

# **Hydrocarbon Air-Surface Exchange from Grasslands**

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# Outline

- Background
- Goals
- Sampling Method Design
- Beginner's Hurdles
- Analysis Methods
- Conclusions & Future Work

# Background

At Fermi labs...

- Established prairie land
  - Soil carbon level at equilibrium
- Restored prairie land
  - Continued increase in soil carbon content

# Eddy Production Patterns of Turbulent Flow



# Goals

At Fermi's restored prairie land site...

- Monitor air-surface exchange of hydrocarbons
  - acetaldehyde, n-butane, methanol, ethanol, 2-Me-butane, acetone, 2-propanol, butanol, 2-butanone, 2-Me-pentane, 3-Me-pentane, methane
  - Determine eddy flux of "up" and "down" currents
- Monitor CO<sub>2</sub>, O<sub>3</sub>, N<sub>2</sub>O, and H<sub>2</sub>O levels in air

# How to go about doing this...

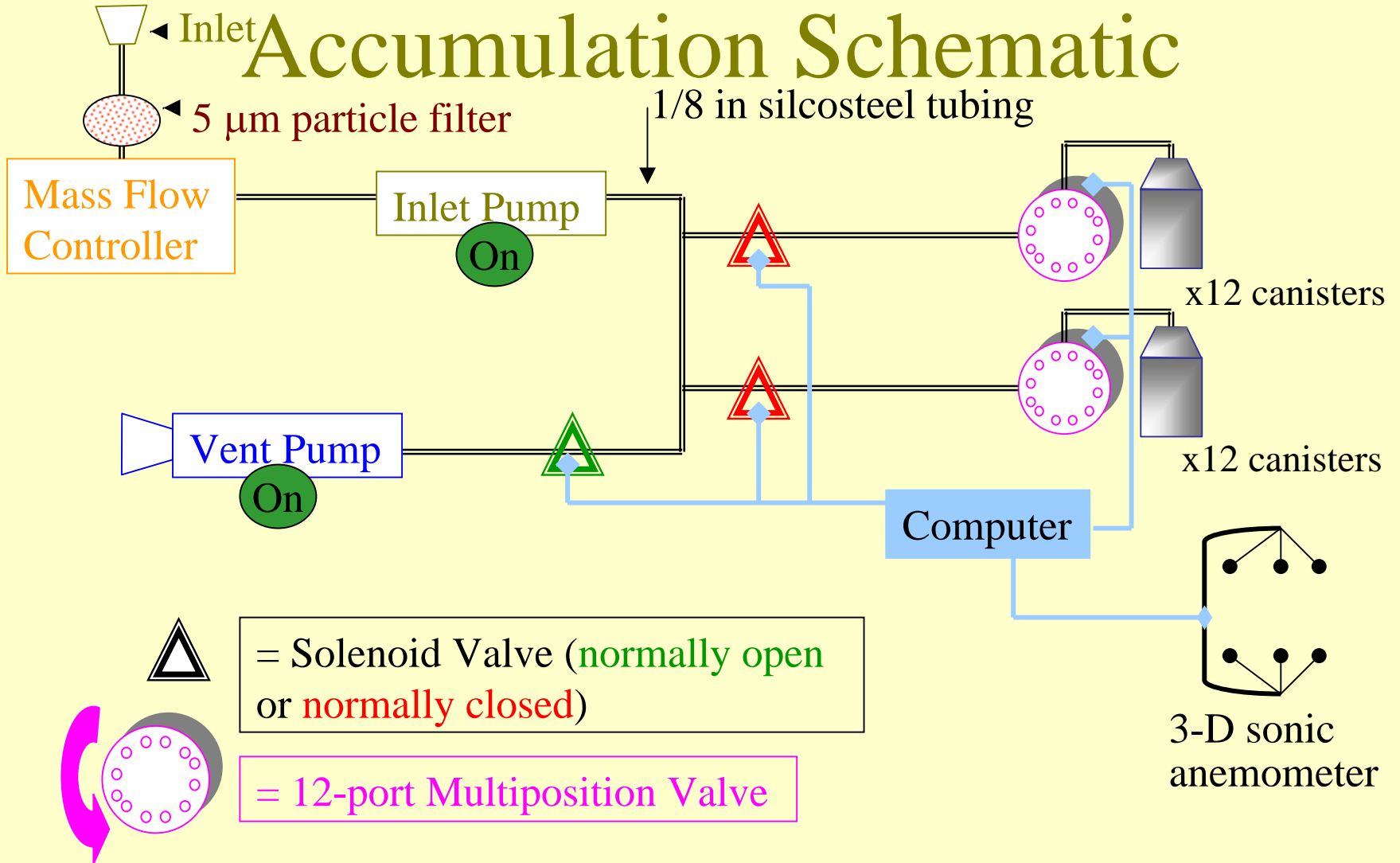
- Ozone
  - real time ozone sensor
- H<sub>2</sub>O and CO<sub>2</sub>
  - real time sensor with IR absorption detection
- N<sub>2</sub>O and hydrocarbons
  - whole air sample collection using Relaxed Eddy Accumulation (REA) system
  - subsequent analysis using various forms of gas chromatography (GC)

