Direct Analysis of Air Samples by GC and GC/MS

Emily M. Bock, Zachary M. Easton, Edmund C. Jong, Mary D. Luxbacher, Paul V. Macek, Harold M. McNair, David O. Mitchem, Raj K. Shrestha, Brian D. Strahm
This work was a cooperative effort between Shimadzu Scientific Instruments and the Biological Systems Engineering, Mining and Minerals Engineering, and Forest Resources & Environmental Conservation Departments at Virginia Tech.
Direct Analysis of Air Samples by GC and GC/MS

Emily M. Bock
Zachary M. Easton
Edmund C. Jong
Kray D. Luxbacher
Paul V. Macek
Harold M. McNair
David O. Mitchem
Raj K. Shrestha
Brian D. Strahm
What is Direct Analysis?

• Direct analysis is a direct injection of a gas sample without any concentration steps
  • No headspace analyzer
  • No thermal desorption
  • No cryogenic focusing
  • No purge & trap
  • No SUMMA Canisters
  • No SPME
So – What’s the Problem?
Should be easy – Right?
Wrong!

Information should be available – Right?
Wrong!
Why Do It?

Low-level analyses are feasible with modern equipment.

Cost
- Headspace, Purge & Trap, Thermal Desorption units are expensive
- Canisters are costly and have very high maintenance costs
- Sorbents must be packed and cleaned and/or conditioned
- SPME fibers are expensive and fragile

Flexibility
- With GC/MS, no need for dedicated instrumentation.

Best (or Only) Way
- Some species are not amenable to P&T, SPME, etc.
Sampling Techniques

Evacuated Vial

- Commonly available
- Easy to sample
- Works well with autosamplers
- Easy to transport and store
- Long shelf life with correct septum
- Contamination can be a problem
- Leaks can be a problem
  - Choose a good septum
  - Can’t cause bent autosampler needles
Sampling Techniques

Syringe

- Easy to sample
- Long shelf life
- Can be easy to inject
- Manual injection / no autosampler

Tedlar Bag

- Commonly Available
- Difficult to fill
- Comparatively fragile and difficult to store
- Leak prone / Short shelf life
Challenges

• This is not an easy analysis
  • Leaks
  • Contamination
  • Standards
  • Reproducibility
  • Sensitivity
Leaks 1

- May occur anywhere there is a connection
- Common Leak Points
  - Syringe
    - Plunger
    - Needle fittings on removable needle syringes
  - Injection port
    - Heavy gauge needles degrade septa
    - <50 Injections. Best to change after 35 injections
  - Sample vial septa
    - Standard Septa won’t always work
Leaks 2

• More Common Leak Points
  • Regulator fittings
    • Interface to vial/syringe
    • Regulator to bottle connection
  • Gas bulb connections
    • Stopcocks
      • Glass is preferred
      • Must use silicon grease on glass stopcock
  • Fill port septa
Leaks 3

Gas Bulb

Fill Port
Contamination 1

• Residual Contamination
  • Insufficient purging
  • Ineffective evacuation
  • Syringe Contamination

• Artificially introduced Contamination
  • From standards preparation
  • From clothing
  • From room air

• **MUST** run blanks – lots of them
Contamination 2

- Air Intrusion – Air gets onto the column
  - Leaks
  - Introduction via injection
    - Injection “air spike”
      - Usually insignificant
      - Not insignificant if you are analyzing methane in air
What co-elutes with CH$_4$ on a Mol-sieve 5A column?

Atmospheric Methane Intrusion at 500 ppb
Contamination 4

- Air Intrusion via injection
  - Easy fix
    - Insert Needle into injection port
    - Hold in injection port long enough to separate air
      - Typically 30 seconds, but is column dependent
    - Make injection
    - Hold in injection port long enough to separate air
      - Typically 30 seconds
Contamination 5

Atmospheric Methane (m/z 15) Intrusion at 100 ppb
Commercial Standards 1

- Commercially made standards
  - Convenient
    - Get a quote and buy
    - Some are “off the shelf”
  - Expensive
    - Typically many hundreds to thousands of dollars
      - Single or two point calibrations
    - Some have short expiration date
Commercial Standards 2

