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# Web Conference Summary of February 25, 2013 Technical Workshop on Analytical Chemical Methods

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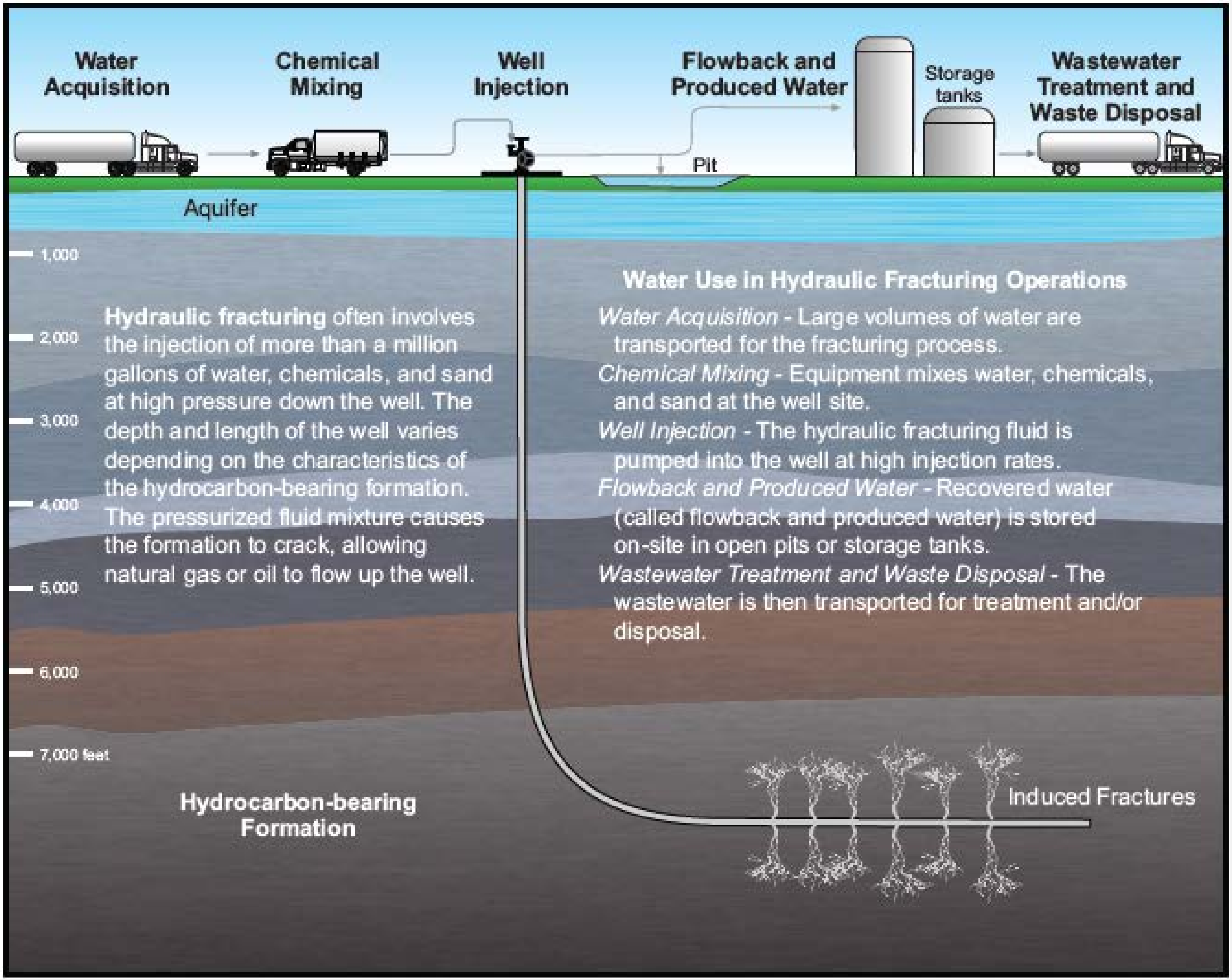
# EPA Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources

