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Improving Quality with Water based QC for Dissolved Gas Analysis in Water

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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

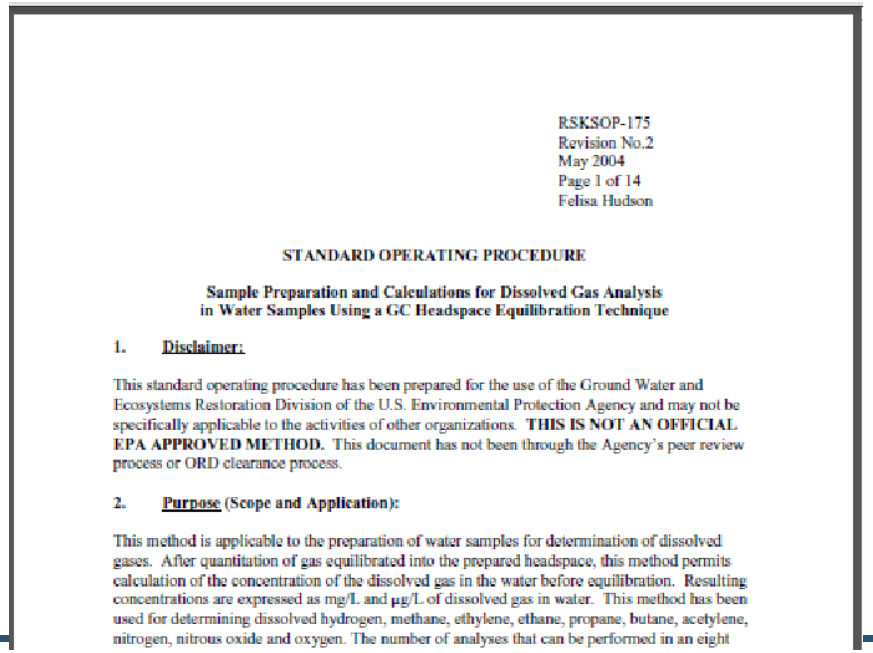
How to measure hydrocarbon gases in groundwater?

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

What limits laboratory data quality?

Lab to lab implementation variability of RSK-175 *method*

~~No commercially available standard reference material~~

Calibration standards are gas phase

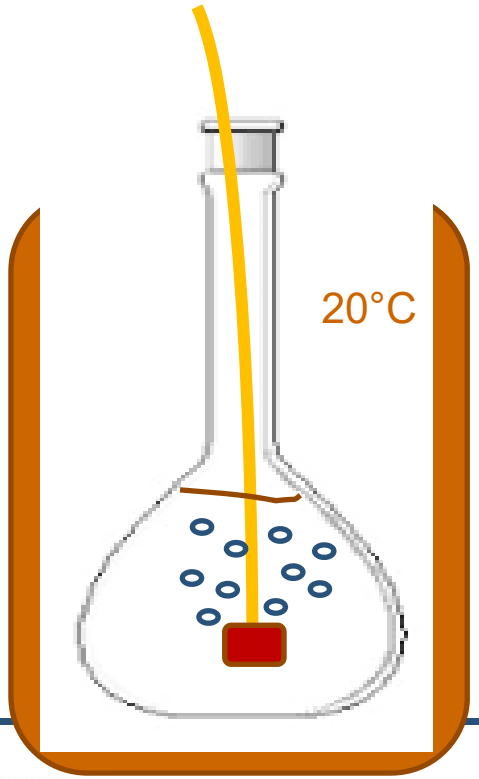
- Samples are water
- Thus standards and samples are not handled identically

