

Units in Mass Spectrometry

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It has been estimated that a billion mass spectra are recorded daily on this planet alone. Even so, mass spectrometrists always seem to find time to argue about units and nomenclature, and they display an incredible energy and enthusiasm in performance of their neologistic duties. Standards for terms have been promulgated and published (1–3). However, in teaching mass spectrometry (MS) and in reading the published literature, it seems common that too little attention is given to units. This column is therefore dedicated to compensating for such a shortfall. The focus will be on the more common units, with commentary on history and usage, and on debate, when appropriate.

We begin with the units for the x axis in the mass spectrum, which have evolved over the years. The current accepted unit is m/z , said aloud as “ m over z .” (I have heard Brits use “ m upon z ,” but then they say “spanner” instead of “wrench,” too.) In this nomenclature, m represents the mass of the ion, and z represents the charge. It has been argued that m/z is a symbol, and should therefore be set in italics (1). However, this is not a uniform typographical practice, and there are those that would debate at length the difference between a symbol and a unit. More to the point, although the unit m/z is universally accepted, it is awkward in that a lowercase m is the SI unit for me-

ter. The correct unit for mass is u , the unified atomic mass unit. A more correct unit for use on the x axis of a mass spectrum would therefore be u/z . Mass spectrometrists simply choose not to use it. The usage “ M/z ” has appeared intermittently, where M is presumably derived from the usage of M^+ to represent the molecular ion of a compound of molecular mass M . A unit in common use before about 1980 was m/e , and this unit appears as the x -axis unit label in many of the ear-

lier classic books on MS. The lower case e , however, is the term for the charge on an electron (1.602×10^{-19} C) rather than the number of such charges, which is designated z .

The u in u/z is the abbreviation for mass in the unified atomic mass scale and is derived from the unified atomic mass unit. The history of this unit establishes its relationship with amu, the abbreviation (sometimes seen as a.m.u.) for atomic mass unit. The relative masses of the various chemical elements were first established by careful study of the stoichiometry of their reactions. Hydrogen, the lightest element, was assigned a relative mass of 1 amu (a suggestion originating with John Dalton). Relative masses of other elements seemed to be simple multiples of that value. For example, oxygen seemed to have a relative mass of about 16. As MS was developed, Aston worked to formulate the whole-number rule. According to this rule, atomic masses are approximately integral masses of the mass of hydrogen (a codification of the stoichiometrically based conclusions), and deviations from the integral values are due to the presence of isotopes of the elements. Aston showed experimentally, in his discovery of the isotopes of chlorine, that the measured relative weight of chlorine (35.45 amu) derives from the fact that the isotopes ^{35}Cl and ^{37}Cl occur naturally in approximately a 3:1 abundance ratio. As knowledge of the masses of isotopes was compiled, Aston made a further valuable contribution in his observation that the integral nature of the isotopic masses is only approximately valid. The exact mass of an isotope (the nucleidic mass) differs slightly from the summed mass value of the component protons, neutrons, and electrons (each in its free unbound state). This difference is known as the mass defect (or mass decrement). The mass defect is equivalent (via $E = mc^2$, where E is energy, m is mass and c is the speed of light) to the binding energy that holds the assembly together. Aston used ^{16}O as the mass standard from which to derive a packing fraction curve that underlies the development of much of modern nuclear physics.

The brief aside into a description of the mass defect mentioned earlier conveys the historical reason for the use of ^{16}O as the standard against which a mass scale for amu was developed. Two scales were developed, however. In the physical

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atomic mass scale, ^{16}O was assigned an exact mass of 16.000000 amu, and all other atomic masses were defined relative to this standard (that is, the amu is defined as $1/16$ the mass of ^{16}O). In the chemical atomic mass scale, the amu was defined as $1/16$ of the average atomic mass of oxygen (which included the contribution of the low-abundance isotopes ^{17}O and ^{18}O). Both scales were internally accurate, but there was a difference factor of 1.000275 between them (physical scale > chemical scale).

The implicit difficulty of maintaining two separate mass scales was apparent, and explicit suggestions for a new scale appeared in 1957. Meetings of the International Union of Physicists (1960) and the International Union of Chemists (1961) agreed to a new mass scale (the unified mass scale) in which the atomic mass unit was defined as $1/12$ the mass of an atom of ^{12}C . Equivalently, the mass of ^{12}C is defined as 12.000000 amu. The numerical value of the amu is $1.66053873 \times 10^{-27}$ kg. In terms of energy, 1 amu equals approximately 931.494 MeV (see the following section on the unit eV).

The description of the situation for units of mass is not yet complete. The unit dalton (Da) has been accepted as an alternate name for the unified atomic mass unit. The unit of dalton is most often used by biochemists (and therefore has appeared much more frequently in MS literature recently), with units of kDa and MDa used to describe the masses of large biomolecules. Even seasoned nomenclators admit that spoken "kamu" and "ku" are not euphonic (nor clear). Terms such as "kilodaltons," therefore, serve a recognized purpose and are accepted — even if not strictly required by the rules. For example, the x -axis label of " $(m/z)/1000$ " recently appeared in print. The typographical simplicity of kDa would seem to be a telling advantage. There is ample room for continued confusion and debate, however. The unit Da

has been coupled directly with the term m/z , as in "For H^+ , $m/z = 1$ Da." This represents continued obfuscation of the difference between the unit m/z , the noun " m/z ratio," and the adjective symbol m/z . More correctly, "The m/z ratio of H^+ is 1" or " H^+ has a mass of 1 Da" or "The ion H^+ is seen at m/z 1."

