

GUIDELINES for MASS SPECTRA 2013

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1. For any ion, report the most abundant isotopomer.
2. For calculating the most abundant isotopomer, FORGET the periodic table; always use a table of isotopes.

Useful links:

<http://ie.lbl.gov/education>

[http://en.wikipedia.org/wiki/Isotope_table %28complete%29](http://en.wikipedia.org/wiki/Isotope_table_%28complete%29)

3. Use an isotope pattern calculator to check your proposal for the assignment of an ion. Print out the theoretical pattern and store it with your data.

Some isotope pattern calculators on the web:

<http://omics.pnl.gov/software/MWCalculator.php> (freeware)

http://www.wsearch.com.au/Tools/molecular_weight_calculator.htm (freeware)

<http://winter.group.shef.ac.uk/chemputer/isotopes.html>

<https://sites.google.com/site/isoproms/>

<http://fluorine.ch.man.ac.uk/research/mstool.php>

4. Sometimes one needs to ask the operators of the mass spectrometer if they determined everything properly.

⇒ You can always ask the operators for a peak list with the relative intensities in the area of interest. This can help you in the comparison.

⇒ Ask the operators if the machine is calibrated with respect to the mass of your compound.

⇒ You can by yourself evaluate the mass accuracy of the instrument using the following formula:

$$\text{Mass accuracy (ppm)} = 10^6 \times \Delta m / m_{\text{observed}} \text{ where } \Delta m = m_{\text{calculated}} - m_{\text{observed}}$$

5. The fragmentation pattern of your compound should be similar to similar compounds measured previously in the group; critically investigate any inconsistencies.

6. Some remarks on FAB-MS:¹

- very frequently a pseudomolecular ion $[\text{MH}]^+$ is observed (especially for neutral compounds).

- all ions may be observed in association with the matrix, $[\text{M}+\text{H}+\text{matrix}]^+$

- be sure that your compound is soluble in the utilized matrix!

- you can normally rationalize most fragments by elimination of a neutral molecule from the molecular ion. Most common are (a) loss of neutral monodentate ligand (for example, CO, NH₃, PR₃), (b) loss of HX (X: halogen) with formation of $[\text{M}-\text{X}]^+$ ion or oxidative addition of a carbon-hydrogen bond of a ligand to the metal center.

- the peak assigned as 100% must be derived from your sample; a matrix peak should NEVER be assigned as 100%, even if it is the most intense ion in the spectrum (you can request a corrected spectrum from the operator if you do not want to manually recalculate the relative intensities).

7. The symbol for a molecular ion is M^+ . If your compound is a salt of the formula $[\text{cation}]^+ [\text{anion}]^-$, the mass of the cation is NOT M^+ . You will need to give the full formula of the

cation, or a different symbol (for example, when [cation]⁺ [anion]⁻ = **9**⁺ BF₄⁻, the mass of the cation can be abbreviated as **9**⁺).

8. Note that with **dications**, ions will normally be doubly charged, with m/z HALF of the ion mass. It may be necessary to report an extra significant digit, e.g. m/z = 865.4.
9. An excellent reference: *Mass Spectrometry of Inorganic and Organometallic Compounds*, Henderson, W.; McIndoe, J. S. Eds.; John Wiley & Sons Ltd: Chichester, England, 2005.