• Commercially made standards
  • Long Lead Time
    • Usually 4 to 8 weeks for custom standards
  • Transfer To Secondary Container/Syringe
    • Purging of the regulator and tubing is necessary
    • Devise removal apparatus
      • Build your own or commercially available
  • Inflexible
    • Can’t change concentrations
    • Can’t add components
“In-House” Standards 1

• Inexpensive
• Flexible
  • Can add components easily
  • Can change concentrations easily
• **VERY** difficult to be prepare/ time consuming
  • Gasses are added one at a time
• Prone to contamination
  • Gas bulbs MUST be cleaned/purged
  • Dedicated syringes for pure components
  • Actual bulb volume must be accurately determined
“In-House” Standards 2

Standards and syringes MUST be allowed to come to atmospheric pressure without introducing air.

Must be temperature and pressure compensated.

Must be validated against a second source.
“In-House” Standards 3

Need to be prepared daily

Limited number of injections
  • Dependent on size of gas bulb and injection volume

Mixing
  • Shouldn’t be necessary, but some data indicate that it is necessary for heavy gasses (e.g. SF$_6$)
  • Nickel plated sewing needles seem to work

Transfer to autosampler vial not tested.
  • No method has been developed yet
    • May not be practical
## In-House Standards 3

**Check Standard (CCV) Results:**

<table>
<thead>
<tr>
<th>Compound</th>
<th>CCV (ppmv)</th>
<th>Cert Std. Conc.</th>
<th>%D</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>4.82</td>
<td>5.0</td>
<td>3.6</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>592.</td>
<td>610</td>
<td>2.8</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.96</td>
<td>1.0</td>
<td>4.0</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>4.89</td>
<td>5.0</td>
<td>2.2</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>598.</td>
<td>610</td>
<td>2.0</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.97</td>
<td>1.0</td>
<td>3.0</td>
</tr>
</tbody>
</table>
In-House” Standards 4

- CO₂ Calibration Curve

RF %RSD : 8.4
R² = 0.9992112
Y = 154191.5X - 31435

Calibration Range:
97.0 ppm to 970 ppm
In-House” Standards 5

• N₂O Calibration Curve

Calibration Range: 0.100 ppm to 29.1 ppm

RF %RSD : 12.4
R² = 0.9998018
Y = 154191.5X - 31435
In-House” Standards 6

- CH₄ Calibration Curve

RF %RSD : 11.8
R² = 0.9999977

Y = 3891.642X - 1977.3

Calibration Range: 0.999 ppm to 495 ppm
Real World Results

Air sample taken 6/1/2015 on the VA Tech campus

Values are consistent with current literature

<table>
<thead>
<tr>
<th>Compound</th>
<th>Conc. (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>2.14</td>
</tr>
<tr>
<td>CO2</td>
<td>391.</td>
</tr>
<tr>
<td>Nitrous Oxide</td>
<td>0.44</td>
</tr>
</tbody>
</table>
Reproducibility 1

• The Most Difficult Problem in Gas Analysis

• Replicate injections should be performed
  • At very least during method development

• Multiple Problem Points
  • Syringe Issues
    • Wear & Tear
    • Contamination
      • Avoid contact with organic solvents
  • Leaks
  • Septum Coring
    • Side Port Needles essential
Reproducibility 2

• Multiple Problem Points (Cont.)

  • Leaks
    • Septum
      • GC
      • Gas Bulb
    • Autosampler Vial
      • Septum selection is critical
      • Crimp-tops seem to work best
Reproducibility 3

• Multiple Problem Points (Cont.)
  • Purging issues
    • Regulator
    • Tubing
    • Syringe
    • Gas Bulb
    • Nitrogen purge gas
    • Helium is convenient but a poor purge gas
  • Must develop a robust purging protocol
  • Must run MANY blanks
Reproducibility 4

• Multiple Problem Points (Cont.)
  • Autosampler Vial Issues
    • Fill Technique
      • Evacuation vs. Purging
  • Septa
    • “Normal” septa will leak for many gas applications
    • Thick, soft, plug type septa
    • Electric crimper
  • Autosampler Needle Issues
  • CTC “Needle Block” Macro
Reproducibility 5

• Multiple Problem Points (Cont.)
  • Evacuation/Purging
    • Technique Dependent on Sample Plan
    • Standards and samples should be treated identically
  • Contamination
    • Multiple introduction points
    • Can be difficult to detect
      • Experiments must be repeated until a reliable protocol is established
Reproducibility 6

