Glossary

A Glossary for Mass Spectrometry

Kenneth L. Busch

Like any scientific discipline, mass spectrometry (MS) uses specialized terms that describe its instruments, procedures, and results. These terms are often used without definition or explanation in technical presentations that involve MS. The purpose of this glossary is to compile some of the more widely used terms that non-mass spectrometrists may encounter, and for which a simple definition would be helpful. The definitions are necessarily brief, but should be sufficient to provide basic understanding.

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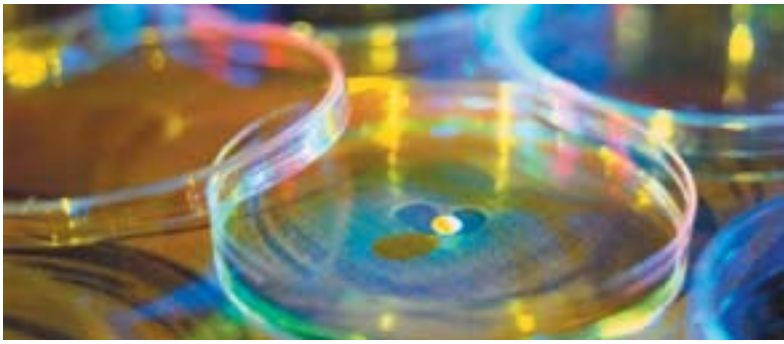
(buschken@hotmail.com) is a scientist at the National Science Foundation (Arlington, VA); any views and opinions expressed in this article are his and not those of the National Science Foundation. He has been involved with mass spectrometry since (almost) the time of Gaede pumps and LBOs. A scientific constant observed during that extended period of time has been the debate over proper nomenclature and its correct definition. The author's teaching of introductory courses in mass spectrometry shows the need for a concise glossary from which beginners can start, and here we have one. This compilation is a short guide rather than lexiconic dictum; the latter is saved for committees with years to consume and tomes to produce. For the rest of us, there are poems to write, places to know, and colleagues to share with us the fact that the ions know what they are doing.

Clearly, a selection process has been exercised by this author. The responsibility for selection and definition of these glossary terms resides solely with the author; complaints from aggrieved nomenclators should be sent directly to him. These definitions in a basic glossary are, as expected, basic. Those in search of more authoritative and comprehensive compilations would do well to begin with the ASMS compilation "Standard Definitions of Terms Relating to Mass Spectrometry: a Report from the Committee on Measurements and Standards of the American Society for Mass Spectrometry," by P. Price in *J. Am. Soc. Mass Spectrom.* **2**, 336–348 (1991) (also available at www.asms.org). IUPAC recommendations for terms for use in MS can be found in J.F.J. Todd, *Pure and Applied Chemistry* **63**, 1541–1566 (1991). Definitions for more-specialized MS terms can also be found in several glossaries found on the web, or the terms can be used as targets for a search engine. The arrangement of terms here is strictly alphabetical, in contrast to some web glossaries that separate terms within broad general areas. After all, if one has to look up the meaning of a term, it's not likely that one would know which category to start with. Many of these terms are associated with acronyms, which are given in parentheses; a more complete listing of acronyms was previously published in "Mass Spectrometry Forum" (1). Positive ions are used as the default descriptive example throughout the text.

Accelerating voltage (V)

The accelerating voltage is applied to the source to move ions formed in the source into the mass analyzer of the instrument. This accelerating voltage can be a few tens of volts in quadrupole mass spectrometers to several thousand volts in sector instruments or in time-of-flight mass spectrometers.



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Accelerator mass spectrometry (AMS)

In this specialized method, atomic ions are formed from the sample by charge stripping in a very high voltage source, usually coupled to a Van de Graff accelerator. Accelerator mass spectrometry is used for low-level analysis of ^{14}C isotopes in radiocarbon dating and biological tracer studies.

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Accurate mass

The accurate mass (or exact mass) of an ion of specified isotopic composition is calculated by summation of the exact masses of the constituent atoms. Conversely, the empirical formula of an ion can be deduced from the measured accurate mass of the ion if the ion mass is low enough to limit the number of formulaic possibilities and if the exact mass value is known accurately enough.

Analyzer

The analyzer is the section of the mass spectrometer in which ions (formed in the source) are differentiated on the basis of their mass-to-charge ratios. The detector of the instrument follows the mass analyzer(s).

