TPRS with MATLAB and quantitative mass spec review

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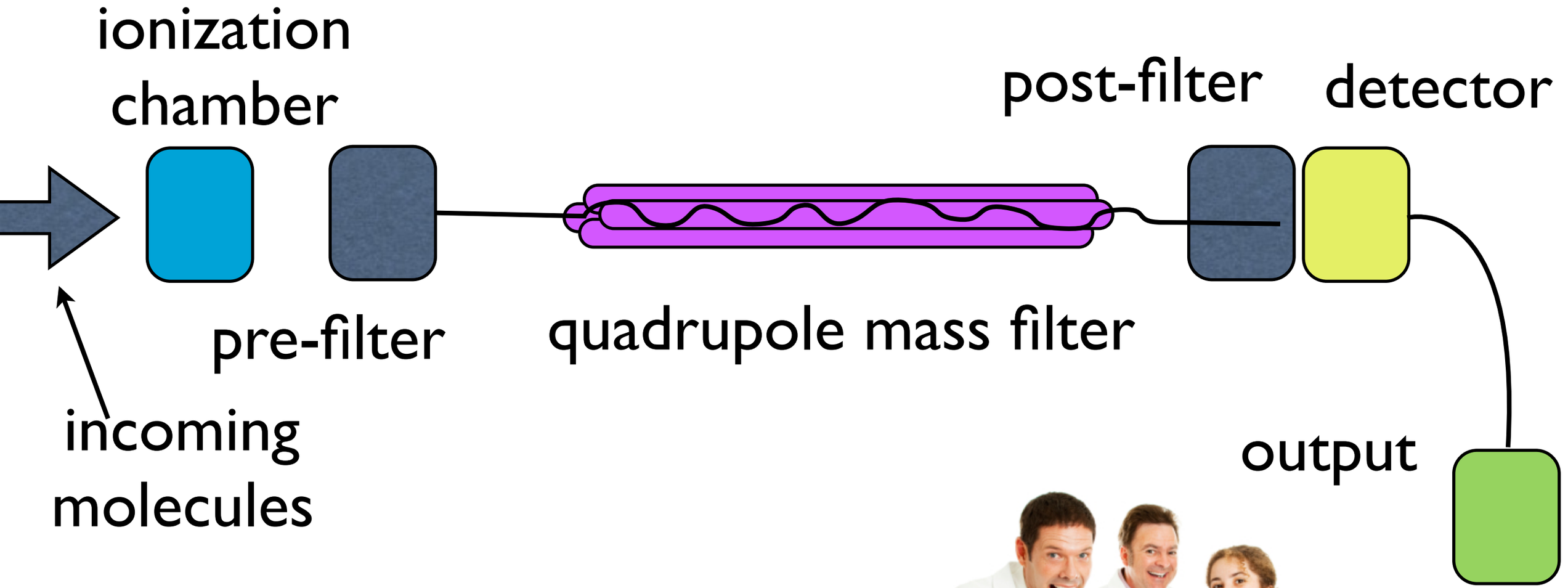
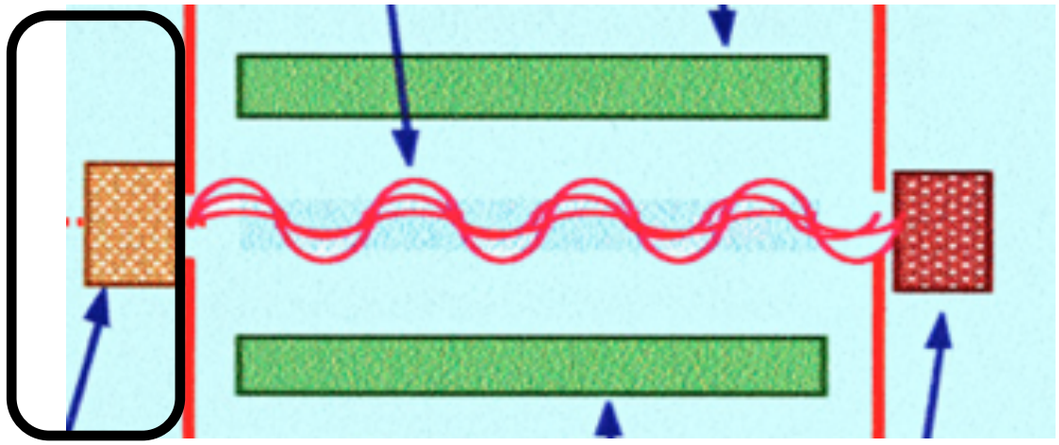
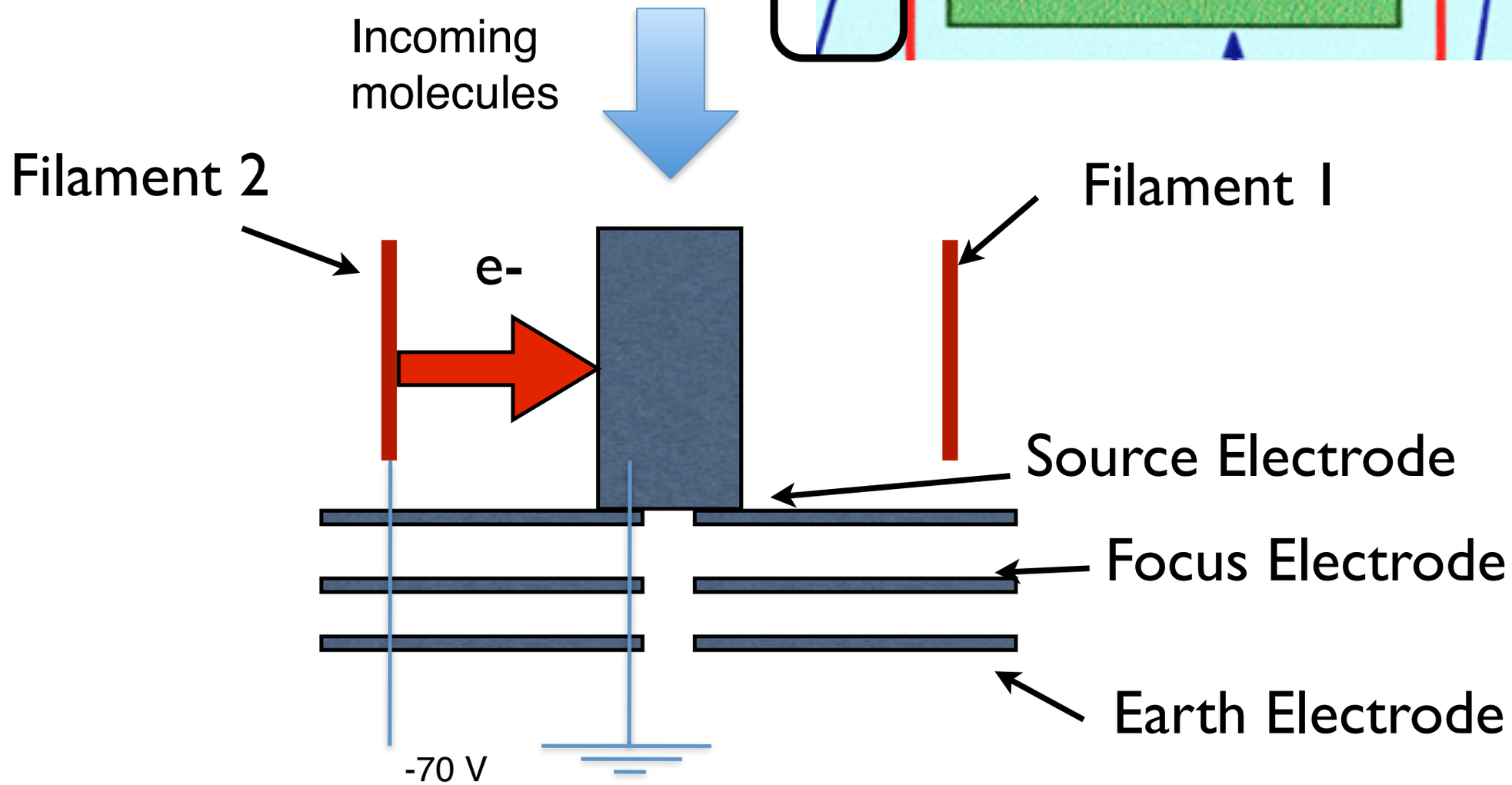
8.12.16

