

**INTERNATIONAL UNION OF
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**ANALYTICAL CHEMISTRY DIVISION
COMMISSION ON ANALYTICAL NOMENCLATURE**

**RECOMMENDATIONS FOR
NOMENCLATURE OF MASS
SPECTROMETRY**

RULES APPROVED 1973

**LONDON
BUTTERWORTHS**

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This report was prepared for the Commission by Professor A. J. B. Robertson. Particular attention was paid to definitions already proposed by the Fachnormenausschuss Vakuumtechnik in Deutschen Normenausschuss and in the Editorial Review on Nomenclature in *Organic Mass Spectrometry*, 2, 249 (1969).

The report has been widely circulated by the Commission to experts in many countries in first and second draft forms and, following publication as a tentative nomenclature report in the IUPAC *Information Bulletin* No. 17 in February 1972, it was modified in the light of comments received over a period of eight months. This final report incorporates many of the suggestions made on previous drafts and is now presented as rules approved 1973.

**RECOMMENDATIONS FOR NOMENCLATURE OF
MASS SPECTROMETRY**

1 Mass spectrometer

An instrument in which ions are separated according to the quotient mass/charge, and in which the ions are measured electrically.

(Note: This term should also be used when a scintillation detector is employed.)

2 Mass spectrograph

An instrument in which beams of ions are separated according to the quotient mass/charge, and in which the deflection and intensity of the beams are recorded directly on photographic plate or film.

3 Mass spectroscopy

A term which may refer to either a mass spectrometer or a mass spectrograph.

4 Mass spectrometry

The branch of science dealing with all aspects of mass spectroscopies and the results obtained with these instruments.

(Note: The term '*Mass Spectroscopy*' seems preferable here, but 'mass spectrometry' has become widely used.)

5 Single-focusing mass spectrometer

An instrument in which an ion beam with a given value of mass/charge is brought to a focus although the initial directions of the ions diverge.

6 Double-focusing mass spectrometer

An instrument which uses both direction and velocity focusing, and therefore an ion beam of a given mass/charge is brought to a focus when the ion beam is initially diverging and contains ions of the same mass and charge with different kinetic energies. The ion beam is measured electrically.

7 Double-focusing mass spectrograph

An instrument which uses both direction and velocity focusing, and therefore an ion beam initially diverging in direction and containing ions of different kinetic energies is separated into beams according to the quotient mass/charge, these beams being focused onto a photographic plate or film.

8 Magnetic deflection

The deflection of an ion beam as a result of the motion of the ions in a magnetic field. Generally the direction of motion of the ions is at right angles to the direction of the magnetic field, and the motion is uniform.

9 Radial electrostatic field analyser

An arrangement of two conducting sheets forming a capacitor and giving a radial electrostatic field which is used to deflect and focus ion beams of different energies. The capacitor may be cylindrical, spherical or toroidal.

10 Nier–Johnson geometry

An arrangement for a double-focusing mass spectrometer in which a deflection of $\pi/2$ radians in a radial electrostatic field analyser is followed by a magnetic deflection of $\pi/3$ radians. The electrostatic analyser uses a symmetrical object–image arrangement and the magnetic analyser is used asymmetrically.

11 Mattauch–Herzog geometry

An arrangement for a double-focusing mass spectrograph in which a deflection of $\pi/4\sqrt{2}$ radians in a radial electrostatic field is followed by a magnetic deflection of $\pi/2$ radians.

12 π Radian magnetic field analyser

An arrangement in which an ion beam is deflected magnetically through π radians.

13 $\pi/2$ Radian magnetic field analyser

An arrangement in which an ion beam is deflected magnetically through $\pi/2$ radians.

14 $\pi/3$ Radian magnetic field analyser

An arrangement in which an ion beam is deflected magnetically through $\pi/3$ radians.

15 Quadrupole mass analyser

An arrangement in which ions with a desired quotient of mass/charge are made to describe a stable path under the effect of a static and a high–frequency electric quadrupole field, and are then measured. Ions with a different mass/charge are separated from the measured ions because of their unstable paths.

16 Time-of-flight mass spectrometer

An arrangement using the fact that ions of different mass/charge need different times to travel through a certain distance in a field-free region after they have all been initially given the same kinetic energy, or the same impulse.

17 Cyclotron resonance mass spectrometer

A high-frequency mass spectrometer in which the ions to be detected, with a selected value of the quotient mass/charge, absorb maximum 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 which satisfy the cyclotron resonance condition and as a result they are separated from ions of different mass/charge.

18 Mass spectrometer operating on the linear accelerator principle

A mass spectrometer in which the ions to be separated absorb maximum energy through the effect of alternating electric fields which are parallel to the path of the ions. These ions are then separated from other ions with different mass/charge by an additional electric field.

