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Analysis of Dissolved Hydrocarbon Gases in Water – Pitfalls and Improvements

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Why measure hydrocarbon gases in groundwater?

- Oil & gas application
  - ~ Predrill site characterization
    - ° Establish baseline for comparison
    - ° Find existing issues
  - ~ Post drill site characterization
    - ° Assess potential changes
- Remediation monitoring
  - ~ Reducing conditions indicator
    - ° Active reductive dechlorination
    - ° Monitored natural attenuation
- Other applications?

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How to measure hydrocarbon gases in groundwater?

- Headspace – GC / FID
  - ~ RSK-175 Rev 0, 1994
  - ~ J Chrom Sci – Kampbell, Vandergrift, 1998
  - ~ M E E Analysis Guidance, US EPA Region 1, 2002
  - ~ RSK-175 Rev 2, 2004
  - ~ RSK-175 Rev 3, 2006
  - ~ RSK-175 Rev 5, 2010
  - ~ PA DEP 3686 Rev 1, 2012
- Purge and Trap
  - ~ PA DEP 9243 Rev 0, 2012

RSKSOP-175
Revision No.2
May 2004
Page 1 of 14
Felisa Hudson

STANDARD OPERATING PROCEDURE

Sample Preparation and Calculations for Dissolved Gas Analysis in Water Samples Using a GC Headspace Equilibration Technique

1. Disclaimer:

This standard operating procedure has been prepared for the use of the Ground Water and Ecosystems Restoration Division of the U.S. Environmental Protection Agency and may not be specifically applicable to the activities of other organizations. **THIS IS NOT AN OFFICIAL EPA APPROVED METHOD.** This document has not been through the Agency's peer review process or ORD clearance process.

2. Purpose (Scope and Application):

This method is applicable to the preparation of water samples for determination of dissolved gases. After quantitation of gas equilibrated into the prepared headspace, this method permits calculation of the concentration of the dissolved gas in the water before equilibration. Resulting concentrations are expressed as mg/L and µg/L of dissolved gas in water. This method has been used for determining dissolved hydrogen, methane, ethylene, ethane, propane, butane, acetylene, nitrogen, nitrous oxide and oxygen. The number of analyses that can be performed in an eight

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What limits data quality?

- Lab to lab implementation variability of RSK-175 *method*
- No commercially available proficiency test samples
- Calibration standards are gas phase
  - ~ Samples are water
  - ~ Thus standards and samples are not handled identically
- Analyte loss during sample preparation
- Maintaining analyte representativeness during sampling

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What limits data quality?

- Lab to lab implementation variability of RSK-175 method
  - ~ Critical process elements
    - ° Sample transfer between containers
    - ° Headspace development
    - ° Equilibration
      - – time
      - – temperature
      - – mixing
  - ~ Process options
    - ° Manual
    - ° Semi-automated
    - ° Fully automated

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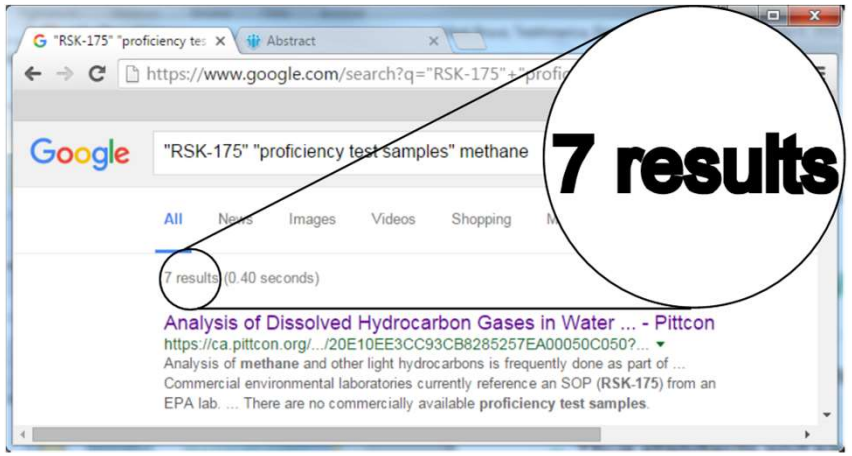
What limits data quality?

- No commercially available proficiency test samples
  - ~ No catalog items
  - ~ No custom PTs available either
  - ~ Limited water solubility
  - ~ Limited organic solvent solubility
  - ~ Limited stability in water
  - ~ Complex preparation process



= expensive to produce, short shelf life & lower quality

>> No independent check on accuracy

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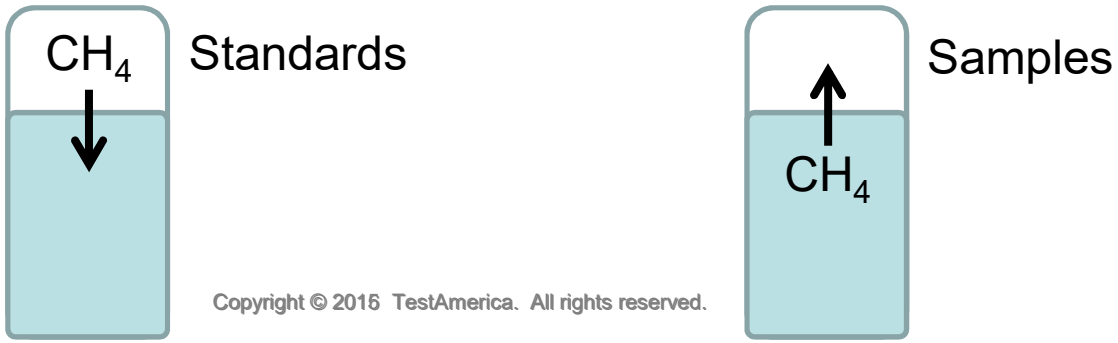
What limits data quality?

