mass of an *ion* or molecule calculated using the mass of the most abundant isotope of each element.

See also *accurate mass*.

From [51].

346. monoisotopic mass spectrum

Mass spectrum containing only *ions* made up of the principal isotopes of atoms of the original molecules.

See also *monoisotopic mass*.

From [5,6].

347. moving belt interface

Liquid sample *mass spectrometer* interface that uses two or more pulleys and a continuous loop of material. Samples are sprayed or deposited from solution onto the belt where they are transported into the vacuum system for vaporization or desorption and ionization.

From [241].

348. MS/MS spectrum

Mass spectrum obtained using *tandem mass spectrometry*.

From [242].

349. MSⁿ

Symbol for *multiple-stage mass spectrometry* experiments designed to record *product ion spectra* where *n* is the number of *product ion* stages (*nth-generation product ions*).

From [243].

350. multicollector mass spectrometer

Mass spectrograph based on a *double-focusing* magnetic analyzer that spatially disperses ions of different m/z values on to an array of *Faraday cup* detectors, generally used with *inductively coupled plasma* ion sources for isotopic composition measurements.

From [244].

351. multidimensional protein identification technology (MudPIT)

Variant of *shotgun proteomics* in which proteins are first digested and then separated by a combination of strong cation exchange and reversed-phase liquid chromatography followed by *mass spectrometry* detection.

From [245].

352. multiphoton ionization (MPI)

Photoionization of an atom or molecule in which two or more photons are absorbed.

From [5,6].

353. multiple ion detection (MID)

This term is deprecated.

See *selected ion monitoring*.

354. multiple reaction monitoring (MRM)

Application of *selected reaction monitoring* to multiple *product ions* from one or more *precursor ions*.

Note: This term should not be confused with *consecutive reaction monitoring*, which involves the serial application of three or more stages of selected reaction monitoring.

From [246].

355. multiple-stage mass spectrometry

Multiple stages of *precursor ion m/z selection* followed by *product ion* detection for successive n^{th} -*generation product ions*.

See also MS^n .

From [243].

356. m/z

Deprecated: mass-to-charge ratio, thomson.

Abbreviation representing the dimensionless quantity formed by dividing the ratio of the mass of an *ion* to the *unified atomic mass unit*, by its *charge number* (regardless of sign). The abbreviation is written in italicized lowercase letters with no spaces.

Note 1: *Mass-to-charge ratio* is deprecated. Mass-to-charge ratio has been used occasionally for the horizontal axis in a plot of a *mass spectrum*, although the quantity measured is not the ion's mass divided by its electric charge (SI units kg C^{-1}). However, m/z is recommended as an abbreviation to represent the dimensionless quantity that is used almost universally as the independent variable in a mass spectrum.

Note 2: The abbreviation m/z should not be used as a variable in a mathematical equation. Instead, the variables m (in kg) and q (in C) should be used to denote mass and charge.

Note 3: The *thomson* (*Th*) unit [13] is deprecated.

From [5,6].

357. nanoelectrospray

Electrospray ionization at a very low solvent flow rate, typically hundreds of nanoliters per minute of sample solution or lower, often without the use of an external solvent delivery system.

Note: *Nanospray* should only be used to describe the commercial product.

See also *microelectrospray*.

From [247].

358. natural isotopic abundance

Of a specified isotope of an element, the isotopic abundance in the element as found in nature, either an average value on planet Earth or from a specified location.

From [5,6].

359. needle voltage

See *nozzle-skimmer voltage*.

360. negative ion

Atomic or molecular species having a net negative electric charge; an anion.

From [5,6].

361. negative ion chemical ionization (NICI)

Chemical ionization that results in the formation of negative *ions*.

From [5].

362. neutralization-reionization mass spectrometry (NRMS)

Procedure by which neutral species are formed from m/z selected *ions* by charge transfer to a collision gas or by dissociation. The neutral species are separated from the remaining *ions* and ionized through collisions with a second gas.

From [248].

363. neutral loss

Loss of an uncharged species from an *ion* during dissociation.

From [5,6].

364. neutral loss scan

Scan used to generate a *constant neutral loss spectrum*.

From [249].

365. Nier–Johnson geometry

Arrangement for a *double-focusing mass spectrometer* in which a deflection of $\pi/2$ rad in a radial electrostatic energy analyzer is combined with a magnetic deflection of $\pi/3$ rad, thus providing a single point of focus for *ions* of the same m/z but with spreads in both trajectory direction and translational energy.

See also *Mattauch–Herzog geometry*.

Revised from [5,6] using additional information from [250].

366. nitrenium ion

Reactive intermediate based on nitrogen with both an electron lone pair and a positive charge and with two substituents (R_2N^+).

Note: The alkylidene derivatives of (H_2N^+), ($R_2C=N^+$), still belong to the class nitrenium ions but are more precisely designated by the term *iminylum ions*.

From [6].

367. nitrogen rule

Rule stating that a neutral organic molecule containing one or more atoms of the elements C, H, O, N, S, P, or any halogen has an odd *nominal mass* if it contains an odd number of nitrogen atoms.

From [24].

368. nominal mass

Mass of a molecular *ion* or molecule calculated using the isotope mass of the most abundant constituent element isotope of each element rounded to the nearest integer value and multiplied by the number of atoms of each element.

See also *monoisotopic mass*.

From [51].

369. normal geometry

See *forward geometry*.

**370. nozzle-skimmer dissociation
in-source collision-induced dissociation**

Collisionally activated dissociation that is caused by collisions in the region between the nozzle and skimmer of an *atmospheric pressure ionization* source such as *electrospray* or *atmospheric pressure chemical ionization*.

Note: The process can be induced by a higher than typical *nozzle-skimmer voltage*.

From [251,252].

**371. nozzle-skimmer voltage
needle voltage**

Electric potential difference applied between the *electrospray needle* and the *skimmer*, which is typically held at the same potential as the *counter electrode*.

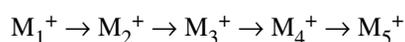
From [252,253].

372. *n*th-generation product ion

Deprecated: granddaughter ion.

Serial *product ions* from dissociation or bimolecular reaction of selected *precursor ions* where *n* refers to the number of stages of dissociation or bimolecular reaction in a series of consecutive reactions that involve successive *product ions*.

Note 1: Given the sequential fragmentation scheme:



M_4^+ is the precursor ion of M_5^+ , a 1st-generation product ion of M_3^+ , a 2nd-generation product ion of M_2^+ , and a 3rd-generation product ion of M_1^+ .

See also *nth-generation product ion spectrum*.

From [8,152,153].

373. *n*th-generation product ion spectrum

Mass spectrum recorded from any *mass spectrometer* in which the appropriate scan function can be set to record the appropriate generation *product ion* or *ions* of *m/z* selected *precursor ions*.