Atmospheric pressure chemical ionization (APCI)

In this method of ionization, an aerosol of sample solution is sprayed at atmospheric pressure into a heated region in which a sharp metal pin held at high potential sustains a corona discharge. The action of the discharge on the solvent creates reagent ions that react with the neutral sample molecules to create protonated ions of the molecule. These ions then pass through a sampling aperture into the mass analyzer of the mass spectrometer.

Atomic mass unit (amu)

The atomic mass unit represents the relative scale in which the mass of ^{1}H is given an integral value of 1, ^{12}C is 12, and so on. The amu is an older unit, replaced by the unified atomic mass unit u.

Average mass

The average mass of an ion of a known empirical formula is calculated by summing the relative average atomic mass of each atom present. For example, carbon has an average atomic mass of 12.01115 Da, hydrogen is 1.00797 Da, and so on. The average mass of the molecular ion of a chemical compound is also the mass that appears on the bottle. However, in a stick representation of a mass spectrum, there is no ion signal at the average mass. Instead, signals appear for ions of various isotopic compositions. The average mass corresponds to the center of the centroid signal recorded for higher mass ions at lower instrumental resolutions.

Base peak

The base peak in a mass spectrum (within the user-selected mass range) is the ion with the highest measured abundance. The relative abundance of the base peak ion is assigned a value of 100, and the abundances of all the other ions plotted in that mass spectrum are normalized to that value. The *y*-axis in a mass spectrum is therefore given in terms of relative abundance.

Charge stripping

Charge stripping is a process by which atomic ions are transformed into a higher charge state, thereby changing their mass-to-charge ratios. Different cross sections for charge stripping of isobaric atomic ions allow their differentiation and subsequent trace level analysis.

Chemical ionization (CI)

Chemical ionization is a process of ionization that involves the reaction of a reagent ion and a neutral molecule to yield a charged ionic form of the molecule. The first step in chemical ionization is creation of the reagent ion through electron ionization of the reagent gas molecules present in great excess. A stable population of reagent ions is formed through ion–molecule reactions, and these ions will eventually react with the neutral gas-phase sample molecules. In a common case, methane gas is ionized to form predominantly CH_5^+, which then reacts with the neutral sample molecule in a process of protonation to form $(M+H)^+$.

Collision-induced dissociation (CID)

In a collision between an ion and a neutral species, a portion of the ion translational energy is converted to internal energy. This internal energy causes dissociation of the ion into smaller fragment ions and can also cause changes in the ion charge. Collision-induced dissociation is also known as collisionally activated dissociation. Collision-induced dissociation is common in MS/MS experiments.

Constant neutral loss scan

In an MS/MS experiment, mass-selected precursor ions are induced to dissociate into product ions, which are then mass-analyzed by a second analyzer. There are three common scans in the single-step MS/MS experiment: the product ion scan, the precursor ion scan, and the constant neutral loss scan. In the latter, both mass analyzers are scanned at the same rate, with a mass offset between them. Therefore, only ions that dissociate by loss of the specified neutral species mass will form a precursor–product ion pair that is passed through to the detector.

Dalton (Da)

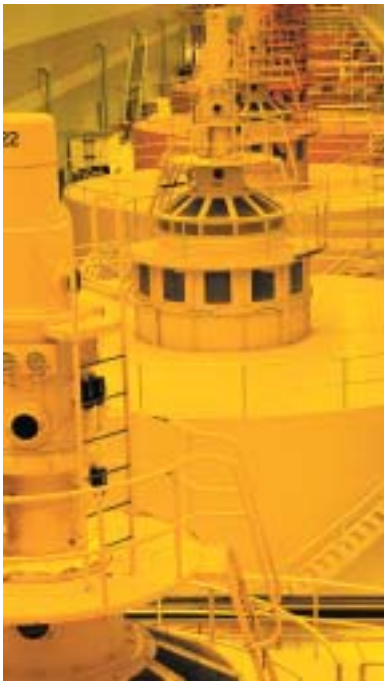
This is a newer unit of mass taken as identical to u (the unified atomic mass unit), but not accepted as standard nomenclature by the IUPAC or IUPAP. The dalton or u is equal in mass to 1/12 the mass of a ^{12}C atom. Mass is often expressed by biologists as kilodaltons and abbreviated kDa, and this unit sometimes appears as the label on the *x*-axis of a mass spectrum.

Delayed extraction (DE)

Delayed extraction is an experimental technique in time-of-flight mass spectrometry in which improved mass resolution is obtained by using a controlled time delay between the initial pulse of ion formation and acceleration of the ions into the flight tube of the instrument. The technique is also called time-lag focusing.