- Calibration standards are gas phase
  - ~ Samples are water
  - ~ Thus standards and samples are not handled identically
  - ~ Equilibrium goes in one direction for samples and the opposite for standards
    - ° Non-equilibrium conditions
      - – High biased standard response
      - – Low biased sample response
      - = low biased calculated sample concentration



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What limits data quality?

- Analyte loss during sample preparation
  - ~ Volatilization during open transfer
    - ° Too slow or turbulent
    - ° PA DEP study demonstrated this can be done right

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What limits data quality?

- Analyte loss during sample preparation
  - ~ Degassing using syringe transfer
    - ° Too fast

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What limits data quality?

- Analyte bias during sample preparation
  - ~ Losses or increases during headspace development
    - ° Transfer water too slow, increases air exposure – low bias
    - ° Transfer HS gas too slow, purges water – high bias
  - ~ Pierced septum leaks
    - ° Headspace / analyte loss while waiting in autosampler

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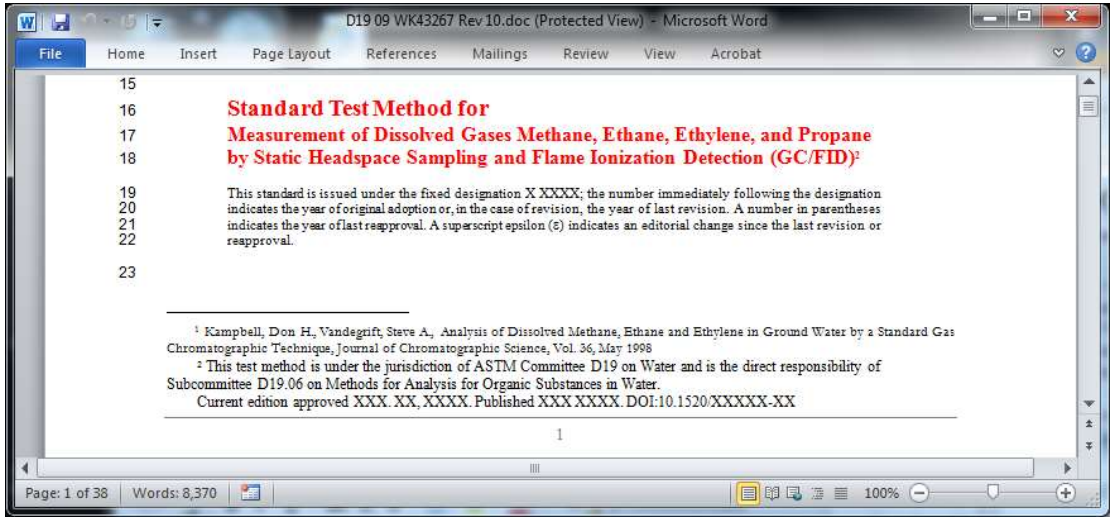
Improvements address limitations

- Multi-lab validated method
  - ~ On track - ASTM D19.09 WK4367 Rev 10 draft Feb 17, 2016
    - ° Single lab validation at present
    - ° Fully automated process with manual option
    - ° Anne Jurek @ EST Analytical
  - ~ Marcellus Shale Coalition
    - ° Revied draft ASTM method
    - ° Identified inter-lab variability as a critical issue



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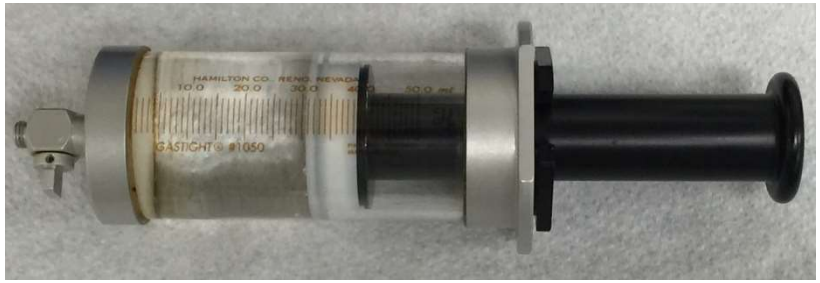
Improvements address limitations

- Water based calibration standards and QC samples
  - ~ In-lab prep of single analyte saturated water standards
    - ° Use literature values at known temperature and pressure
      - – PA DEP 3686 Rev 1, 2012
      - – ASTM D19.09 WK4367
    - ° Immediate dilution to working standards
      - – Store in VOC vials – no headspace, 14 days
  - ~ Commercial providers attempting to develop standards
    - ° Not ready yet
  - ~ Store stock standard in gas tight syringe with valve
    - ° Hours of stability
    - ° Not weeks

Methane 23.2 mg/L
Ethane 62.0 mg/L
Ethene 149.0 mg/L
Propane 76.7 mg/L



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Improvements address limitations

- Water based calibration standards and QC samples
  - ~ What hasn't worked (methane)
    - ° Inject methane bubble into vial filled with water
    - ° Inject methane bubble into vial filled with methanol
    - ° Refrigerate to improve solubility
    - ° Apply pressure with syringe plunger