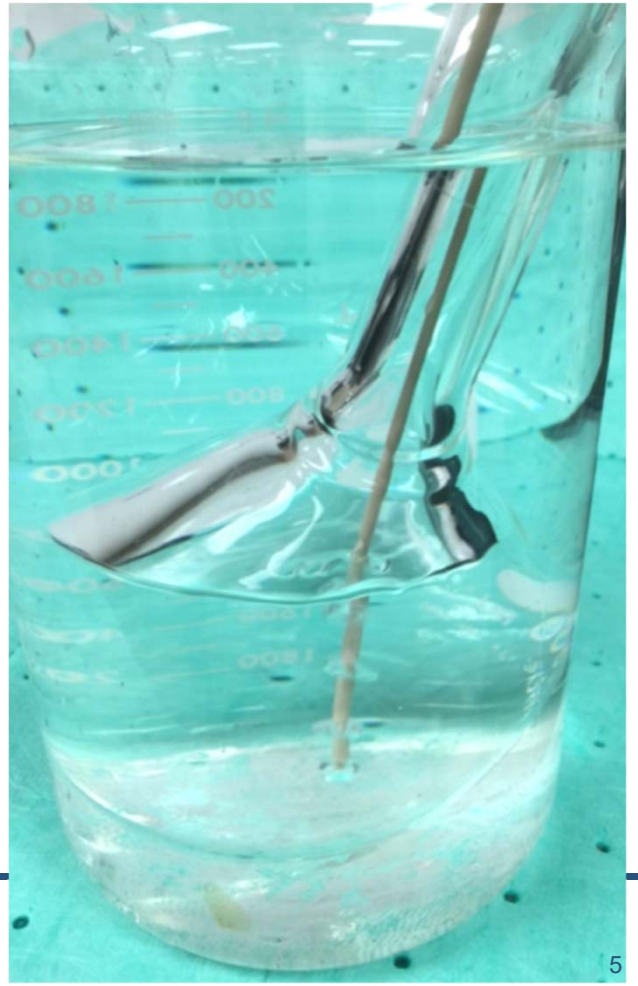
Analyte loss during sample preparation

Preparing Reference Materials

Water based calibration standards and QC samples

- PA DEP 3686 Rev 1, 2012
- ASTM D8028-2017





MEEP Reference Material Sources

MEEP = Methane, Ethane, Ethene and Propane

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 D8028-2017
  - Immediate dilution to working standards
    - Store in VOC vials – no headspace, 14 days

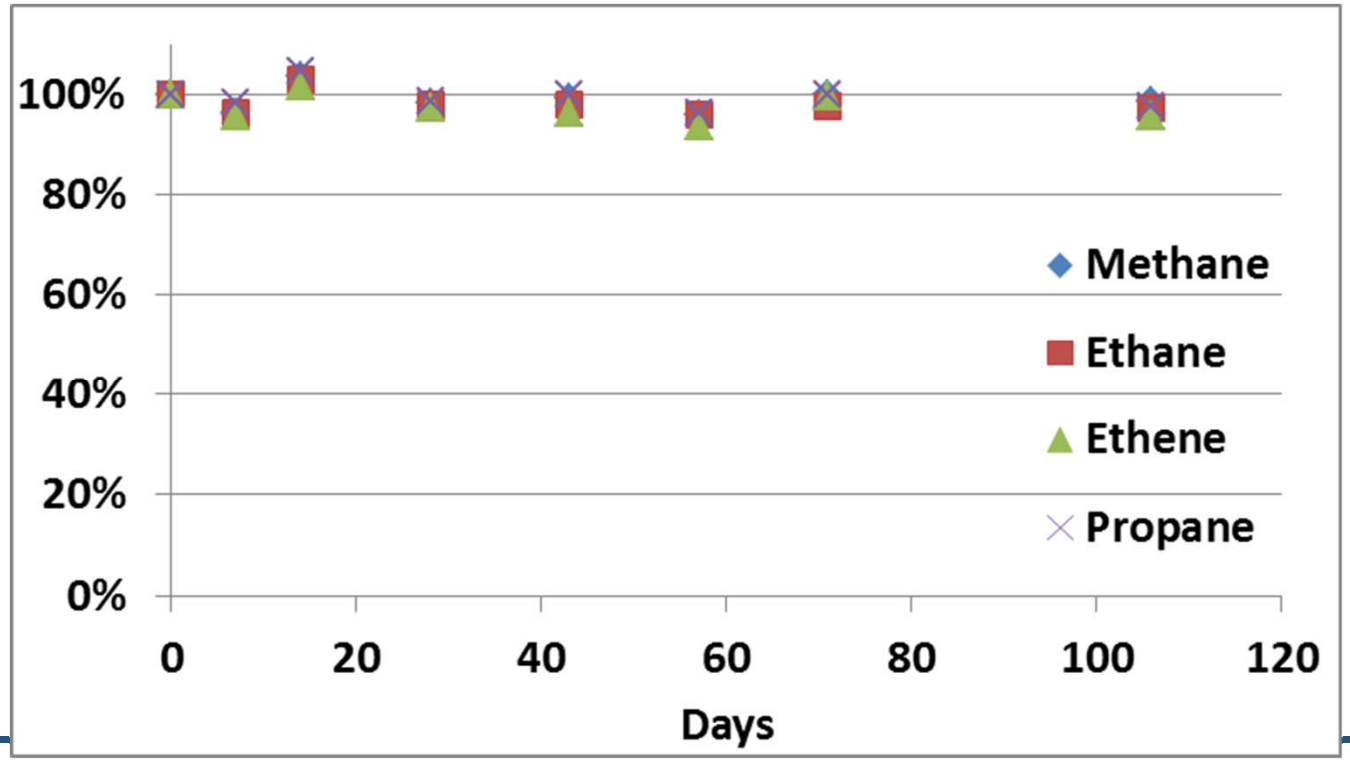
Methane 23.2 mg/L
Ethane 62.0 mg/L
Ethene 149.0 mg/L
Propane 76.7 mg/L

