Thermal Decomposition Characterization of Filter Inlet for Gases and AEROsols (FIGAERO) coupled with Chemical Ionization Time-of-Flight Mass Spectrometer (ToF-CIMS)

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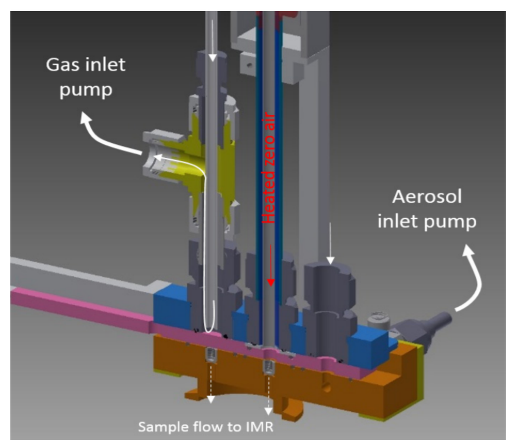
Introduction



FIGAERO Schematic
[Aerodyne Research, Inc.]

FIGAERO Features
- 2 separate inlets
  - gas and particle
- Coupled with CIMS
- Less fragmentation than AMS

Thermal Decomposition of FIGAERO
- FIGAERO is ramped up to 200 ℃
- Temperature as low as 200 ℃ can lead to thermal decomposition (Stark et al., 2017)
- Limited knowledge on potential impact of thermal decomposition

Objective of the Study
- To fully characterize the mechanisms of thermal decomposition (e.g., decarboxylation, dehydration, etc.) in the FIGAERO using a suite of standard compounds with different functional groups
- To assess the impact of ramping rate on thermal decomposition

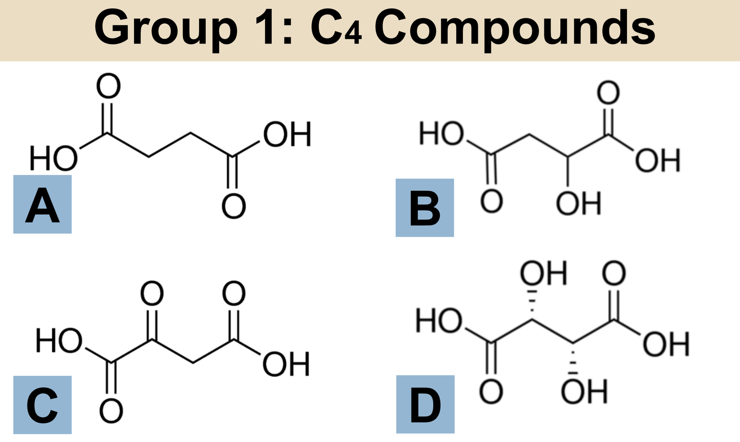
Method

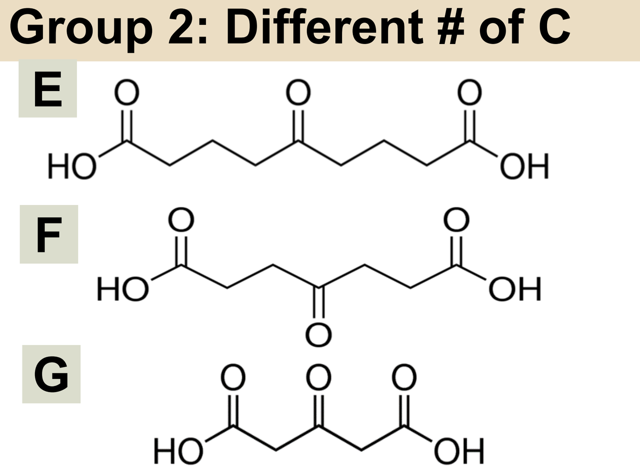
FIGAERO Instrument
- Coupled with ToF-CIMS
- Reagent ion: Iodide
- Mode: Desorption mode