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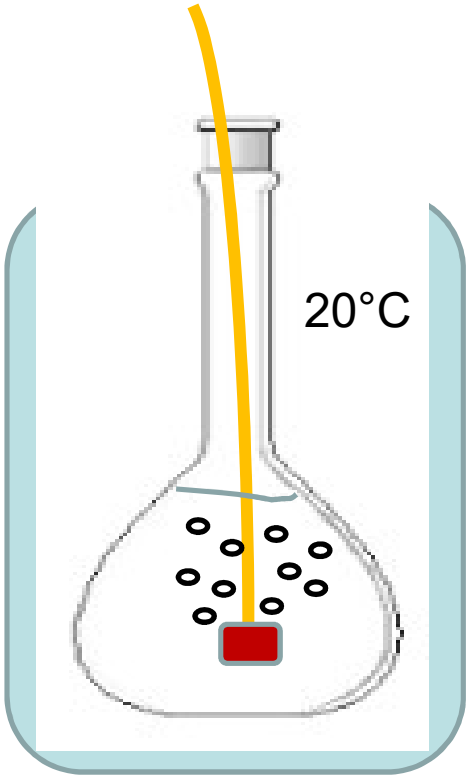
Improvements address limitations

- Water based calibration standards and QC samples
  - ~ PA DEP 3686 Rev 1, 2012
  - ~ ASTM D19.09 WK4367



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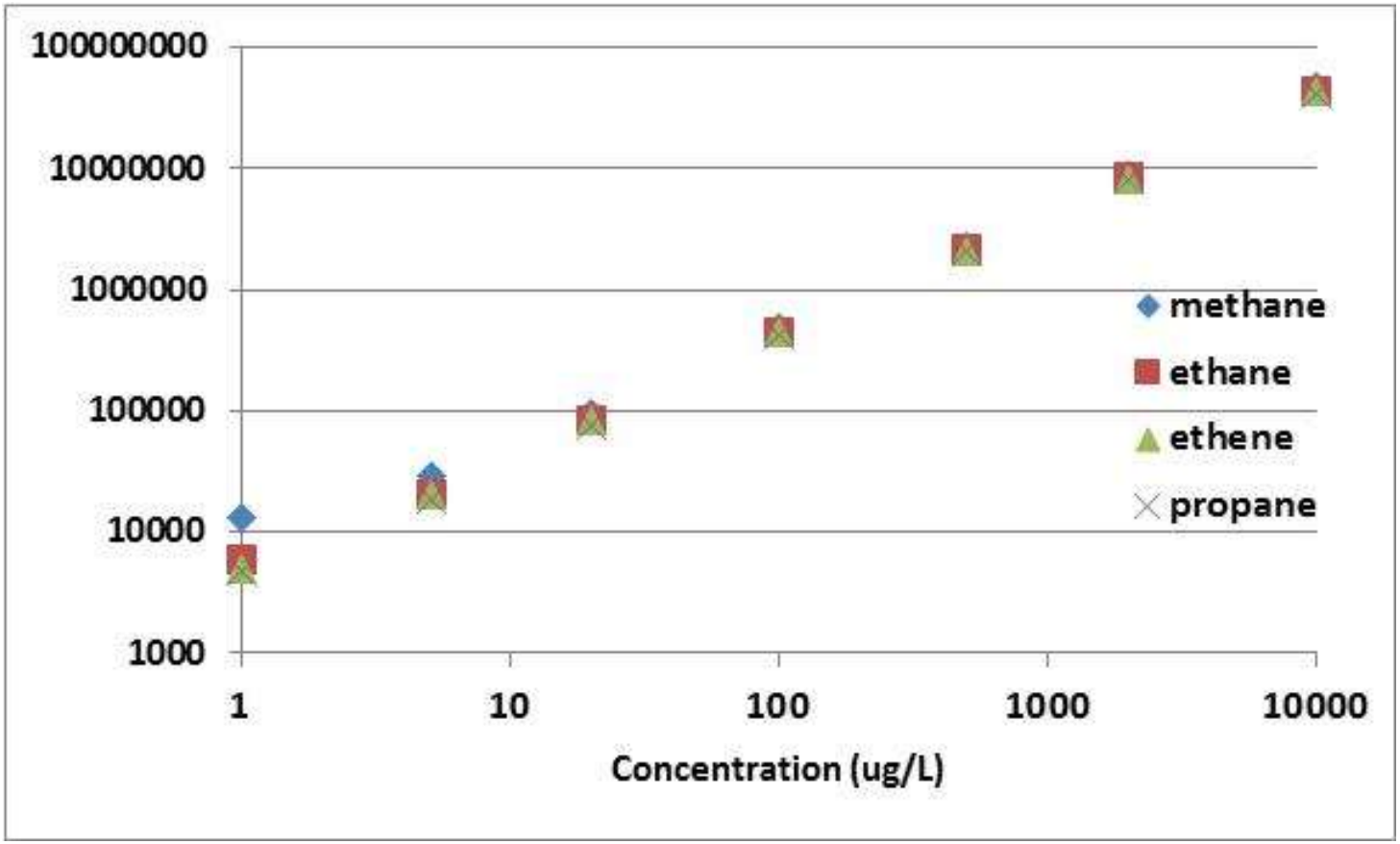
Improvements address limitations

- Water based calibration standards
  - ~ 4 analytes in the same standard



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Improvements address limitations

- Water based calibration standards
  - Individual analyte ICVs (second source)
    - ~100 ug/L
    - Methane 103%R
    - Ethane 101%R
    - Ethene 83%R
    - Propane 91%R