Desorption ionization (DI)

This is a general term used to group various methods (secondary ion mass spectrometry, fast atom bombardment, californium fission fragment desorption, and plasma desorption) in which ions are generated directly from a sample by rapid energy input into the condensed phase sample. There may be no discrete process of desorption (in the thermal sense), but instead a transfer of usually nonvolatile sample molecules into the gas phase as ions that can subsequently be mass-analyzed.



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Detection limit

The detection limit of an instrument or system is the smallest flow of sample into the source of the mass spectrometer (or the lowest partial pressure of sample gas) that gives a signal that can be distinguished from background noise. Often this is listed as the limit of detection, and specified at a signal-to-noise ratio of 3. The limit of quantitation is usually higher. The detection limit of a method is not the sensitivity of the method. The detection limit is a value. It is not "lower than" some value, a statement that is as meaningless as it is common.

Direct exposure probe (DEP)

This is a variant of the direct insertion probe (or direct probe) in which the sample is coated on a surface that is inserted within the ion source of the mass spectrometer, and thus exposed to the ionization beam in the source directly. The direct exposure probe can be used to generate mass spectra of otherwise nonvolatile sample molecules.

Direct insertion probe (DIP)

The direct insertion probe is a shaft having a sample holder at one end. The probe is inserted through a vacuum lock to place the sample holder near to the ion source. The sample is vaporized by heat from the ion source or by heat from a separate heater surrounding the sample holder. The sample molecules are evaporated into the ion source where they are then ionized as gas-phase molecules.

Double-focusing mass spectrometer

A magnetic analyzer and an electric analyzer are combined in a specified geometrical configuration and sequence to accomplish both direction and velocity focusing of an ion beam from an ion source. This combination provides a higher instrumental resolving power and the ability to make more accurate mass measurements for ions.

Electric sector (E)

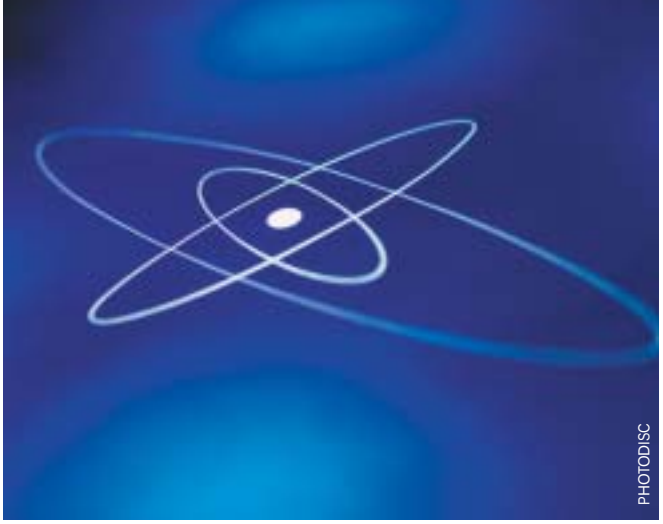
The electric sector is a device constructed of curved, parallel metal plates that creates an electrostatic field perpendicular to the ion path. The sector (or analyzer) selects and focuses ions of the same kinetic energy. The electric sector does not separate ions according to mass or charge, and therefore is always used in conjunction with a magnetic analyzer, often in a double-focusing mass spectrometer. The electric sector is also sometimes called an electrostatic sector or electrostatic analyzer.

Electron attachment

Electron attachment is a process in which an electron of thermal energy is added to an atom or molecule (M) to form a stable ion ($M^{-\cdot}$). The molecule must have a positive electron affinity (for example, be electrophoric). Thermal electrons are required so as not to cause dissociation of the molecular ion.

Electron energy

The electron energy is the potential difference through which electrons are accelerated in the ionization source; these electrons are those used to initiate the electron ionization process. The term ionizing voltage is sometimes used in place of electron energy. The electron energy for standard electron ionization mass spectra is 70 eV, chosen to maximize ion production and provide reproducible mass spectra.



Electron ionization (EI)

Electron ionization is the process of molecular ionization initiated by interaction of the gas-phase molecule with an energetic electron. The beam of electrons is emitted from a heated metal filament in the source, and the electrons accelerated through a potential difference of 70 V. The collision between the molecule and the electron causes the ejection of an electron from the molecule (M), and produces a radical molecular ion in which the unpaired electron is indicated by the superscripted dot ($M^{+\cdot}$). The overall process is: $M + e^- \geqslant M^{+\cdot} + 2e^-$. An older term for electron ionization is electron impact.