# Relaxed Eddy Accumulation (REA) design

- 3-D sonic anemometer
  - calculate wind direction and speed
  - signals to open a sampling line's solenoid valve during a sampling hour when **both**:
    - wind direction is "UP" or "DOWN"
    - wind speed reaches and/or exceeds critical value
- 24 hour whole-air sampling apparatus
  - sample every other hour on the hour (12 whole hours of possible sample intake)
  - 24 canisters total: 12 "UP" & 12 "DOWN"

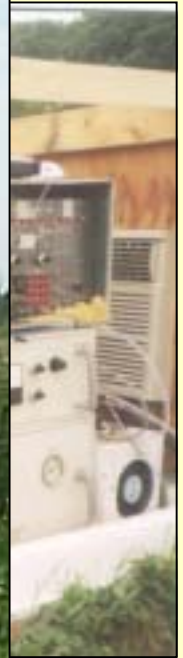
# Relaxed Eddy

## Accumulation Schematic





# Field Site: Up and Running



Sonic

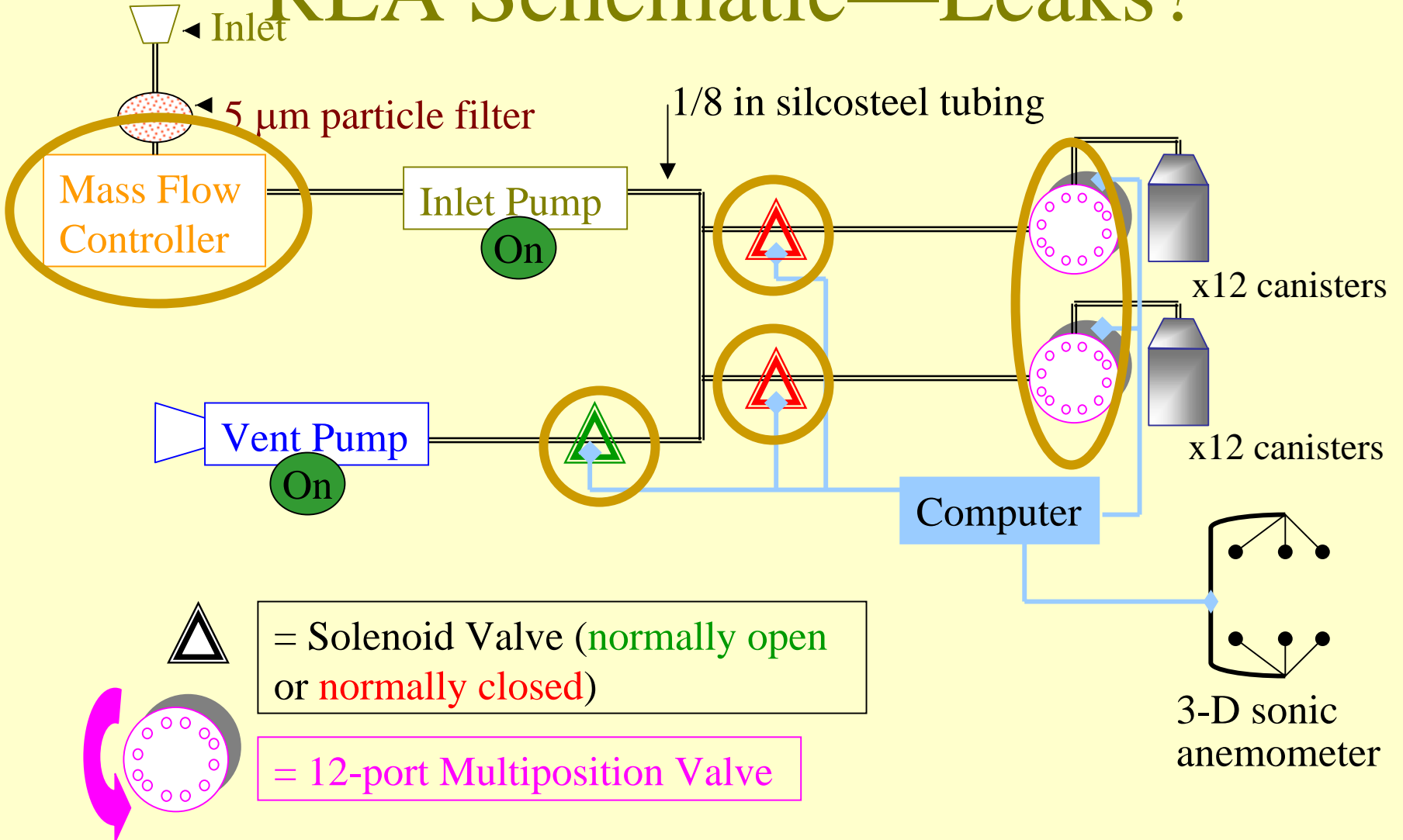
# Beginner's Hurdles

- Problem
  - Pressures in each canister after 24 hr sampling period ended:
    - most were still under vacuum pressure!  
(-8 to -14 inHg)
    - few had reached atmospheric pressure (0 psig)
    - a couple had positive pressure (+1 psig)
    - desired pressure → 15 psig



# What is causing the lack of pressure in the canisters?

- Not enough air pumped into the canisters?
  - mass flow controller increased—74 mL/min to 200 mL/min
  - no noticeable change in final pressures
- Leaks?
  - capped off inlet, ran 24 hr REA program
  - canisters returned to atmospheric pressure
  - air must be entering through another path!