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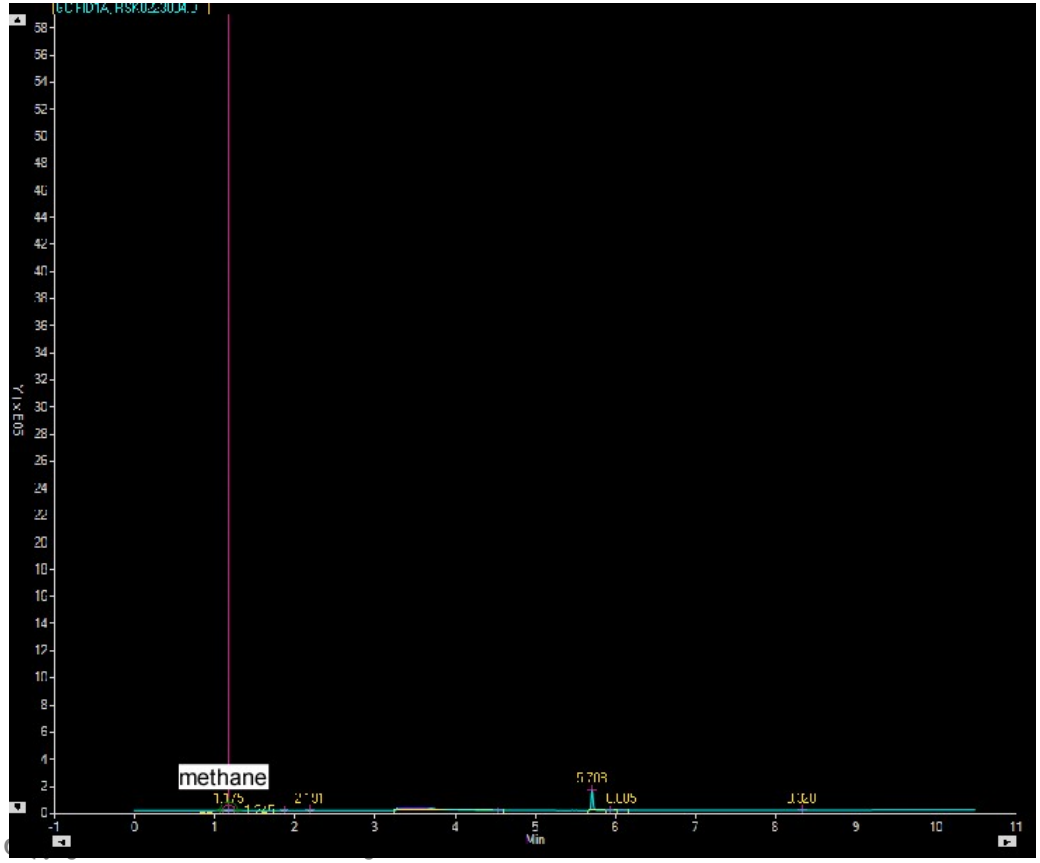
Improvements address limitations

- Surrogate - monitor sample prep & analysis quality
  - ~ How to know when you have a good headspace injection?
  - ~ Int. Std.
  - ~ Surrogate
  - ~ ASTM
    - ° MTBE



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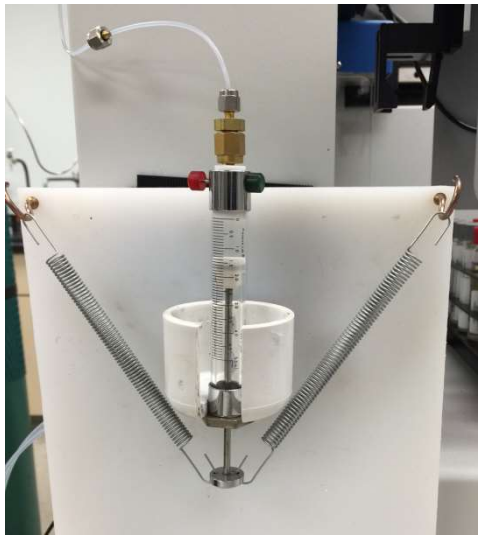
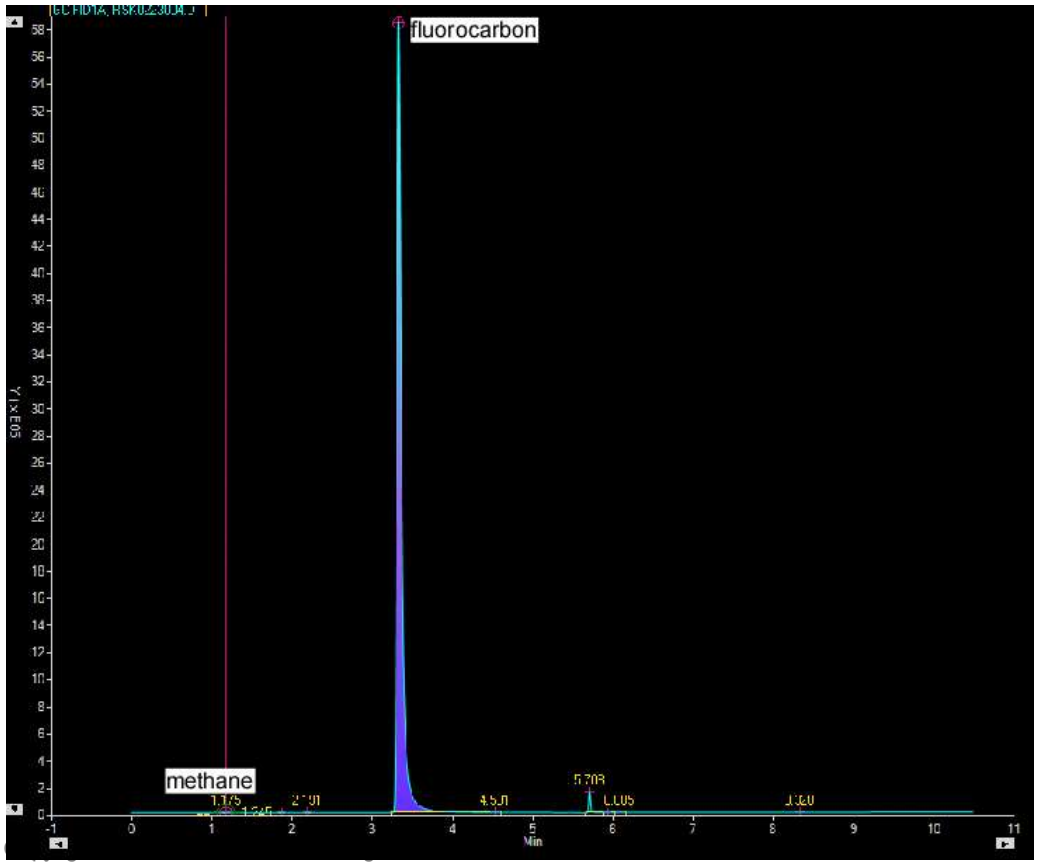
Improvements address limitations