See also *nth-generation product ion*.

From [152,153].

374. odd-electron ion

See *radical ion*.

From [5,6].

375. onium compounds

Cations derived by addition of a H^+ to a mononuclear parent hydride of the nitrogen, chalcogen, and halogen families.

Note: Examples are ammonium (NH_4^+), oxonium (H_3O^+), and fluoronium (H_2F^+) ions.

See also *lyonium ion*.

From [6].

376. orthogonal acceleration

See *orthogonal extraction*.

377. orthogonal electrospray

Configuration for *electrospray* ionization in which the axis of the spray is at a right angle to the axis of the *sampling cone*.

From [254].

**378. orthogonal extraction
orthogonal acceleration**

Pulsed acceleration of *ions* perpendicular to their original direction of travel into a *mass spectrometer*, typically *time-of-flight*.

Note: *Ions* may be extracted from a directional *ion source*, drift tube, or *m/z* separation stage. From [252].

379. parent ion

This term is deprecated.

See *precursor ion*.

380. parent ion spectrum

This term is deprecated.

See *precursor ion spectrum*.

381. partial charge exchange reaction

See *partial charge transfer reaction*.

**382. partial charge transfer reaction
partial charge exchange reaction**

Reaction of an *ion* with a neutral species in which some but not all of the ion charge is transferred to the neutral.

From [5,6].

383. partial isotopic scrambling

Partial random mixing of isotopes among specified atom positions in an ion or neutral species.

Note: In *mass spectrometry*, this term usually refers to the partial random mixing of isotopes in isolated *ions* that were formed with a fixed isotopic composition.

Revised from [5,6] using additional information from [255].

384. particle beam interface

Method for coupling liquid chromatography to *mass spectrometry* in which the effluent is passed through a heated capillary to form an expanding jet of vapour and aerosol particles. After passing through a skimmer that acts as a momentum separator, the beam impinges on a heated surface to form *ions* through *chemical ionization* at the surface or ionization of the resulting vapour in a *chemical ionization* or *electron ionization* source.

From [256,257].

**385. Paul ion trap
quadrupole ion trap
quadrupole ion storage trap**

Ion trapping device that depends on the application of radio frequency potentials between a ring electrode and two end-cap electrodes to confine the ion motion to a cyclic path described by an appropriate form of the Mathieu equation. The choice of these potentials determines the m/z value below which ions are not trapped.

From [10,52,62].

386. peak (in mass spectrometry)

See *mass peak*.

387. peak height

Height of a recorded *peak* in a *mass spectrum*.

From [5].

388. peak matching

Procedure for measuring the *accurate mass* of an *ion* using scanning *mass spectrometers*, in which the *peak* corresponding to the unknown ion and that for a *reference ion* of known m/z are displayed alternately and caused to overlap by adjusting appropriate electric fields.

From [258].

389. peak parking

Method used to extend the amount of time available for *mass spectrometric* analysis of the components in a narrow chromatographic peak. The eluent flow rate is reduced to an ultra-low level at the leading edge of the peak and held at this low flow rate for the duration of compound elution, thus enabling collection of sufficient data for reliable statistical analysis.

From [259].

390. peak stripping

Data analysis technique used in elemental *mass spectrometry* to correct the intensity of an unresolved multiplet peak monitored for a specific element for contributions from a multi-isotopic contaminant. The correction is calculated from the measured intensity of a different isotopic peak of the contaminant and the known *natural isotopic abundance* ratio.

From [260].

391. Penning ionization

Ionization via electron removal that occurs through the energy transfer from a neutral species (N) internally excited to a metastable state (such as a high Rydberg state) to a neutral species (M) with lower *ionization energy*, as represented by the following reaction: $N^* + M \rightarrow N + M^{+\bullet} + e^-$.

Note: Penning ionization differs from *chemi-ionization* in that no chemical change is involved.

From [5].

392. Penning ion trap

Ion trapping device using a static magnetic field and a static electric potential well. The magnetic field confines the ion motion to circular orbits around the magnetic force line direction, which aligns with the direction of the trap axis, whereas the electric potential well confines the ion motion axially.

Note: This device is used for the mass analyzer of *Fourier transform-ion cyclotron resonance-mass spectrometers*.

From [261].

393. peptide mass fingerprinting (PMF) mass mapping

Method for protein analysis where an unknown protein is chemically or enzymatically cleaved into peptide fragments whose masses are determined by *mass spectrometry*. The peptide masses are compared to peptide masses calculated for known proteins in a database and analyzed statistically to determine the best match.

See also *accurate mass tag*.

From [262].

394. peptide sequence tag

Sequence of peptide ion fragment masses that can be used to aid in the identification of the amino acid sequence.

Note: *Sequence tags* are often obtained in *tandem mass spectrometry* analysis of peptides from an unknown protein that has been chemically or enzymatically cleaved into peptide fragments.

From [263].

395. photodissociation

Process wherein the reactant *ion* or molecule is dissociated as a result of absorption of one or more photons.

From [264].

396. photographic plate recording

Recording of *ion* currents by allowing them to strike a photographic plate, which is subsequently developed.

Note: This technique is typically associated with *ion*-beams that have been spatially separated by *m/z* and focused across a focal plane as in a *Mattauch–Herzog geometry magnetic sector* instrument.

From [5].

397. photoionization (PI)

Deprecated: photon impact.

Ionization of an atom or molecule by a photon, written $M + h\nu \rightarrow M^{+*} + e^{-}$.

See also *multiphoton ionization*.

From [5,6].

398. photon impact

This term is deprecated.

See *photoionization*.

399. π/n rad ($180^\circ/n$) magnetic sector

Arrangement in which an ion beam is deflected magnetically through π/n rad, where $n > 1$.

From [5].

400. plasma (in spectrochemistry)

Gas that is at least partly ionized and contains particles of various types: electrons, atoms, *ions*, and molecules. The plasma as a whole is electrically neutral.

From [5,6].

**401. plasma desorption ionization (PDI)
fission fragment ionization**

Ionization of material in a solid sample by bombarding it with *ions* and/or neutral atoms formed as a result of the fission of a suitable nuclide, typically ^{252}Cf .

From [5,6].

402. pneumatically assisted electrospray ionization

Electrospray ionization in which the nebulization of the liquid stream is assisted by a concentric stream of gas.

Note: *Ionspray* should only be used to describe the commercial product.

From [265].

403. point detector

Detector in which the ion beam is focused onto a small area, for example, defined by a *collector slit*, rather than dispersed by m/z spatially across a focal plane.

From [266].

404. positive ion

Atomic or molecular species having a net positive electric charge; a cation.