• Multiple Problem Points (Cont.)
  • Injection Techniques
    • Syringe pressure must be at atmospheric pressure
    • Fast vs. Slow
      • Conventional wisdom says “not too fast”
      • Fast is better in most cases
    • Pre-pressurized vs. non-pressurized injection
      • For most species either technique will work
      • For early elutors pre-pressurize the syringe
Reproducibility Example

- AutoSampler Standard Vial Fill Problems 2012

<table>
<thead>
<tr>
<th>RT</th>
<th>Area</th>
<th>Vial</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.50</td>
<td>1,652,271</td>
<td>4</td>
</tr>
<tr>
<td>7.50</td>
<td>1,662,573</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>sequential injections</td>
<td></td>
</tr>
<tr>
<td>7.50</td>
<td>1,681,641</td>
<td>4</td>
</tr>
<tr>
<td>7.50</td>
<td>1,750,929</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>sequential injections</td>
<td></td>
</tr>
<tr>
<td>7.50</td>
<td>1,753,305</td>
<td>6</td>
</tr>
<tr>
<td>7.50</td>
<td>1,750,934</td>
<td>6</td>
</tr>
</tbody>
</table>
Reproducibility Example

• Autosampler Vial Fill Procedure
• Develop a procedure that works for your app
• In this case:
  • Multiple N2 purge (3 in this case)
  • Add a known amount of gas standard to vial
Reproducibility Example

- Autosampler Standard Vial Fill Data 2014

<table>
<thead>
<tr>
<th>RT</th>
<th>Area</th>
<th>Vial</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.54</td>
<td>1,640,890</td>
<td>1</td>
</tr>
<tr>
<td>7.54</td>
<td>1,633,041</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.54</td>
<td>1,628,391</td>
<td>24</td>
</tr>
<tr>
<td>7.54</td>
<td>1,630,448</td>
<td>15</td>
</tr>
<tr>
<td>7.54</td>
<td>1,602,760</td>
<td>6</td>
</tr>
<tr>
<td>7.54</td>
<td>1,601,797</td>
<td>29</td>
</tr>
</tbody>
</table>

- sequential injections
- non-sequential injections
Sensitivity 1

- Detectors are becoming more sensitive
- For CO and CO$_2$ use a methanizer/FID
  - Low ppm range vs hundreds of ppm for TCD
- For some apps, use He discharge detector
  - Barrier Ionization Detector
    - More robust than PDHID
    - Some sacrifice in sensitivity
  - Pulsed Discharge Helium Ionization Detector
    - Very sensitive
    - Not as robust as a Barrier Ionization Detector
Modern Mass Specs are MUCH more sensitive:

- 10x to 500x more sensitive than earlier MS
  - Lower oil background
  - Better oils
  - Turbomolecular pumps
- Quieter electronics
- Better source design
- Better electron multipliers
- Differential pumping
- Better (lower bleed) columns

Lower maintenance than earlier instruments:

- Pre-quad mass filters
- Robust filaments
Sensitivity 3

• Modern Mass Specs work well for gas analysis
  • Air background can be avoided in most cases
  • Increased sensitivity rivals or exceeds GC Detector
    • With NCI, sensitivity is greater than ECD for some compounds
    • EI sensitivity exceeds FID sensitivity by >10x for most compounds
  • Good PLOT columns now available
    • No need to use multiple columns/column switching
    • Use a PLOT column filter
      • Protect turbo
      • Doesn’t appear to cause unintended problems
Conclusion

• Direct analysis of gas samples is feasible.
• There are obstacles to overcome that may not be obvious to chromatographers who are used to working with liquid samples or extracts.
• Accurate standards can be prepared in the laboratory.
• Reproducible results can be obtained.
• GC/MS has the potential to become the technique of choice for gas analysis.
References

Emily Bock, Paul Macek, Zachery Easton
"Analysis of Greenhouse Gasses by GC/MS“ Poster Presented at NEMC 2014

Edmund C. Jong, Paul V. Macek, Inoka E. Perera, Kray D. Luxbacher, Harold M. McNair
“An Ultra-Trace Analysis Technique for SF6 Using Gas Chromatography with Negative Ion Chemical Ionization Mass Spectrometry”


Questions?