19 Static fields mass spectrometer

An instrument which can separate a selected ion beam with fields which do not vary with time. The fields are generally both electric and magnetic.

20 Dynamic field(s) mass spectrometer

A mass spectrometer in which the separation of a selected ion beam depends essentially on the use of fields, or a field, varying with time. These fields are generally electric.

21 Prolate trochoidal mass spectrometer

A mass spectrometer in which the ions of different mass/charge are separated by means of crossed electric and magnetic fields in such a way that the selected ions follow a prolate trochoidal path.

(Note: The usual term '*Cycloidal*' used sometimes is incorrect because the path used is not cycloidal. A cycloid is a special case of a trochoid.)

22 Crossed electric and magnetic fields

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

23 Resolution: 10 per cent valley definition

Let two peaks of equal height in a mass spectrum at masses m and $m - \Delta m$ (a.m.u.) be separated by a valley which at its lowest point is just 10 per cent of the height of either peak. For similar peaks at a mass exceeding m , let the height of the valley at its lowest point be more (by any amount) than ten per cent of either peak height. Then the resolution (10 per cent valley definition) is $m/\Delta m$. It is usually a function of m . $m/\Delta m$ should be given for a number of values of m . This definition implies that, for an isolated symmetrical peak, at a distance $\pm \frac{1}{2}\Delta m$ along the mass scale from the peak maximum the peak height is 5 per cent of the maximum peak height.

24 Resolving power (mass)

The ability to distinguish between ions differing in the quotient mass/charge by a small increment. It may be characterized by giving the peak width, measured in mass units, expressed as a function of mass, for at least two points on the peak, specifically for fifty per cent and for five per cent of the maximum peak height.

25 Electron impact ionization

Ionization resulting from the interaction of an electron with any particle, e.g. a molecule or atom.

26 Ionizing voltage

The voltage difference through which electrons are accelerated before they are used to bring about electron impact ionization.

(Note: To obtain the true ionizing voltage corrections for any contact or surface potentials must be made.)

(Note: The term '*electron energy*' is frequently used in place of 'ionizing voltage'.)

27 Field ionization

Ionization resulting from the effect of a very strong electric field on any particle. The strong electric field may produce ionization in space or in a region very close to a metal or other surface.

28 Photoionization

Ionization resulting from the interaction of a photon with any particle which is, in consequence, ionized.

29 Thermal ionization

Ionization of particles brought about by a high temperature—for example, emission of ions from an adsorbed layer on an incandescent metal surface.

30 Chemical ionization

Ionization resulting from the collision of a particle with a positively or negatively charged ion.

31 Chemi-ionization

Ionization resulting from the collision of a particle with a neutral species (generally excited) such as a metastable helium atom.

32 Spark source ionization

Ionization resulting from a spark between electrodes.

33 Ionization by sputtering

Ionization by bombardment of a solid specimen with accelerated ions or electrons or fast neutrals.

34 Laser beam ionization

Ionization by irradiation of a specimen with a laser beam.

35 Faraday cup (or cylinder) collector

A hollow collector, open at one end and closed at the other, used to collect beams of ions.

36 Secondary electron multiplier

A device to multiply current in an electron beam (or in a photon or particle beam by first conversion to electrons) by incidence of accelerated electrons upon the surface of an electrode which yields a number of secondary electrons greater than the number of incident electrons. These electrons are then accelerated to another electrode (or another part of the same electrode) which in turn emits further secondary electrons so that the process can be repeated.

37 Vibrating reed electrometer

A device to measure small currents which uses a vibrating reed forming part of a capacitor which has, in consequence, a periodically varying capacity allowing the measured signal to be modulated for a.c. amplification.

38 Photographic plate recording

The recording of ion beams by allowing them to strike a photographic plate which is subsequently developed.

39 Mass spectrum

This may refer to:

(i) The spectrum produced by a mass spectrometer which shows ion current as a function of the quotient mass/charge as a series of peaks corresponding to different ions.

(ii) The spectrum produced by a mass spectrograph which shows a series of lines on a photographic plate or film.

(In the limiting case a mass spectrum may show only a single ionic species rather than a series of lines or peaks, but this is unlikely in practice.)

Generally the term 'mass spectrum' refers to a spectrum of positive ions.

40 Negative-ion mass spectrum

A mass spectrum of negative ions.

41 Molecular ion

The ion produced when a molecule loses or gains an electron.

42 Molecular cation

A molecular ion produced by loss of one electron from a molecule.

43 Molecular anion

A molecular ion produced when a molecule gains an electron.

44 Rearranged molecular ion

A molecular ion which has rearranged to a structure different from that of the original molecule.

