Sampling with TOFWERK
Vocus Chemical Ionization Mass Spectrometers

Part 1: Basic Principles
Webinar Overview

- Understanding inlet effects on time response and sensitivity
- Practical considerations for building an inlet:
  - Ground rule: Put the instrument close to the sample
  - Geometry, flows, and temperature
  - Materials
- Common problems with sampling and how to avoid them
- Inlet passivation and depassivation
- Correcting data for inlet effects
Inlet Design Is Important

A bad inlet can change the instrument response to certain compounds by:
1. Destroying or producing a compound.

Hydroxyperoxide conversion to carbonyls on metal surfaces

Rivera-Rios et al., GRL 2014
doi.org/10.1002/2014GL061919

NO$_2$ conversion to HONO on acidic surfaces

Based on Kleffmann, Atmos. Environ. 1998
doi.org/10.1016/S1352-2310(98)00065-X
Inlet Design Is Important

A bad inlet can change the instrument response to certain compounds:
2. By changing the response time.

Alkanes in car exhaust through an unheated 5m PFA inlet
Understanding Analyte-surface Interactions

Important factors:
- Surface material
- Temperature
- Air contact time with surface
  - Flow rate
  - Tubing length
  - Tubing diameter
- Analyte chemical properties
  - Volatility
  - Henry’s law coefficient
  - Diffusion coefficients
- Humidity and other chemicals (replacements) in the air

Adapted from Pagonis et al., AMT (2017) and Huang et al., EST (2018)
**Understanding Analyte-surface Interactions**

**Delay Time:** Metric for surface interactions
Long delay time = bad

Model for exploring tubing response from the University of Colorado:

https://tinyurl.com/PartitioningDelays

![Graph showing concentration over time with short and long delay times, indicating low-volatility and high-volatility compounds](image)
Understanding Analyte-surface Interactions

**Delay Time**: Metric for surface interactions
Long delay time = bad

Model for exploring tubing response from the University of Colorado:

https://tinyurl.com/PartitioningDelays

Surface interactions:
- Sampling line geometry
- Flow rate
- Sampling line material
- Diameter
- Shape

Extreme case with almost 100% loss
Which analytes are likely to have inlet problems?

Most VOC interactions with inlets can be described by volatility.

Small polar molecule behavior depends on Henry’s law coefficient.

Liu et al., AMT. 2019
Inlet Materials – Practical Advice

*For VOCs, choose an inlet material with a low delay time.

**Materials to avoid (this includes fittings!):**
- Tygon tubing – emits VOC
- Silicone tubing – emits VOC
- Stainless steel – adsorbs VOC
- Copper – adsorbs VOC

Avoid particle filters if possible! Filters greatly increase surface area and will increase delay time and prevent the measurement of I/SVOC.

PFA is generally the best choice

* Deming et al. 2019  [https://doi.org/10.5194/amt-12-3453-2019](https://doi.org/10.5194/amt-12-3453-2019)
Inlet Materials – Practical Advice

For other analytes, research which materials are best.

**Example:** Nitric acid. Adapted from Neuman et al., EST 1999.

Other examples:
- Ethylene oxide: polyethylene is best (Teflon permeability is too high)
- Amines and some other sticky compounds: heated (100°C) Siltek stainless steel
Other Material Considerations

<table>
<thead>
<tr>
<th>Property</th>
<th>PFA</th>
<th>PEEK</th>
<th>Stainless steel (304)</th>
<th>Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Softens at... (&quot;heat distortion temperature&quot;)</td>
<td>70-77°C</td>
<td>160°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Usable temperature</td>
<td>Up to 200°C</td>
<td>Up to 250°C</td>
<td>Up to 900°C (corrodes)</td>
<td>Up to 420°C (corrodes)</td>
</tr>
<tr>
<td>Thermal conductivity W/m*K</td>
<td>0.209</td>
<td>0.26</td>
<td>17</td>
<td>400</td>
</tr>
<tr>
<td>CO₂ permeability cm³ m⁻² day⁻¹, 1 bar, 100 um thickness, room temperature</td>
<td>7000</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cost For 1 m of 1/8” tubing</td>
<td>$5</td>
<td>$50</td>
<td>$10</td>
<td>$2</td>
</tr>
</tbody>
</table>

**PEEK** is more resistant to high temperatures than PFA. For hot experiments (like thermal desorption), can’t use PEEK or PFA.

Copper will heat evenly. Stainless can have cold spots. Use it to connect hot and ambient temperature components.

VOCs can permeate through thin-walled PFA tubing. (PTFE is worse: 15000)
Inlet Configurations – Example 1

Direct attachment to the front inlet

Simplest Configuration:
- No additional pumping: ~100 SCCM flow
- Shortest possible path to capillary
- Use a bored-through fitting or mate with larger and smaller diameter tubing to get close to the capillary
- Useful for simple experiments close to the instrument (e.g., headspace vial)
- Not good if you have high particle concentration
Inlet Configurations – Example 2

Attachment to Onboard-Pump Using Front-Inlet

How:
Overflow attaches to sampling inlet.