From [5,6].

405. post-acceleration detector (PAD)

Detector in which a high potential is applied after m/z separation to accelerate the *ions* and produce an improved signal.

See also *conversion dynode*.

From [267].

406. post-source decay (PSD)

Technique specific to *reflectron time-of-flight mass spectrometers* where *product ions* of metastable transitions or *collision-induced dissociations* generated in the flight tube prior to entering the reflectron are separated according to *m/z* to yield *product ion spectra*.

From [268].

**407. precursor ion
progenitor ion**

Deprecated: parent ion.

Ion that reacts to form particular *product ions* or undergoes specified *neutral losses*. The reaction can be of different types including *unimolecular dissociation*, *ion/molecule reaction*, change in charge state, possibly preceded by isomerization.

Revised from [5,6] using additional information from [8,16,17].

408. precursor ion spectrum

Deprecated: parent ion spectrum.

Mass spectrum in which the appropriate *m/z* separation function records the *precursor ions* of selected *product ions* or specified neutral loss.

Note: The *ion current* recorded by the detector is that from the product ion but the *m/z* values corresponding to the peaks in the resulting spectrum are those of precursor ions that fragmented in the fashion specified by the *m/z* separation function of the *tandem mass spectrometer*.

See also *product ion spectrum*.

From [8,16,17].

409. pre-ionization state

Electronic state capable of undergoing *autoionization*.

From [5,6].

410. principal ion

Most abundant *ion* of an *isotope cluster*.

Note 1: An example is the $^{11}\text{B}^{79}\text{Br}_2^{81}\text{Br}^{+\bullet}$ ion of *m/z* 250 of the cluster of *isotopolog molecular ions* of BBr_3 .

Note 2: Principal ion has also been used to describe ions that have been artificially isotopically enriched in one or more positions such as $^{13}\text{CH}_3^{+\bullet}$ or CH_2D_2^+ , but those are best defined as *isotopolog ions*.

From [5,6].

411. probability-based matching

Automated system for computer examination of the *mass spectrum* of an unknown mixture for the presence of a specific compound for which a standard spectrum is available in a library. The probability that the compound is present is given by a confidence index *K* such that 2^K is the average number of ran-

domly selected compounds whose *mass spectra* would have to be examined to find data which match the target spectrum to the same degree as does the unknown.

From [269].

412. product ion

Deprecated: daughter ion.

Ion formed as the product of a reaction involving a particular *precursor ion*.

Note: The reaction can be of different types including *unimolecular dissociation* to form *fragment ions*, an *ion/molecule reaction*, or simply involve a change in the number of charges.

Revised from [5,6] using additional information from [8,16,17].

413. product ion analysis

Deprecated: daughter ion analysis.

Process whereby a *precursor ion* of a particular *m/z* is selected by *m/z*, fragmentation is induced, and the *mass spectrum* of the resulting *product ions* is recorded.

Revised from [5] using additional information from [152,153].

414. product ion spectrum

Mass spectrum in which the appropriate *m/z* separation analysis function is set to record the *product ions* of a selected *precursor ion* selected by *m/z*.

See also *precursor ion spectrum*.

From [8,16,17].

415. profile mode

Method for acquiring a *mass spectrum* where each *peak* is displayed as a curve, with the data points defining the curve corresponding to the signal intensities at each particular *m/z* value.

See also *centroid acquisition*.

From [270,271].

416. progenitor ion

See *precursor ion*.

From [5,6].

417. prolate trochoidal mass spectrometer

Deprecated: cycloidal mass spectrometer.

Mass spectrometer in which the *ions* of different *m/z* are separated by means of crossed electric and magnetic fields in such a way that the selected ions follow a prolate trochoidal path.

From [5,6].

418. proton affinity (PA)

For a species M, the negative of the enthalpy change for the gas phase reaction $M + H^+ \rightarrow [M + H]^+$ at a specified temperature, usually 298 K.
From [5,6].

419. protonated molecular ion

This term is deprecated.
See *protonated molecule*.

420. protonated molecule

Deprecated: protonated molecular ion, pseudo-molecular ion, quasi-molecular ion.

Adduct ion, represented by $[M + H]^+$, formed by the interaction of a molecule with a proton (*hydron*).

Note 1: Multiply protonated molecules are represented by $[M + nH]^{n+}$ where n is the number of protons.

Note 2: *Protonated molecular ion* is deprecated; for example, for a molecular ion $M^{+\bullet}$ this would correspond to a species carrying two positive charges plus an unpaired electron.

Note 3: *Pseudo-molecular ion* and *quasi-molecular ion* are deprecated; a specific term such as *protonated molecule*, or a chemical description such as $[M + H]^+$ should be used.

See also *adduct ion*.

Revised from [5,6] using additional information from [16].

421. proton-bound dimer

Dimeric *ion* consisting of two similar or dissimilar molecules bound together by hydrogen bonding with a shared proton.
From [272,273].

422. pseudo-molecular ion

This term is deprecated.
See *protonated molecule*.

423. pyrolysis mass spectrometry (PyMS)

Mass spectrometry technique in which the sample is heated to the point of decomposition and the gas-phase decomposition products are characterized by mass spectrometry.
From [274].

424. quadratic field reflectron

Reflectron in which the electric field varies with the square of the distance from the entrance and compensates for kinetic energy spread to all orders.
From [275].

425. quadrupolar axialization

Technique for *axialization* in *Fourier transform-ion cyclotron resonance-mass spectrometers* in which magnetron motion is converted into *cyclotron motion* by subjecting the trapped *ions* to a quadrupolar excitation field while they undergo collisions.

From [276,277].

426. quadrupole ion storage trap (QUISTOR)

See *Paul ion trap*.

427. quadrupole ion trap (QIT)

See *Paul ion trap*.

428. quadrupole mass analyzer

See *transmission quadrupole mass spectrometer*.

429. quadrupole mass filter (QMF)

See *transmission quadrupole mass spectrometer*.

430. quadrupole mass spectrometer (QMS)

See *transmission quadrupole mass spectrometer*.

431. quadrupole time-of-flight (QTOF)

Hybrid mass spectrometer consisting of a *transmission quadrupole mass spectrometer* coupled to an *orthogonal acceleration time-of-flight mass spectrometer*. A *collision quadrupole* is typically inserted between the two *mass spectrometers*.

From [278].

432. quantitation by concatenated tryptic peptides (QCAT)

Method for absolute quantitation of a protein or proteins in a multiplexed fashion using isotope-labeled peptides as *surrogate internal standards*. The labeled peptides are produced by synthesizing a gene coding for all desired peptides, expressing this gene in *E. coli* culture containing appropriately labeled substrate, and digesting with trypsin the expressed protein composed of the desired concatenated peptides.