45 Parent ion

Ion precursor or progenitor of a fragment ion or of a metastable intermediate. The term is generally given the same meaning as 'molecular ion'.

46 Precursor or progenitor ion

The precursor or progenitor of a fragment ion or of a metastable intermediate.

(Note: A fragment ion may be the precursor or progenitor of other fragment ions.)

47 Fragment ion

An ion produced by the loss of one or more fragments from a parent molecular ion.

48 Isotopic ion

In organic mass spectrometry this term generally means an ion containing one or more atoms of a less abundant isotope. In spark source mass spectrometry involving an element or elements with isotopes, any ion of any nuclide is an isotopic ion.

49 Rearrangement ion

An ion with a structure not obtainable from the parent ion by the simple cleavage of bonds.

50 Metastable decomposition

The decomposition of an ion of mass m_1 into an ion of mass m_2 ($m_2 < m_1$) occurring during passage of the ion through the mass spectrometer. The decomposition is on a time-scale longer than that generating a normal fragment ion.

51 Metastable ion peak (or metastable peak)

The peak resulting from a metastable decomposition, often referring to the peak at $m^* = m_2/m_1$ resulting from decomposition in a single-focusing magnetic deflection mass spectrometer. It may be observed also in time-of-flight instruments by means of suitable retarding voltages.

52 Appearance energy (or appearance potential)

The lowest energy which must be imparted to the parent molecule to cause it to produce a particular specified ion. This energy, usually stated in electron volts, may be imparted by electron impact, by photon impact, or in other ways.

(Note: It is recommended that the term '*appearance energy*' should replace the term '*appearance potential*' and that the energy should be stated in SI units.)

53 Base peak

The most intense peak in a mass spectrum. This term may be applied to the spectra of pure substances or mixtures.

54 Intensity relative to base peak

The ratio of the ion current of a peak to that of the base peak. A process of normalization is generally used with the base peak current taken as 100.

55 Peak height

The height of a recorded peak in a mass spectrum.

56 Total ion current

(a) After mass analysis

The sum of all the separate ion currents carried by the different ions contributing to the spectrum.

(b) Before mass analysis

The sum of all the separate ion currents for ions of the same sign (usually positive) before mass analysis.

57 Additivity of mass spectra

The process by which each chemical species present in the ion source at a certain partial pressure makes a contribution to the total mass spectrum which is the same as that which it would give if that chemical species alone were present in the ion source at a pressure equal to this certain partial pressure.

58 Interference

The modifying effect on the mass spectrum of a particular chemical species due to the presence of other chemical species in the ion source.

59 Ion-molecule reaction

A chemical interaction between a positive or negative ion and an uncharged molecule.

60 Auto-ionization

The spontaneous ionization of an atom, molecule, or fragment of a molecule which is in a sufficiently excited state.

(Note: The term 'Pre-ionization' is also used with the same meaning, particularly in the case of molecules.)

61 Ionization efficiency curve

A curve showing the ion current of a particular ion plotted against the energy of the ionizing electrons or photons.

62 Sensitivity

(a) *Ion source*

The value obtained when the ion current (before any amplification) for a specified ion from a specified species is divided by the partial pressure of the species in the ion source.

(b) *Inlet system*

The sensitivity with respect to an inlet system for a gaseous sample should be given as a similar quotient using the partial pressure of the species in the inlet system or reservoir system.

(c) *Direct probe*

The sensitivity using a direct probe inlet should be given by stating the ion current for a specified ion from a specified species under specified conditions of operation.

It is usually very difficult to measure the partial pressure of the species in the ion source under standard operating conditions. For practical purposes it may be better to state the total ion current for a specified species using the direct probe inlet or other types of inlet systems.

63 Background mass spectrum

The mass spectrum observed when no sample is intentionally introduced into the mass spectrometer or spectrograph.

64 α -Cleavage

Fission adjacent to a heteroatom or functional group producing a radical and an ion.

65 β -Cleavage

Fission next but one to a heteroatom or functional group producing a radical and an ion.

66 McLafferty rearrangement

β -Cleavage with concomitant specific transfer of a γ -hydrogen atom in a six-membered transition state in mono-unsaturated systems irrespective of whether the rearrangement is formulated by a radical or an ionic mechanism and irrespective of the position of the charge.

SYMBOLS

m/e	The quotient mass/charge
m^*	(i) Metastable peak (an asterisk denotes metastability) (ii) Value along the m/e scale for a metastable peak
*	Denotes a decomposition, the occurrence of which is supported by a metastable peak
+. or †	Odd-electron ion
+	Even-electron ion
⤴	Single electron movement
⤵	Electron-pair movement
M	Mass number of molecular ion