- Commercially available standard reference material
  - LGC has developed reference materials
    - Water SRM for MEEP compounds
    - 90 day shelf life, 4-6 mg/L
    - VHG-MEEP-5-40

Stability Testing

Water based calibration standards and QC samples

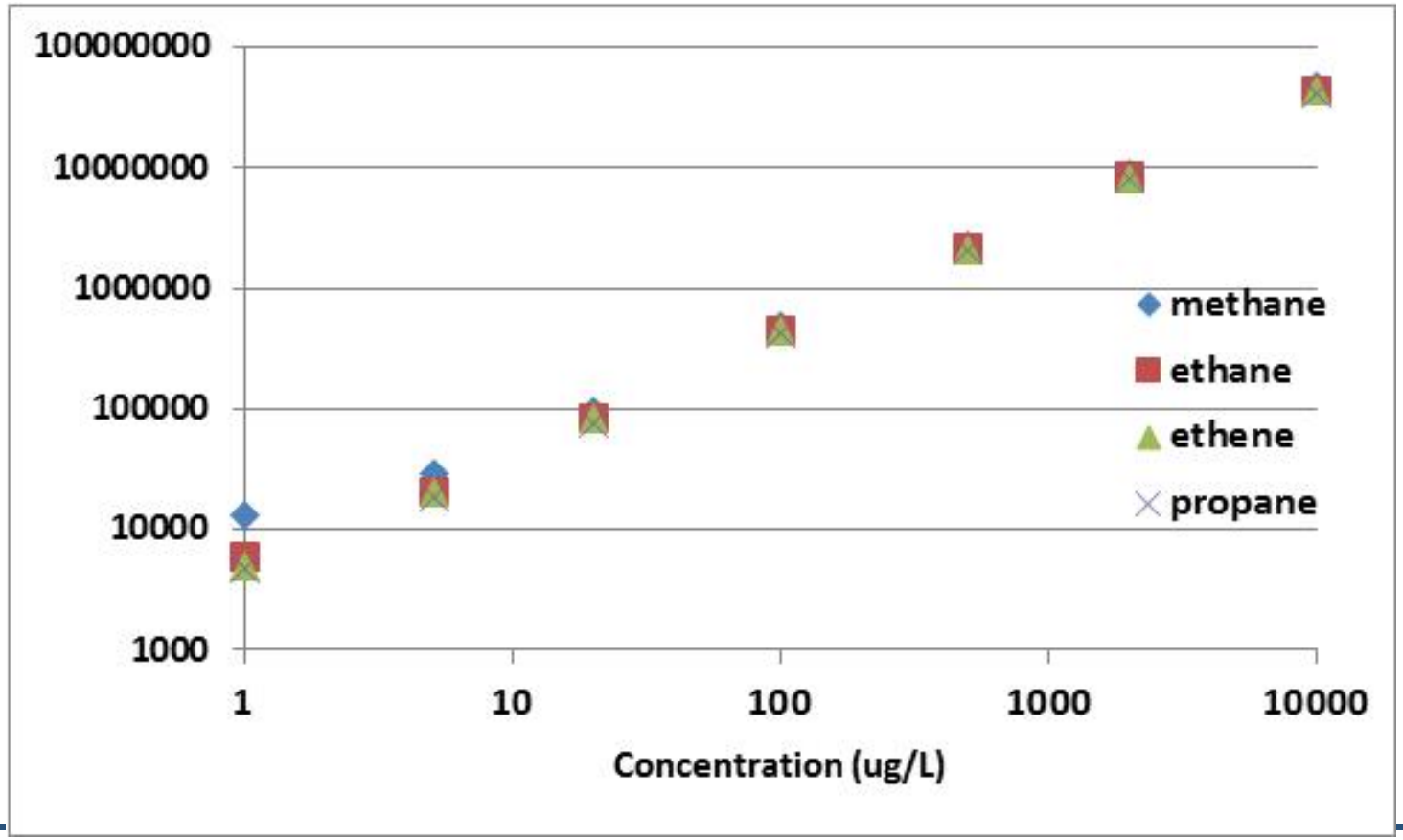
- Eurofins TestAmerica
  - 4 analyte formulation @10 mg/L
  - Months of stability - alternative storage container



