

EPA Methods 202 and 5F: Overcorrecting For Sulfates?



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Statement of the Problem

- M202 and M5F allow subtraction of mass from particulate catch based on sulfate concentrations
- The aliquot for sulfate analysis is taken before processing the samples
- Some sulfate may be lost due to evaporation during processing
- Therefore corrections associated with the sulfate measurement may be overstated



Topics of Discussion

- How this phenomena affects each method
- Process and stoichiometry of sulfate corrections
- Data and references illustrating loss of sulfate during processing
- Suggestions for solving the problem



Issue With M5F

- Measures non-sulfate particulate
- Therefore sulfate and combined anions are subtracted from the gravimetric particulate result
- If substantially all of the particulate is sulfate (e.g. some cat crackers) then negative particulate results can occur



Issue with M202

- Sulfate is not subtracted.
However, the weight of the associated cations is subtracted.
- Because sulfate is not subtracted, loss of sulfate leads to lower than real particulate catches
- Relevant when pH of impingers is less than 4.5



Some Chemistry

- Sulfate exists in the impinger catch as dissociated sulfate ion $\text{SO}_4^{=}$
- Extra electrons are shared with loosely associated waters of hydration
- Different numbers of waters of hydration can be present at up to 8 H_2O s per sulfate ion
- Upon drying some waters of hydration may be retained and add to particulate catch.



Some Chemistry

- To “even the playing field” waters of hydration are replaced with ammonium cation NH_4^+ - 2 per sulfate ion
- Bonding with ammonium is ionic and much stronger than with waters of hydration
- Therefore all waters of hydration are replaced by NH_4
- $\text{SO}_4^{*} 8\text{H}_2\text{O} + \text{NH}_4\text{OH} \rightarrow (\text{NH}_4)_2\text{SO}_4$



Correction M5F

- Aliquot of refluxed H₂O is measured for sulfate
- Sulfate catch is corrected to (NH₄)₂SO₄ stoichiometrically
- Entire catch of (NH₄)₂SO₄ is subtracted from particulate catch



Correction M202

- Aliquot of impinger liquid is taken and analyzed for sulfate before processing starts
- Only ammonium is subtracted. Therefore sulfate catch is corrected to ammonium by multiplying by the stoichiometric ratio of 0.354