- Surrogate - monitor sample prep & analysis quality
  - ~ How to know when you have a good headspace injection?
  - ~ Surrogate in water?
  - ~ Automated delivery?





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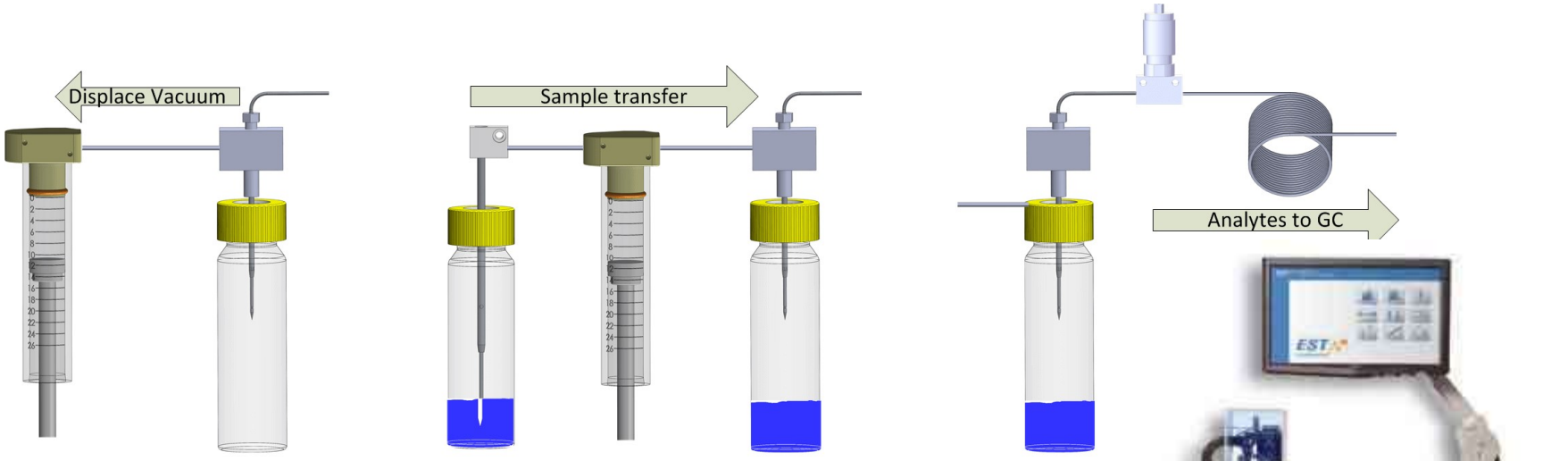
Improvements address limitations

