Direct Analysis of Air Samples by GC and GC/MS

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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.

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Biological Systems Engineering

Mining and Minerals Engineering Virginia Tech

Forest Resources & Environmental Conservation

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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

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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 equipmen

Cost

- Headspace, Purge & Trap, Thermal Desorption units are expensive
- Canisters are costly 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

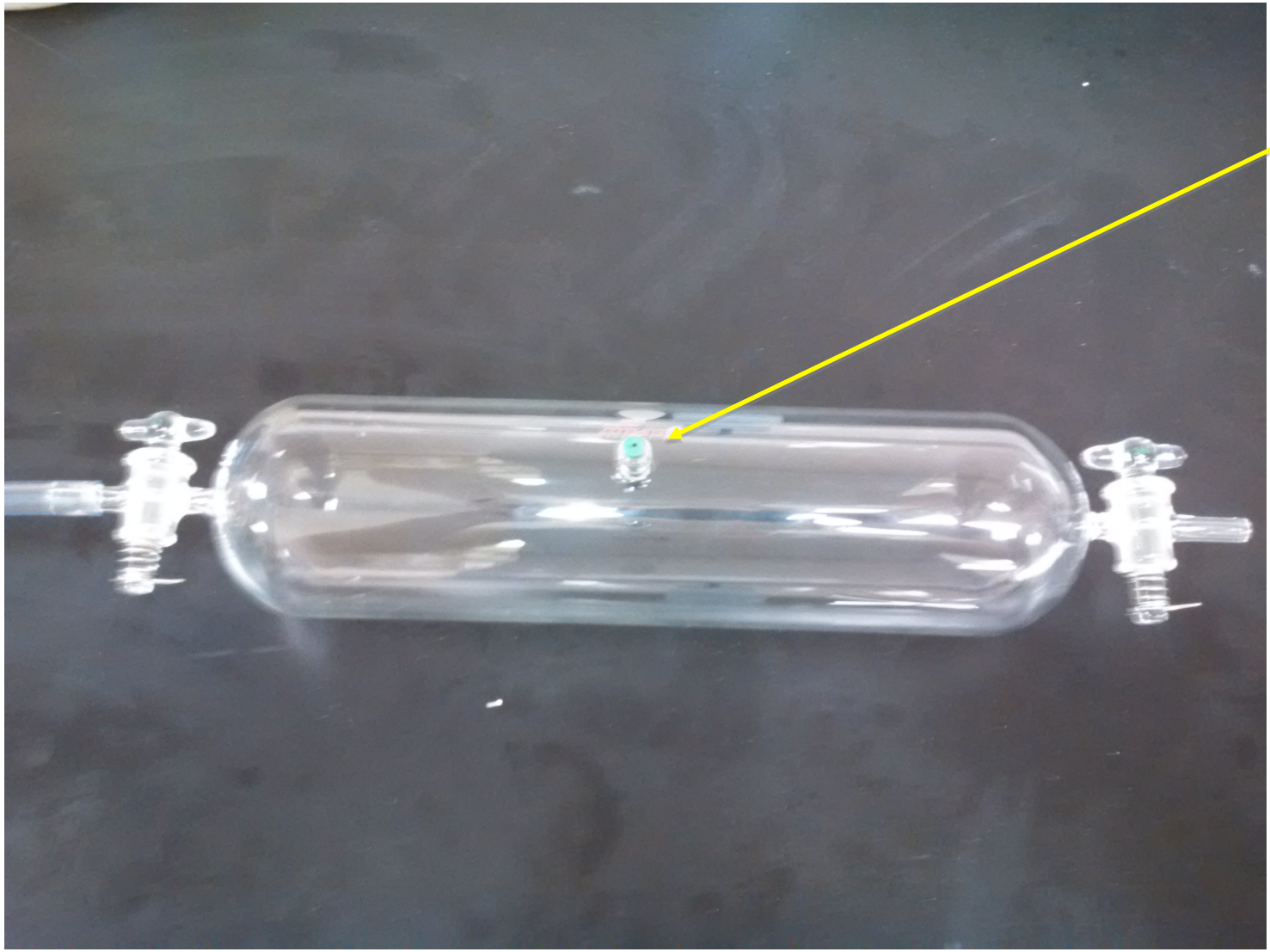
Leaks 1

- 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

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

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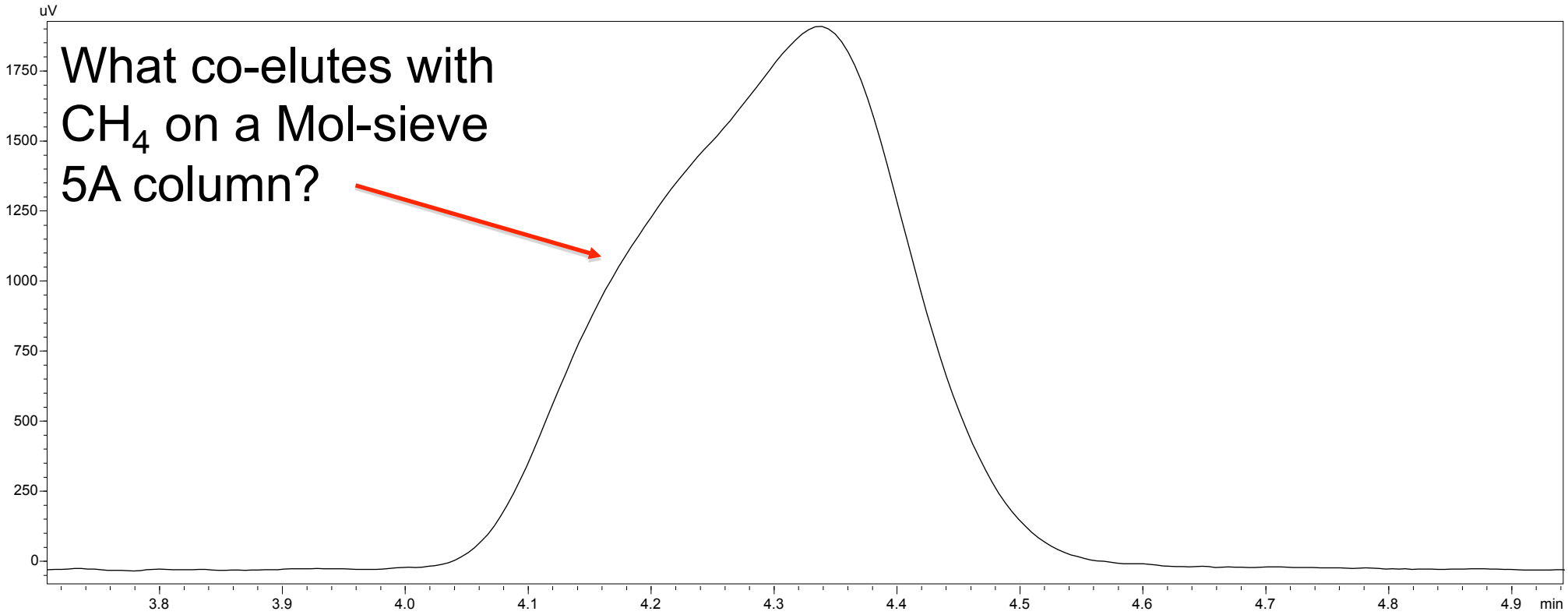
Contamination 3