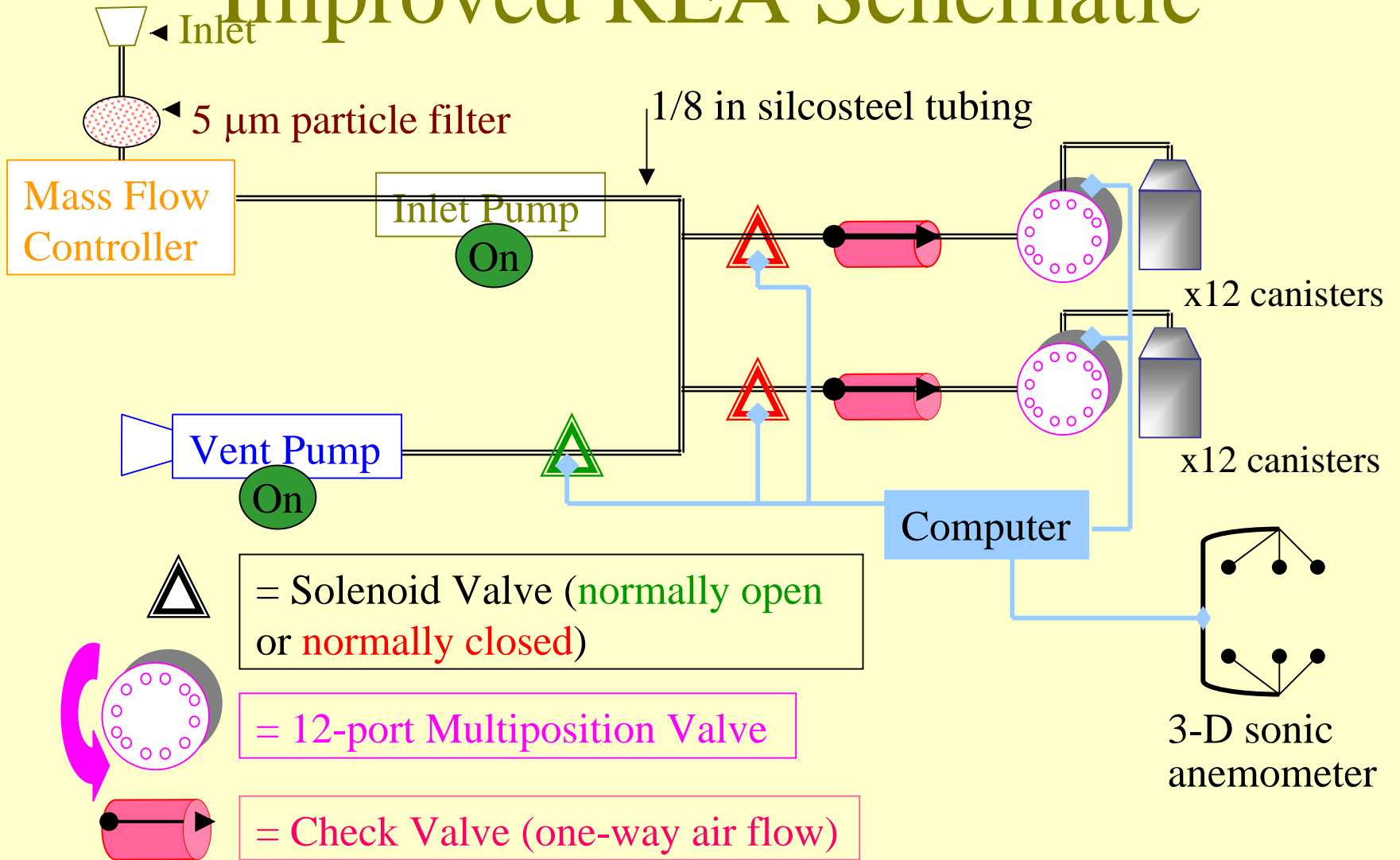
# REA Schematic—Leaks?



# One Problem Identified

- Leaky solenoid valves  normally closed  normally open
  - canisters not fully protected from continuous vent pump
  - canisters evacuated after filling
  - canisters never completely filled
  - total air leakage ~900 mL (1800 mL canister)