- Automated headspace preparation
  - ~ EST Analytical – LGX 50



60°C, 10 min, high speed stir

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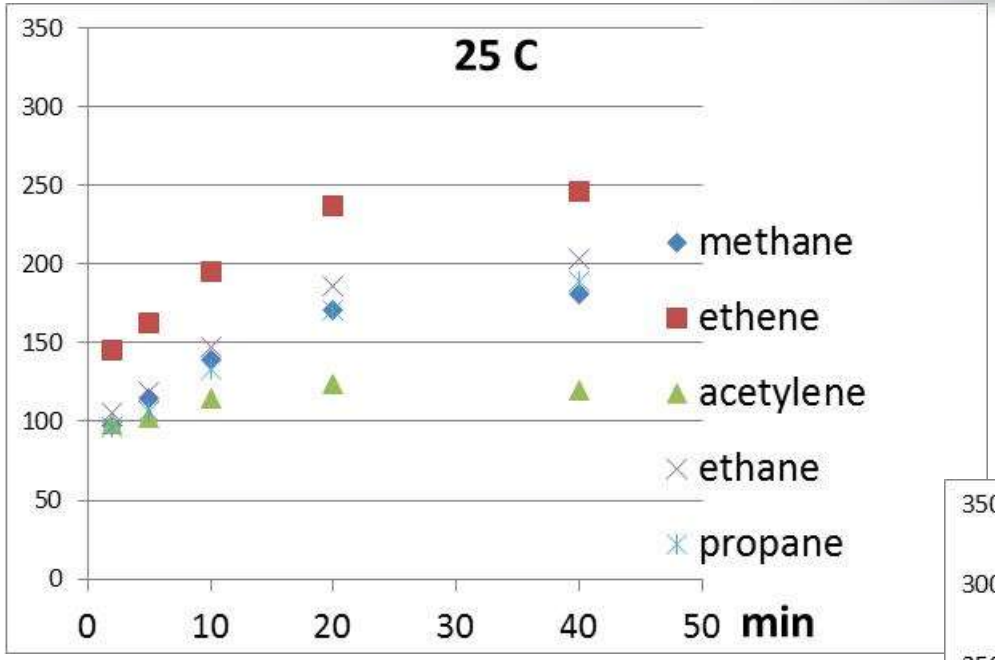
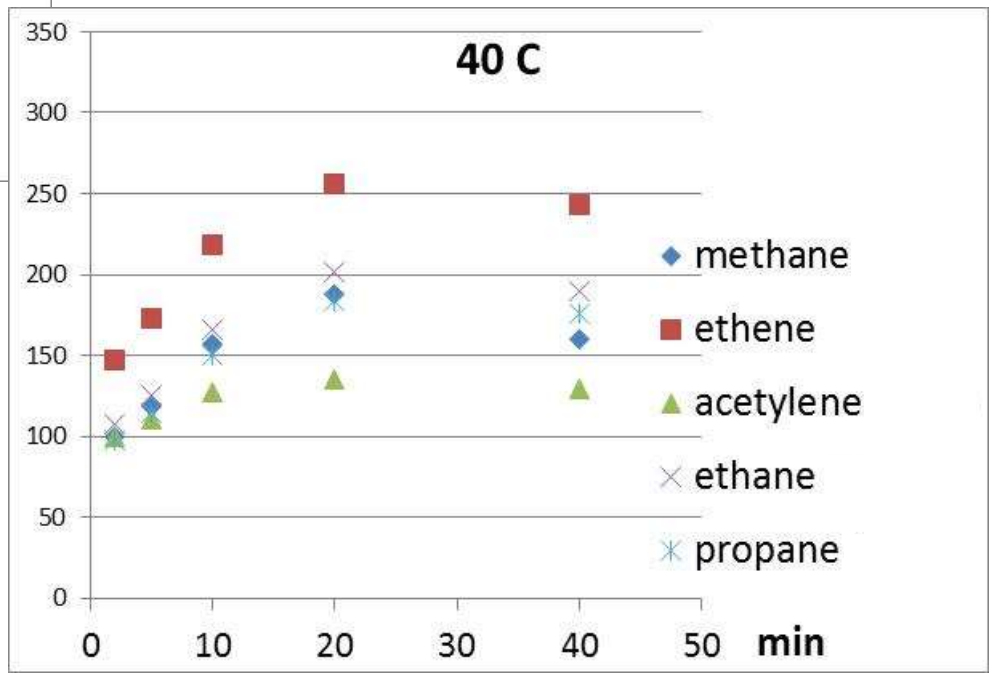
Headspace Equilibrium Optimization





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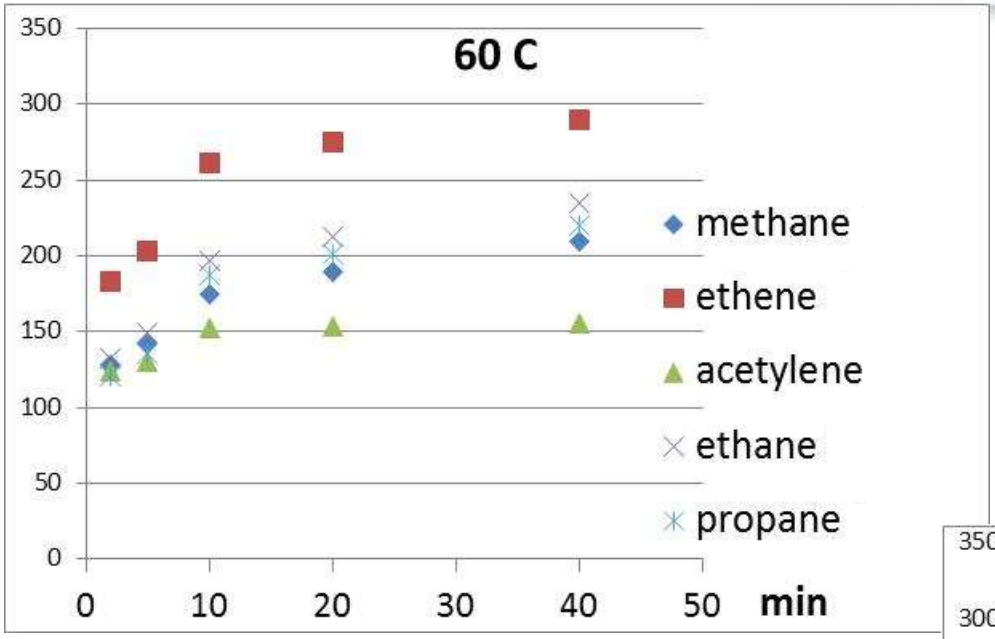