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

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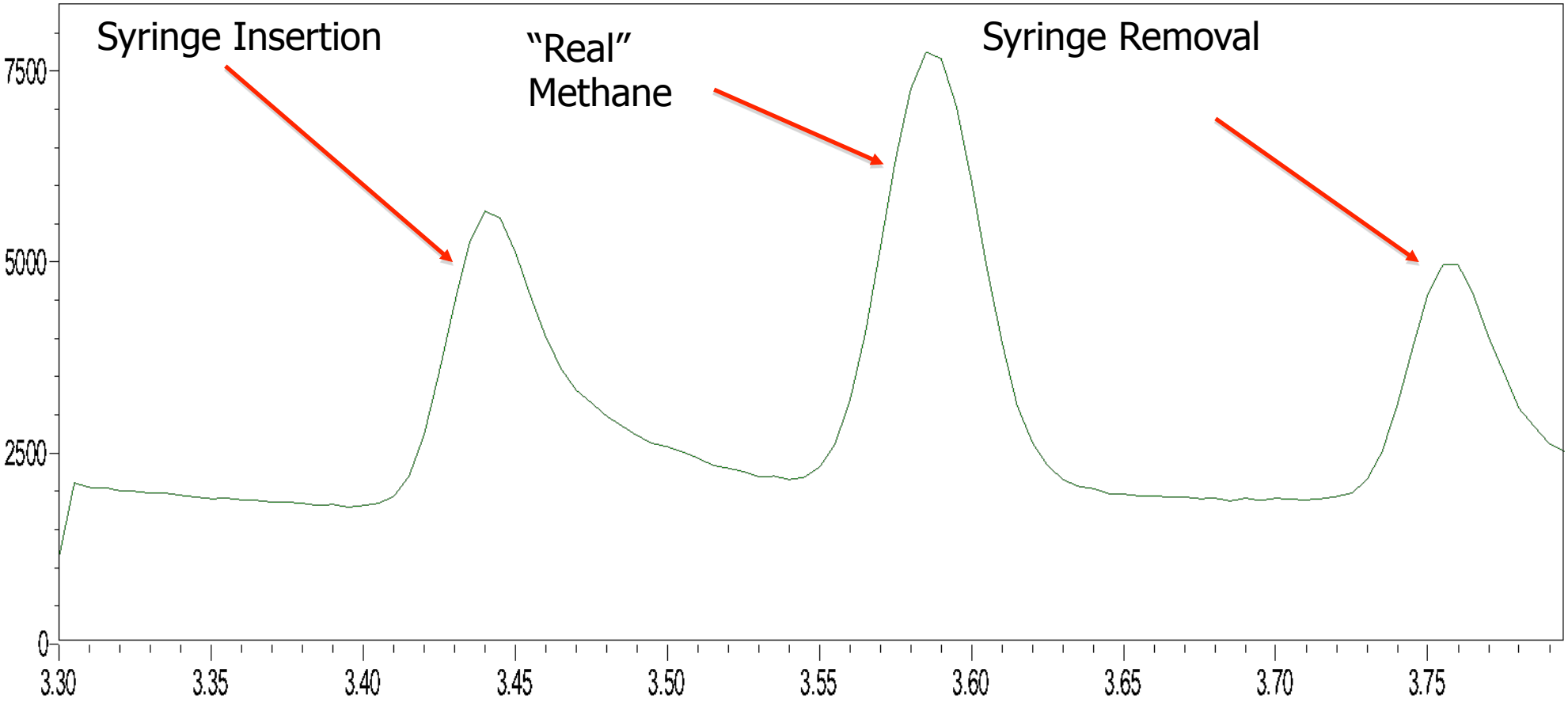
Contamination 5



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

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"In-House" Standards 3

Check Standard (CCV) Results:

Compound	CCV (ppmv)	Cert Std. Conc.	%D
CH_4	4.82	5.0	3.6
CO_2	592.	610	2.8
H_2O	0.96	1.0	4.0
CH_4	4.89	5.0	2.2
CO_2	598.	610	2.0
H_2O	0.97	1.0	3.0