Hiden Triple Filter QMS: a basic schematic



Electron Ionization





σ_i: ionization cross-section
likelihood of ionization of an incoming molecule (units of area)

$$I_i = c * n_i * \sigma_i$$

I_i: corrected ion current of molecule, i
c: proportionality constant
n_i: incoming flux/area density of molecule, i

Ionization cross-section

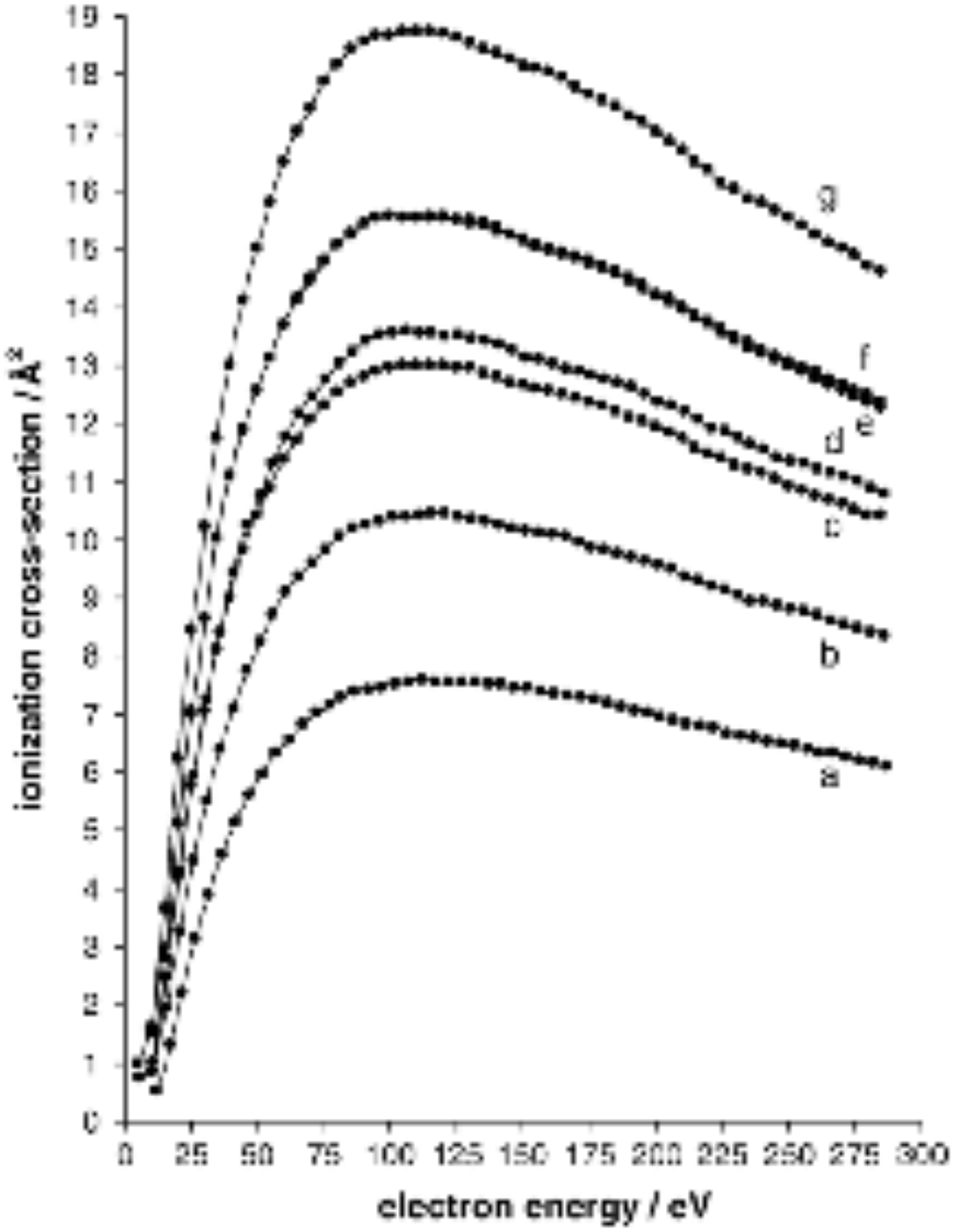


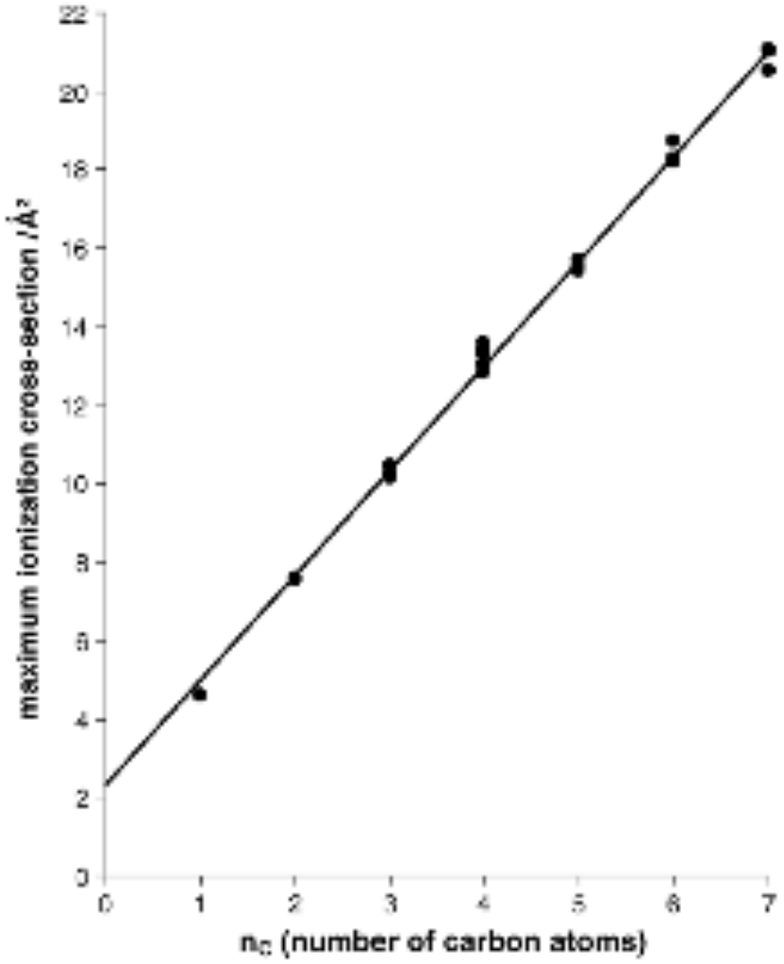
Fig. 1. Ionization cross-section vs. electron energy for the methanoates: a, methyl methanoate; b, ethyl methanoate; c, *iso*-propyl methanoate; d, *normal*-propyl methanoate; e, *iso*-butyl methanoate; f, *normal*-butyl methanoate; g, *normal*-amyl methanoate.