LOSS OF SULFATE

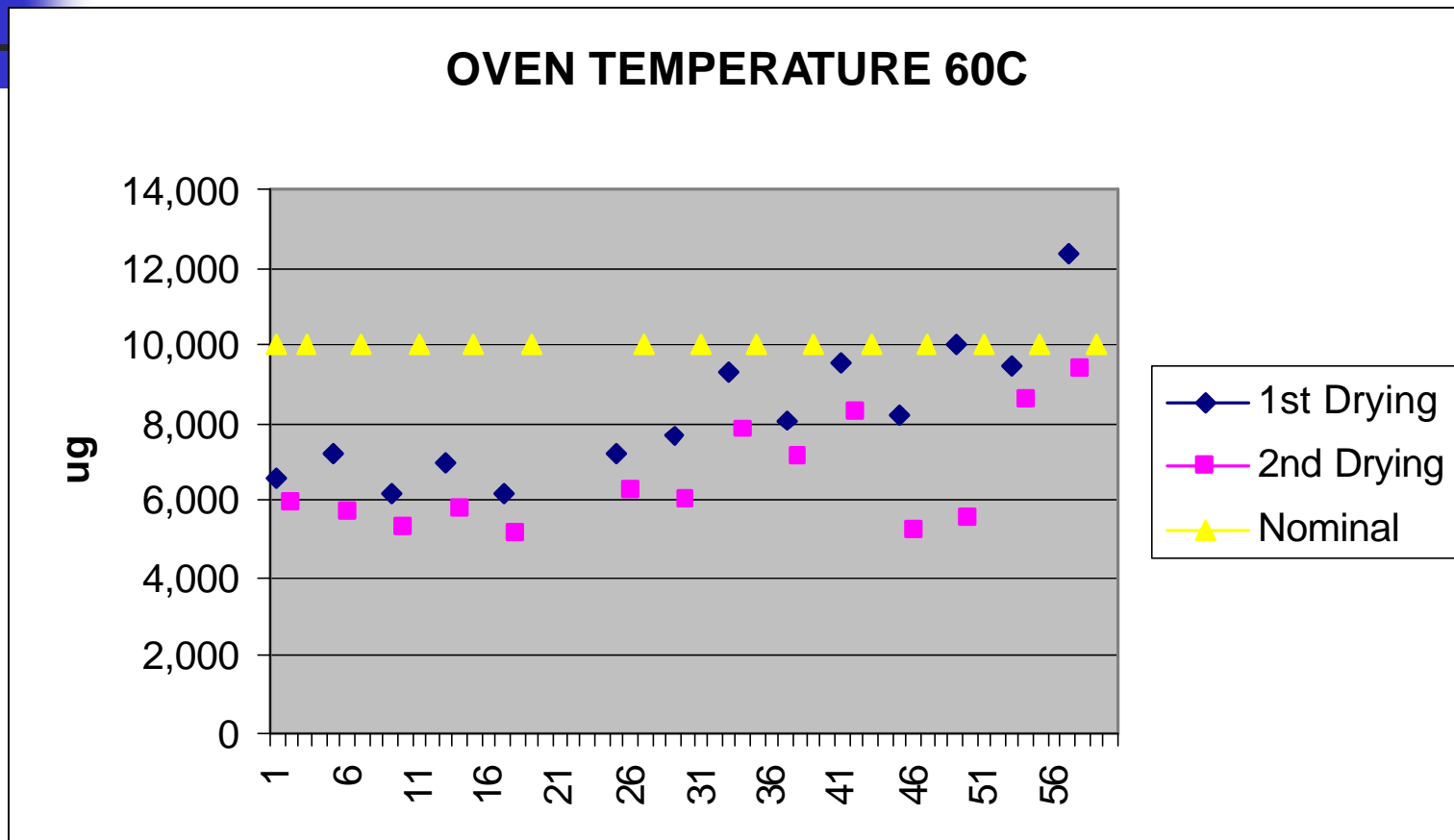
- Noticed negative catches for M5F
- Noticed increased blank values for sulfate after drying
- Noticed that sulfate concentrations were lower when measuring chloride corrections at end of process. (chloride and sulfate appear on same anion analysis)
- Hypothesized that all of these could be explained by evaporation of the sulfate during drying.