From [279].

433. quasi-equilibrium theory (QET)

Statistical theory of unimolecular reaction rates (isomerization or fragmentation) of molecular species that assumes that reaction occurs from the ground electronic state of the reactant regardless of its mode of formation, at a rate determined by the free statistical redistribution of internal energy into those vibrational and rotational modes that must be activated sufficiently to reach the appropriate transition state for the specified reaction to occur. The QET applies to isolated molecular species in the absence of collisions, as for *ion* fragmentations in a *mass spectrometer*. Early formulations assumed the reactant con-

tained s identical harmonic oscillators of frequency ν , with a transition state corresponding to just one critical oscillator containing at least m quanta corresponding to the critical energy for reaction $\varepsilon^* = m\nu$. A further assumption that $m \gg s$ leads to an ultra-simple expression for the unimolecular rate constant at total internal energy ε : $k(\varepsilon) = \nu[(\varepsilon - \varepsilon^*)/\varepsilon]^{(s-1)}$. Elimination of most of these simplifying assumptions followed development of the *Rice–Ramsperger–Kassel–Marcus (RRKM) theory*.

See also *Rice–Ramsperger–Kassel (RRK) theory*.

Revised from [6] using additional information from [280,281].

434. quasi-molecular ion

This term is deprecated.

See *protonated molecule*.

435. radial ejection

Ejection of an *ion* from an *ion trap* in a direction perpendicular to the longitudinal axis of the trap.

From [282].

436. radial electrostatic field analyzer

Arrangement of two conducting sheets forming a capacitor and giving a radial electrostatic field which is used to deflect and focus *ion* beams. The degree of deflection varies with the ratio of translational energy to charge. The capacitor may be cylindrical, spherical, or toroidal.

Revised from [5,6].

437. radical ion odd-electron ion

Cation or anion containing unpaired electrons in its ground state. An unpaired electron is denoted by a superscript dot following the superscript symbol for charge, such as for the *molecular ion* of a molecule M, that is, $M^{+\bullet}$. Radical *ions* with more than one charge and/or more than one unpaired electron are denoted using parentheses, for example, as $M^{(2+)(2\bullet)}$.

Note 1: Unless the positions of the unpaired electron and charge can be associated with specific atoms, superscript charge designation should be placed before the superscript dot designation.

Note 2: The order of the unpaired electron and charge are reversed from that recommended for organic and inorganic chemistry in which the dot representing the unpaired electron precedes the symbol for the charge. This convention is widely used in the *mass spectrometry* field and has been in place for many decades, and is retained here for that reason.

Note 3: It is not recommended that the charge designation be placed directly above the centrally placed dot because of the difficulty of extending it to ions bearing more than one charge and/or more than one unpaired electron.

From [6].

438. Rayleigh limit

Limiting droplet size at which self-fragmentation will occur for charged droplets generated in *electrospray* or other *ionization* processes. Self-fragmentation occurs when the electrostatic repulsion force generated by the excess charge exceeds the surface tension that maintains the integrity of the droplet.

From [283].

439. reagent gas

Gas that reacts with *ions* to produce *product ions* through *ion/molecule reactions*; for example, a gas such as methane, ammonia, or isobutane used in *chemical ionization* to create *reagent ions* or a gas used in *ion traps* or *collision cells* to perform gas-phase ion/molecule reactions.

From [284].

440. reagent ion

Ion that reacts with a neutral to produce an ionized form of such species through an *ion/molecule reaction*, for example, as in *chemical ionization*.

From [284].

441. rearrangement ion

Ion that results from molecular rearrangement; in which its atoms or groups of atoms have transferred from one portion of the molecule to another during or following ionization.

From [5,6].

442. recombination energy

Energy released when an electron is added to an ionized molecule or atom.

Note: This is the energy required for the reverse process of *vertical ionization*.

From [285].

443. reconstructed ion chromatogram

See *extracted ion chromatogram*.

444. reconstructed total ion current chromatogram

See *total ion current chromatogram*.

445. rectilinear ion trap

Quadrupole ion trap whose electrodes form a rectilinear polygon, the simplest form of which consists of two pairs of rectangular electrodes supplied with radio frequency (RF) potentials and a pair of electrodes to which a DC potential is applied. Slits or apertures in the electrodes allow injection and ejection of charged particles.

From [286].

446. reference ion

Stable *ion* whose structure or elemental formula is known with certainty. These ions are formed by direct ionization of a molecule of known structure or elemental formula, and are used to verify by comparison the structure or thermochemistry of an unknown ion or to calibrate the m/z scale of the *mass spectrometer*.

From [287–289].

447. reflectron

Component of a *time-of-flight mass spectrometer* that uses a static electric field to reverse the direction of travel of the *ions* and improves mass resolution by assuring that ions of the same m/z but different translational energy arrive at the detector at the same time.

From [290].

**448. relative detection limit
detection limit**

Smallest amount of material detectable in a matrix relative to the amount of material analyzed, given in atomic, mole, or weight fractions.

Note 1: The meaning of “detectable” must be specified, for example, three times the standard deviation of the measurement (3σ criterion).

Note 2: Often incorrectly referred to as sensitivity.

From [6]

449. relative difference of isotope ratios

See *relative isotope-ratio difference*.

450. relative intensity (in mass spectrometry)

See *intensity relative to base peak (in mass spectrometry)*.

From [8].

**451. relative isotope-ratio difference, δ
delta notation
isotope delta
relative difference of isotope ratios**

Measure of an isotope ratio in a sample of interest relative to a reference defined by the relation

$$\delta = (R_{\text{sample}} - R_{\text{standard}})/R_{\text{standard}}$$

where R is the *isotope ratio* of the element.

Note 1: The reference is often an international measurement standard.

Note 2: The same relative differences are used to calculate delta values from the abundance of *isotopomers* and *isotopologs*, ion currents, frequencies, or optical extinctions.

Note 3: Relative isotope ratio differences are usually small and are therefore often expressed in units of parts per mil with symbol ‰.

Note 4: Units of parts per thousand (ppt, 10^{-3}) or parts per million (ppm, 10^{-6}) are deprecated [7].

From [196,197].

452. residual gas analyzer (RGA)

Mass spectrometer used to measure the composition and pressure of gases in an evacuated chamber and to test for leaks in pressurized systems.

From [291].

453. residual spectrum

Mass spectrum with peaks recorded in the absence of sample and due either to small air leaks or to the presence of molecules desorbed from the walls of the introduction device, the *ion source*, or from vacuum pump fluids.

See also *background mass spectrum*.

From [11].

454. resolution (in mass spectrometry) mass resolution

In a *mass spectrum*, the observed m/z value divided by the smallest difference $\Delta(m/z)$ for two *ions* that can be separated: $(m/z)/\Delta(m/z)$.