70 eV maximizes ionization for most molecules, but also causes increased **fragmentation.**

At standard operating parameters, approximately 1/1000 molecules
are ionized.

Hudson, J., Weng, Z., Vallance, C. & Harland, P. INTERNATIONAL JOURNAL OF MASS SPECTROMETRY 248, 42-46 (2006).

Ionization cross-section

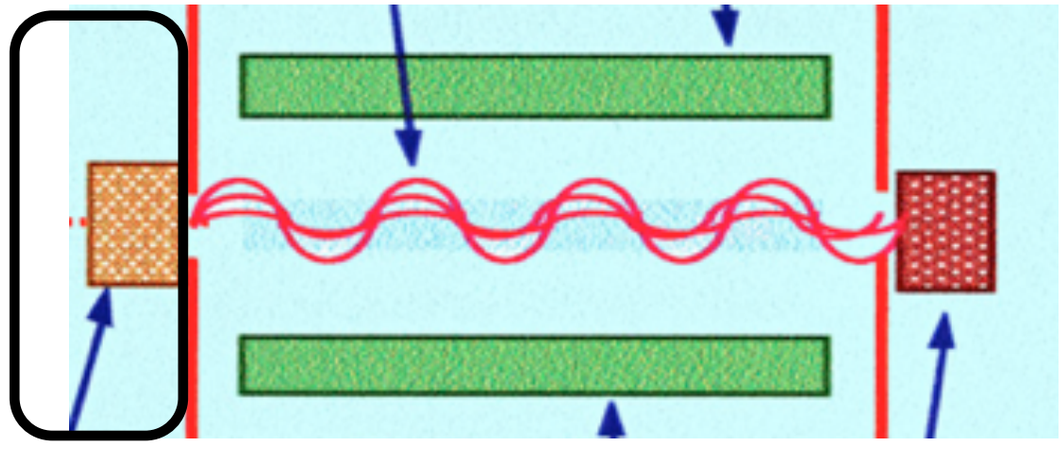


C2-C6 formates
C3-C7 acetates

$$\sigma_{max} = 2.67n_C + 2.34$$

Hudson, J., Weng, Z., Vallance, C. & Harland, P. INTERNATIONAL JOURNAL OF MASS SPECTROMETRY 248, 42-46 (2006).

Fragmentation



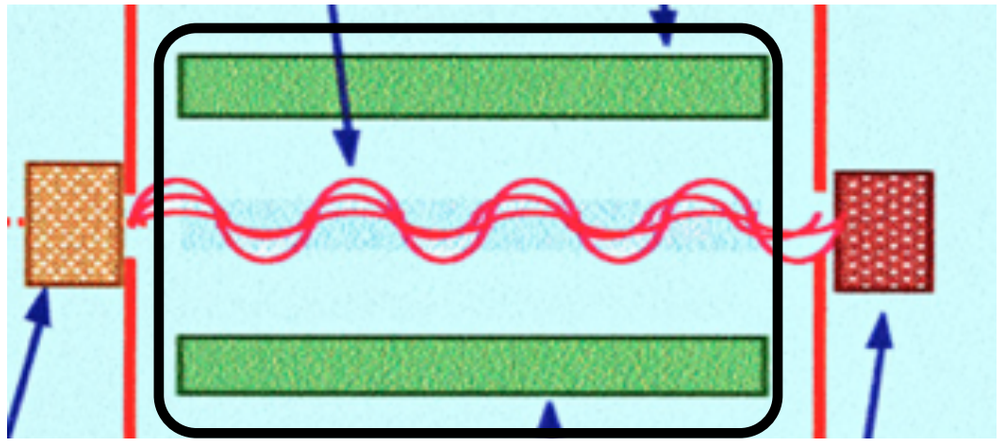
- Molecules break into fragments in reliable patterns: **cracking pattern**
- These can be found in NIST, but to do quantitative analysis, we take our own of all neat samples (both reactants **and** products), as things can vary by MS.