Electron multiplier (EM)

An electron multiplier is a detection device inside the vacuum of the mass spectrometer that converts the arrivals of ions at its front dynodes into a detectable, amplified electron current at the back lead of the device. The overall gain (signal out/signal in) can be as high as 10^4–10^8. Positive ions exiting from the mass analyzer impact the first dynode surface, and the impact causes the release of several electrons, which are then accelerated through a potential to the next electrode. There, each electron impact causes the release of several secondary electrons, which are accelerated into the next dynode for a repetition of the impact–release process. A cascade of electrons is produced, generating a current that is further amplified and then sampled by an analog-to-digital converter to be recorded by the data system.

Electrospray ionization (ESI)

In the electrospray ionization process, a solution containing the molecules of interest is pumped through a metal capillary tube held at a high potential. The solution is sprayed from the tube into a chamber held at ground and open to atmospheric pressure. The sample solution spray creates small droplets that carry a charge induced by the needle potential. The droplets in the mist become progressively smaller as the neutral solvent molecules evaporate. The charge is maintained on the surfaces of the droplets, eventually causing an instability that results in the expulsion of solvent-less, highly charged ions of the dissolved sample molecules. Multiple protonation can occur to form highly charged sample molecules of the form $(M+nH)^{n+}$.

Even-electron ion

An even-electron ion contains no unpaired electrons; for example, CH_3^+.

Faraday cage

A Faraday cage is a hollow metal cylinder used as an ion detector. Ions enter the open end and then impact the metal walls or the closed end. The summed ion current carried by the ions is measured directly. Each singly charged ion carries a charge of 1.6×10^{-19} coulombs.

Fast-atom bombardment (FAB)

Fast-atom bombardment uses a beam of neutral atoms (created by neutralization of ions of about 5 keV energy) to sputter sample molecules from a liquid solution held on the surface of a beam-intersecting sample probe. The atom impact deposits energy into the semivolatile matrix, causing desorption of many species including ions, neutral molecules, and clusters of solvent and sample molecules. Desolvation follows desorption, and molecules (M) are usually ionized in a process of protonation to form $(M+H)^+$. The mass spectra usually contain a large background of ions from the energy-moderating solvent. Glycerol was the first widely used FAB solvent, but many others have been developed.

Field-free region (FFR)

In the flight path of an ion from the source of the mass spectrometer through the mass analyzer to the detector, the ion may pass through regions in which there is no specific magnetic or electric field. These are field-free regions, as in the portion of the ion path between the electric and magnetic analyzers in a double-focusing mass spectrometer, or between the source and the first sector of both single- and double-focusing mass spectrometers. Unimolecular ion dissociations in these regions can occur to give rise to signals in the mass spectrum recorded under normal conditions (metastable ions), or can be specifically investigated.

Fragment ion

A fragment ion is the charged product of an ion dissociation. A fragment ion may be stable itself or may dissociate further to form other charged fragment ions and neutral species of successively lower mass. Molecular ions formed in the initial ionization process dissociate to fragment ions because of the excess internal energy that remains after ionization. Note that ions dissociate rather than decompose.

Ion cyclotron resonance (ICR)

An ion cyclotron resonance mass spectrometer is a device for storage and mass analysis of ions. The ions are held in the cell by a combination of a static magnetic field and a coincident electrical field generated by potentials applied to all walls of the metal cell. Ions attain a coherent cyclotron orbit with frequency proportional to mass. Ions are detected by monitoring the alternating electrical current generated in detector plates by their regular orbits. A Fourier transformation converts the monitored frequency to ion mass.

Ionization energy

The ionization energy is the minimum energy required to remove an electron from an atom or molecule in order to produce a positive ion.

Ion/molecule reaction (I/M rxn)

This reaction occurs between an ion and a neutral gas-phase molecule to cause ionization (as in protonation in chemical ionization), or changes in the internal energy of one or both of the reactants.

Ion trap analyzer

An ion trap analyzer consists of two end caps and a ring electrode assembled into a compact device that serves as a mass analyzer. The three-dimensional rotationally symmetric quadrupole field stores ions (externally generated) at its center. An additional electrical signal is then applied to mass-selectively eject ions to an external detector.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Isobaric ion

Isobaric ions have identical masses (at whatever level of accuracy chosen) but have different atomic compositions. A common example is a positive ion at *m/z* 28, which can have the empirical formulas of CO^+, N_2^+, or $C_2H_4^+$.

