



Dissolved Methane Sampling and Analysis Techniques

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Background



The analysis for dissolved methane in water is an important parameter in baseline monitoring.

Methane can occur naturally in water wells.

The analysis of methane and other dissolved gases is important for determining if bioremediation is occurring.

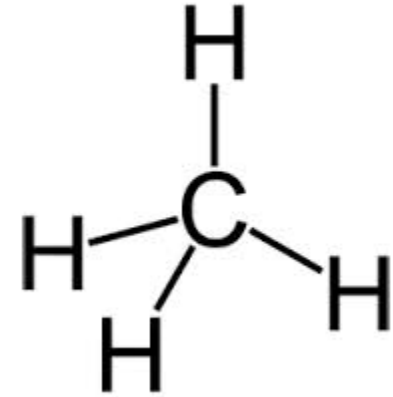
Therefore, the assessment of “clean” drinking water or water aquifers is significant.

Background



Methane

- Boiling point = -161°C
- Molecular Weight = 16.04 g/mol
- Solubility in Water = 22.7 mg/l



Background



Several analytical approaches have been used for the analysis of methane (and dissolved gases);

- RSK-175
- PA DEP 3686
- PA DEP 9243
- EPA 8015 (coupled with 5021)
- ASTM (proposed)

Background



Dilemma

There are differences between the methods and differences between laboratories performing the “same” method.

Statement from MSC Proposal to Investigate Dissolved Methane Methods,

“Dissolved methane results from water samples collected from the same source at the same time are comparable when analyzed within an individual laboratory but are not comparable when analyzed by different laboratories.”



RSK-175

- Originally developed at R.S. Kerr Environmental Research Center, Ada, OK.
- The method is an EPA Lab SOP. Each version of the procedure contains the following disclaimer;

“This standard operating procedure has been prepared for the use of the Ground Water and Ecosystems Restoration Division of the US EPA and may not be specifically applicable to the activities of other organizations. **This is not an official EPA approved method.**”



RSK-175 (cont'd)

- Method (“sop”) uses headspace for sample introduction.
- Gas Chromatography with Flame Ionization Detection (GC/FID) is determinative step.
- Multi-point calibration with gas standards.
- Use of Henry’s constants
- Samples collected in serum bottles of unspecified volume. Practice is to use 40 ml VOA vials.
- Analysis technique set-up to accommodate several dissolved gases in addition to methane including ethane, ethene, propane, butane and acetylene



RSK-175 (cont'd)

- Recommends use of acid preserved vials, which allows a sample holding time of up to 14 days
- Sample handling by helium displacement
- Samples warmed to “room temperature” for analysis



PA DEP 3686

- Developed by PA Bureau of Laboratories (BOL).
- Revision 0 date April of 2012, but in-house version in use for several years prior.
- Headspace GC/FID.
- Multi-point calibration with aqueous standards. Aqueous standards prepared by bubbling gas into laboratory water until water is saturated.
- Only a single compound can be calibrated at a time.
- Listed as applicable to methane, ethane and propane.



PA DEP 3686 (cont'd)

- Holding time of 7 days in unpreserved 40 ml vial
- Samples handled/transferred by opening 40 ml sample vial
- Presentation at NEMC in Washington, DC substantiating handling technique
- Dilutions prepared in headspace vials, able to be stored up to 7 days at $<6^{\circ}\text{C}$



PA DEP 9243

- Developed by PA BOL in conjunction with an instrument manufacturer (Tekmar)
- Revision 0 from October of 2012
- Uses Purge and Trap (P&T) with GC/FID
- Multi-point calibration using aqueous standards prepared similar to 3686.
- Only a single compound can be calibrated at a time.
- Method makes several references to “sequestering” of methane within the system.



PA DEP 9243 (cont'd)

- As written, method applicable to methane, ethane, ethene and propane
- Requires maintaining sample temperature at $<10^{\circ}\text{C}$ while handling for analysis
- Holding time of 7 days in an unpreserved 40 ml vial



EPA 8015/5021

- Very generic EPA method
- Headspace GC/FID
- Multi-point calibration
- Preparation of calibration standards defined by laboratory SOP
- Based on use of gas standards or gas injected into water standards, multiple compounds calibrated for at same time



ASTM (proposed)

- Uses headspace GC/FID
- Multi-point calibration using an instrument manufacturer's (EST) equipment for the sample handling
- Calibration based on use of aqueous standards.
- Only a single compound calibrated for at a time.
- Handling of sample automated by instrument
- Method applicable to analysis of methane, ethane, ethene and propane



ASTM (proposed)

- Holding time of 7 days in unpreserved 40 ml vials
- Samples allowed to warm to “room temperature” prior to handling and analysis

Example



Comparison of Methane Results – RSK-175 vs PA-3686

ELLE Sample Number	RSK 175	DL		PA-3686	DL	%D
6967112	2212	20		1487		-32.8%
6967124	87	1		95		9.0%
6969152	8.9	1		12		35.3%
6967155	16	1		18		9.9%
6967159	5.7	1		8.4		48.4%
6967171	63			34		-45.8%
6967181	5565	50		3597		-35.4%
6968046	127	1		81		-36.5%
6971873	51083	250		40210	10	-21.3%
6971874	80834	250		50384	10	-37.7%

So Why the Differences?



1. Sample Handling

- What is the sample collected in?
- How is it transferred to the analytical system?
- At what temperature is the analysis performed?

2. Calibration/Calibration Standards

- How are calibration standards prepared?
- What calibration range is covered?

Example



Evaluation of Calibration Types

Parameter		RSK 175			PA3686
	Conc	% Error		Conc	% Error
Calibration level 1	5 ppb	-6%		11.6	24.0%
Calibration level 2	15 ppb	-0.9%		23.2	14.1%
Calibration level 3	60 ppb	7.3%		116	-12.6%
Calibration level 4	100 ppb	5.9%		580	6.1%
Calibration level 5	150 ppb	4.1%		2320	1.1%
Calibration level 6	500 ppb	3.3%		5800	-3.9%
Calibration level 7	na			11600	-3.4%
Calibration level 8	na			17400	-9.9%
Calibration level 9	na			23200	-15.4%
Avg % Error		4.60%			10.00%
Coefficient of Determination		0.9976			0.9649

So Why the Differences?



3. Surrogate Standard Use

- Is a surrogate standard used?
- How is it introduced?

4. Specifics of Sample Analysis

- Does chromatographic system discriminate methane from other dissolved gases?
- How are dilutions performed?
- Is sample injection manual or automated

So Why the Differences?



5. Sample Collection

- How is sample collected?
- Is a preservative used?
- What is timeframe for analysis?

Next Steps



Marcellus Shale Coalition (MSC) is conducting an inter-laboratory study for the analysis of dissolved gases, specifically methane.

Goal is to identify the critical values that lead to variability in results between laboratories.

Try to identify a consensus standard for the analysis of light gases in groundwater.



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