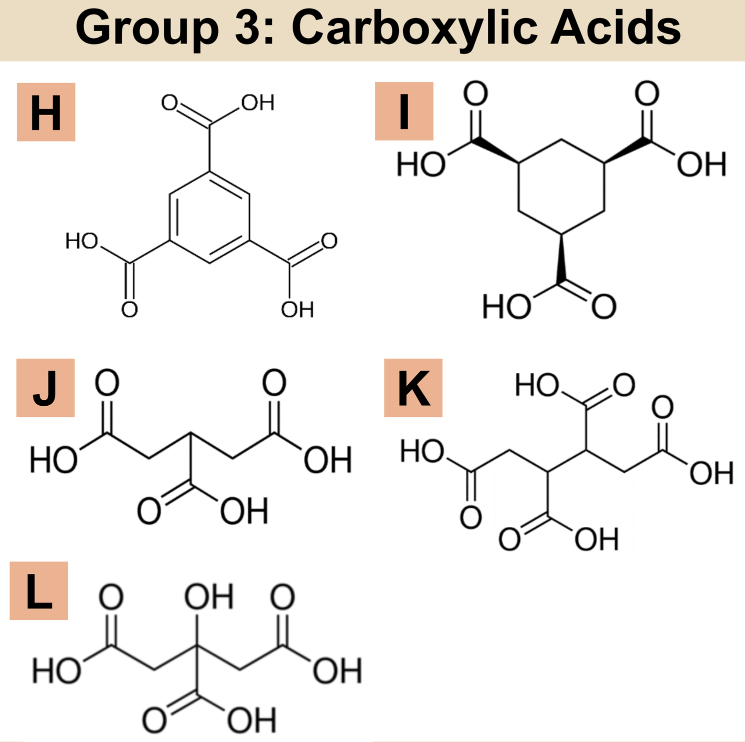
Experiment
- Solvent: acetone
- [Standard] prepared: 0.05g/L
  - Mass loaded: 100ng

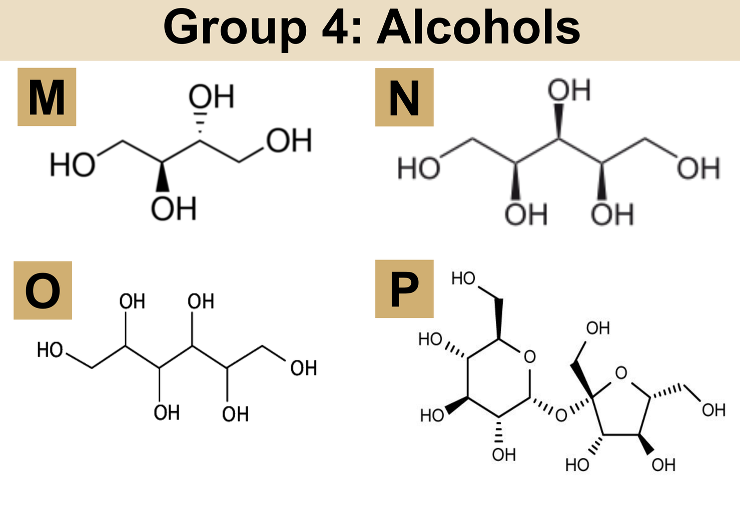
Standard Setting
- Ramping (15 min)
  - Ramped up to ~194 ℃ from room temperature
  - Average rate: 10 ℃/min
- Soaking (15 min)
  - At a max. temperature
- Cooling (10 min)