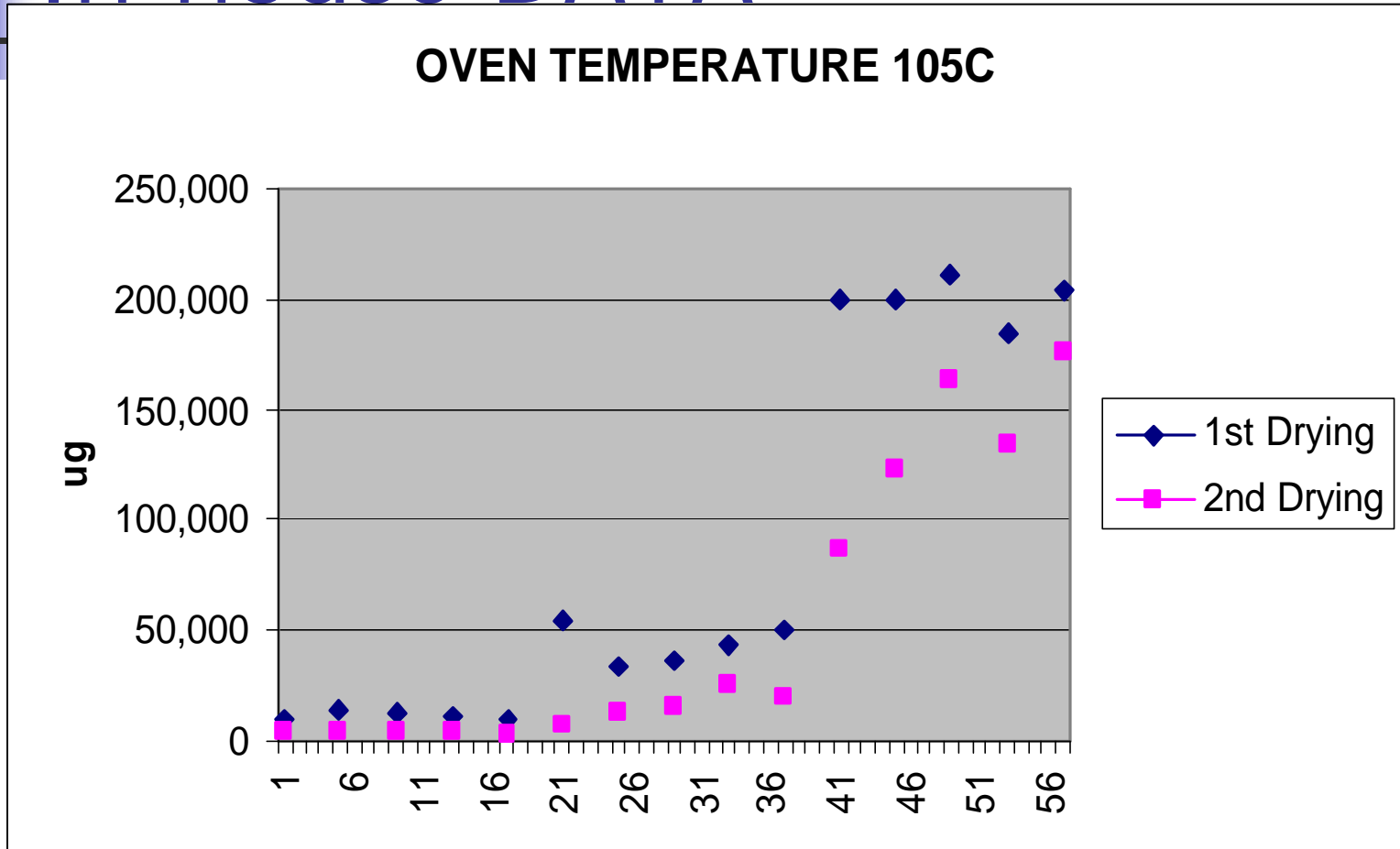
Collected DATA

- Began having sulfate analysis done on refluxed H₂O and on resuspension of particulate for all M5F projects.
- Began second analysis for sulfate on selected M202 projects.
- Initiated in-house lab study to confirm data