Note 1: The m/z value at which the measurement was made should be reported.

Note 2: The definition and method of measurement of $\Delta(m/z)$ should be reported. Commonly this is performed using *peak* width measured at a specified percentage of *peak* height.

Note 3: Alternatively $\Delta(m/z)$ is defined as the separation between two adjacent equal magnitude peaks such that the valley between them is a specified fraction of the *peak* height, for example as measured by *peak matching*.

See also *resolving power (in mass spectrometry)*.

Revised from [5,10] using additional information from [292,293].

455. resolution: 10 per cent valley definition

Value of $(m/z)/\Delta(m/z)$ measured for two *peaks* of equal height in a *mass spectrum* at m/z and $m/z \pm \Delta(m/z)$ that are separated by a valley which at its lowest point is 10 % of the height of either *peak*. For *peaks* of similar height separated by a valley, let the height of the valley at its lowest point be 10 % of the lower *peak*. Then the resolution (10 % valley definition) is $(m/z)/\Delta(m/z)$ and should be given for a number of values of m/z .

See also *resolution: peak width definition*.

From [5,6].

456. resolution: peak width definition

For a single *peak* corresponding to singly charged *ions* at mass m in a *mass spectrum*, the resolution may be expressed as $(m/z)/\Delta(m/z)$, where $\Delta(m/z)$ is the width of the *peak* at a height which is a specified fraction of the maximum peak height. It is recommended that one of three values 50, 5, or 0.5 % should always be used.

Note: For an isolated symmetrical peak recorded with a system which is linear in the range between 5 % and 10 % levels of the peak, the 5 % peak width definition is equivalent to the 10 % valley definition. A common standard is the definition of resolution based upon Δm being full width of the peak at half its maximum (FWHM) height.

See also *resolution: 10 per cent valley definition*.

From [5,6].

457. resolving power (in mass spectrometry)
mass resolving power

Measure of the ability of a *mass spectrometer* to provide a specified value of *mass resolution*.

Note: The procedure by which $\Delta(m/z)$ was defined and measured, and the m/z value at which the measurement was made, should be reported.

Revised from [5,6].

458. resonance-enhanced multiphoton ionization (REMPI)
resonance ionization

Multiphoton ionization in which the ionization cross section is significantly enhanced because the energy of the incident photons is resonant with an intermediate excited state of the neutral.

From [294,295].

459. resonance ion ejection

Mode of *ion ejection* in an *ion trap* that relies on an auxiliary radio frequency potential that is applied to the end-cap or trapping electrodes. The potential is tuned to the classical oscillation frequency of a particular ion to eject it.

From [296].

460. resonance ionization (RI)

See *resonance-enhanced multiphoton ionization*.

461. retro Diels–Alder reaction

Ion fragmentation mechanism in which the *molecular ion* $M^{+\bullet}$ of a cyclic alkene fragments to form a neutral diene and an alkene radical cation or a diene radical cation and an alkene. The reaction is the reverse of the Diels–Alder reaction of organic synthesis.

From [297].

462. reverse geometry

Double-focusing mass spectrometer configuration in which the *ion beam* traverses the *magnetic sector* prior to the *electric sector*.

See also *forward geometry*.

From [149].

463. reverse library search

Process of comparing a subset of the *peaks* in the *mass spectrum* of an unknown compound with peaks present in the library mass spectrum. Any peaks in the mass spectrum of the unknown compound that are not in the library spectrum are disregarded.

Note: A reverse library search measures the extent to which the peaks in a reference spectrum are present in the unknown spectrum and is more effective than a *forward library search* when peaks arising from two or more components are present in the unknown spectrum

See also *forward library search*.

From [230].

464. RF-DC ion mobility spectrometry

See *high-field asymmetric waveform ion mobility spectrometry*.

465. RF-only quadrupole

Transmission quadrupole device in which a sinusoidal radio frequency (RF) potential is applied between the connected pairs of opposite rod electrodes in a linear quadrupole, providing a transmission device for all *ions* with m/z values above a cut-off value.

Note: Higher-order multipoles can also be used in this manner.

See also *collision quadrupole*.

From [78].

466. Rice–Ramsperger–Kassel–Marcus (RRKM) theory

Statistical theory of unimolecular reaction rates of gas-phase molecular species that removes most of the simplifying assumptions in the *Rice–Ramsperger–Kassel (RRK) theory*. Account is taken of the way in which the different normal-mode vibrations and rotations contribute to reaction, and allowance is made for the zero-point energies. The total internal energy is partitioned into active and inactive components, such that only the active component can flow freely among the internal modes and thus contribute to reaction. The assumed equilibrium ratio of active-to-inactive components is evaluated using partition functions. In applications where gas-phase collisions are important, the rates of activation and deactivation take into account their energy dependence, and in the high-pressure limit the transition state is in equilibrium with non-activated reactants and RRKM reduces to conventional transition-state theory.

Note: The theory is also used (with some modification) for reactions in condensed phases. Revised from [6] using additional information from [298–300].

467. Rice–Ramsperger–Kassel (RRK) theory

Statistical theory of unimolecular reaction rates of gas-phase molecular species that is equivalent to the *quasi-equilibrium theory*, but with the added consideration that the effects of gas-phase collisions in activation to and deactivation from the transition state are taken into account.

Note: Elimination of most of the simplifying assumptions led to development of the *Rice–Ramsperger–Kassel–Marcus (RRKM) theory*.

Revised from [6] using additional information from [281,301,302].

468. ring and double bond equivalent

Deprecated: rings plus double bonds.

Conventional measure of the degree of unsaturation of an organic molecule given by $X - Y/2 + Z/2 + 1$ where X is the number of carbon atoms, Y is the number of hydrogen or halogen atoms and Z is the number of nitrogen and phosphorus atoms.

From [24,303].

469. rings plus double bonds

This term is deprecated.

See *ring and double bond equivalent*.

470. saddle field gun

Compact *ion* and fast atom sources for use when small size and high beam intensity are required, as in *fast atom bombardment mass spectrometry*. The discharge is produced by electrons oscillating between two cold cathodes in an electric field that possesses a single saddle point. To produce and intensify the *plasma* the electrons must have long path lengths, achieved by allowing the electrons to have an oscillatory motion in the saddle-shaped electric field between the cathodes separated by the anode.

From [304].

471. sampling cone

Component of a *spray ionization* interface that consists of a cone with a small orifice through which the spray passes into a differentially pumped chamber

Note 1: In interfaces that have both a sampling cone and *skimmer*, the spray passes first through the sampling cone and then through the skimmer.

Note 2: A capillary can also be used in place of a cone.