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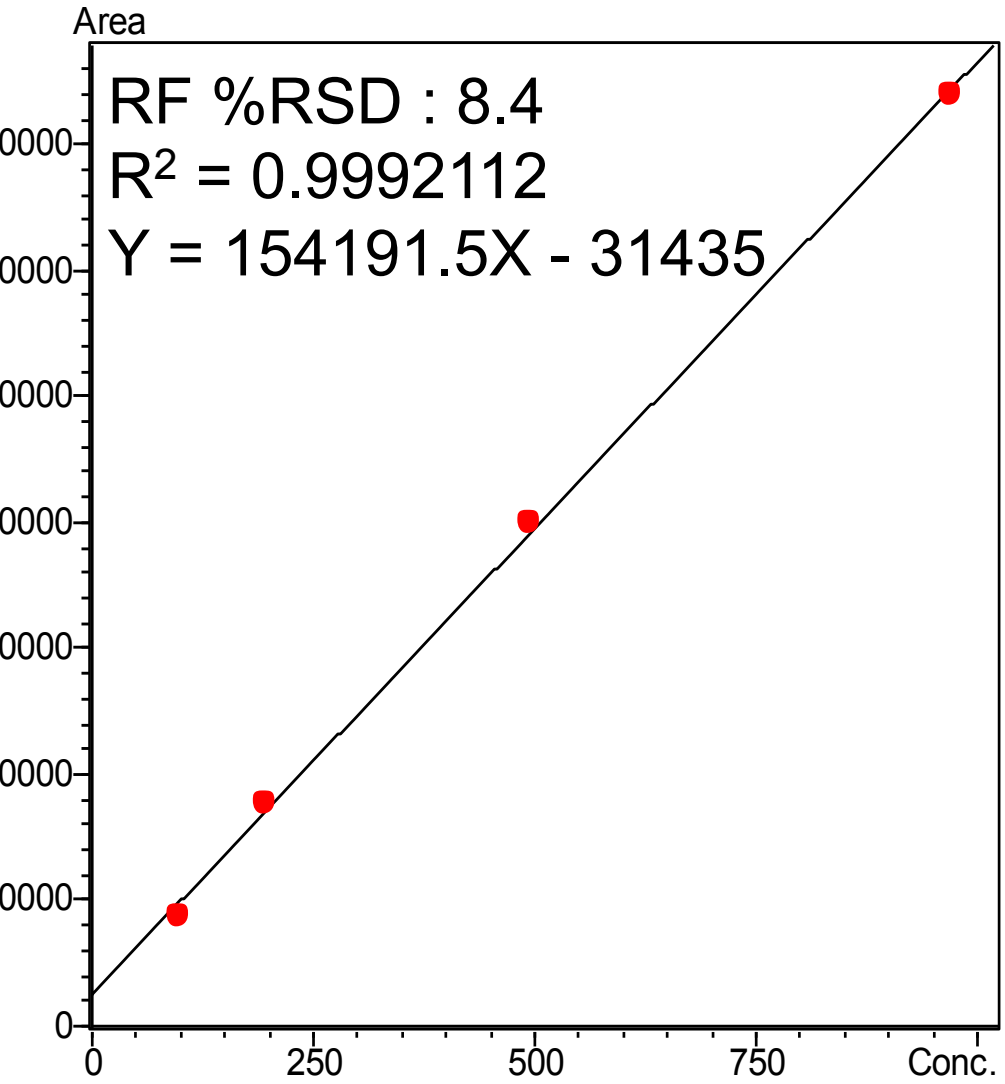
In-House" Standards 4