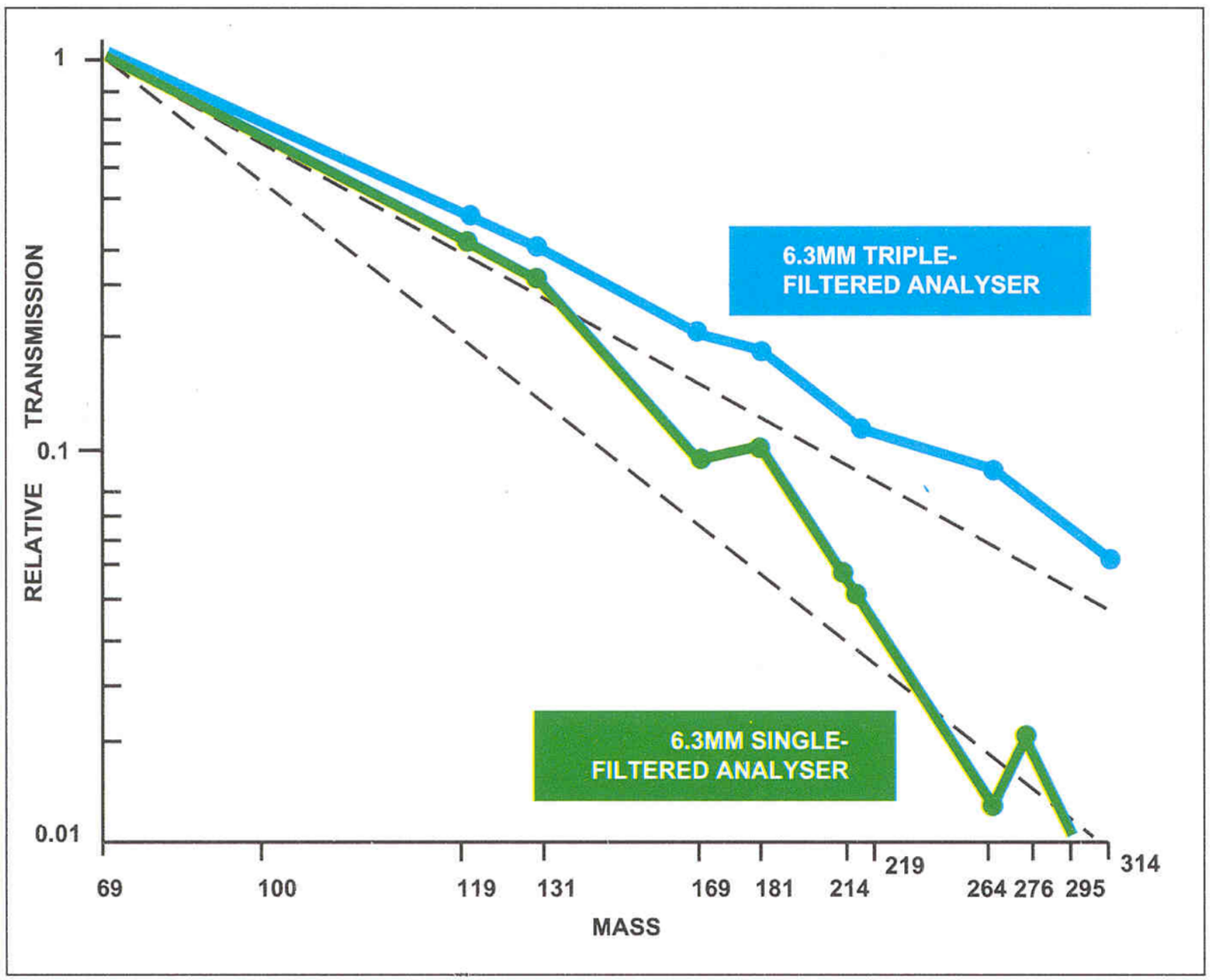
$$I_i = \sum_{j}^{z} I_{ij}$$

I_{ij}: ion current of molecule i fragment m/z j

j-z: all fragments of molecule i

Transmission coefficient





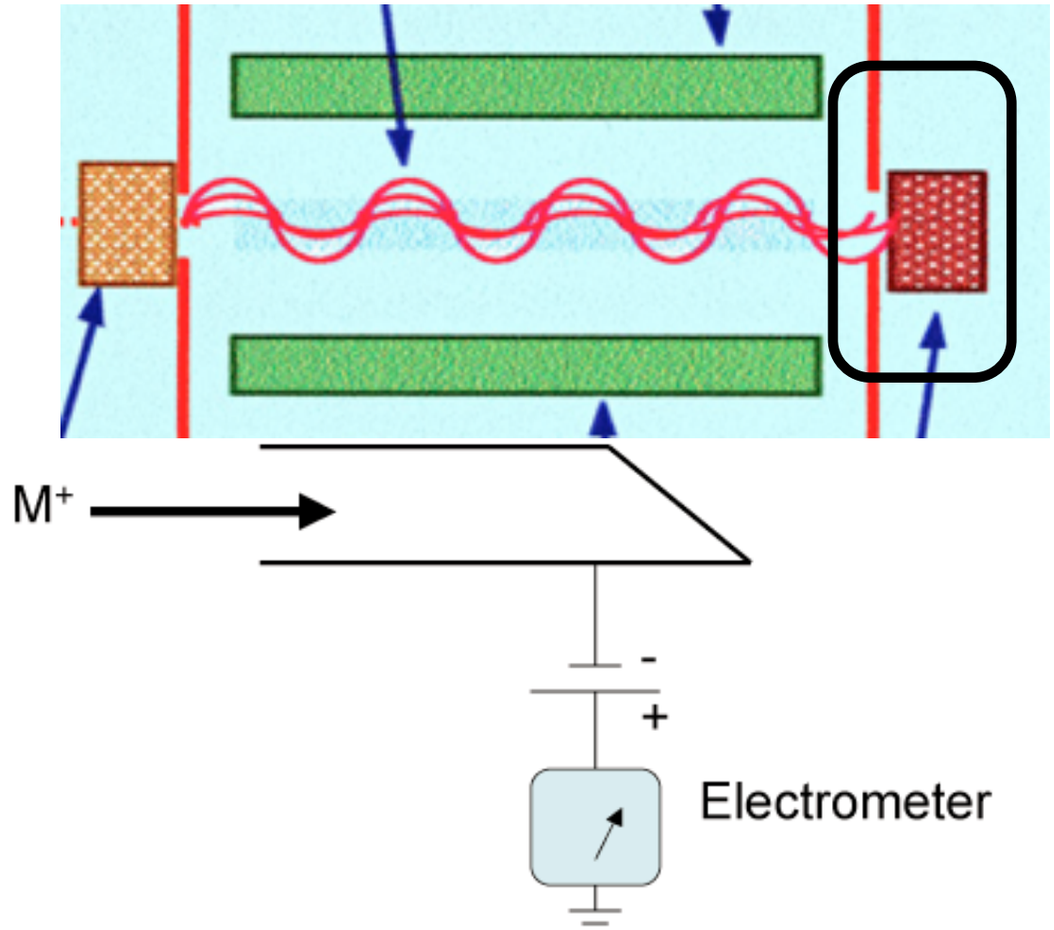
Triple filter masspec has prefocus stage, so that the incoming ions are more focused