From [49,254,305].

472. scan cycle time

Time required to obtain a *mass spectrum* (or other mass spectrometric data quantity) such as in a separation coupled to *mass spectrometry*.

From [137,306].

473. secondary electron

Electrons ejected from a sample surface as a result of bombardment by a primary beam of atoms, *ions*, electrons, or photons.

From [307].

474. secondary ionization

Process in which *ions* are ejected from a sample surface as a result of bombardment by a primary beam of atoms or *ions*.

See also *secondary ion mass spectrometry (SIMS)*.

From [6].

475. secondary ion mass spectrometry (SIMS)

Technique in which a focused beam of primary *ions* produces secondary ions by sputtering from a solid surface. The secondary ions are analyzed by *mass spectrometry*.

See also *dynamic secondary ion mass spectrometry (DSIMS)*, *static secondary ion mass spectrometry (SSIMS)*.

From [308].

476. secondary neutral mass spectrometry (SNMS)

Mass spectrometry technique in which neutral species ejected from a sample surface as a result of bombardment by a primary beam of atoms or *ions* are ionized, most often by *photoionization*, prior to analysis.

See also *secondary ion mass spectrometry (SIMS)*.

From [309,310].

477. sector mass spectrometer

Mass spectrometer consisting of one or more *magnetic sectors* for recording a *mass spectrum* of a monoenergetic beam of *ions*. Such instruments may also have one or more *electric sectors* for energy dispersion that can be arranged for velocity-focusing by compensating for dispersion by the magnetic sector if the beam is not truly monoenergetic. Such a combination provides double focusing of ions of the same m/z , i.e., focusing with respect to both direction and speed.

From [311].

478. selected ion flow tube (SIFT)

Device in which m/z selected *ions* are entrained in an inert carrier gas and subsequently undergo *ion/molecule reactions* with molecules introduced into the gas flow.

See also *drift tube*.

From [312].

479. selected ion monitoring (SIM)

Deprecated: multiple ion detection, mass fragmentography, selected ion recording.

Operation of a *mass spectrometer* in which the abundances of *ions* of one or more specific m/z values are recorded rather than the entire *mass spectrum*.

See also *selected reaction monitoring (SRM)*.

Revised from [5,6] using additional information from [313].

480. selected ion recording (SIR)

This term is deprecated.

See *selected ion monitoring (SIM)*.

481. selected reaction monitoring (SRM)

Data acquired from one or more specific *product ions* corresponding to m/z selected *precursor ions* recorded via two or more stages of *mass spectrometry*.

Note 1: Selected reaction monitoring in multiple-stage mass spectrometry is known as consecutive reaction monitoring.

Note 2: Selected reaction monitoring applied to multiple product ions from one or more precursor ions is known as multiple reaction monitoring.

See also *selected ion monitoring (SIM)*.

From [314].

482. self-chemical ionization (self-CI)

Chemical ionization of an analyte where the *reagent ion* is an ionized form of the *analyte* or one of its *product ions*.

From [315].

483. sensitivity, A

Slope of the calibration curve.

Note 1: If the curve is not a straight line, sensitivity will be a function of *analyte* concentration or amount.

Note 2: If sensitivity is to be a unique performance characteristic, it must depend only on the chemical measurement process, not upon scale factors.

From [5,6].

484. sheath flow interface

Capillary electrophoresis to *electrospray ionization* interface that uses a coaxial flow of *make-up liquid* that is introduced through a tube that is concentric with the separation capillary.

From [216,217].

485. sheath gas

Gas introduced through a tube that is coaxial with the *electrospray emitter* to pneumatically assist the formation of the sprayed droplets.

From [316].

486. sheath liquid

Make-up liquid in a *sheath flow interface*.

From [26].

487. shotgun proteomics

Protein identification using a combination of high-performance liquid chromatography and *mass spectrometry* in which the proteins in a mixture are digested, usually by a specific enzyme, and the resulting peptides are separated by liquid chromatography and identified by *tandem mass spectrometry*.

See also *bottom-up proteomics*.

From [317].

488. skimmer

Cone with a central orifice that intercepts the center of a spray or jet expansion to sample the central portion of the expansion, for example, as in a *momentum separator*.
From [253].

489. soft ionization

Formation of gas-phase *ions* without extensive fragmentation.
See also *hard ionization*.
From [318].

490. sonic spray ionization (SSI)

Process in which both anions and cations are produced at atmospheric pressure from an ionic solution due to a statistically unbalanced charge distribution in the minute droplets formed by the action of a sonic atomizer.
See also *spray ionization*.
From [319].

491. space charge effect

Result of mutual repulsion of particles of like charge (*ions*, electrons, etc.) that can limit the current in a charged-particle beam and can also cause some motion of ions in a beam or packet in addition to that caused by external fields.

Note: Space charge effects on ion trajectories are most noticeable in *ion trap* instruments that confine large numbers of ions in a small volume.

From [320].

492. spark ionization

Formation of *ions* from a solid material by an intermittent electric discharge.
From [5,6].

493. spectral skewing

Deviation of the *peak* intensities in a *mass spectrum* from their expected values that occurs when the relative concentration of the various *analytes* change during acquisition of the mass spectrum.
From [321].

494. spray ionization

General term used to describe a range of ionization techniques for *analytes* in solution that involve dispersing the liquid into fine droplets as a component step.

Note: Most of these techniques are examples of *atmospheric pressure ionization*.
From [322].

495. stable ion

Ion with internal energy sufficiently low that it does not rearrange or dissociate prior to detection in a *mass spectrometer*.

From [5,6].

496. stable isotope mass spectrometry

See *isotope ratio mass spectrometry*.

497. stable isotope ratio analysis of amino acids in cell culture (SILAC)

Proteomics technique that detects differences in protein abundance between cultured cell samples using stable isotopic labeling achieved with labeled amino acids in one cell culture and unlabeled ones in a separate culture.

From [323–325].

498. stable isotope standards and capture by anti-peptide antibodies (SISCAPA)

Method for absolute quantitation of a protein or proteins in a multiplexed fashion using isotope-labeled peptides as *surrogate internal standards*. The labeled peptides are produced by synthesizing a gene coding for each desired peptide, cell-free transcription, and translation of this gene in a medium containing $^{13}\text{C}_6$ -labeled lysine, and digesting with trypsin the expressed protein composed of the desired concatenated peptides. For low-abundance proteins the sensitivity is increased by selective enrichment of the target peptides by antibody capture.

From [326].

499. stability diagram

See *Mathieu stability diagram*.

500. static field

Electric or magnetic field that does not change in time.

From [327].

501. static secondary ion mass spectrometry (SSIMS)

Method of *secondary ion mass spectrometry* using low current densities for analysis of sample surface components, in contrast with *dynamic secondary ion mass spectrometry*, which is used for analysis of components in the depth direction.