Experimental Group

Group 1: C_4 Compounds


Group 2: Different # of C


Group 3: Carboxylic Acids


Group 4: Alcohols


Compounds' Names

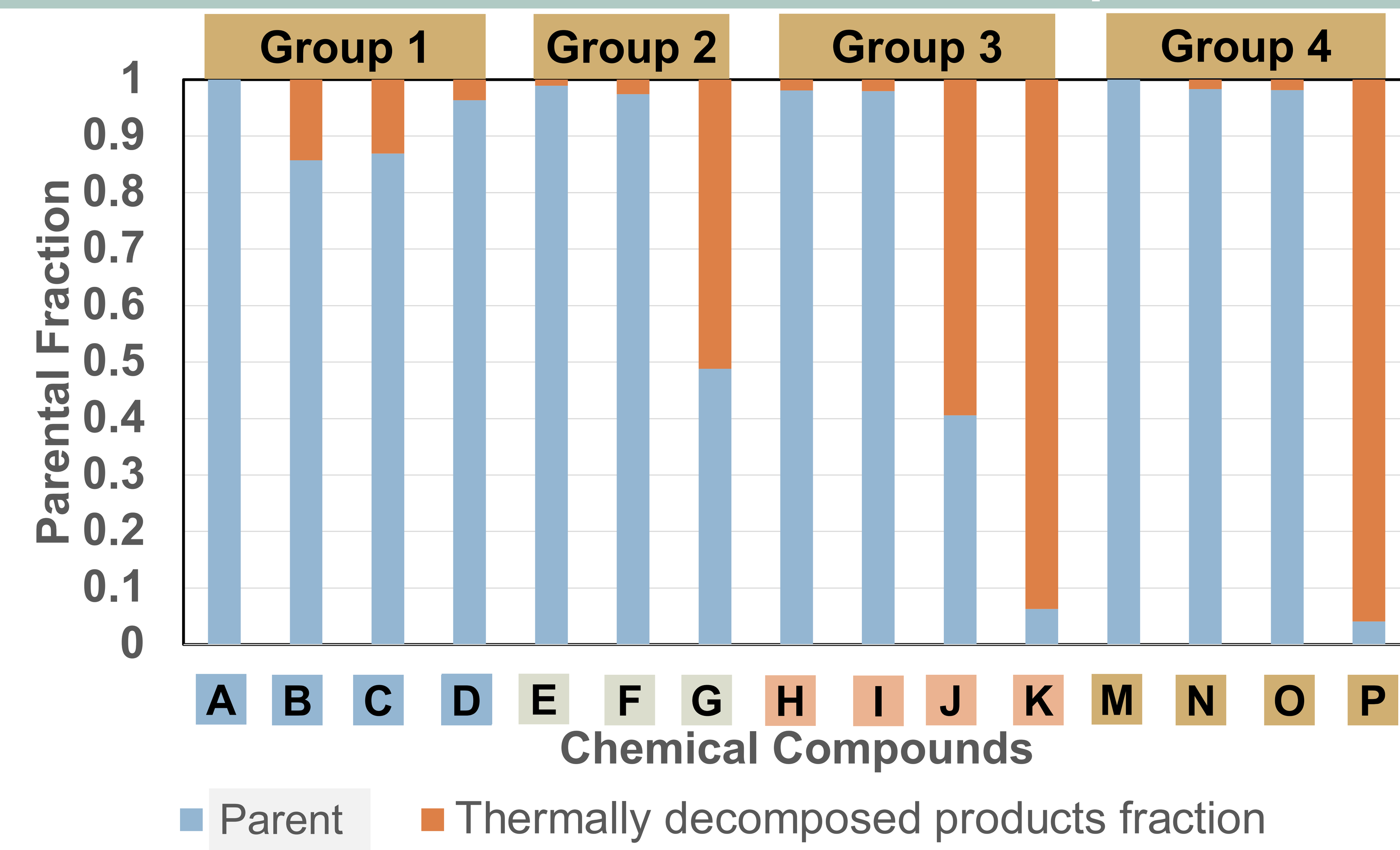
Group 1
- **A** Succinic acid
- **B** Malic acid
- **C** Oxaloacetic acid
- **D** Tartaric acid

Group 2
- **E** 5-oxoazaleic acid
- **F** 4-oxoheptanedioic acid
- **G** 1,3-acetonedicarboxylic acid

Group 3
- **H** 1,3,5-benzenetricarboxylic
- **I** 1,3,5-cyclohexanetricarboxylic
- **J** Tricarballylic acid
- **K** 1,2,3,4-butanetetracarboxylic
- **L** Citric acid

