Precision estimation for PMF of CIMS datasets

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Overview

Error sources in mass spectra

- Poisson statistics
- “Other” noise (electronic, ...?)
- Simplest case: no averaging (after A/D conversion):

\[
\sigma_{cts/sec} = \sqrt{\frac{cts}{sec} \times \frac{cts}{sec}}
\]

Error (including units)

needed for correct error unit

measurement

expected

Signal (cts/sec)

Signal (cts/sec)
Using average spectra

- Additional scaling factor for uncertainties:

\[ \sigma = \sqrt{\frac{\text{avgsignal} \cdot \frac{cts}{sec}}{N \text{sec}}} \]

\( N\text{sec} \): number of seconds used for average

Duty cycle correction

- Duty cycle accounts for \( m/Q \) dependence of ion density in extraction region

\[ \sigma = \sqrt{\frac{\text{avgsignal}_{\text{drc}} \cdot \frac{cts}{sec} \cdot \frac{m/Q_0}{m/Q}}{N \text{sec}}} \]

\( \text{avgsignal}_{\text{drc}} \): duty-cycle-corrected average signal
\( m/Q_0 \): reagent ion mass-to-charge ratio
Additional uncertainty

- To account for different ion sizes:
  \[ 1 + \alpha^2 = 1.2 \]

\[
\sigma = \sqrt{\frac{\text{avgsignal}_{d/c,N}}{N \text{ sec}} \cdot \frac{\text{cts}}{\text{sec}} \cdot (1 + \alpha^2) \cdot \frac{m/Q_0}{m/Q} \cdot \sqrt{\frac{m/Q_0}{m/Q}}}
\]

Question: why does this factor not show up in the “poisson plots”? 

How to deal with normalized signals?

- For CIMS, one often normalizes to a selected reagent ion intensity

\[
\sigma = \sqrt{\frac{\text{avgsignal}_{d/c,N}}{N \text{ sec}} \cdot \frac{\text{cts}}{\text{sec}} \cdot (1 + \alpha^2) \cdot \frac{m/Q_0}{m/Q} \cdot \frac{1}{CF_0}}
\]

\text{avgsignal}_{d/c,N}: \text{normalized, duty-cycle-corrected average signal}

\text{CF}_0: \text{normalization factor (}=I_0/I_t)
What about “other noise”?

- Directly determined from background regions of individual spectra, no correction necessary
- Accounts for electronic noise and ion scattering
- Here: slight dependence on near ion counts (or m/Q?)

\[ \sigma_{ON} = \sigma_{bkg} \]
Calculation example

- Ion signal = 100 Hz at m/Q = 236 Th
- Averaging time: 30 sec
- Other noise = 0.6 Hz
- Acetate signal = 5×10^5 Hz at m/Q = 59 Th
- Normal acetate signal = 1×10^6 Hz
- First term: \( \frac{100}{30} \cdot 1.2 \cdot \sqrt{\frac{59}{236}} = 1 \)
- Second term: 0.6
- Addition in quadrature: \( \sqrt{1+0.36} \approx 1.17 \)

\[
\left( \frac{1}{\sqrt{t_{avg}}} \right) \left( \sqrt{1.2 \cdot \frac{I_{signal}}{CF_{reagent \ ion}} \cdot \frac{m/Q_{reagent \ ion}}{m/Q}} \right)^2 + (\sigma_{ON})^2
\]

UMR sticks errors

- Non-linear effect due to varying integration widths
- Formula becomes a (good) approximation
- Non-zero baseline needs to be taken into account in addition to all other factors

\[ \sigma = \sqrt{(signal + baseline)} \]
• Additional uncertainty: fit errors: see Mike’s presentation

• Larger peak: 30±3
• Smaller peak: 10±3
• Uncertainty proportional to signal level rather than stick height?