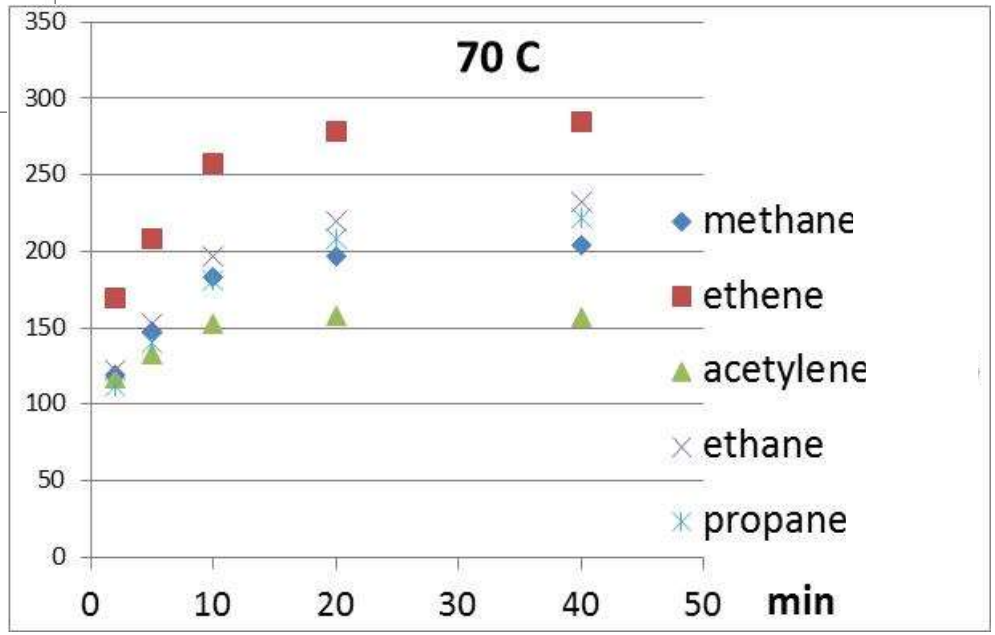

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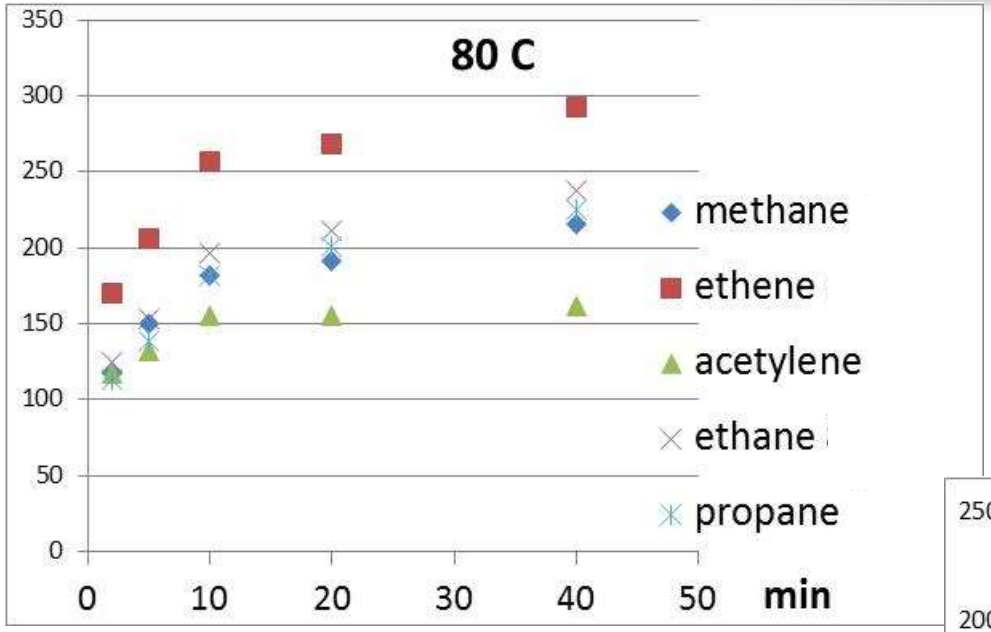

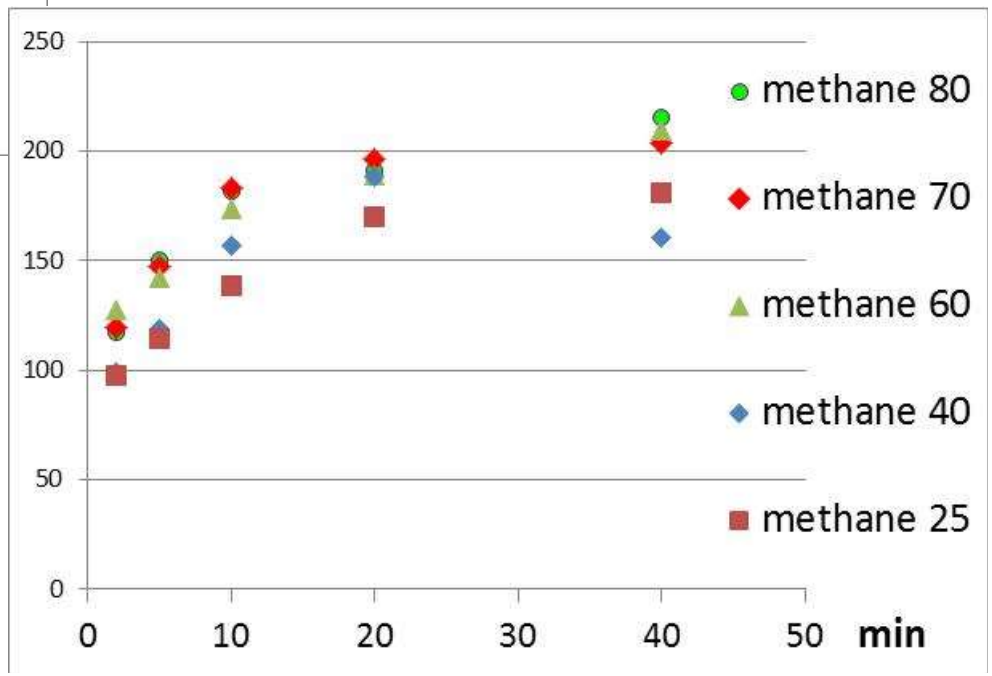

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Headspace Equilibrium Optimization

