Improving Dissolved Hydrocarbon Gas Analysis in Water

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Background/Objectives. Groundwater analysis for methane and other light hydrocarbon gases is an important component of monitoring biological processes for in situ remediation and natural attenuation at chlorinated solvent contaminated sites. It is also used for predrill background studies to support hydraulic fracturing activities in the various shale plays as a common risk management strategy. Post drill characterization can also be performed when changes in groundwater are suspected. There is no fully validated USEPA method for this type of analysis. ASTM recently released D8028 to address many of the limitations of the previous analytical options. Other organizations are also considering development of improved analysis methods. One company is developing water-based reference materials that can be used as external proficiency test samples, analysis batch QC samples and calibration standards. This will provide laboratories with the opportunity to diagnose internal process problems and impartially demonstrate method performance to clients and auditors.

Approach/Activities. Analytical process differences between handling of water samples and gas phase based standards can introduce a low bias in the final results. These biases arise from analyte losses and non-equilibrium conditions. Use of water-based reference materials facilitates evaluation of each step in the analytical process. Switching to water-based calibration standards and QC samples can significantly improve the accuracy of the final results. The stability of water-based standards for methane, ethane, ethene and propane have been studied in several different storage scenarios. Adding a representative surrogate compound to the sample at the beginning of the sample preparation process tracks the integrity of the process for every sample. Different techniques for sample transfers between containers and dilutions have also been studied.

Results/Lessons Learned. Water-based reference material stability ranges from a few hours to several months depending on the container and storage conditions. Many different hydrofluorocarbons were evaluated as surrogate options. Selecting the optimal difluoro-, trifluoro- or tetrafluoro-ethane compound will depend on the specific hydrocarbon gases of interest, the chromatographic column and GC parameters. When determining the C1-C4 hydrocarbons and using a Q PLOT column, 1,1,1-trifluoroethane elutes at an acceptable retention time and has similar volatility and solubility characteristics to the hydrocarbons. Water-based reference materials with dissolved hydrocarbons have been used to investigate and correct a variety of laboratory sample handling processes. These include water sample and standard storage, transfer from field vial to autosampler vial, dilution, headspace development and equilibration. Cumulative losses have been corrected in order to consistently meet the expected 70-130% recovery range.