Note: When the sample is an organic molecule in solid form the term is often changed to organic SIMS or molecular SIMS.

From [124].

502. Stevenson's rule

Rule stating that in competing fragmentations the *product ion* formed from its neutral species counterpart with the lower *ionization energy* will usually be the more abundant.

Note: The original version of this rule referred to reliability of determination of thermochemical data obtained for an *ion* produced by fragmentation of a single σ -bond in an *odd-electron ion* $X-Y^{+\bullet}$, but was later extended to the version in more common use since then.

From [328–330].

503. stored waveform inverse Fourier transform (SWIFT)

Technique to create excitation waveforms for *ions* in *Fourier transform-ion cyclotron resonance-mass spectrometers* or *Paul ion traps*. An excitation waveform in the time-domain is generated by taking the inverse Fourier transform of an appropriate frequency-domain programmed excitation spectrum, in which the resonance frequencies of ions to be excited are included.

Note: This procedure may be used for selection of *precursor ions* in MS^n experiments.

From [331].

504. supercritical fluid chromatography-mass spectrometry (SFC-MS) supercritical fluid chromatography/mass spectrometry (SFC/MS)

Combined technique in which a mixture of *analytes* is separated into solutions of individual components by chromatography that uses a supercritical fluid as mobile phase, followed by the ionization of the separation effluent in the *ion source* of a *mass spectrometer*.

From [332].

505. surface-assisted laser desorption/ionization (SALDI)

Class of matrix-free *laser desorption ionization* techniques for biological macromolecules.

Note: An example is *desorption ionization on silicon (DIOS)*.

From [333].

506. surface-enhanced affinity capture (SEAC)

See *surface-enhanced laser desorption/ionization (SELDI)*

507. surface-enhanced laser desorption/ionization (SELDI)

Variant of *matrix-assisted laser desorption/ionization (MALDI)* in which the matrix is replaced by a surface coating of a chromatographic stationary phase designed to selectively retain different subsets of proteins or peptides from a mixture depending on their physico-chemical properties or biochemical affinity characteristics.

Note: Originally this technique was named *surface-enhanced affinity capture (SEAC)* to distinguish it from *surface-enhanced neat desorption (SEND)* where the surface coating is designed to increase the efficiency of *laser desorption*.

From [334,335].

508. surface-enhanced neat desorption (SEND)

See *surface-enhanced laser desorption/ionization (SELDI)*.

509. surface-induced dissociation (SID)

Fragmentation that results from the collision of an *ion* with a surface.
From [336].

510. surface-induced reaction (SIR)

Process wherein a reactant *ion* interacts with a surface to produce either chemically different species or a change in the internal energy of the reactant ion.
From [337].

511. surface ionization (SI)

Ionization of a neutral when it interacts with a solid surface with an appropriate work function and temperature.
From [5,6].

**512. surrogate internal standard
internal standard**

Compound added in accurately known amounts to a sample to be analyzed for a specified *analyte*. The surrogate internal standard is chemically similar to the analyte so that losses in the analytical procedure are the same for both and thus the analyte concentration can be determined relative to that of the standard.

Note 1: In quantitative *mass spectrometry* the preferred type is an isotope-labeled version of the analyte.

Note 2: The abbreviated term *internal standard* is often used.
See also *volumetric internal standard*.
From [338].

513. sustained off-resonance irradiation (SORI)

Procedure associated with *Fourier transform-ion cyclotron resonance-mass spectrometers* to facilitate *ion/neutral reactions* such as *low-energy collision-induced dissociation* in which a radio-frequency electric field, slightly off-resonance with respect to the cyclotron frequency of the reactant *ion*, cyclically accelerates and decelerates the reactant ion that is confined in the *Penning ion trap*. As a consequence, the orbit does not exceed the dimensions of the ion trap but maintains a high average translational energy for an extended time that activates an ion/neutral process.
From [339].

514. tandem mass spectrometer

Mass spectrometer designed for *mass spectrometry/mass spectrometry*.
From [5,6].

515. tandem mass spectrometry

See *mass spectrometry/mass spectrometry (MS/MS)*.

516. tandem mass spectrometry in space

Tandem mass spectrometry procedure in which *product ion spectra* are recorded for *ion* beams in *m/z* analyzers separated in space. Specific *m/z* separation functions are designed so that in one section of the instrument ions are selected, dissociated in an intermediate region, and the *product ions* are then transmitted to another analyzer for *m/z* separation and data acquisition.

From [340].

517. tandem mass spectrometry in time

Tandem mass spectrometry procedure in which *product ion spectra* are recorded in a single *m/z* analyzer (such as a *Paul ion trap*, *linear ion trap*, or *Fourier transform-ion cyclotron resonance-mass spectrometer*) in discrete steps over time. *Ions* in a specific *m/z* range are selected, dissociated, and the *product ions* analyzed sequentially in time.

Note: *Mass spectrometers* that can perform tandem mass spectrometry in time can also perform *MSⁿ*.

From [340].

518. target gas

This term is deprecated.

See *collision gas*.

519. Taylor cone

Conical shape of the liquid emanating from a capillary under high potential, as in *electrospray* or other electrohydrodynamic spray processes.

From [341,342].

520. thermal ionization (TI)

Ionization of a neutral through contact with a high-temperature surface.

From [5,6].

521. thermospray ionization

Spray ionization in which a liquid is flowed through a heated capillary to produce a spray of droplets and solvent vapor. *Ions* are formed due to the statistical imbalance of charges in the droplets or by a heated filament.

From [343,344].

522. thin layer chromatography-mass spectrometry (TLC-MS)**thin layer chromatography/mass spectrometry (TLC/MS)**

Technique by which a mixture of *analytes* is separated into individual components by liquid chromatography, followed by the ionization of the separated species by an *ion source* of a *mass spectrometer*.

From [345].

523. thomson, Th

This term is deprecated.

See *m/z*.

524. time-lag focusing (TLF)

Energy focusing of *ions* formed in the gas phase in a *time-of-flight mass spectrometer* that is accomplished by introducing a time delay between the formation of the ions and the application of the *accelerating potential* pulse.

See also *delayed extraction*.

From [346].

525. time-of-flight mass spectrometer (TOF-MS)

Mass spectrometer that separates *ions* by *m/z* in a *field-free region* after acceleration through a fixed *accelerating potential*. Ions of the same initial translational energy and different *m/z* require different times to traverse a given distance in the field-free region.

From [5,6].

526. tolyl ion

Even-electron $C_7H_7^+$ *ion* with the same carbon skeleton as toluene that has lost a hydrogen atom from one of the ring carbons that carries the positive charge.