- CO_2 Calibration Curve



Calibration Range:
97.0 ppm to 970 ppm

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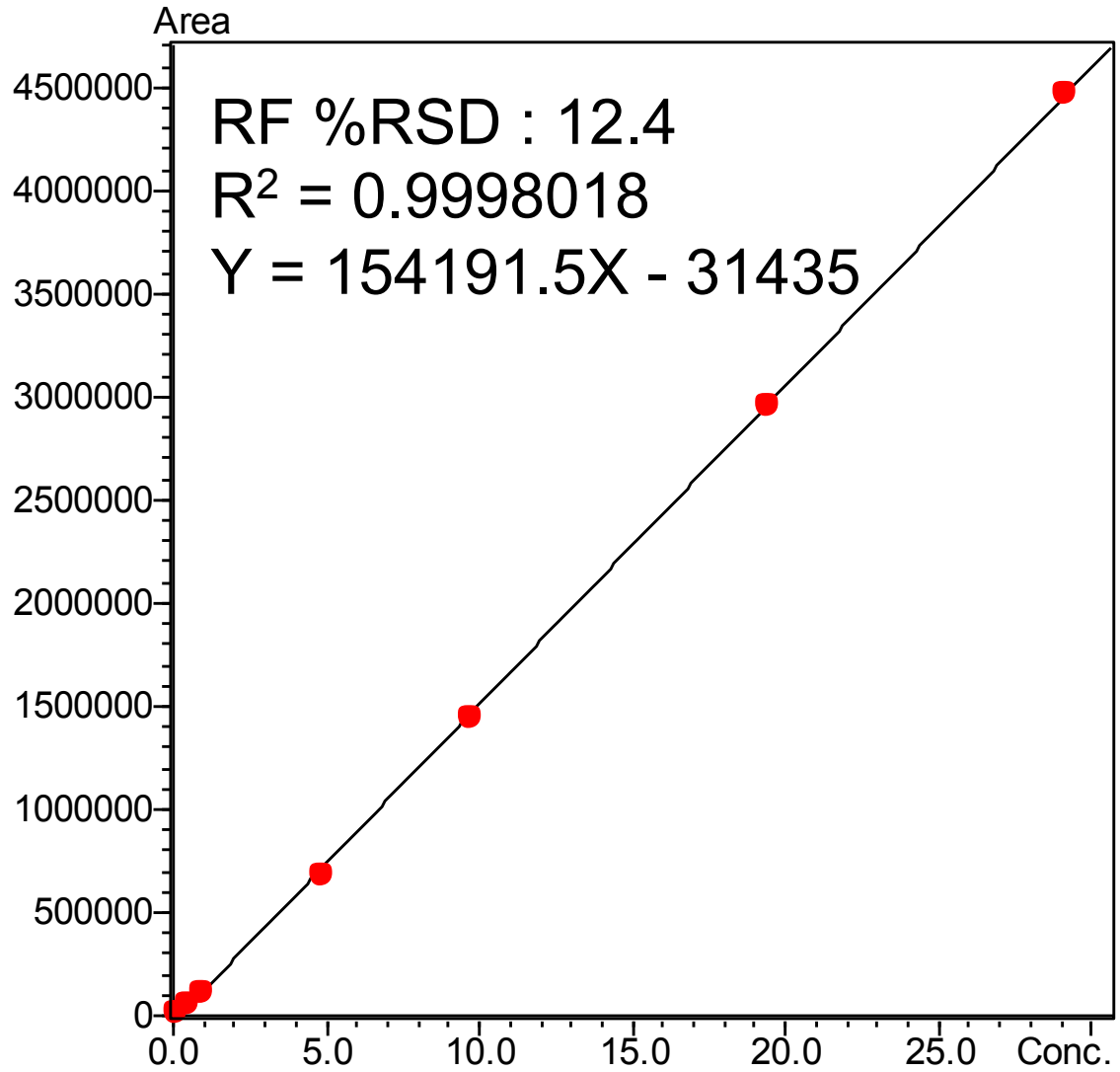
In-House" Standards 5