Isotope

Isotopes are atomic forms of elements that contain the same numbers of protons and electrons, but different numbers of neutrons. For example, chlorine consists of two naturally occurring isotopes: ^{35}Cl, atoms of which consist of 17 protons, 17 electrons, and 18 neutrons; and ^{37}Cl, which has atoms containing 17 protons, 17 electrons, and 20 neutrons. Mass spectrometry does not usually deal with radioactive isotopes, except in special instances such as isotope ratio mass spectrometry.

Isotope ratio mass spectrometry (IRMS)

Isotope ratio mass spectrometry provides high accuracy, high precision measurements to determine ratios of atomic isotopes, usually in small amounts of gaseous samples. These ratios are used in geochemistry, cosmological chemistry, dating, and tracer studies.

Linked scan

In a sector instrument with both magnetic and electric sectors, a linked scan is an experiment in which both sector field values (the magnetic and the electric sector values) are changed simultaneously so that ion mass- and

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charge-changing reactions that occur after the ion source, but before the sectors, or in the field-free region between the sectors, can be recorded in a mass spectrum.

Magnetic analyzer (B)

A magnetic analyzer creates a magnetic field perpendicular to the ion path and, in conjunction with entrance and exit slits along the flight path, selects and focuses ions of a selected momentum (and, nominally, then, with the same mass-to-charge ratio) through to the detector. A magnetic analyzer is also called a magnetic sector. An instrument that includes magnetic or electric analyzers is called a sector mass spectrometer.

Mass defect

The term mass defect has an "official" meaning that is quite different from one of its meanings in mass spectrometry. Officially, the mass defect is the difference in the mass of a polyatomic atom and the sum of the masses of all of the particles (electrons, protons, and neutrons) of which it is composed. This mass defect occurs because matter is converted into energy according to the Einstein equation; this energy binds the nucleus together and overcomes the mutual repulsion between protons. In mass spectrometry, the mass defect is the term also used for the difference (whether positive or negative) between the exact mass of an ion, and the nearest integer mass.

Mass spectrometry/mass spectrometry (MS/MS)

MS/MS is a concept that recognizes ions as reactive entities that can be interrogated. The prototype MS/MS instrument consists of two independently operated mass analyzers linked by a reaction region in which the ion can be induced to react. Induction often occurs through collision (collision-induced dissociation) in which a selected higher-mass ion dissociates to a smaller product fragment ion. Even in this simple conceptual instrument, three experiments are possible: precursor ion scan, product ion scan, and constant neutral loss scan. MS/MS that recurs over multiple steps is known as MS^n. MS/MS is also known as tandem mass spectrometry, but this latter term does not reflect the full analytical capabilities of the experiment.

Mathieu stability diagram

A graphical representation for reduced variables that incorporate the values of dc and ac voltages applied either to the four rods of a quadrupole mass filter or to the electrodes of an ion trap. The stability diagram illustrates areas of ion stability and ion instability and designates scan lines for the changes in those voltages so that the device can serve as an ion mass-to-charge ratio analyzer.

Matrix-assisted laser desorption ionization (MALDI)

In MALDI, sample molecules are mixed with an excess of an energy-absorbing (usually solid) matrix. The mixture is cocrystallized in a thin film on an inert metal support. Repetitive irradiation of the film with a pulsed laser releases ions from the surface, which are usually accelerated into a time-of-flight mass spectrometer. Since the matrix is usually a solid organic acid, the predominant mode of ionization is protonation of the sample molecule M to form $(M+H)^+$.

Membrane inlet mass spectrometry (MIMS)

A membrane inlet system consists of a semipermeable membrane that permits passage of gas-phase volatile sample molecules directly into the mass spectrometer ion source, which is usually operated as an electron ionization or chemical ionization source.

Metastable ion

A metastable ion is a precursor ion that dissociates into a fragment ion and neutral species after leaving the ion source (that is, after acceleration) but before reaching the detector. The dissociation is most readily observed when it takes place in one of the field-free regions of a sector mass spectrometer.

Molecular ion

A molecular ion is formed by the removal (positive ions) or addition (negative ions) of one or more electrons from a molecule M to form $M^{+\cdot}$ or $M^{-\cdot}$. The mass of the molecular ion corresponds to the nominal or monoisotopic mass of the molecule, with the mass of the electron added or lost usually consequential. Of course, the mass of such a molecular ion reflects the isotopic composition of the ion, rather than the average molecular mass of the molecule. Thus the molecular ion mass is the sum of the relative masses of the most abundant naturally occurring isotopes of the various atoms that make up the molecule.