*EPA Study Goals*

- To assess the potential impacts of hydraulic fracturing on drinking water resources
- To identify the driving factors that affect the severity and frequency of any impacts

# Hydraulic Fracturing



# Hydraulic Fracturing Water Cycle

| Water Use in Hydraulic Fracturing Operations | Fundamental Research Questions |
|---|---|
| Water Acquisition | How might large volume water withdrawals from ground and surface water impact drinking water resources? |
| Chemical Mixing | **What are the possible impacts of releases of hydraulic fracturing fluids on drinking water resources?*** |
| Well Injection | What are the possible impacts of the injection and fracturing process on drinking water resources? |
| Flowback and Produced Water | **What are the possible impacts of releases of flowback and produced water on drinking water resources?** |
| Water Treatment and Waste Disposal | **What are the possible impacts of inadequate treatment of hydraulic fracturing wastewaters on drinking water resources?** |

**Bold lettering indicates research areas requiring analytical methods*

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# HF Water Cycle

| Water Use in Hydraulic Fracturing Operations | Secondary Research Questions Requiring Analytical Method Development |
| --- | --- |
| Chemical Mixing | What are the identities and volumes of chemicals used in hydraulic fracturing fluids, and how might his composition vary at a given site and across the country? |
| Flowback and Produced Water | What is the composition of hydraulic fracturing wastewaters, and what factors might influence this composition? |
| Water Treatment and Waste Disposal | What are the potential impacts from surface water disposal of treated hydraulic fracturing wastewater on drinking water treatment facilities? |

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# HF Water Cycle

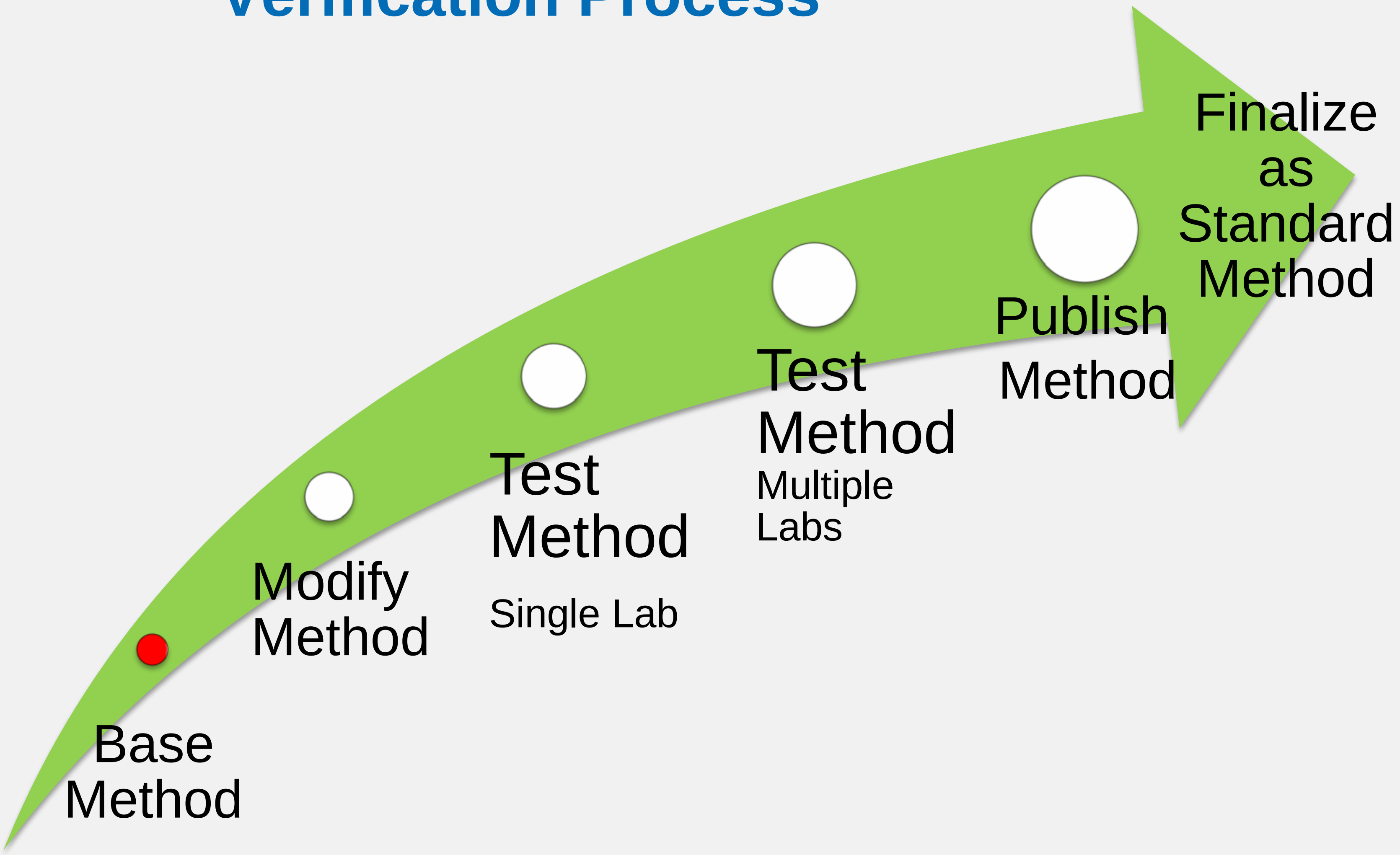
## Water Use in Hydraulic Fracturing Operations

