HR-ToF-AMS
High Resolution Stick Analysis

Pete DeCarlo
U. of Colorado

Peak Integration by Key Analysis

- PIKA is part of SQUIRREL
- Pikas* are not related to Squirrels

*Pikas are closely related to rabbits (Wikipedia)
PIKA Acknowledgements…

• Marrying SQUIRREL and PIKA and usability improvements– Donna
• Algorithm Development Input
  – Marc, Doug, Jose, Allison
• Beta-Testers

Field-Deployable, High-Resolution, Time-of-Flight Aerosol Mass Spectrometer

PIKA Approach - Gaussian Model

• Mass Calibration: (t₀)
  – Needs to be accurate
• Peak Width: (α)
• Peak Shape f(α,t-t₀)
  – Modified Gaussian
  – Integration of overlapping signals is more robust with peak shape than straight gaussian.
• Fit Peak Height: A
• Ion Signal = f(α,t,A)
• Simultaneous fitting of up to 20 ions at each m/z

\[
\text{RawSpectrum}_{m/z} = \sum_{\text{ions}=1}^{\text{max ions}} f(\alpha_{m/z}, t-t_0, A_{ion}) + \text{baseline}
\]
Mass Calibration

- Already integrated into Squirrel
- Fit Peaks to determine peak center in iToF
  - Use a variable power law
  - $\text{iToF} = \text{slope} \times m^{\text{power}} + \text{intercept}$
    - Typically power $\sim 0.5$
  - Robust, highly accurate
    - for low $m/z$ (< 200 amu)

Peak Width ($\sigma$)

- Appears $\sim$ Linear up to $m/z$ 100
- PIKA determines slope and intercept based on user selected peaks

\[ a + b \times m/z = \sigma \]

Coefficient values:
- $a = 2.09$
- $b = 0.00988$

- USER RESPONSIBILITY (Defaults are a starting point, not always the best ions to use)
Modified Gaussian Peak Shape

From DeCarlo et al. 2006

From the Data we’ll be using today

Peak width is an empirical function scaled \( \frac{t-t_0}{\text{peak width}} \) which introduces no new parameters into the fitting of the peaks.

Gaussian vs Peak Shape

- Reduces residual
- Improves apportionment of signal to different ions
- 1.42 factor difference in CO\(^+\) fitted signal
- Factor of 2.7 difference in N/C ratio
- (N/C is most sensitive because of N containing peaks in shoulder of larger peaks)
- Gaussian okay for “first look”, highly recommend peak shape for serious data analysis
Put it together …

- List of ions at each $m/z$
- Fit the ions Gaussians need 3 parameters
  - Peak Center, $t_0$
    - fixed by exact mass and mass cal
  - Peak Width, $\sigma$
    - fixed by predetermined relation to $m/z$
  - Peak Height, $A$
    - fit by Levenberg-Marquardt least squares fitting
- “Fourth parameter” is peak shape…is also predetermined
- Step through $m/z$’s and fit all ions selected

Data Processing (m/z 81)

- Custom algorithm to integrate ion signals
  - Modified Gaussian Peak Shape
• 1 hour averages on 12x VACES aerosol concentrator (USC)
• Unit resolution instrument would only measure black curve.
• High resolution allows detailed investigation of size resolved chemistry.

• 5 minute afternoon average from SOAR-1
• Unit resolution instrument would only resolve peak height