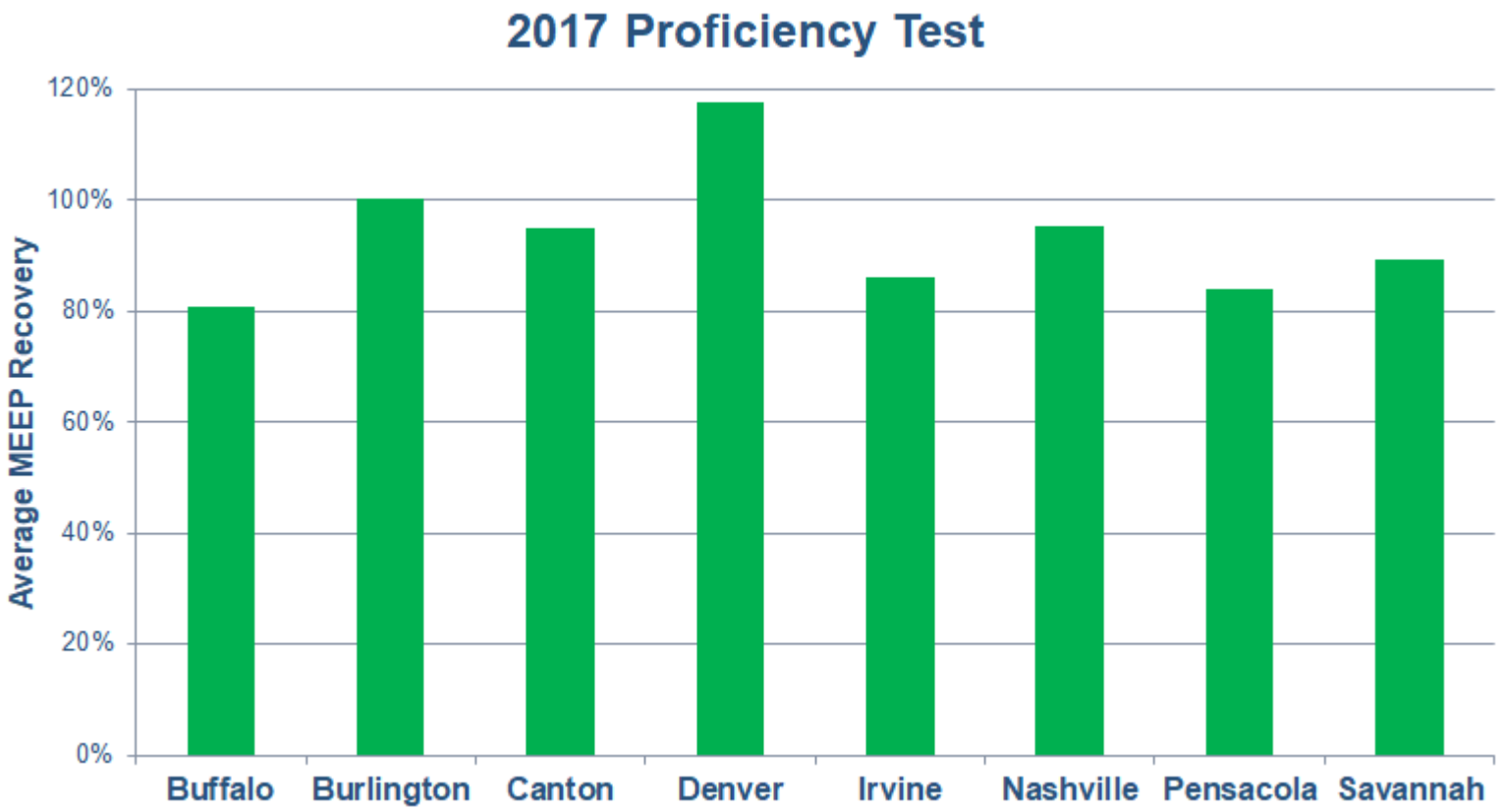
Calibration

Water based calibration standards

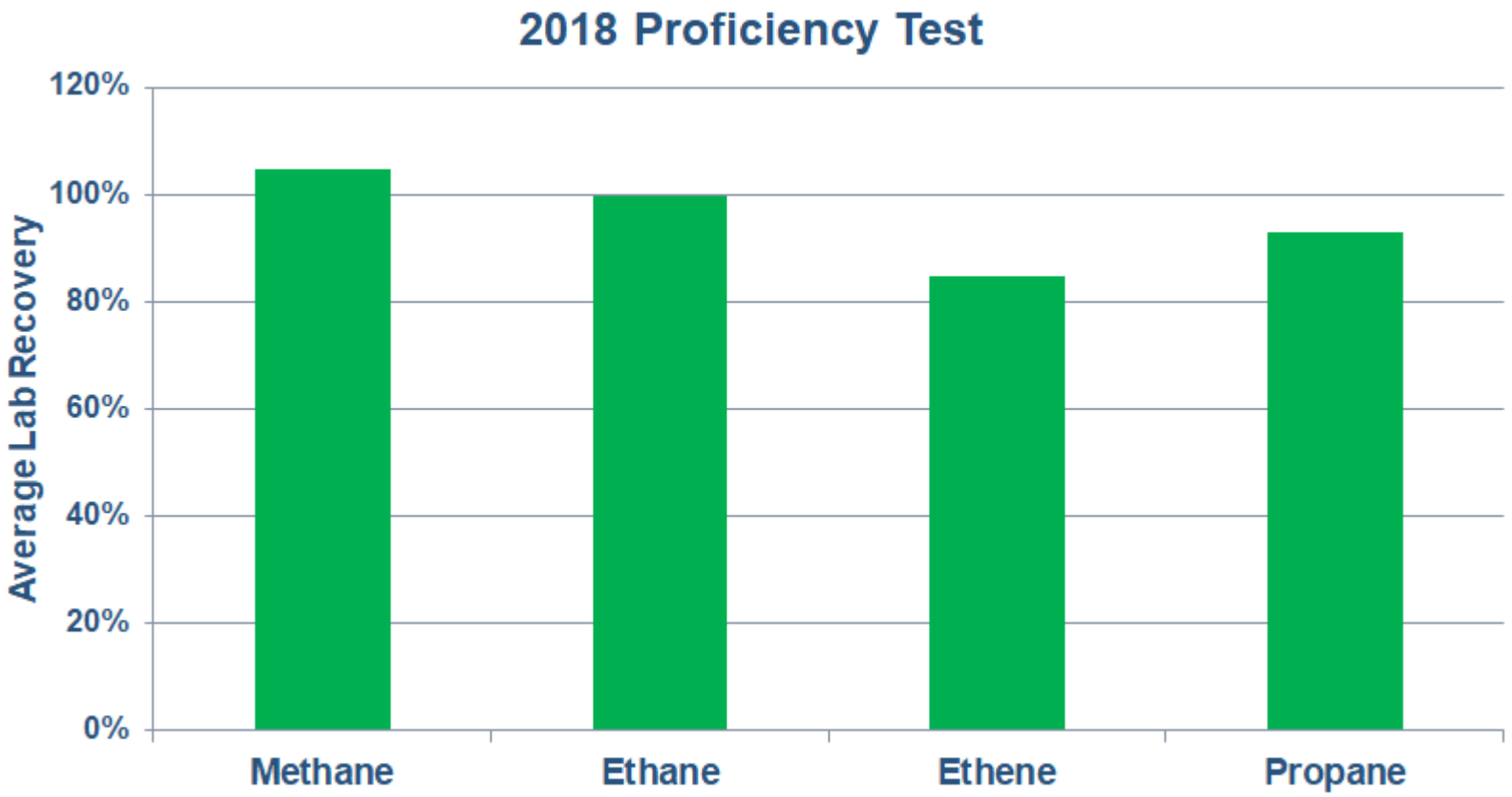
- 4 analytes in the same standard