**Chemical Mixing** → Glycols, Ethoxylated Alcohols, Alcohols, Alcohol amines, Amides, Aldehydes, Aromatic Hydrocarbons, Inorganic Elements, Halogens

**Flowback and Produced Water** → Glycols, Ethoxylated Alcohols, Alcohols, Alcohol amines, Amides, Aldehydes, Aromatic Hydrocarbons, Inorganic Elements, Radionuclides, Halogens

**Water Treatment and Waste Disposal** → Disinfection Byproducts, Inorganic Elements, Radionuclides

# Analytical Method Testing and Verification Process



# Analytical Methods Research

- Base Methods
  - SW-846
  - SDWA
  - CWA
  - ASTM
  - Peer reviewed journal articles

***NOTE:*** *Methods are available for the majority of analytes.*

*Goal of EPA research is to improve accuracy, precision and sensitivity of methods for hydraulic fracturing related matrices*

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# Analytical Methods Challenges

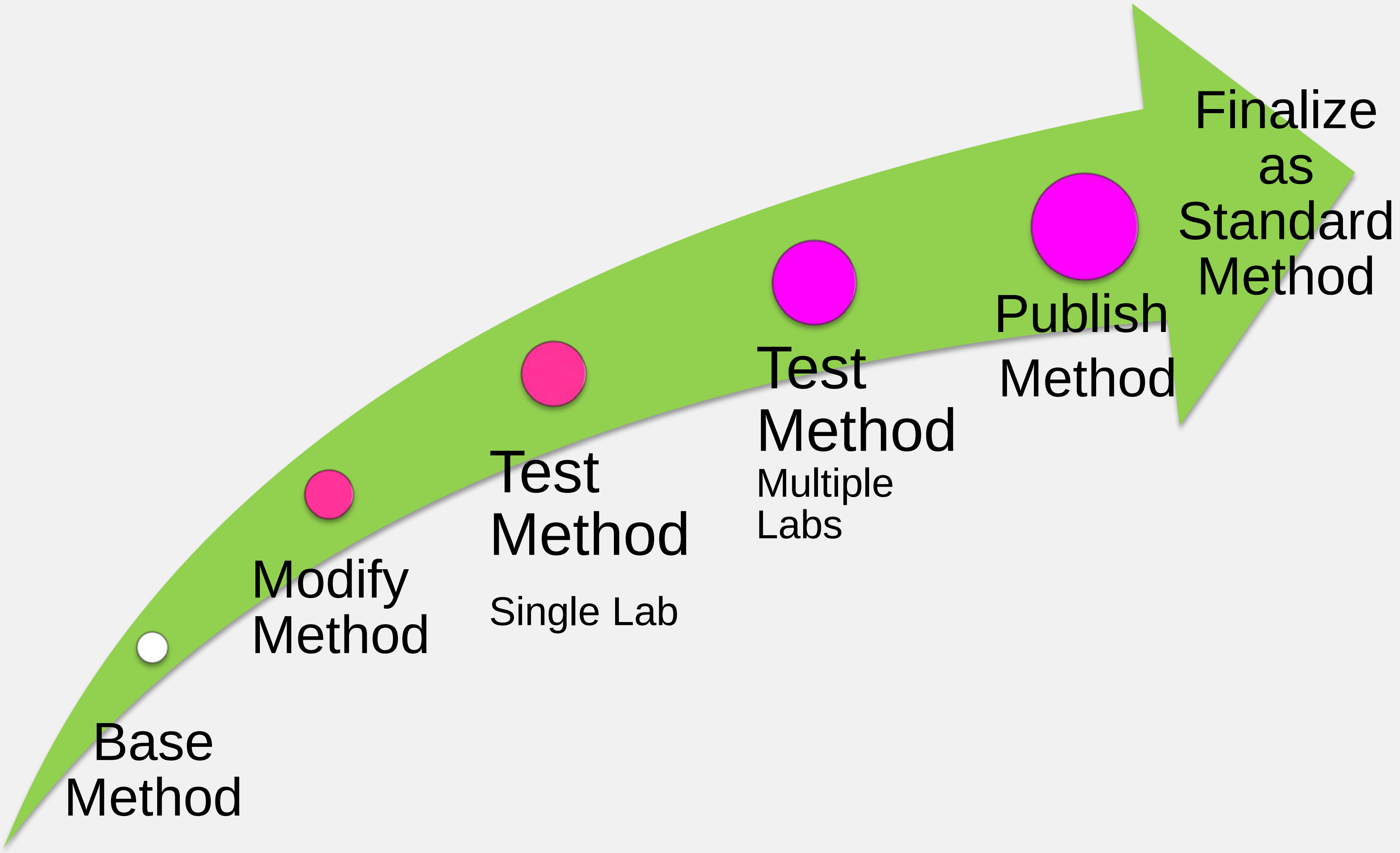
| Chemical Name | Base Method | Challenge |
|---|---|---|
| Glycols & related compound | SW-846 Methods 8000C and 8321B + ASTM D7731-11 | No standard method available to cover all compounds; detection limits too high |
| Ethoxylated Alcohols | ASTM D7485-09 | No standard method available to cover all compounds |
