Frag Table vs. HR analysis

Jesse Kroll
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Frag table


Necessary for quantifying individual aerosol components because:
1) at unit m/z resolution several (most) masses correspond to more than one ion
2) some ions may be formed from the fragmentation of different aerosol components (e.g., H$_2$O$^+$)
Frag table example

<table>
<thead>
<tr>
<th>m/z</th>
<th>frag_nitrate</th>
<th>frag_organic</th>
<th>frag_air</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td></td>
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<td></td>
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<tr>
<td>23</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td></td>
<td>24: frag_sulphate[24]</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td></td>
<td></td>
<td></td>
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<td>26</td>
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<td>27</td>
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<tr>
<td>28</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>29</td>
<td></td>
<td>29: frag_ni[29]</td>
<td>0.00736%frag_ni[29]</td>
</tr>
<tr>
<td>30</td>
<td>0.00465%frag_nitrate[30]</td>
<td>0.002%frag_organic[29]</td>
<td>0.000013%frag_air[29]</td>
</tr>
<tr>
<td>31</td>
<td>0.002%frag_nitrate[30]</td>
<td>31: frag_nitrate[31]</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>0.002%frag_nitrate[30]</td>
<td>32: frag_sulphate[32]: frag_nitrate[32]</td>
<td>0.000763%frag_air[32]</td>
</tr>
<tr>
<td>33</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>34</td>
<td></td>
<td>0.00402%frag_air[32]</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>36</td>
<td></td>
<td>0.00330%frag_air[40]</td>
<td></td>
</tr>
<tr>
<td>37</td>
<td></td>
<td>37: frag_chloride[37]</td>
<td></td>
</tr>
<tr>
<td>38</td>
<td></td>
<td>38: frag_chloride[38]: frag_ni[38]</td>
<td>0.000633%frag_ni[40]</td>
</tr>
<tr>
<td>39</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Values in frag table

Details of (specific values within) the current frag list come from a number of AMS studies from several groups.

Not fixed values: users’ responsibility to adjust to specific experiments/conditions.
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Details of (specific values within) the current frag list come from a number of AMS studies from several groups

Not fixed values: *user’s responsibility* to adjust to specific experiments/conditions

High-resolution AMS

HR-ToF-AMS of high enough resolution (5000) to distinguish multiple peaks at a single unit mass (m/z < 100)

Allows for unambiguous identification of individual ions

→ Provides a powerful check for values in the frag list; will help for future refinements

Focus here is on frag list/HR comparison; details of HR-AMS analysis discussed Monday (Allison, Pete, Donna)
HR example: m/z 43

Both ions are classified as organic (but different classes of organic)

Inorganic species are even easier to distinguish

Frag List / HR-AMS comparison

Data taken from FLAME 1 (Missoula, MT; June 2006): biomass burning aerosol from 18 different burns (16 fuels)

One average mass spectrum per burn (1-2 hour averages)

High organic loadings (5-190 μg/m³) – the effects of any interferences by organic species will be obvious here (much more than in the atmosphere)

One major ambiguity: H₂O⁺ (+ OH⁺, O⁺) could be from sulfate, or organic, aerosol water, or water vapor. Default frag list rules used in this case: H₂O⁺(org)=CO₂⁺(org)
Organic

HR: ~7% higher than frag list

Organic (low loading)

HR: ~7% higher than frag list
**Chloride**

m/z 35, 36: nearly unique

**Ammonium**

m/z 16: NH$_3^+$, O$^+$
m/z 17: NH$_2^+$, OH$^+$
Ammonium

**Outliers**: interferences from inferred organics at m/z 48 and m/z 64:

SO$_4^{64}$ = 64 - org$_{64}$

org$_{64}$ = 0.5 ( org$_{50}$ + org$_{78}$ )

(negative values possible!)

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Sulfate

**Outliers**: interferences from inferred organics at m/z 48 and m/z 64:

SO$_4^{64}$ = 64 - org$_{64}$

org$_{64}$ = 0.5 ( org$_{50}$ + org$_{78}$ )

(negative values possible!)
Nitrate

Nitrate (low loadings)

Main interference:
CH$_2$O$^+$ (m/z 30)

0.1% of organic
Potassium

Interference: $\text{C}_3\text{H}_3^+$ (m/z 39); major organic peak in biomass burning

Organic (corrected for K error)

HR: ~4.5% higher than frag list
Source of remaining error

Air peaks: m/z 28 (CO+, C₂H₄⁺)
          m/z 40 (C₃H₄⁺, C₂O⁺)
          m/z 32 (CH₄O⁺)

Because this aerosol is not as oxidized as OOA, neglect of CO⁺
might not make as big a difference as it does in the atmosphere

Possible offset: H₂O⁺(org) may be overestimated

Change to frag table in the works

Summary

In general, frag list and HR analysis are in very good agreement

As always, caution is needed, esp. for specific aerosol types (such
as present case: fresh biomass burning)

Outliers include NO₃ and K, because of interferences by CH₂O⁺
and C₃H₃⁺; need ambient HR data for comparison

Contributions from “air peaks” (CO⁺) to organic mass non-
egligible, but also probably cancelled out by assumed H₂O⁺.
Roles of these two ions requires further study.