Internal Proficiency
Test samples



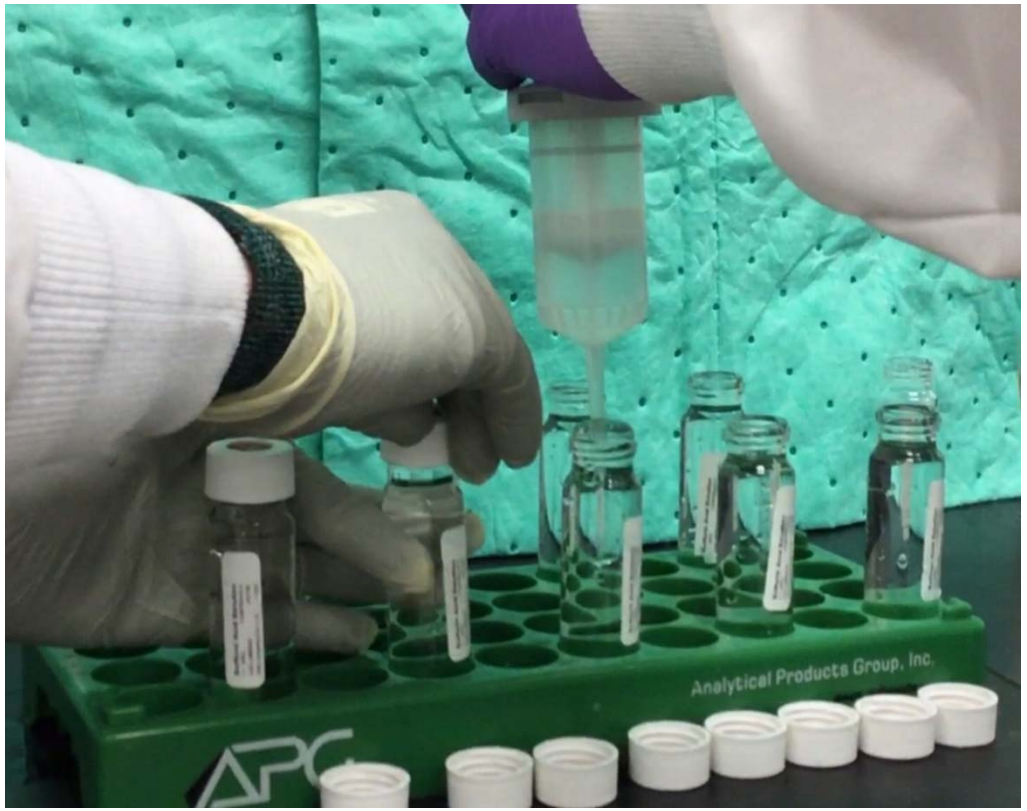
External Proficiency
Test samples



Implementing the Water SRM as LCS

Typical concentration:

- **4-6 mg/L**