| Alcohols | SW-846 Method 5030 and 8260C | Confirmation in hydraulic fracturing related matrices |
| Alcohols, amine (diethanolamine) | No Standard Method | No standard method available |
| Amides (acrylamide) | SW-846 Method 8032A | Matrix interferences, and poor extractability |
| Disinfection Byproducts (bromide, bromate and haloacetic acids) | SDWA Methods 521, 551, and 552 | Matrix interferences |

# Analytical Methods Challenges

| Chemical Name | Base Method | Concerns |
|---|---|---|
| Aldehydes | SW-846 Method 8315 | Complex method, confirmation in hydraulic fracturing matrices; detection limits too high |
| Aromatic Hydrocarbons | SW-846 Methods 5030 and 8260C | Confirmation in hydraulic fracturing related matrices |
| Inorganic Elements | SW-846 Methods 6010C and 6020A or CWA 200.7 | Matrix interferences |
| Radionuclides (gross alpha & beta) | SW-846 Method 9310 | Matrix interferences |
| Halogens | SW-846 Method 9056A | Matrix interferences |

† - DWA methods may be found at http://water.epa.gov/scitech/methods/cwa/index.cfm). CWA methods may be found at http://water.epa.gov/scitech/methods/cwa/index.cfm. SW-846 Methods may be found at http://www.epa.gov/epawaste/hazard/testmethods/sw846/online/index.htm. ASTM – American Society for Testing and Materials, International.