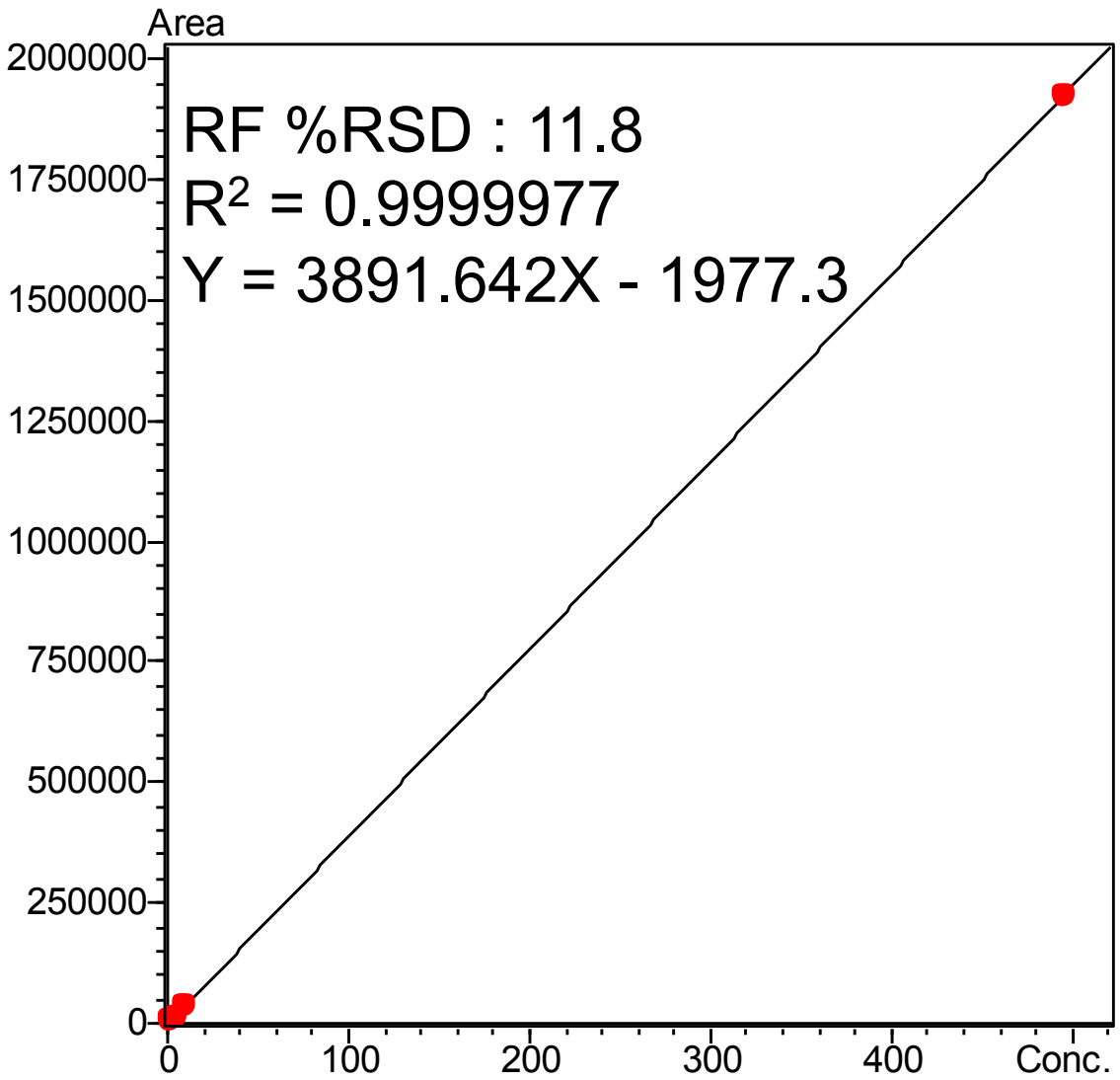
- N_2O Calibration Curve



Calibration Range:
0.100 ppm to 29.1 ppm

In-House" Standards 6

- CH_4 Calibration Curve



Calibration Range:
0.999 ppm to 495 ppm

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Real World Results

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

Values are consistent with current literature

Compound	Conc. (ppm)
Methane	2.14
CO2	391.
Nitrous Oxide	0.44

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

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Reproducibility Example

- AutoSampler Standard Vial Fill Problems 2012

RT	Area	Vial	
7.50	1,652,271	4	
7.50	1,662,573	4	sequential injections
7.50	1,681,641	4	
7.50	1,750,929	6	
7.50	1,753,305	6	sequential injections
7.50	1,750,934	6	

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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

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Reproducibility Example

- Autosampler Standard Vial Fill Data 2014

RT	Area	Vial	
7.54	1,640,890	1	sequential injections
7.54	1,633,041	1	
7.54	1,628,391	24	non-sequential injections
7.54	1,630,448	15	
7.54	1,602,760	6	
7.54	1,601,797	29	

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

Sensitivity 2

- 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.

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Questions?