  - **Methane**
  - **Ethane**
  - **Ethene**
  - **Propane**



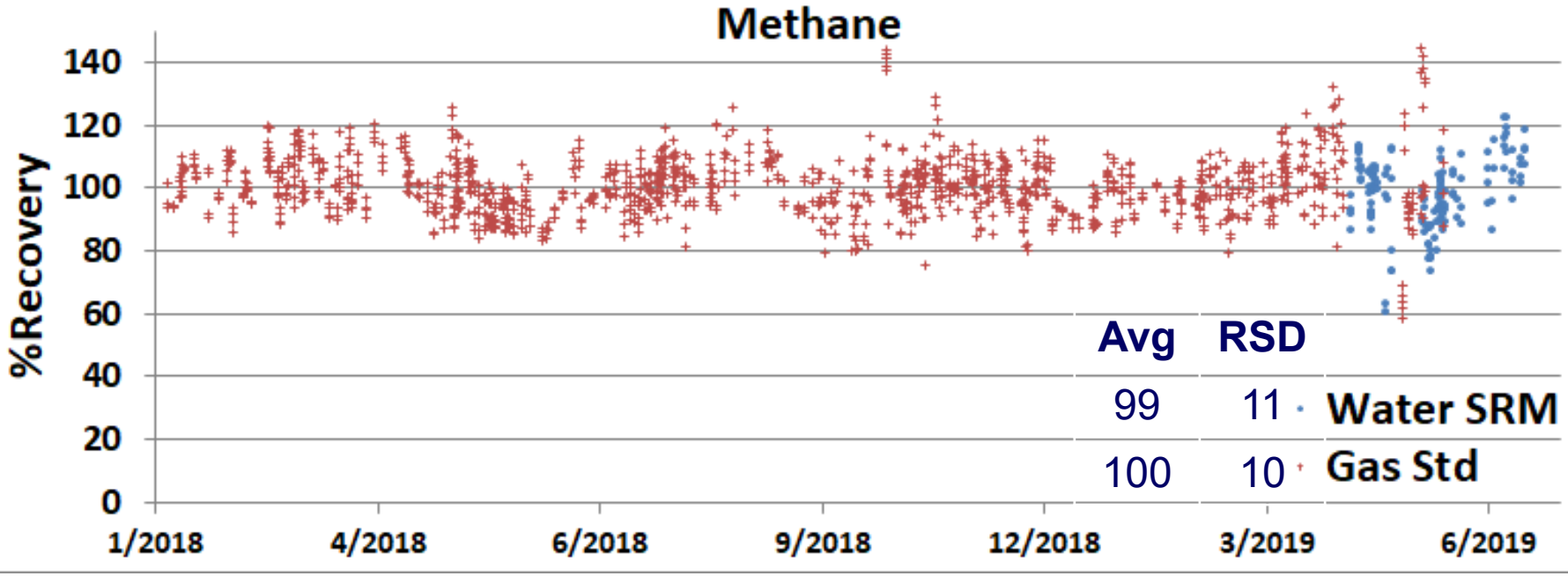
Dilute to 100-500 ug/L in VOC vial with butyl rubber septum