Monoisotopic ion mass

The monoisotopic mass of an ion is defined as the mass of an ion for a given empirical formula calculated using the exact mass of the most abundant isotope of each element; for example, C = 12.000000 Da (exactly), H = 1.007825 Da, O = 15.994915 Da.

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Multiple reaction monitoring (MRM)

The MS/MS experiment uses two sequential stages of independent mass analysis. In the product ion MS/MS scan, a precursor ion is selected by mass with the first mass analyzer, and the fragment ions formed as a result of collision-induced dissociation are measured with a scan of the second mass analyzer and recorded in a mass spectrum. In an analogy to selected ion monitoring, if both mass analyzers in an MS/MS instrument are set on a specific mass, the signal represents the precursor-to-product ion transition for a specific ion pair. This experiment is called reaction monitoring. If several different precursor–product ion pairs are monitored, as is most often the case, the experiment is multiple reaction monitoring.

m/z

The *x*-axis of a plotted mass spectrum is often labeled in units of *m/z*, where *m* denotes the mass of the ion (in daltons), and *z* represents the total number of charges on the ion (in units of the elementary charge). An older abbreviation is *m/e*, where *e* represents the charge. The term Thomson has also been suggested. Da (daltons) and kDa are also used as labeling units for the *x*-axis of a mass spectrum.

Nanospray

The term describes a design for a miniaturized electrospray ionization source using a pulled and coated glass capillary as the spray tip. This design achieves a flow rate of 20–50 nL/min, much lower than the usual electrospray ionization source.

Nominal ion mass

The nominal ion mass is the mass of an ion for a given empirical formula calculated using the integer mass of the most abundant isotope of each element (for example, C is 12 Da, H is 1 Da, and O is 16 Da).

Odd-electron ion

An odd-electron ion contains an unpaired electron; for example, $CH_4^{+\cdot}$. The superscripted dot denotes the unpaired electron. The molecular ion initially formed in electron ionization is an odd-electron ion.

Parent ion

The term parent ion is synonymous with the term precursor ion and denotes the ion that dissociates to a smaller fragment ion, usually as a result of collision-induced dissociation in an MS/MS experiment. Precursor ion is the preferred term.

Percent accuracy

In the experimental measurement of an exact mass, the percent accuracy is calculated as the (true mass − observed

mass)/true mass × 100%. The percent accuracy is often expressed in parts per million (ppm). For example, 0.01% accuracy is 100 ppm. A 100 ppm accuracy for an ion with a mass of 1000 Da is 0.1 Da.

Postsource decay (PSD)

Postsource decay processes are ion dissociations that occur within the drift region of a time-of-flight mass analyzer. After initial ion formation and acceleration out of the source into the flight tube, ions may dissociate or neutralize. In a linear time-of-flight instrument, these fragment ions and neutral species reach the detector at the same time as the precursor ions from which they are formed. However, these reactions can be specifically studied by using a reflectron (adjusting the ratio of accelerating to reflectron voltages in a stepwise manner) to bring fragment ions formed in postsource decay processes into focus at the detector.

Precursor ion scan

In an MS/MS experiment, mass-selected precursor ions are induced to dissociate into product ions, which are then mass analyzed by a second analyzer. The three common scans in the single-step MS/MS experiment are: product ion scan, precursor ion scan, and then the constant neutral loss scan. In the precursor ion scan, the second mass analyzer is set at the mass of the selected product ion, and then the first mass analyzer is scanned from that mass upwards. The result is a mass spectrum that contains signals for all the precursor ions that dissociate to that selected product ion.

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Product ion scan

In an MS/MS experiment, mass-selected precursor ions are induced to dissociate into product ions, which are then mass analyzed by a second analyzer. The three common scans in the single-step MS/MS experiment are: product ion scan, precursor ion scan, and then the constant neutral loss scan. In the product ion scan, the first mass analyzer is set at the mass of the selected precursor ion, and then the second mass analyzer is scanned from that mass downwards. The result is a mass spectrum that contains signals for all the product ions formed from that selected precursor ion.


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Protonated molecule

A protonated molecule is (usually) an ion formed by addition of a proton to the neutral molecule M , namely $(M+H)^+$. The process of chemical ionization using a reagent gas such as methane forms such a protonated molecule. The transfer of a proton from one molecule to the other in the gas phase is an acid/base reaction in which the relative proton affinities of the reacting species describe the energetics of the reaction. Protonated molecules formed in other ionization sources (such as fast atom bombardment, electrospray ionization, or MALDI) may not be the end result of such well-defined acid/base reactions. The term protonated molecular ion has been used to describe $(M+H)^+$ but is usually discouraged.

