

Analytical Considerations During Natural Gas Fracturing Activities

Technical Workshop on Analytical Chemical Methods
EPA Research Triangle Park Campus
Research Triangle Park, NC
February 25, 2013

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 - Case Study
 - Lesson Learned

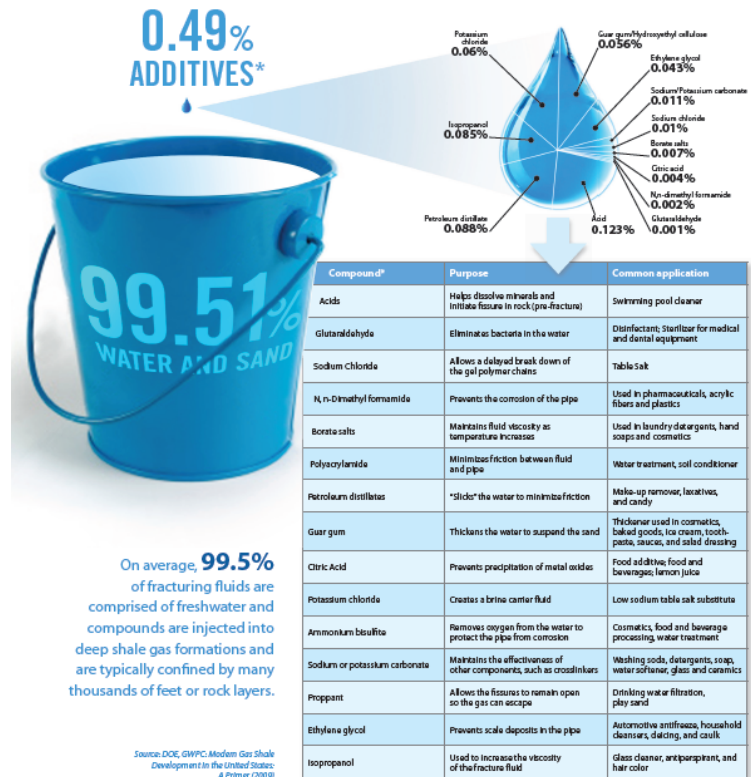
Opening Comments

- High-quality analytical data before, during, and after production processes increasingly important to document baseline and post-drilling groundwater and surface water quality
 - Thorough knowledge of the pre-existing conditions
 - Thorough documentation of S&A activities
 - bottleware, sampling and handling processes
 - sample preparation and instrumentation and methodology used for testing
- Equally important is the characterization and analysis of unusual analytes that may be present in fracturing solutions

Fracturing Fluids

- Typically - 98-99% water and 1% chemical additives (e.g., dilute acids, bactericides, corrosion inhibitors, gelling agents, friction reducers, surfactants) and silica sand and man-made ceramics
- Many chemical additives are not routinely tested for by laboratories
 - Bottleware and preservatives are not certified for these non-routine parameters
 - For analytes that are not included on published method lists, a robust method development process is necessary to ensure a complete characterization, preferably *before* a release takes place.

A FLUID SITUATION: TYPICAL SOLUTION* USED IN HYDRAULIC FRACTURING



*The specific compounds used in a given fracturing operation will vary depending on source water quality and site, and specific characteristics of the target formation. The compounds listed above are representative of the major material components used in the hydraulic fracturing of natural gas shales. Compositions are approximate.

Case Study One: Overview

- Unknown amount of flowback water released
- Sampling program of 45 residential water wells
- Team chemists observed large number of glycol detections and suspected contamination given the similarity in concentrations
- Suspected contamination; investigation revealed
 - Field blanks not collected – no need for tap sampling?
 - Preserved vials used for sampling were not pre-tested
 - Vials used for lab method blank were not preserved
 - Analysis of vial lot # confirmed glycol contamination
 - Resampling using certified vials yielded ND for glycol

Case Study One: Lessons Learned

- Standard Operating Procedures including field QC must be in place
 - A single documented lot of bottleware and preservatives must be used for a sampling event
 - Field blanks must be collected using the same lot number of bottleware used for samples
 - Any bottleware/preservatives used for sample collection must be pre-tested prior to use for the analytes of interest to the reporting sensitivity
 - Do not assume the laboratory has already done this
 - Laboratory method blanks should be stored in the same type of preserved bottles used for samples
- Sampling teams should undergo periodic third-party field audits

Case Study Two: Overview

- Surface release of large volume of fracturing fluid
- Material Safety Data Sheets for the chemical additives revealed two compounds, directly indicative of the additives, are not routinely tested for by laboratories
- Emergency method development was required
 - Extraction and analysis techniques, including method detection limit (MDL) studies, precision and accuracy and definitive analytical finishes (one by LC/MS and one by GC/MS)
 - And we need it YESTERDAY

Case Study Two: Lessons Learned

- Analytical methods may not exist for the contingent characterization data needs of hydraulic fracturing activities
- It is prudent to have analytical methods on line for selected marker compounds being used during fracturing activities
- Time, cost, capacity, and TAT need to be considered when developing methods whether proactively or on an emergency basis in the event of a release

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