Looks like a field sample at this point

The handling process is now identical to field samples

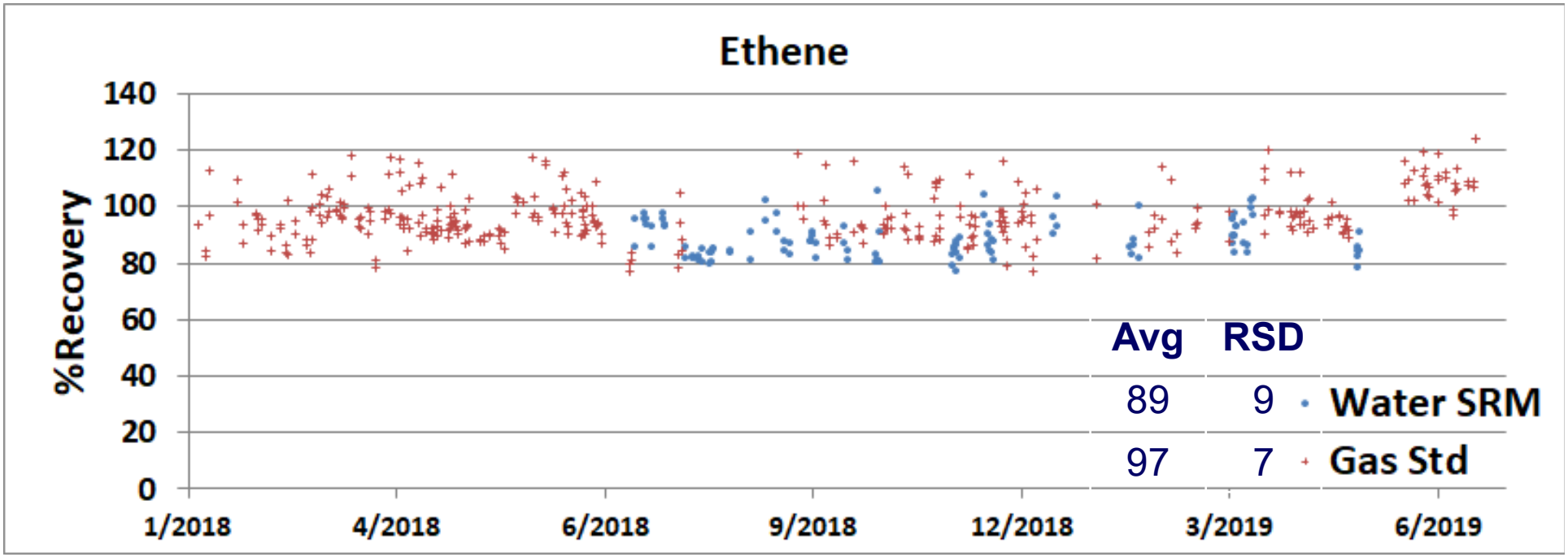
Does the LCS data change?

Sometimes not much



Does the LCS data change?

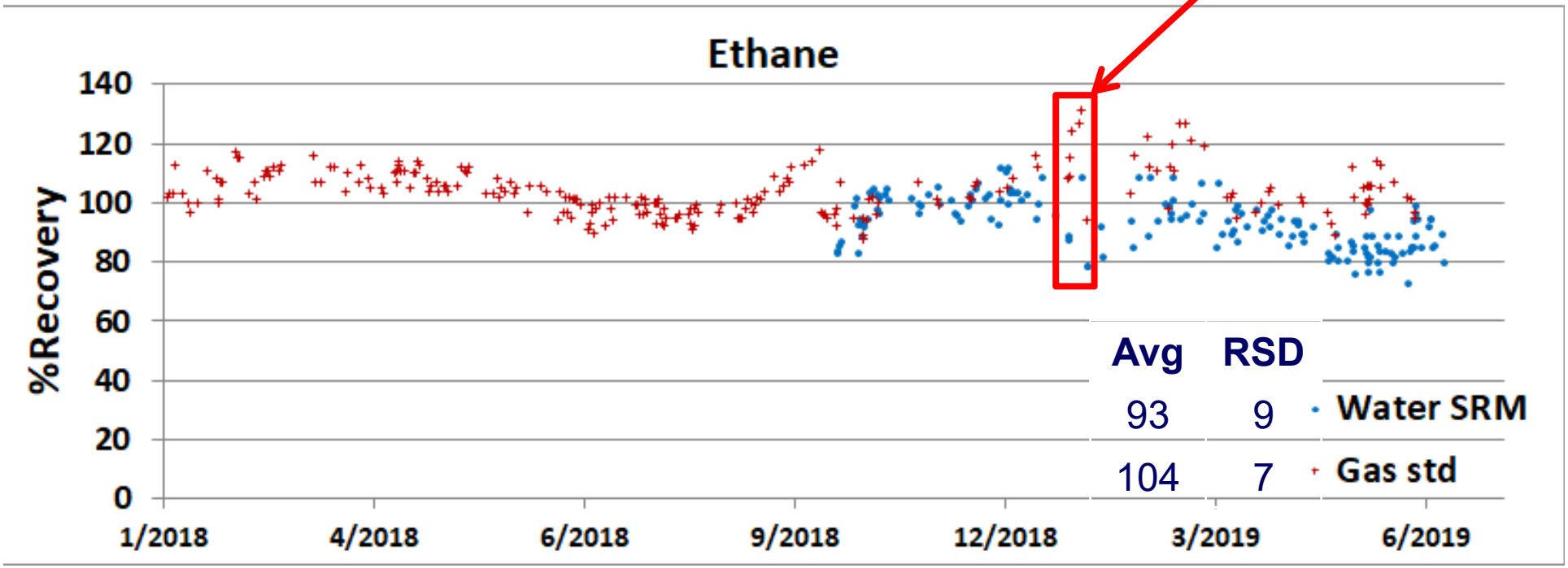
Sometimes a small reduction in recovery & small increase in RSD