T_{ij}: Transmission coefficient for m/z j of molecule i

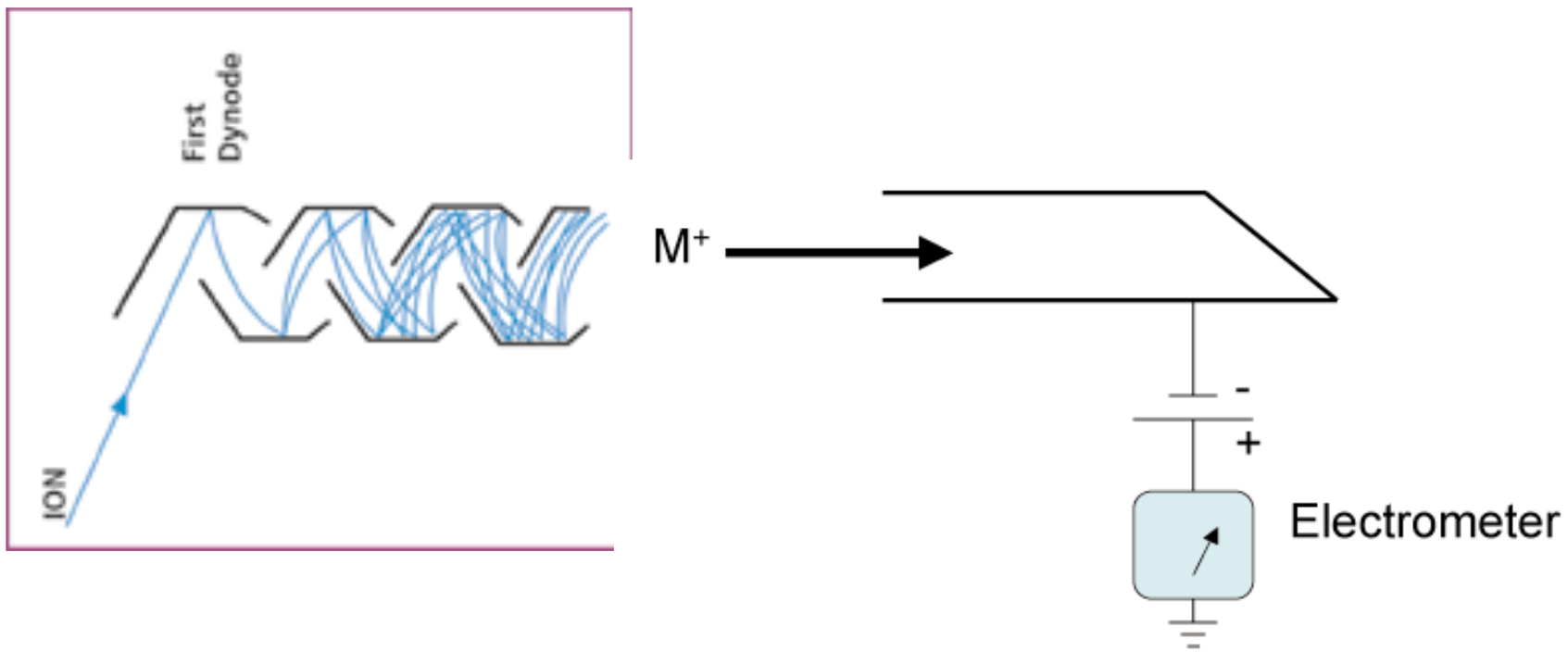
how much of the ion is transmitted through the quadrupole?