Group 4
- **M** Erythritol
- **N** Xylitol
- **O** Mannitol
- **P** Sucrose

Results I. Standard Chemical Compounds



Group 1: C_4 Compounds

C4 diacid
- No decomposition

→ +1 Alcohol
- Dehydration
- 14% of parent

→ +2 Alcohols
- Dehydration
- 4% of parent

→ +1 Ketone
- Decarboxylation
- 14% of parent

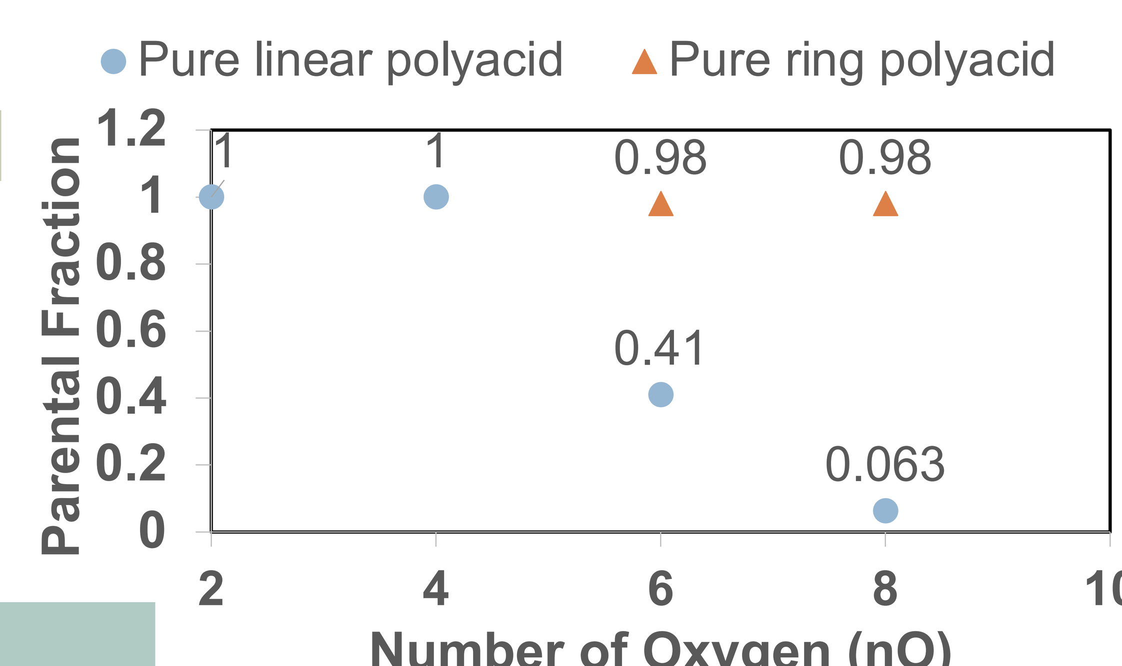
Group 2: Different # of C

Compound E	Compound F	Compound G
• Negligible dehydration (2%)	• Negligible dehydration • ~2%	• Decarboxylation • ~50% parent decomposed

Decrease in carbonyl proximity
Increase in thermal decomposition

Group 3: Carboxylic Acids

Structure
- Linear & Branched → nO
  - ≤ 4
    - No Decomp.
  - ≥ 6
    - Parental Fraction
      - less than 0.4
    - Dehydration
- Ring
  - Minor decomp. (2%)