Pros and cons:
+ Short, high-flow path → high transmission
+ No extra equipment needed
- Particles can clog capillary

Recommended for:
• Samples with low particle concentration
• Measurements that need fast time response
  (moves air more quickly through inlet)
Attachment to External-T With Orthogonal Flow Into Instrument

How:
Use of external pump to pull sample flow

Pros and cons:
+ Keeps large particles from going to capillary
- Needs an external pump
- Lower transmission of less volatile compounds

Recommended for:
• Samples with high particle concentration
• High analyte concentration or only VOC

** You can also accomplish this by swapping inlet and overflow ports (diagram on previous slide)
Identifying Common Inlet Issues

Clogged capillary

*Can happen if you are sampling smoke, dirty urban air, samples with high concentration or condensable VOC, insects...*

**Symptoms:**

1) Cannot maintain pressure in Vocus reactor (number steps = 0 but pressure is low).
2) Low inlet flow – measure directly or with calgas (should be 60-100 sccm).

**Solution:** Clean or replace capillary – instructions in Knowledge Base.

Water drops in inlet

*Can happen if rain or condensation from sample collects in the line.*

**Symptoms:** Sudden pressure pulse in drift tube; strange cluster behavior.

**Solution:** Heat cold spots along inlet; orient ambient sampling lines downwards to avoid rain.

Leaks

1. Check that fittings are tight.
2. Check overflow and calgas ports on the Vocus inlet.
3. Hold a swab dipped in acetone (or other safe analyte) near joints to check for leaks inwards.

*Dust and Particles:*

Clean your inlet before attaching to the instrument by flowing air through it.
Inlet Passivation & Depassivation

Competition for Adsorption Sites *(Dependent on Species and Material)*

From Deming et al. (2019)
Inlet passivation & Depassivation

Competition for Adsorption Sites

Roscioli et al. (2016)

Perfluoroalkanoic Acid used to reduce HNO₃ response time
*we do not recommend (toxic!!, could titrate primary ions)

https://doi.org/10.1021/acs.jpca.5b04395

Other:
- Ammonia “doping” can help with time response to simple amines
- “Conditioning” tubing with low-volatility VOC can change the time response – be careful with “dirty” tubing!

Water can occupy adsorption sites:
Humidification can help time response

Note: Rapid changes in humidity can create desorption artifacts.
Current Approaches to Data Correction

Approaches

• Ignoring this entirely (see slide 7 for how bad an error this can produce)
• Calibrate at the upstream end of your inlet
• Fast background subtraction
• Slow background subtraction (when it’s relevant; when it’s not)
• Deconvolution

Comments

• CI community does not agree yet about the “best” way to correct for inlet effects
• What makes the most sense for your experiment and your target compounds?
• It is **ok** to have inlet effects **if** you understand them
Approaches to Data Correction

What is “Background”?

1) **Persistent** Background
   - Electronic noise
   - Contaminant in carrier gas
   - Persistent contaminant inside instrument

2) **Inlet or Surface** Background
   - Reversible interaction of analyte with surface
   - Variable over time

Subtract signal measured during complete absence of analyte = long backgrounds (wait until inlet and surfaces are clean)

Trickier...
Approaches to Data Correction

Concept & figures from Palm et al. AMT (2019)

Flux to the walls

Flux from walls to detector (leads to background signal)

Flux to detector without wall interaction (leads to background-subtracted signal)

“Fast-zeros” measure this background
Fast-Zero Example

Notes:
- This only works if inlet response is fast
- Less time spent measuring sample
Deconvolution

Figures & concepts from Pagonis et al. (in prep), with permission

Inlet effects (="partitioning delays") can be described by an equation I(t)

\[ M(t) = F(t) \ast I(t) = \int_{0}^{\infty} [F(t - \tau) \times I(\tau)] \, d\tau \]

Measurement is the convolution of input \( F(t) \) and the instrument response function \( I(t) \)

\[ \tau_1 = 1.64 \, \text{s}; \, A_1 = 0.57 \]
\[ \tau_2 = 20.0 \, \text{s}; \, A_2 = 0.43 \]
Deconvolution

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Measurement is the convolution of input \( F(t) \) and the instrument response function \( I(t) \)

Idea: **Deconvolute** the measurement \( M \) using the known inlet function \( I \) to recover the actual behavior \( F \)

- Estimate it experimentally
- Mathematical deconvolution (e.g. Fourier transform)
Contacts, Sources, and Resources

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Supply sources for tubing and fittings:
Swagelok – metal, PFA fittings
Entegris fittings – PFA fittings
IDEX -- PEEK fittings and tubing
McMaster – PFA tubing
MSC industrial – PFA tubing
Savillex – PFA jars, lids, funnels etc.
Vici – PEEK tubing and metal/silica capillary

Bibliography: see Tofwerk.com webinar page

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