H₂O for Elemental Analysis

Current Default HROrg Frag Entry for organic related H₂O is as follows:

\[
HR\text{\_frag\_organic} = 0.225 * HR\text{\_frag\_organic}([CO_2])
\]

This value of 0.225, is based on following assumptions:

a) Even under 0% RH, we can’t get rid of chemisorbed H₂O from highly oxidized organic (from hulis literature). So, assume the chemisorbed H₂O is 50% of measured organic-related H₂O

Chemisorbed Org Particle H₂O = 0.5 * measured H₂O

b) RIE (H₂O)=2 (for both organic H₂O and chemisorbed H₂O)

If we remove these assumptions, the “raw” organic related H₂O would be:

\[
\text{Org H}_2\text{O}/\text{CO}_2 = (0.225/0.5)*(2/1.4) = 0.64 \quad (1.4 \text{ is RIE of org})
\]

(This is closer to the values that have been mentioned earlier by Qi Chen, Yele etc.)

H₂O for Elemental Analysis cont..

- What do we do if measured H₂O/CO₂ is different?
  - Change default frag proportionally

- If you disagree with assumptions (a or b) then need to decide how to approach it. Specific lab studies may need a different frag wave than that used for the “average” ambient organic. Right now we don’t have enough information to automatically change H₂O related entries in the ambient organic frag wave

- If you modify H₂O entry in HR_Frag_org, you need to change RIE of org, to conserve org mass

- If publishing results based on different frag waves, it is important to explicitly say how the frag waves were modified.
Defining Errors for HR-ToF-PMF

Manjula Canagaratna

Some slides from James Allan, Ingrid Ulbrich,

\[ \text{ORG} = C \times MS + E \]

**OA Components: Multivariate Analyses**
Quick Review of PMF

- We minimize $Q$

$$Q = \sum_{i=\text{ions}} \sum_{j=\text{columns}} \left( \frac{\text{residual}_{ij}}{\text{error}_{ij}} \right)^2$$

- $Q_{\text{exp}} = (m \times n) - p^*(m + n)$

- $$Q/Q_{\text{exp}} = \frac{\sum_{i=\text{ions}} \sum_{j=\text{columns}} \left( \frac{\text{residual}_{ij}}{\text{error}_{ij}} \right)^2}{(mn) - p(m + n)}$$

Ideally, would get close to 1

IF

Residual close to error

ERROR on each point is important for guiding minimization of fit!

Why do we care about the noise

- Weighting of each data point in fit determined by prescribed noise
- DEGREE TO WHICH AN ION GIVES USEFUL INFORMATION TO THE FIT IS CONTROLLED BY ITS S/N

IONS WITH HIGHER S/N ARE MORE USEFUL THAN OTHERS
IONS WITH VERY POOR S/N SHOULD BE DOWNWEIGHTED OR REMOVED!!!
SNR < 2 is “weak”: signal ≈ noise

Pittsburgh, 2002
(Q-AMS)

In this dataset, most m/z’s > 180 are “weak”

Handling “bad” and “weak” m/z’s

- Recall that the PMF fit is error-weighted
  \[ Q = \sum_{i,rows} \sum_{j,columns} \left( \frac{\text{residual}_{ij}}{\text{error}_{ij}} \right)^2 \]
  
  \[ \rightarrow \text{Increasing the error would decrease the Q-contribution or “downweight” the influence of these points} \]

  **Downweighting “bad” and “weak” m/z’s**

  0.2 < SNR < 2  “weak”  Downweight (x 2-3)
  
  SNR < 0.2  “bad”  Remove or strongly downweight (x 5-10)

**NOTE**: THERE IS A PMF Error Preparation *.ipf that can be used for this
A. Precision
B. Accuracy
C. Both
D. Depends

What do we use as the ‘error’ for PMF?

\[ C_{j,t}^{(\text{ugm}^3)} = \frac{10^{12} \times MW_{\text{NO}_3}}{CE_s \times RIE_s \times E_{\text{NO}_3} \times QN_A} \cdot I_{j,t}^{(\text{Hz})} \]

Accuracy
- Unit conversions, AB corrections, Transmissin Efficiency Corrections, Flow rate Corrections
- Factors that multiply Entire Row or Column
- Don’t affect temporal correlations of m/zs
  - Change Factor MS? NO
  - Change Factor time trend? NO (only differ by multiplier)

Precision
- What is the uncertainty in the Ion Count rate?
- m/z dependent
- Affects Individual Points differently
  - Change Factor MS? YES
  - Change Factor time trend? YES
What noise do we include in PMF?

A) Precision  
B) Accuracy  
C) Both  
D) Depends

Sources of Precision Error

1) Counting Error - Number of ions you generate for a given number of parent molecules is variable (POISSON STATISTICS)

2) Ion to Ion Variability - MCP response to ions is variable (Width of single ion histogram measurements)

3) Electronic Noise – provides minimum error, decreases with sqrt(t)
Sources of Error in Precision

- $\Delta I_{\text{electronic}} = \alpha \sqrt{T}$
- $\Delta I_{\text{ion2ion}} = \beta \sqrt{I}$
- $\Delta I_{\text{counting}} = \sqrt{I}$

$\Delta I = \sqrt{\alpha^2 T + \beta^2 I + I}$

$\Delta S = \frac{\Delta I}{T} = \frac{\sqrt{\alpha^2 + (1 + \beta^2)S}}{\sqrt{T}}$

SAME for all AMSs (Q-AMS, All ToF_AMS s)

Other Errors Particular to ToF systems

- Effect of Baseline Subtraction
- $m/z$ calibration shifts, peak width uncertainties
- Peak Fitting Errors (Effect of neighbor intensity and spectral distance on )

How good are the errors output by current PIKA program? Donna has new diagnostic to look at this..
Procedure for HR-PMF

- Output HROrg, HROrg_err, min error waves
- Apply Ingrid’s PMFerror preparation routines (PMF_ErrPrep_AMS_V2_3.ipf)

Error

- Apply minimum error criterion
  - if error_{i,j} < limit, then set it to limit
- Remove nans and m/z 19,20
- Downweight weak/bad variables
- Downweight m/z 44-related peaks
  (Reducing contribution of multiple copies)

NOTE: we would have same issue with isotopes as well- In general, we remove isotopes from organic matrix to minimize this issue.
Clicker Question
What is difference between ugm3 units reported on axis of Average MS and ugm3 reported in label?

A) This is a Trick question- they are the same
B) Label uses species RIE, axis does not
C) Axis uses RIE, label does not
D) They differ by the CE
E) When do we go skiing?

Clicker Question
What is the HR analog of Org 44 from squirrel?

A) HROrg44
B) HRPCO2
C) HROrgCO2
D) There isn’t one
E) Ions at 44 don’t contribute to HROrg
Clicker Question

What is the purpose of the DC regions in PToF mode?

A) Define where particles appear in SD
B) Define where AB appears in SD
C) Define the appropriate Zero (Baseline) Level for P-TOF signals
D) Don’t know
E) They are not used at all