Detection of Methane from Water Sources

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Introduction

With the Marcellus shale drilling in Pennsylvania, there has been a concern for the ecological effects on water sources. Some of the contaminants that could be released into these water sources are natural gases like methane and ethane. This research aims to optimize the method for detecting and quantifying these dissolved gasses in water sources. Once the method is optimized, it will be implemented for future water quality studies.

This study will expand on methodology used in the Marcellus Shale Gas Drilling and Tioga County Well Water Quality research done over the summer of 2015 with Drs. Michele Conrad, Shaker Ramasamy, and Paul Wendel. The U.S. Environmental Protection Agency procedure for collection of the water was followed, where water was collected in airtight vials and sealed after acidification of water.

Experimental Setup

Standards were made by bubbling natural gas from a fume hood into a volumetric flask for 3-5 hours at constant temperature of 23°C. The samples were then made based on calculation of solubility that the concentration of methane in the water at 23°C is 23.59 ppm.

Immediately preceding analysis, a headspace was introduced in the methane sample vials by removing 7 mL with a syringe. To reach equilibrium, the vials were agitated on a rotary shaker for ten minutes and heated in a constant temperature bath at 35°C for ten minutes. The headspace gas was injected with a 100 µL gas-tight syringe into the GC/MS. The GC oven was held at 30°C for 2 minutes, ramped at 15°C/min to 120°C and held for 1 minute. The carrier gas used was helium, and the overall time was nine minutes. The retention time for methane was 1.75 minutes.

The GC/MS parameters were held steady, while the testing method was improved by observing the parameters of deterioration of samples over time, effects of headspace, and equilibrium temperature. Calibration curves were collected for various equilibrium temperatures.

Calibration Curves

Differences in Water Bath Temperatures

- (35°C) y = 203127x - 162500
  R² = 0.9893
- (45°C) y = 179825x + 46315
  R² = 0.9942
- (60°C) y = 147171x + 59449
  R² = 0.9789

Headspace Analysis

 effect of headspace removal were observed by preparing two identical samples. One had the headspace removed on the day it was prepared and the second was stored for a week before the headspace was removed.

Reproducibility

Multiple samples prepared at the same concentration and measured under the same conditions to determine reproducibility of standard samples.

Example chromatogram from the GC/MS and the peak for methane is highlighted.

Results and Discussion

Calibration Curves for Different Equilibrium Temperatures

Effect of Time on Sample Concentration

Samples of 0.214 and 23.59ppm were measured over time. The samples were stored in a refrigerator.

Conclusions and Future Plans

The conclusions so far in this research that the temperature of equilibrium of the water bath does not have an effect on the calibration curve, the effects of deterioration is linear over time, and that the effect of when a headspace removed has no effect over time. These results can be applied to improve the methodology in the well water testing phase four done by students at Mansfield University.

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