See also *tropylium ion*, *benzyl ion*.

From [57].

527. top-down proteomics

Method of protein identification that uses the *m/z* selection of intact proteins followed by fragmentation and *m/z* separation in a second stage of *mass spectrometry*. Mixtures of proteins must first be separated by liquid chromatography or other separation method prior to analysis by mass spectrometry.

From [347,348].

528. toroidal ion trap

Ion trapping device based on the three-dimensional structure formed by rotating the cross-section of a *quadrupole ion trap* about the edge perpendicular to the plane of the ring electrode. The resulting trapping region is toroidal.

From [349].

529. total ion chromatogram

This term is deprecated.

See *total ion current chromatogram (TICC)*.

530. total ion current (TIC)

Obsolete: after mass analysis, before mass analysis

Sum of all the separate *ion* currents carried by the ions of different m/z contributing to a complete *mass spectrum* or in a specified m/z range of a mass spectrum.

From [5,6].

**531. total ion current chromatogram (TICC)
reconstructed total ion current chromatogram**

Deprecated: total ion chromatogram.

Chromatogram created by plotting the *total ion current* in a series of *mass spectra* recorded as a function of retention time.

From [350].

**532. total ion current electropherogram
total ion current electrophorogram**

Plot of the *total ion current* in each of a series of *mass spectra* that are recorded as a function of electrophoresis time.

From [351].

533. total ion current electrophorogram

See *total ion current electropherogram*.

534. total ion current profile

Any plot of *total ion current* in a series of *mass spectra* recorded as a function of time, including *total ion current chromatogram*, *total ion current electropherogram*, *flow injection mass spectrometry*, or any other time dependent sampling.

See also *extracted ion profile*.

From [352].

535. transmission efficiency

Ratio of the number of *ions* leaving a region of a *mass spectrometer* to the number entering that region.

From [5,6].

**536. transmission quadrupole mass spectrometer
quadrupole mass analyzer
quadrupole mass filter
quadrupole mass spectrometer**

Mass spectrometer that consists of an array of four parallel rod electrodes whose centers form the corners of a square and whose opposing electrode pairs are connected. The electric potential applied between the connected pairs of rods is a superposition of a static potential and a sinusoidal radio frequency potential. The motion of an *ion* in the x - y plane perpendicular to the length direction of the rod

electrodes is described by the Mathieu equation whose solutions show that ions in a particular m/z range can be transmitted along the z -axis.

Revised from [5,6] using additional information from [353].

537. transport region

Region in a *mass spectrometer* in which an ion beam is transported from the ion source to the *ion optics* or from one ion optical element to the next.

From [354].

538. triple quadrupole mass spectrometer

Tandem mass spectrometer comprising two *transmission quadrupole mass spectrometers* in series, with a (non-selecting) *RF-only quadrupole* (or other multipole) between them to act as a *collision cell*.

From [78].

539. tropylium ion

Delocalized *carbenium ion*, cycloheptatrienylium, $C_7H_7^+$, derived formally by detachment of one *hydride ion* from the CH_2 group of cyclohepta-1,3,5-triene and substitution derivatives thereof.

See also *benzyl ion*, *tolyl ion*.

From [6].

540. unified atomic mass unit, u dalton

Non-SI unit of mass defined as one-twelfth of the mass of one atom of ^{12}C at rest in its ground state and equal to $1.660\,538\,921(73) \times 10^{-27}$ kg where the digits in parentheses indicate the estimated uncertainty in the final two digits of the value. Equivalent to the dalton (Da) unit.

Note: The abbreviation *amu* for *atomic mass unit* is deprecated; it has been used to denote atomic masses measured relative to a single atom of ^{16}O , or to the isotope-averaged mass of an oxygen atom, or to a single atom of ^{12}C .

Revised from [6] using additional information from [46].

541. unimolecular dissociation

Fragmentation reaction in which the molecularity of the reaction system is unity. The dissociation may arise from the extra energy acquired by a *metastable ion* produced in the *ion source* or that provided by *collisional excitation* of a *stable ion*.

From [355].

542. unit mass resolution

Mass resolution such that it is possible to clearly distinguish a *peak* corresponding to a singly charged *ion* from its neighbors 1 u away, usually with no more than 5–10 % overlap.

Note: This term is most frequently used to describe resolution obtained using a *Paul ion trap* or a *transmission quadrupole mass spectrometer*.

From [356].

543. unstable ion

Nascent *ion* that is either inherently unstable or formed with sufficient energy to dissociate within the region of formation such as the *ion source* or *collision cell*.

Revised from [5,6].

544. vertical ionization

Process in which one or more electrons are removed from or added to a molecule without a change in the positions of the atoms.

Note 1: The resulting *ion* is typically in an excited vibrational state.

Note 2: Such a “frozen nuclei” process is called a Franck–Condon process in optical spectroscopy.

From [5,6].

545. v-ion

High-energy *product ion* of a protonated peptide formally equivalent to a *y-ion* with the ionizing proton on the N-terminus, but with elimination of HR from the N-terminus where R is the side-chain on the C-atom of the N-terminal residue, to give a $(\text{H}_2\text{N}^+=\text{CH}-\text{CO}-)$ structure.

From [112].

546. volumetric internal standard

Compound added in a fixed reproducible amount to a solution to be analyzed by gas chromatography to permit corrections for uncontrolled variations in injected volumes.

See also *surrogate internal standard*.

From [357].

547. Wahrhaftig diagram

Diagram illustrating the relative contributions in *unimolecular dissociation* of an *ion*, for example, by homolytic cleavage of a single bond, and fragmentation following rearrangement. The diagram is in two parts with a common horizontal axis representing the internal energy of the *ion*. The vertical axis in one part of the diagram shows the two types of rate constant on a logarithmic scale, and that for the other portion of the diagram indicates the distribution function for internal energy of the ion.

From [24,358].

548. Wien filter

Mass spectrometer in which *m/z* separation is achieved using *crossed electric and magnetic fields*.

Note: It can also be operated as a charged particle energy analyzer or monochromator.

From [359].

549. w-ion

High-energy *product ion* of a protonated peptide formally equivalent to a *z-ion* that has lost the part of the N-terminal side-chain starting at the γ -carbon (if any).

From [112].

550. x-ion

Fragment ion containing the peptide C-terminus formed upon dissociation of a peptide *ion* at the peptide backbone C–C bond.

From [28].

551. y-ion

Fragment ion containing the peptide C-terminus formed upon dissociation of a peptide *ion* at the peptide backbone C–N bond.

From [28].

552. z-ion

Fragment ion containing the peptide C-terminus formed upon dissociation of a peptide *ion* at the peptide backbone N–C bond.

From [28].

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