# Improved REA Schematic



# Analysis Methods

## Gas Chromatography

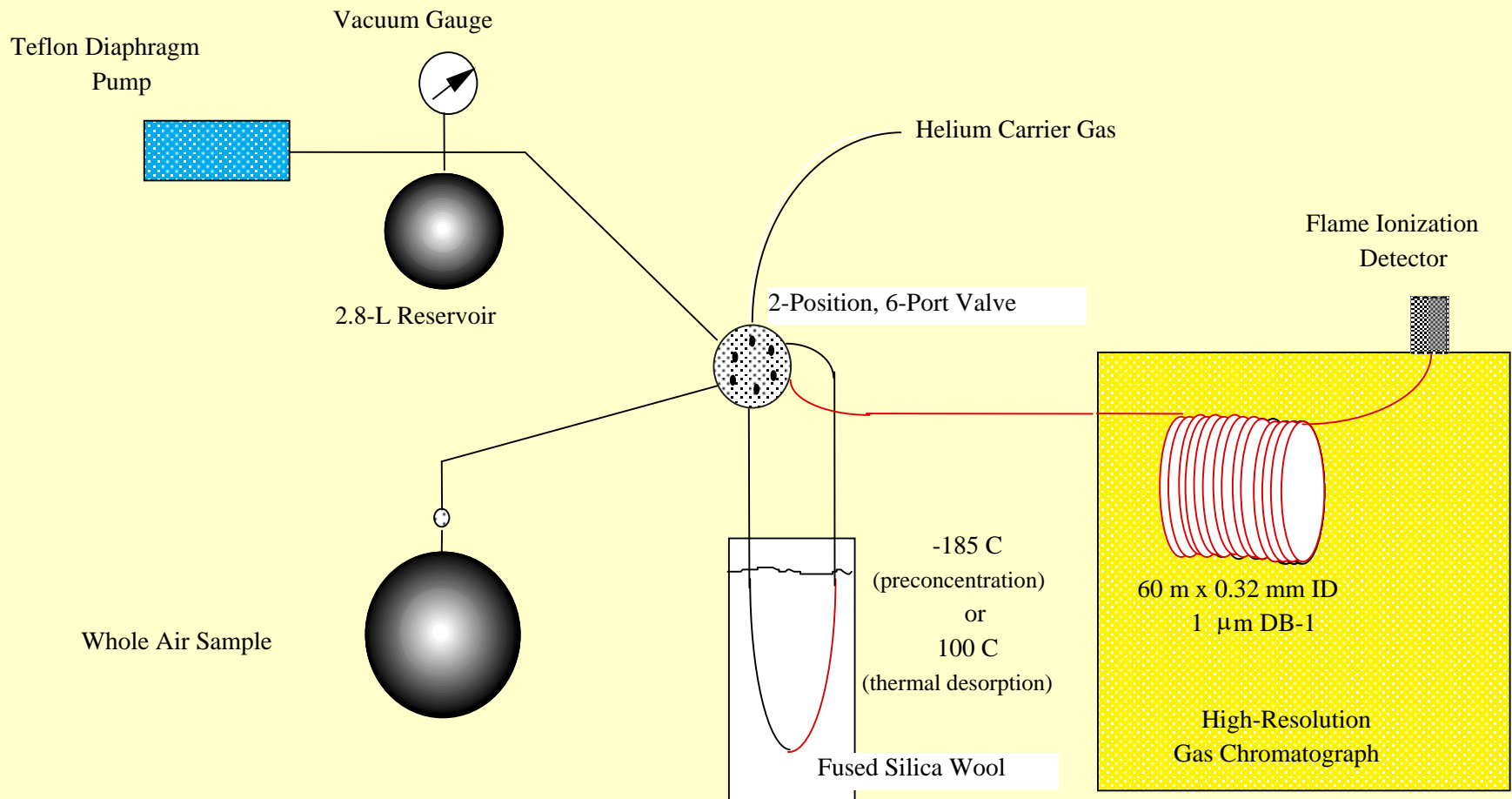


GC with Flame Ionization Detector ( $\text{CH}_4$ ) and  
Electron Capture Detector ( $\text{N}_2\text{O}$ )