Detector

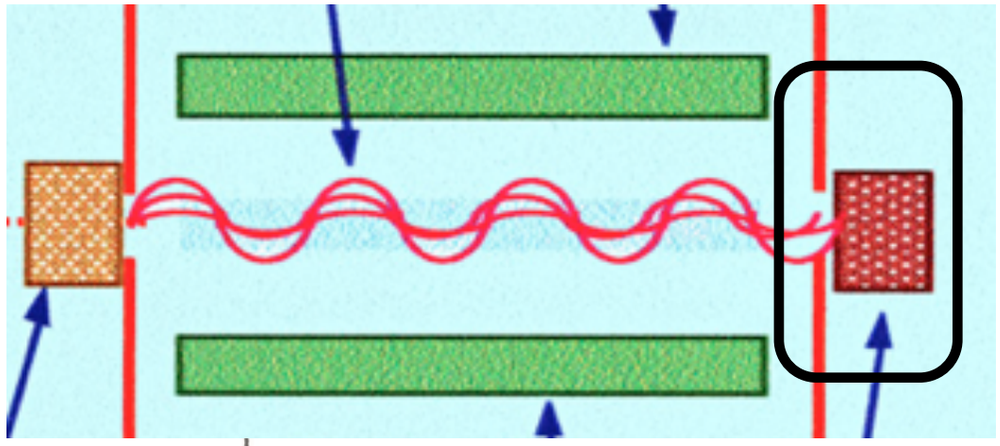
- Faraday cup
  - –Detection limit 10^{-14}A