# Analytical Method Verification Process



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# Analytical Methods Status

| Modify/Develop Method | Test Method Single Lab | Test Method Multiple Labs | Publish Method | Finalize Standard Method |
|---|---|---|---|---|
| Aldehydes | Radionuclides | Glycols | Ethoxylated alcohols | |
| Inorganic elements | Ethoxylated alcohols | | Acrylamide | |
| Halogens | Acrylamide | | | |
| DBPs (bromide, bromate and haloacetic acids) | | | | |

Future research will focus on alcohols, diethanolamine, and aromatic hydrocarbons.

# Analytical Method Development: Glycols as an Example†

- Glycols in drinking water wells
  - Di-, tri-, and tetraethylene glycol + 2-methoxyethanol and 2-butoxyethanol

– EPA SW-846 Method 8015C lists diethylene glycol but no others and not sensitive enough

– EPA Method 8321B, 8000C, and ASTM D7731-11 used in combination to create new method

  - Direct inject LC/MS/MS method

† - participating laboratories include: EPA Regions 3 and 5; EPA ORD Laboratories in Cincinnati and Las Vegas; Metropolitan Water District of Southern California; Philadelphia Water District; Eurofins Lancaster Laboratories; and TestAmerica, Inc.

# Analytical Method Development: Radionuclides – Gross α and β

- Radionuclides in produced waters and wastewaters
  - Gross α and β as a screening technique
  - Radium, Uranium, Thorium

- SW-846 Method 9310 is for gross α and β
  - Not sensitive enough and subject to high interferences from total dissolved solids and salts

- National Air and Radiation Environmental Laboratory in Montgomery, AL
  - Goal is method with minimum detectable activity of 30 and 50 with a method uncertainty of 30%

# Workshop Structure

- 2 Sessions
  – Analytical methods for chemical analytes
  – Future trends in hydraulic fracturing chemical usage and implications for analytical methods

- Participants were from EPA, USGS, DOE, states, industry, academia and non-governmental organizations
  – industry included: oil & gas companies, commercial laboratories, analytical standard producers and instrument manufacturers
  – just over 50 participants present

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# Questions for Consideration

- Participants were asked to consider the following six questions during the discussion:
  - What other/different/new methods or modifications should EPA consider for its analytes, and why (i.e., what limitations do these other methods overcome)?
  - What other analytes should EPA be testing for, and why? What methods would we use for other analytes? Are there any that EPA should *not* be testing for?
  - What considerations arise relative to the differences between various matrices (injection fluids, produced and flowback water) and the effects of high TDS, radionuclides,interference?

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# Questions for Consideration (cont)

- What levels of sensitivity are needed for analytical methods to detect effects or serve as indicators of connection to hydraulic fracturing?
- What defines “how low is low enough” in testing for an analyte?
- What has been your experience in addressing analytical challenges?

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# Session One Discussion Themes

## Baseline Information

- Importance of collecting baseline data to understand the quality of formation water & to be able to determine if a change has occurred
  - concentrations of organic matter and methane may be important
- Robust dataset needed because of temporal variability (e.g., seasonal variations, natural variability, and issues related to construction of private water supply wells)

## Sampling Procedures

- Guidance on baseline sampling (e.g., where, when, questions to ask about well operating conditions) would be helpful
- Sampling includes sample collection, timing of collection, preservation, holding times and storage
- Field turbidity measurements before and after sampling were recommended

# Session One Discussion Themes (cont)

## Analytical approaches

- Tiered approach suggested, first evaluating for key indicators such as high TDS, chlorine and sodium. Significantly elevated concentrations of these indicators would then trigger additional analyses

- Purpose of analysis is primarily for forensics (determining the source of contamination) rather than for evaluation of toxicity or water quality impacts, but should be doing both

- Natural temporal variability of water over time and the need for multiple lines of evidence
  - Additional parameters identified include: total Kjeldahl nitrogen (TKN), total organic carbon (TOC), and BTEX in wet gas locations