The standard values of mass and charge used in MS are collected in Table I. It was noted earlier that the z in m/z is a dimensionless value that corresponds to the number of charges on the ion. The symbol z is distinct from e , which is the actual value of the charge on an electron, measured in the units of coulombs. If one electron is removed from a neutral molecule to create a molecular ion M^+ , then the molecular ion has a positive charge equal to the value of the negative charge on the electron that was removed (1.602×10^{-19} C). Similarly, a proton has that same value of charge, and therefore so does a protonated molecule $(\text{M}+\text{H})^+$. A multiply protonated molecule $(\text{M}+n\text{H})^{n+}$ has a charge z that is equal in numerical value to $n \times e$.

There are units in MS that appropriately retain the use of the symbol e . One of these is commonly seen in descriptions of electron ionization mass spectra, in which it might be noted that the proffered mass spectra are standard "70 eV" spectra. This unit is spoken aloud as "electron volt," and has several related definitions. The (single word) electronvolt or (hyphenated) electron-volt (eV) is a unit of energy that is defined by the energy required to move a single electron through a potential difference of 1 V. The accurate numerical value of 1 eV is 1.602×10^{-19} J. In an electron ionization source, an electron emitted from a hot metal filament is directed to a collector that is held at a potential 70 V more positive than the filament itself. Each electron therefore moves through a potential difference of 70 V, and acquires the appropriate kinetic energy for that potential difference. Remember that the units for e are coulombs, and the units for the potential difference are volts, and therefore the product is expressed in units of joules (that is, $\text{C} \times \text{V} = \text{J}$).

The electronvolt is also a unit of mass, used

in some areas of particle physics. Mass and energy are related by $E = mc^2$. An energy of 1 eV is therefore equivalent to a mass of about 1.782662×10^{-36} kg, or about 1.073544×10^{-9} amu. Most particle masses are expressed in units of MeV or GeV.

The unit eV appears in other guises in MS. In MS-MS experiments, a mass-selected precursor ion is induced to dissociate into product ions in an energization step separate from the ionization process itself. The energization can occur in a collision in which the selected precursor ion (at a chosen kinetic energy) collides with a neutral target gas molecule. The faster the precursor ion is moving, the more energy is deposited into it as a result of such a collision, and the greater the degree of dissociation. Therefore, MS-MS spectra that involve collision-induced dissociation vary with the collision energy, which is expressed in units of eV. A singly charged ion accelerated to a kinetic energy by a 50 V potential difference will produce an MS-MS spectrum at 50 eV collision energy. This energy scale is common in MS-MS performed with multiple-quadrupole or ion trap instrumentation. Note that a doubly charged ion that is accelerated through the same 50 V potential will achieve a different velocity. How then to label the MS-MS spectrum? Implicitly, the units should be $n\text{eV}$, where n is the number of charges. This would lead to a descriptive label of 100 eV. But such a simple label fails to reflect the fact that the precursor ion is a doubly charged ion. The solution to date has been to use a unit of volts in the lab frame (simply saying that the instrumental potential difference is 50 V) and then to specify elsewhere the identity and charge of the precursor ion. This issue of nomenclature and units will surely become a topic of future debate. In the in-

Table I. Standard units of mass and charge used in mass spectrometry.

Mass unit	u	1.66043×10^{-27} kg
Electron charge	e	1.60210×10^{-19} C
Proton rest mass	m_p	1.67252×10^{-27} kg 1.00727663 u
Neutron rest mass	m_n	1.67482×10^{-27} kg 1.008665 u
Electron rest mass	m_e	9.10908×10^{-31} kg 5.48597×10^{-4} u
Velocity of light in a vacuum	c	2.997925×10^8 m s $^{-1}$

terim, careful descriptions of the experiments leading to such MS-MS spectra must be documented.

The charge on the ion reappears for consideration in ion detection at a Faraday cup or an electron multiplier. Remember that the charge on a singly charged ion is 1.602×10^{-19} C. If a million ions of the same mass arrive at the detector

(3) O.D. Sparkman, *Mass Spectrometry Desk Reference* (Global View Publishing, Pittsburgh, PA, 2000).

Kenneth L. Busch's interest in units dates back to his tinkering with stereo equipment during his gawky teen years (1962–1987). The stereo equipment at that time had panel indicators for signal strength called VU meters (now mostly replaced by

red LEDs). Being retentive in nature, Busch investigated the origin of the name VU (see www.sound.au.com/project55.htm). As described in this column, MS has its own collection of (commonly used and sometimes misused) units. The field seems also to find delight in a panoply of acronyms, which will be the topic of a future column. ♦

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within 1 s, the accumulated current is $(1.6 \times 10^{-19} \text{ C} \times 10^6 \times 1 \text{ s}) = 1.6 \times 10^{-13} \text{ A}$. Remember that a current of 1 A flowing for 1 s transports a charge of 1 C (that is, $1 \text{ A/s} = 1 \text{ C}$ or $1 \text{ A} = 1 \text{ C s}$). The need for very sensitive ammeters (in Faraday cup detection) or amplification by many orders of magnitude (usual gains in electron multipliers are 10^6 to 10^7) is clear. A previous column discussed in detail the operation of the electron multiplier detector.

Finally, we have left aside for now the y axis of the mass spectrum, which can be ion counts, number of ions, or (commonly) relative abundance or relative intensity. Because the term “intensity” usually refers to the height of a peak or the strength of an ion beam, the term “relative abundance” is better used to refer to the number of ions in the mass spectrometer, which should be reflected in the y-axis value. Isotopic abundances, their precise and accurate measurement, and applications of such measurements will be the subject of an upcoming installment of “Mass Spectrometry Forum.”

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