Pyrolysis MS

In a pyrolysis source interfaced with a mass spectrometer, the sample is thermally decomposed in a reproducible pyrolysis. The gaseous products formed are then analyzed either as a mixture by mass spectrometry, or are analyzed by GC/MS. Pyrolysis mass spectrometry can be used for the analysis of otherwise nonvolatile samples.

Quadrupole mass filter (Q)

In the quadrupole mass filter, the application of a particular combination of dc and rf voltages to four parallel metal rods creates a filtering device through which only ions of a defined *m/z* value are transmitted. Changing the ratio of the voltages changes the *m/z* value of the ion that is passed through to the detector. The quadrupole mass filter can also be operated in other modes, such as passing a mass range of ions through to the detector. If only the rf portion of the voltage is applied to the rods, essentially all ions are passed through to the detector.

Rearrangement ion

A rearrangement ion is a fragment ion formed in a dissociation in which atoms or groups of atoms have transferred from one part of the molecule to another during the fragmentation process. Because the structural requirements to form rearrangement fragment ions are

constrained, the identification and rationalization of rearrangement fragment ions are especially important in spectral interpretation.

Reconstructed ion chromatogram

A normal mass spectrometric data set consists of full mass spectra recorded sequentially in time as sample is admitted to the ion source, either from a direct-insertion probe or from a chromatograph (for example, GC/MS). The total ion current trace is the sum of ion abundances in each mass spectrum plotted versus time. Clearly each mass spectrum will also contain a pattern of molecular and fragment ions. Ions of these particular masses can be specified, and the data system can plot the scan-by-scan abundances of these specific ions versus time, which is known as a reconstructed ion chromatogram. The reconstructed ion chromatogram can be used to identify all ions that belong together in a single mass spectrum by virtue of their coincident peaks in time (and discriminate against background ions), and can also be used to screen a GC/MS run for related classes of compounds by reconstruction of ion chromatograms for common structurally specific ions.

Reflectron time-of-flight mass spectrometer

A reflectron is a device incorporated into the flight tube of a time-of-flight mass spectrometer that operates as an electrostatic mirror. Ions with a range of kinetic energies from the ionization source traverse the first portion of the flight tube and then spend different amounts of time in the reflectron. The net result is that these (reflected) ions all come into focus at the detector located at the end of the second portion of the flight tube, leading to higher mass resolution.

Relative abundance (RA)

The relative abundance of an ion is the measured intensity for the ion beam at that designated *m/z* value. To be precise, ion beams have intensities, and ions have abundances. Relative abundance is a term related to the practice of assigning the most abundant ion in a measured and plotted mass spectrum a relative abundance of 100% and normalizing all other ion abundances to that value.

Resolution

Resolution is defined in several different ways relative to the commonly given formula of $m/\Delta m$, where m is the mass of the ion at which resolution is specified. For two adjacent, symmetric peaks of equal height in a mass spectrum, the instrumental (physical or electrical) parameters are adjusted such that the peaks at masses m and $(m - \Delta m)$ are separated by a valley that, at its lowest point, is just 10% of the height of either peak. Then, the resolution (10% valley definition) is $m/\Delta m$. The definition can be given also for 50% valley or 5% valley separations. For a single peak, the resolution is still calculated as $m/\Delta m$, but now Δm is the width of the peak at a height that is a specified fraction of the maximum peak height. A 5% peak width definition is technically equivalent to the 10% valley definition of resolution. A common standard is the definition of resolution based on Δm being the full width of the peak at half its maximum height (fwhm).

Resolving power (RP)

Resolving power is the ability of a mass spectrometer to distinguish between ions that differ only slightly in their *m/z* ratios. It is a definition that is distinct from resolution.


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Secondary ion mass spectrometry (SIMS)

In secondary ion mass spectrometry, a beam of energetic ions (usually around 5 keV energy) is used to sputter sample atoms and molecules from a thin solid film or surface (classic SIMS), or organic molecules that may be present as a thin film or dissolved in a liquid or solid solution (molecular SIMS or liquid SIMS) held on the surface of a beam-intersecting sample probe. In liquid SIMS, the ion impact deposits energy into the semivolatile matrix, causing desorption of many species, including ions, neutral molecules, and clusters of solvent (when present), matrix, and sample molecules. Desolvation follows desorption, and molecules (M) are usually ionized in a process of protonation to form $(M+H)^+$. The mass spectra or liquid SIMS usually contain a large background of ions from the energy-moderating solvent or matrix, if used. The same matrix solvents are used in liquid SIMS and FAB.