# Session One Discussion Themes (cont)

## Analyte Selection/Method Development

- Need to consider lab capability, availability of equipment, and costs for specific analytical methods (e.g., isotopic analysis of B)
- Analyses recommended for disinfection byproduct (DBP) precursors (not just DBP compounds themselves) that could render waste water more difficult and costly to treat to meet the waste water disposal regulations
- Radionuclides, radium-226 and radium-228 data valuable but gross alpha data was not as useful
- Methylene Blue Active Substances (MBAS) assay, a colorimetric analysis test method to detect the presence of anionic surfactants, not recommended
- For evaluating isotopic signatures, participants suggested considering existing information such as Compound-Specific Isotope Analysis (CSIA)

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# Session One Discussion Themes (cont)

## Quality Assurance/Quality Control (QA/QC)

- Importance of developing a strategic sampling plan was discussed
- In the field:
  - Important to take preserved and unpreserved samples, equipment blanks, field collection blanks and replicates.
- In the laboratory:
  - Important to developing methods specific to the matrix of concern (i.e., determine sensitivity and detection limits based on the actual matrix and not try to make a method applicable to everything)
  - Run blanks to catch contamination (e.g., glycol in HCl preservant)
- Suggestion that EPA determine meaningful holding times for archiving and for regulatory acceptance

# Session 2

- 2 Sessions
  – Analytical methods for chemical analytes
  – Future trends in hydraulic fracturing chemical usage and implications for analytical methods

- Participants were asked to consider the following 2 questions during the discussion:
  - What is changing in the chemical makeup of hydraulic fracturing injection fluids, and what are the implications for chemical selection or field sample analysis?
  - What has been your experience with artificial tracers for tracking hydraulic fracturing fluids? What analytical methods are suitable?

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# Session Two Discussion Themes

## Changes in hydraulic fracturing fluid composition and implications for chemical selection and analysis

- Makeup of hydraulic fracturing fluid is changing, as companies learn what works best, look for more environmentally friendly chemicals with the same performance, and strive to use less fresh water
- List of additives is shrinking and is not static. It is continually evolving as some new compounds are added for specific needs depending on geology
- Reuse of flowback and produced water is on the rise, and the makeup of reused water can decrease the need for chemical additives
  - There are limits regarding the quality of reused water, and treatment costs must be considered
- The issue of matrix interferences and the need for standard/certified reference materials was also raised in the context of water reuse

# Session Two Discussion Themes (cont)

## Tracers and associated analytical methods

- Use of tracers (as distinct from indicators) necessitates scientific assessment (e.g., what happens to tracers under high temperature/pressure conditions) before EPA incorporates them into the study
    - Tracer is chemical added to movement of fluids
    - Indicators are in HF fluids and generally used to check well integrity

- Current tracers include perfluorocarbon tracers (PFTs) and isotopic tracers.
    – For PFTs, it was noted that there are tradeoffs, such as the high global warming potential of PFTs, disposal costs and suitability
    – For radioisotopes, limited number of suppliers complicates use

# Session Two Discussion Themes (cont)

## **Detection limits -** "How low is low enough?"

- Questions raised about the use of a statistically determined method detection limit (MDL) as identified in 40CFR Part 136
  - Dichotomy identified in regulatory programs.
    - In SW-846, recommend use of the lower limit of quantitation (LLOQ) instead of the MDL
    - Clean Water Act and Safe Drinking Water Act regulations specify the MDL

## Field sampling for methane

- Grab sampling versus capturing methane in a submerged collection system discussed
    - A retrospective case study in Colorado was looking at the reproducibility of the submerged method
- In-line sampling at hydrostatic pressure and laser-based devices to measure methane and carbon isotopes also available
- Recommendation that EPA establish field protocols and quality assurance/quality control procedures for methane sampling

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# Next Steps

- This Analytical Chemical Methods workshop is the first in a series of five technical workshops related to EPA's Hydraulic Fracturing Study.
- Info on upcoming April and June 2013 workshops can be found at: http://www.epa.gov/hfstudy/techwork13.html
- Interested parties are requested to submit data and scientific literature to inform EPA's Hydraulic Fracturing Study by April 30, 2013, as described in the November 9, 2012 Federal Register notice at: http://www.gpo.gov/fdsys/pkg/FR-2012-11-09/html/2012-27452.htm