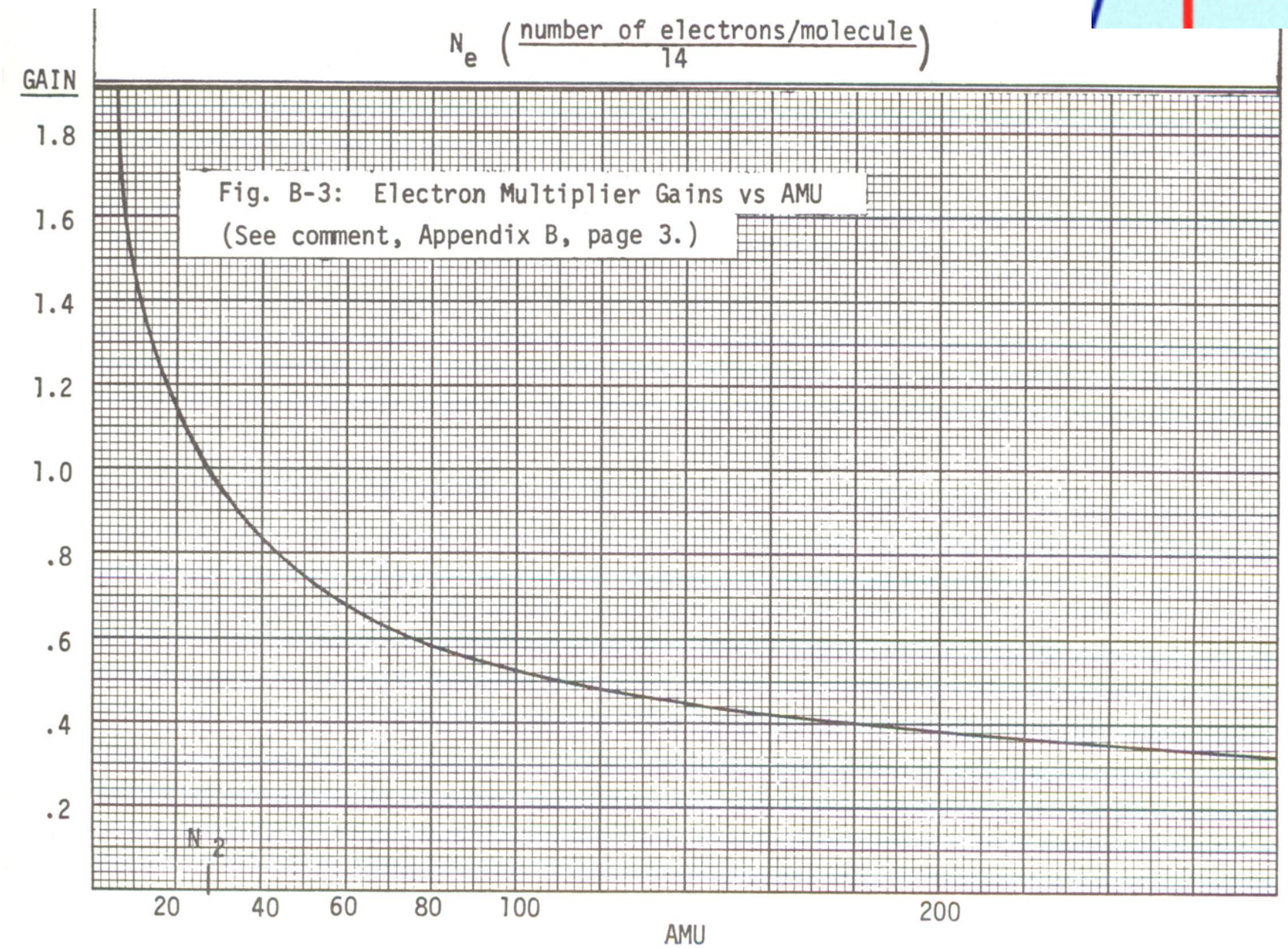


- Secondary Electron Multiplier (SEM)
  - –10^{-18}A



Detection efficiency

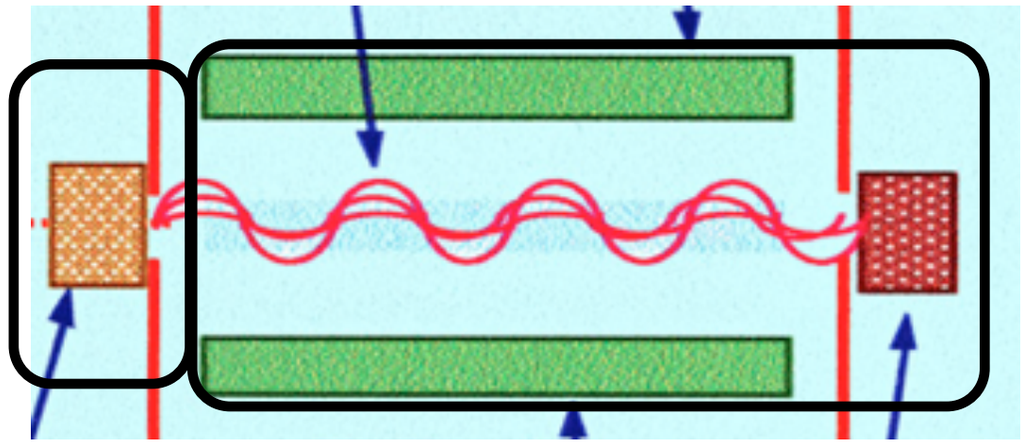




δ_{ij}: Detection Efficiency
for m/z j of molecule i

Adopted from UTI manual

Formalism



$$I_i \propto \sigma_i \bullet n_i \qquad I_i = \sum I_{ij} \qquad I_{ij} = \frac{s_{ij}}{T_{ij} \bullet \delta_{ij}}$$

$$n_i \approx I_i \approx \sum_j I_{ij} = \sigma_i^{-1} \bullet \sum_j \frac{s_{ij}}{T_{ij} \bullet \delta_{ij}} = \frac{\sigma_i^{-1} \bullet s_{ik}}{T_{ik} \bullet \delta_{ik}} \bullet \left(1 + \sum_{j,\, j \neq k} \frac{s_{ij} \bullet T_{ik} \bullet \delta_{ik}}{s_{ik} \bullet T_{ij} \bullet \delta_{ij}} \right)$$

$$X_i = \frac{n_i}{\sum_j n_j} = \frac{I_i}{\sum_j I_j}$$

s_{ik} is the mass spectrometer signal of the signature mass of molecule *i*,
T_{ik} is the transmission coefficient of a fragment with m/z *k* of molecule *i*,
δ_{ik} is the detection coefficient of a fragment with m/z *k* of molecule *i*,
j are all cracking fragments from molecule *I*,
n_i is the number density of molecule *i* in the mixture coming into the ionization chamber of the mass spectrometer.
X_i is the molar fraction of molecule *i* in the mixture.

Hiden sensitivity and TIPS

- To increase S/N on higher mass, you want to set a lower sensitivity level (ie 10^{-10} instead of 10^{-9})
- This increases the time to collect the signal of the given mass. (increases signal)
- The output of the Hiden is given in torr. This means that time average, already accounting for this increased time.
- To read HYDROGEN: put "2" as the second mass-- never first. Also, look at your analog scan-- 2.3 may be a better number for the middle of the hydrogen peak.
- To increase the number of fragments/time:
  - Turn off: auto zero, auto scale for sensitivity
  - Go to advanced options:
    - turn off Beam on/beam off. Turn beam on on first mass. That's all.

TPRS with MATLAB

- The idea: use least squares regression in MATLAB to make the tedious, error-prone process of hand subtraction and analysis a bit more reliable (and ideally faster).

- inputs: fragmentation patterns and ionization cross sections for all molecules (reactants and products)— you need ALL fragments, not just the ones you're looking at in your final TPRS. Fragmentation should ideally be done on a neat sample with a low coverage to minimize error.

- outputs: reconstructed TPRS, error between estimated reconstructed TPRS and raw data, relative corrected areas for the peaks of all products

The Code:

- Needed inputs into the TPRS.m file:
  - Temperature beginning and end for integration (this can be helpful if you only want to integrate over a certain temperature range)
  - Temperature voltage to T conversion equation

Library Files

- simple text file
- must be in the library folder, which must be in the Matlab path
- format

ionization cross section

mass (space) relative abundance

- The units do not matter (it all gets normalized)
- The order of masses does not matter