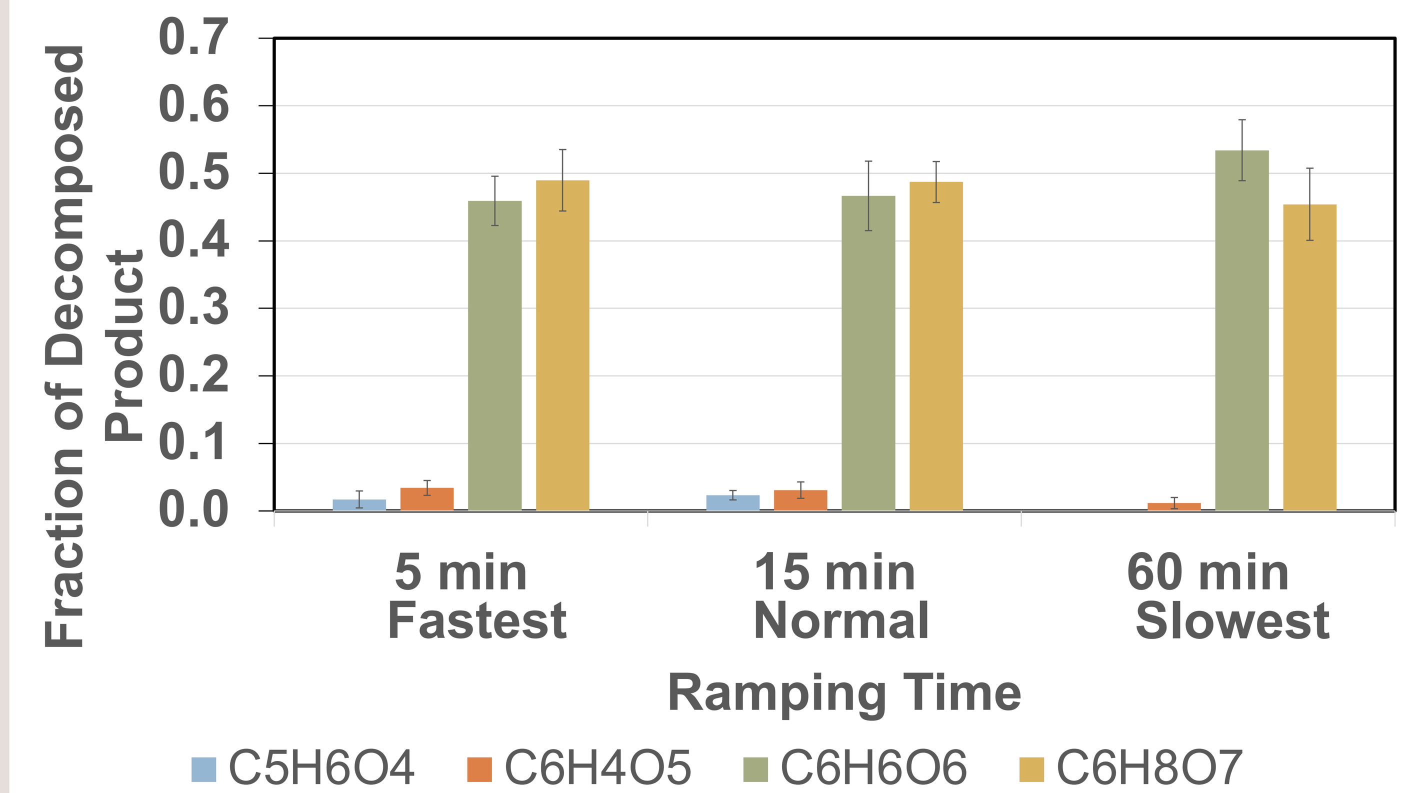


Group 4: Alcohols

Alcohol
- Pure → **Negligible decomposition** 98% parental compound retained
- Sucrose → **Significant dehydration** ~6% parental compound retained

Results II. Ramping Rate Experiment

Ramping Rate Experiment with Citric acid



- Slowest ramping rate differs the most from the fastest and the normal ramping rates
- Slowest ramping rate leads to less fragmented decomposition products and least decomposition
- Fastest and normal ramping rates have miniscule difference

Discussion & Conclusion

- **Decarboxylation vs. Dehydration**
  - Dehydration
    - Most compounds
  - Decarboxylation (Compounds C,G, and H)
    - Stable resonance structure with ≥ 2 carboxylic acids
      - Beta-carbonyl adjacent to two carboxylic acids
    - Presence of ring that can form resonance structure (i.e. benzene) with more than 2 carboxylic acids
- **Characterization of Thermal Decomposition**
  - Degree of Thermal Decomposition
    - Most direct measure: Parental fraction
      - FIGAERO-CIMS's intrinsic parameters as x-axis
      - Did not observe a clear trend between degree of thermal decomposition and Molecular weight, nO, nC, O/C, etc.
- **Potential Implication of Thermal Decomposition in Data Interpretation**
  - Most common compounds in the ambient air are alkanes, diacids, and terpenes (Kroll et al., 2011 & Khan et al., 2000)
    - Alkanes and diacids → No thermal decomposition
    - Terpenes → Minor decarboxylation (2%)
  - For more oxidized products with abundant carboxylic acids with alcohols or carbonyls, thermal decomposition must be factored in → Ongoing research

References & Acknowledgement

➢ References

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