Selected ion monitoring (SIM)

Selected ion monitoring is the practice of monitoring and recording ion currents at one or more selected ion *m/z* values with time, rather than recording full mass spectra, as sample is introduced into the ion source. Because the detector is integrating signal for a longer time at the relevant ion, limits of detection can be lowered, albeit at a cost of susceptibility of the experiment to unexpected interferences. Use of the terms multiple ion detection, multiple ion (peak) monitoring, and mass fragmentography have also been used but are discouraged. The terms single ion monitoring or multiple ion monitoring are sometimes used.

Sensitivity

The proper definition of sensitivity is that of a system response measured per amount of sample placed in the system. In mass spectrometry the units are most often given in terms of coulombs per microgram. An electron ionization source may provide 2×10^{-7} C/μg for a standard test compound at a specified instrumental resolution, and a specified means of

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introducing sample into the ionization source. Clearly sensitivity is a system parameter. An alternative specification for sensitivity is based on the change of ion current correlated to the change of partial pressure of the sample in the ion source. Here the unit is amperes per pascal, and system parameters must be specified. Most often, sensitivity is documented by examples of applications of system response for given conditions and sample input. System performance is then evaluated by the confluence of performance results exemplified by all the examples. Sensitivity is distinct from detection limit, which is the amount of sample required for a signal of a prescribed signal-to-noise ratio.

Single-focusing

In a single-focusing mass spectrometer, a single magnetic sector is used to generate the magnetic field that differentiates ions according to their *m/z* values (strictly, according to their momenta). The addition of an electric sector in a specified configuration provides a double-focusing mass spectrometer that can achieve higher mass resolution than a single-focusing mass spectrometer.

Source

The source is the device within the mass spectrometer in which ionization of sample molecules occurs. The source may be under vacuum, or it can operate at atmospheric pressure. A chromatographic method may interface with the source, or samples may be introduced via a probe or an automated sample introduction system. Ions are accelerated out of the source into the mass analyzer of the instrument.

Surface-induced dissociation (SID)

Surface-induced dissociation is the fragmentation of an ion induced by an energetic collision of that ion with a solid surface, which can be placed between two mass analyzers. The surface then takes the place of the neutral gas molecule that is the collision target in collision-induced dissociation.

Time-of-flight (TOF) mass analyzer

A time-of-flight mass spectrometer is a mass analyzer that provides a measurement of mass via determination of the flight time of ions having the same kinetic energy over a fixed distance. Ions are formed in the same place at the same time, and are given the same energy by an acceleration voltage as they pass into a flight tube. The time-of-flight mass spectrometer acts as a racetrack for ions, with the lower mass ions moving with higher velocity and the higher mass ions moving with slower velocities. Determination of the time of arrival of ions after the start signal then serves as a means of differentiating their masses.

Total-ion current (TIC)

The total-ion current trace is the sum of the relative abundances of all the ions in each mass spectrum plotted against the time (or number of scans) in a data collection sequence. For example, the total-ion current trace in a GC/MS run is analogous to the output of a single-channel gas chromatography detector. The trace allows eluted peaks to be identified by an increase in the total-ion current over background. The scans corresponding to the eluted peak are averaged together to create the mass spectrum of the sample corresponding to that peak.

Unified mass scale (u)

IUPAC & IUPAP (1959–1960) agreed on a standardized mass scale in which 1 u (the unified atomic mass unit) is defined as equal to $\frac{1}{12}$ the mass of the most abundant form of carbon, the ^{12}C isotope. There had previously been two slightly different mass scales — the physical scale and the chemical scale. The unified scale brought coherence to mass metrology.

Unimolecular dissociation

Unimolecular dissociation is the isolated, spontaneous dissociation of a neutral or an ion, based on the amount and distribution of its internal energy. In the electron ionization source, initial ionization of the molecule by the electrons leads to molecular ions, which then undergo rapid unimolecular dissociations leading to the fragment ions observed in the mass spectrum. Unimolecular dissociation that occurs after the ions leave the source and in the field-free regions of the mass spectrometer leads to metastable ions that can be observed with special methods. Unimolecular dissociation is contrasted with collision-induced dissociation, at least in concept. True unimolecular dissociation evolves into collision-induced dissociation as the operating pressure of the mass spectrometer increases.

Reference

1. K.L. Busch, *Spectroscopy* 16(11), 28–31 (2001). ■

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