In-house Data



In-house DATA



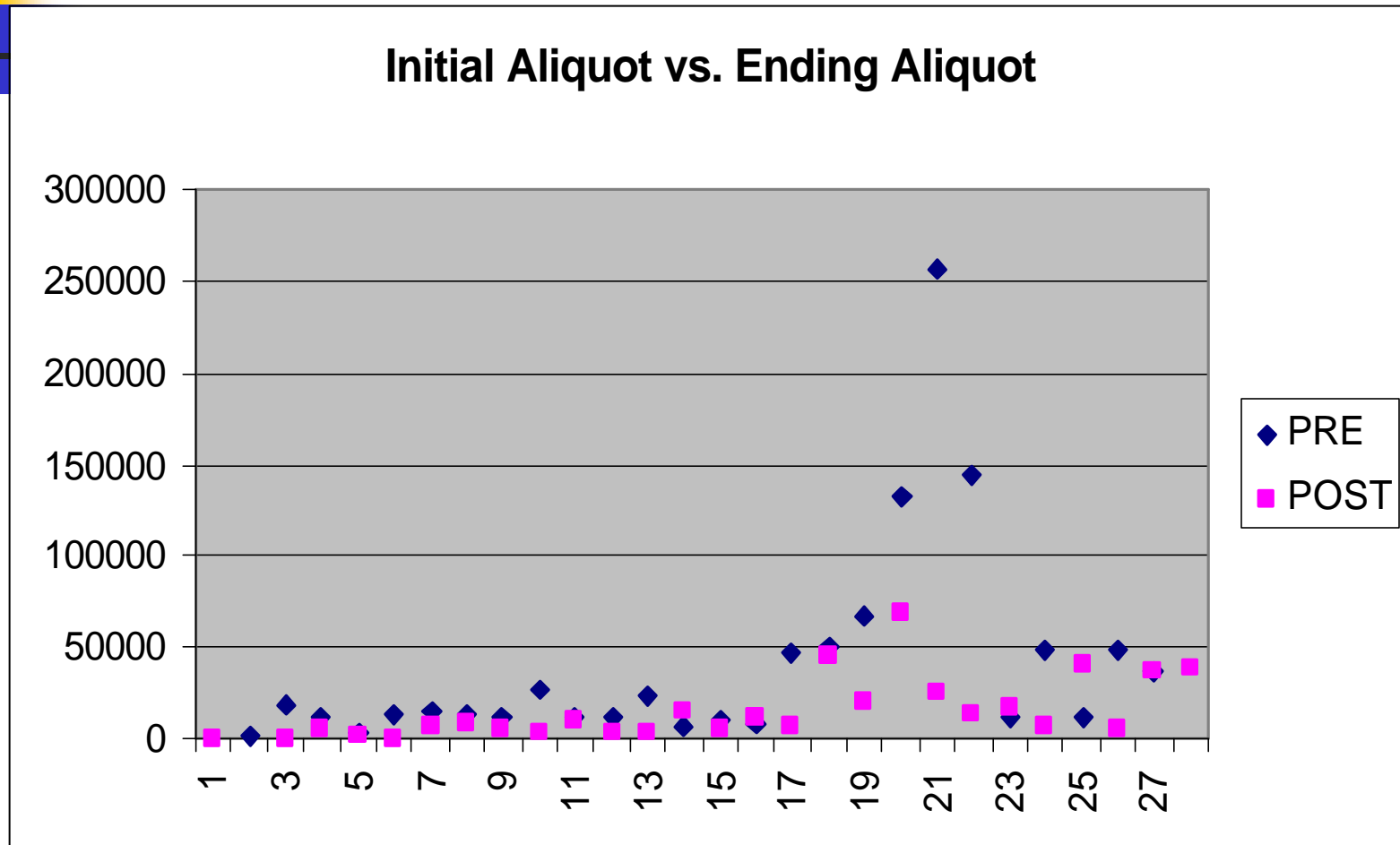


In-house DATA

- At 105 °C average loss of sulfate was 53%

- At 60 °C average loss of sulfate was 22%

Data From Real Samples





Confirmation From Another Source

- From NIOSH survey of sulfuric acid ambient methods
 - “After an ^{32}S labeled sulfuric aerosol sample was collected on a membrane filter and placed in a petri dish whose cover was coated with NaOH maximum diffusion of the acid occurred when the petri dish was heated for 1-6 hours at 125 °C.”



Confirmation From Another Source

- “investigators found that sulfuric acid diffused readily from Teflon and graphite filters whereas little or no acid was released from glass fiber or cellulose acetate filters. The authors attributed the latter to neutralization in-situ by resident cations”
 - Maddalone et al Radiochemical evaluation of the separation of H₂SO₄ aerosol by microdiffusion Mikrochim Acta 1974



Confirmation From Another Source

- ... the entire assembly was heated for 2 hours at 125 °C in a nitrogen purged oven. Under these conditions, it was reported that $(\text{NH}_4)_2\text{SO}_4$ and NH_4SO_4 were not volatilized



Does this apply to stack testing?

- M5F specifies evaporation of refluxed water at 105 °C until <100 mL remains
 - Enthalpy uses Teflon beakers for this
 - Enthalpy typically performs this at 75 °C to 90 °C
- M202 specifies 105 °C to < 50 mL
 - Enthalpy uses Teflon beakers for this
 - Enthalpy typically performs this at 75 °C to 90 °C



Suggestions

- Be very diligent about N₂ purge for M202 – if sulfate is kept out of sample then this is not an issue
- Add ammonium hydroxide before starting the drying. As stated in NIOSH report this species does not evaporate.
- Perform sulfate analysis after particulate catch is complete. This will add time to the analytical phase because the sulfate analysis can not be done concurrent to drying



Suggestions

- Beware of sources where NH_4Cl may be present and counted as particulate
 - In that case revert to current procedure and dry at lower temperature
 - Some loss may occur when samples become dry in oven overnight. So, turn oven off when not attended.
- Allow correction for other anion species as they will become non-volatile with addition of ammonium