Does the LCS data change?

Sometimes a small reduction in recovery & small increase in RSD

- Sometimes gas and water reference materials diverge



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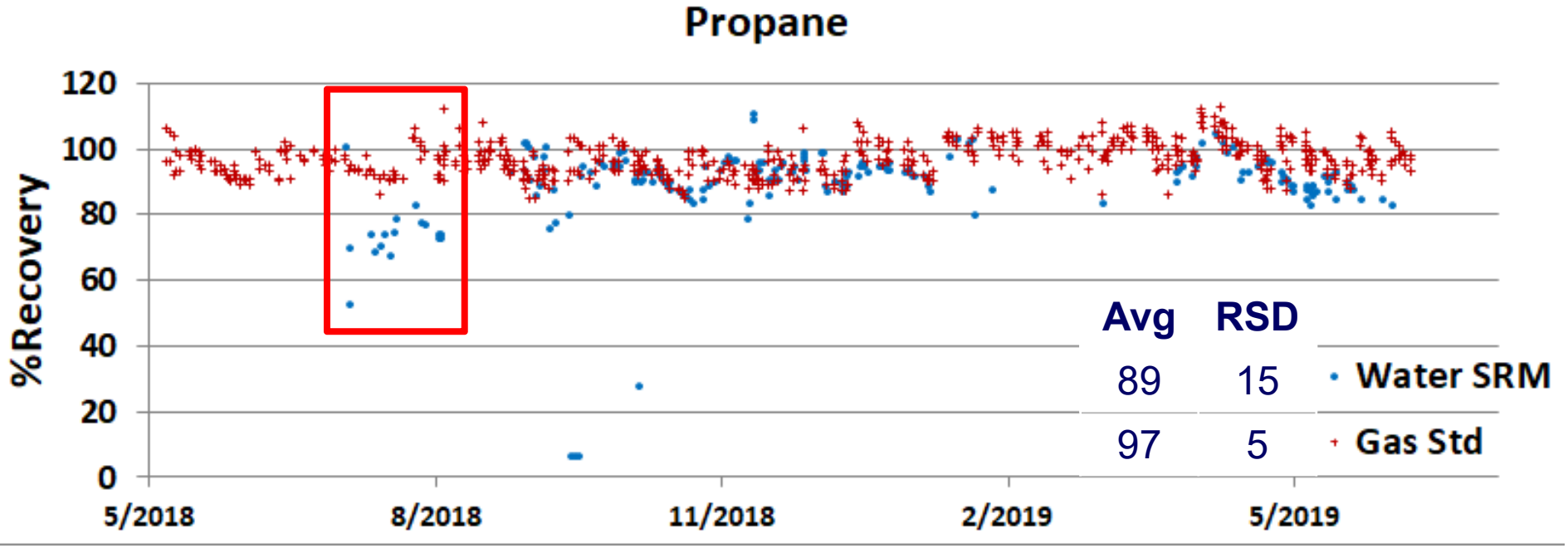

Lower bias and higher RSD are indicators

Possible causes

- Loss in transfer
  - Too much air exposure
  - Analyte outgassing in syringe
- Leaks
  - Holes in septa coupled with long delay to analysis
  - Autosampler plumbing connections
- Non-equilibrium headspace conditions
  - Key vulnerability when using gas phase calibration

Overall Averages

	Average %R	RSD
Methane		
Gas Std	101	8%
Water SRM	92	11%
Ethane		
Gas Std	101	7%
Water SRM	92	11%
Ethene		
Gas Std	101	7%
Water SRM	94	10%
Propane		
Gas Std	101	7%
Water SRM	87	13%

Summary

Multi-lab validated method

- ASTM D8028-2017 – study approved by ASTM, not scheduled
- Marcellus Shale Coalition – study planned soon

Water based PT, QC and calibration standards

- Lab based saturated stock water solutions
- LGC is the first commercial provider
- Use water based reference materials to find your “issues”

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