

Glossary (updated 6/23/2008):

Average mass: the atomic weight or mass to charge ratio of a species assuming all elements in that species are present at their natural isotopic abundances (e.g. 98.93%  $^{12}\text{C}$ , 1.07%  $^{13}\text{C}$ , 99.985%  $^1\text{H}$ , 0.0115%  $^2\text{H}$ , 75.78%  $^{35}\text{Cl}$ , 24.22%  $^{37}\text{Cl}$ ).

CI: chemical ionization, an ionization method that creates analyte ions by reacting gaseous molecules with ions created from a reagent gas. The reagent gas is ionized by EI. The MAT-95 has three gasses available for CI, methane, isobutane, and ammonia. CI is a much less energetic process than EI, so it is easier to obtain molecular ions. Ions of the type  $(\text{M-H})^+$ ,  $\text{M}^+$ ,  $(\text{M+H})^+$ ,  $\text{M}^-$ , and  $(\text{M-H})^-$  can be created by CI.

Da: Dalton, a unit of molecular weight.  $1 \text{ Da} = 1 \text{ atomic mass unit} = 1.66 \times 10^{-27} \text{ kg}$

Deconvolution: The process of computing the zero charge molecular weight of a molecule from a distribution of multiply charge mass spectral features generated by electrospray ionization. The basic formula for the observed  $m/z$  ratio for a multiply protonated is given by:  $m/z_{\text{obs}} = [\text{MW} + (n \times 1.0073)]/n$  where  $n$  is the charge state and MW is the zero charge molecular weight of the molecule in question (1.0073 Da is the mass of a proton). If the charge state is unknown, two adjacent peaks may be used to compute the charge state of one of them, the molecular weight of the molecule can be discerned. Mixtures of multiply charged mass spectral features often need computer analysis to handle the calculations.

EI: electron ionization (aka electron impact), an ionization method that involves bombarding gaseous samples with 70 eV electrons. The 70 eV electrons ionize molecules by ejection of an electron from the analyte. The relatively high energy of these collisions often leads to extensive fragmentation of the analyte ions. The fragmentation patterns can be used to deduce the chemical structure of the analyte ion. Radical ions of the type  $\text{M}^{\cdot+}$  are most often created by EI.

ESI: electrospray ionization, an ionization method that involves dissolving the compound in a conductive solution of a polar solvent. This solvent also contains an source of cations (e.g. volatile organic acids (acetic, formic) for  $\text{H}^+$ , salts of organic acids, e.g. sodium acetate or ammonium formate for  $\text{Na}^+$  or  $\text{NH}_4^+$ ) for positive ionization or anions (e.g. ammonia, triethylamine, ammonium bicarbonate) for negative ionization). The solution is then infused through a needle placed in a strong electric field (several kV/cm). The high electric field forms a spray of very highly charged, very fine droplets. As these droplets evaporate, they will fission when the charge-charge repulsion exceeds the surface tension and/or evaporate analyte ions from their surfaces. ESI often generates multiply charged ions for species over 1,000 Da. Multiply charged ions require mass spectral deconvolution to compute the mass of the uncharged analyte molecule.

eV: electron volt, an energy unit commonly used in nuclear chemistry and ion physics.  
 $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$

external calibration: denotes an experiment in which the mass scale was calibrated at some time other than when the analyte data were recorded. This is the calibration used by both of the quadrupole instruments (API III and HP 5971).

internal calibration: denotes an experiment in which compounds of known molecular weight are added to sample prior to the recording of the mass spectrum. These calibrants are then used to refine mass calibration in the sample mass spectrum. Since both the calibrant and analyte mass spectra are recorded simultaneously, instrument drift and matrix effects are negated, facilitating very precise calibration. All formula matching experiments with the MAT-95 or LCT require the addition of internal calibrants (usually perfluorokerosene or renin substrate peptide). Internally calibrated mass spectra can also be recorded with the Biflex III. Lists of commonly used internal calibrants can be found on the Useful Info page.

LDI: laser desorption ionization, an ionization method that involves irradiating a dried sample with a laser to create photo-ions. In the Biflex III, a 337 nm nitrogen laser is used to irradiate samples already in the vacuum chamber. Radical ions of the type  $M^+$  are most often created by LDI.

MALDI: matrix-assisted laser desorption/ionization, an ionization method that involves mixing the analyte with a molar excess (usually 10,000:1 or greater) of an organic dye known as a matrix. The analyte and matrix are co-crystallized prior to being introduced into the mass spectrometer. In the Biflex III, a 337 nm nitrogen laser interrogates the matrix/analyte spot. Each laser shot causes a small amount of the dye to sublime into the gas phase, volatilizing some of the entrained analyte in the process. Proton transfer reactions in the sublimation plume (possibly involving matrix molecules in an excited state) allow the simultaneous creation of positive and negative analyte molecules. Ions typically result from successive protonations (e.g.  $[M+H]^+$ ) or deprotonations (e.g.  $[M-H]^-$ ) of analyte molecules.

MALDI matrix: a UV-absorbing dye molecule added to biological and polymer samples prior to MALDI mass spectrometry. Common MALDI matrices include  $\alpha$ -cyano-4-hydroxycinnamic acid (a.k.a. CHCA or CCA), 3-methoxy-4-hydroxycinnamic acid (a.k.a. ferulic acid or FA), 2,5-dihydroxybenzoic acid (a.k.a. DHB), and 3,5-dimethoxy-4-hydroxycinnamic acid (a.k.a. sinapinic acid or SA)

monoisotopic mass: the atomic mass or mass to charge ratio of a species assuming all elements in that species are present in a single isotopic form. This is most commonly used to refer to species containing all  $^1\text{H}$ ,  $^{12}\text{C}$ ,  $^{14}\text{N}$ ,  $^{28}\text{Si}$ ,  $^{32}\text{S}$ ,  $^{35}\text{Cl}$ ,  $^{79}\text{Br}$ , etc. (e.g. no  $^{13}\text{C}$  or  $^{37}\text{Cl}$ ), and is typically observed as the lowest mass peak in an

isotopic distribution of a small molecule. This number is often given in place of the average mass (see average mass).

ppm: part per million, a measure of relative error. Use the following formula to convert ppm of relative error to absolute error:  $(E / 10^6) * X = S$  where E is the relative error in ppm, X is the value which the error is associated with, and S is the absolute error. Thus, 200 ppm of error at 3149.7 Da give an absolute error of 0.63 Da  $[(200/10^6)*3149.7]$ , while 200 ppm of error at 379.1 Da corresponds to 0.076 Da of absolute error.

Th: Thompson, a unit of molecular weight per charge given by  $MW/n$  where MW is the molecular weight of the species in Da, and n is the number of charges (given as an integral multiple of the charge on an electron). It can be thought of as  $Da/z$  where z is the charge of the ion. For example, the +15 charge state of bovine cytochrome C (made by adding 15 protons to a cytochrome C molecule) has a molecular weight of 12375.11 Da  $(12360 + 15*1.0073)$  and a mass/charge ratio of  $12375/15 = 825.01$  Th. For singly charge species, Da and Th are effectively interchangeable.

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