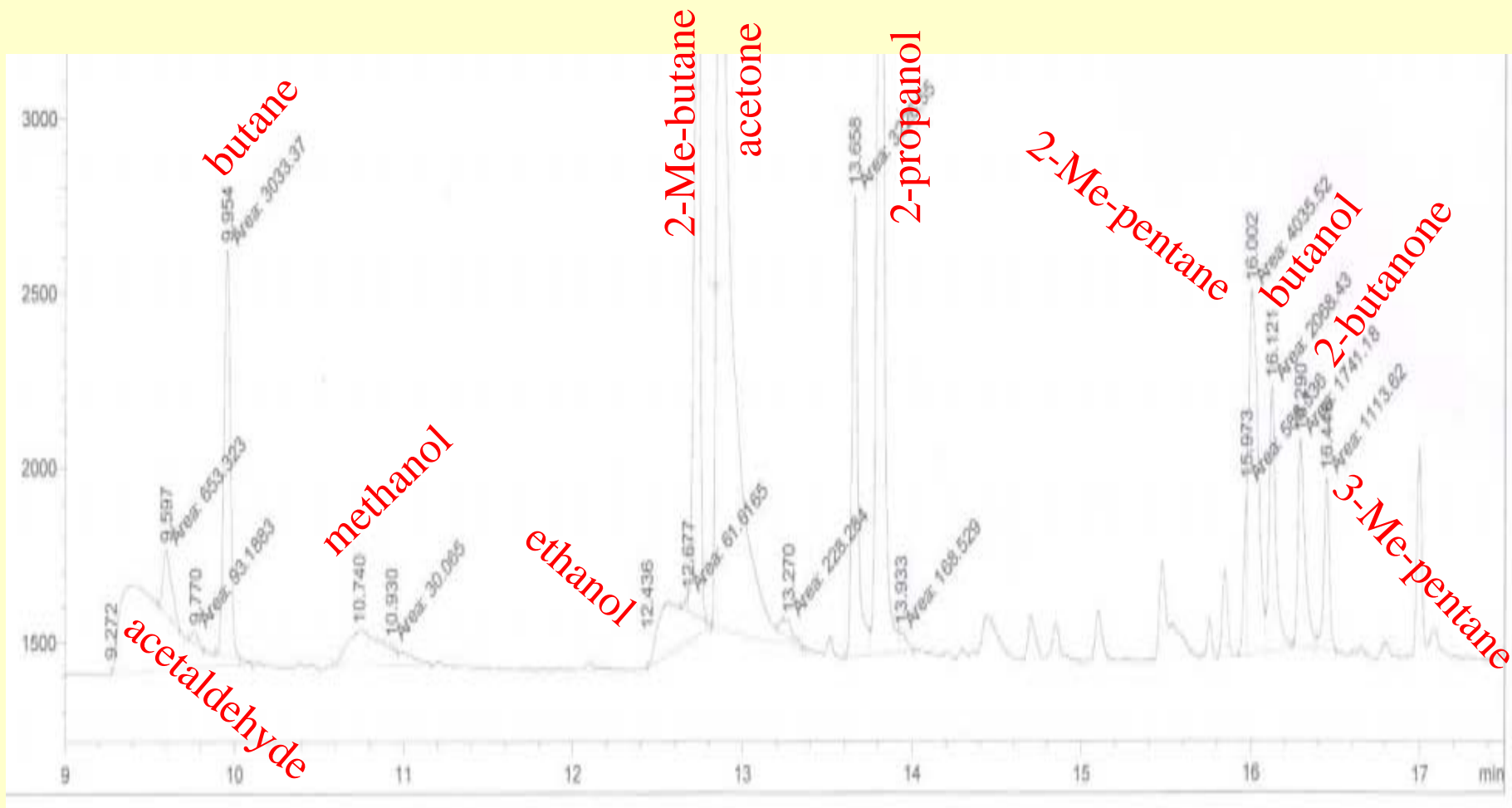


# Cryogenic pre-concentration GC with FID

– For most of our desired hydrocarbons



# Example Chromatogram



# Conclusions & Future Work

- Install check valves in REA system
- Make adjustments to 12-port multiposition valves, leak check
- Perform test runs at ANL
- Move REA system to Fermi for actual field sampling

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