- Stir bars
  - ~ Standard mini (12 mm)
  - ~ Spinfin (12.7 & 19 mm)
  - ~ Starburst (9.5 and 19 mm)
- Short Equilibration
  - ~ 60°C
  - ~ 3 min
  - ~ Maximum stir speed

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Selecting a Stir Bar

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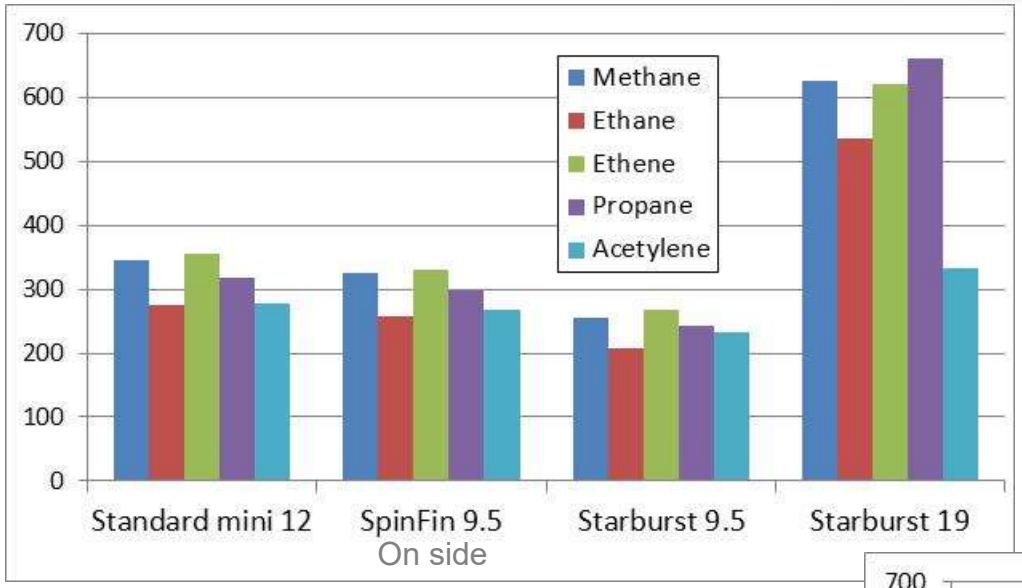
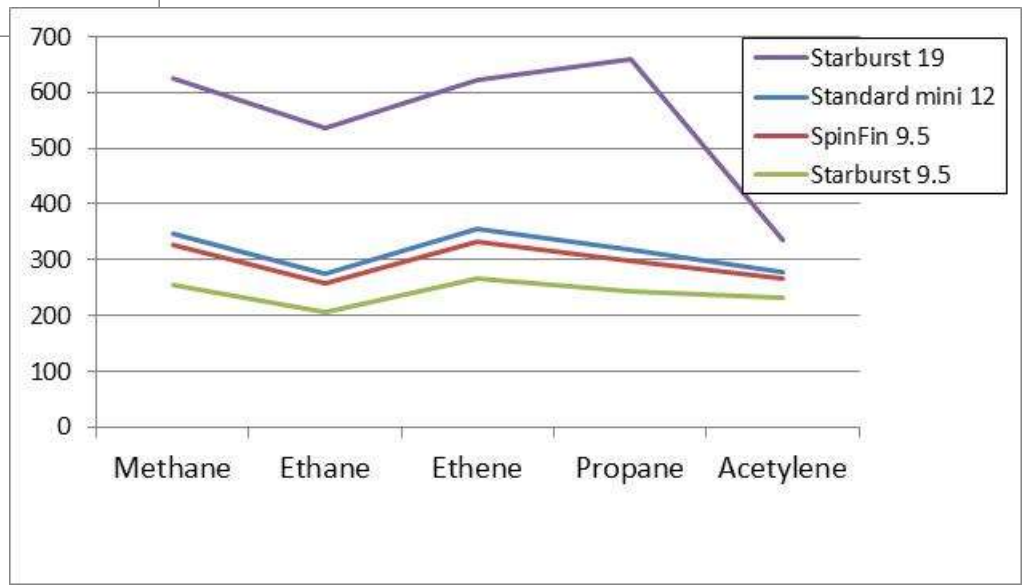
Selecting a Stir Bar





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Improvements address limitations

- External Proficiency Test samples

Future state – Regular independent accuracy verification

Current state - No independent accuracy verification

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Summary

- Multi-lab validated method
  - ~ On track - ASTM D19.09 WK4367
- Water based calibration standards and QC samples
  - ~ Open opportunity for commercial provider
  - ~ Lab based saturated stock water solutions
- Surrogate - monitor sample prep & analysis quality
- Automated headspace preparation
  - ~ 60°C, 10 min, high speed stir with 19 mm starburst
- External Proficiency Test samples
  - ~ Open opportunity for commercial provider

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