Automated, Rapid and Reliable Determination of Dissolved Gases in Water by Static Headspace – Gas Chromatography

A. Caruso, M. Santoro, F. Bedini, P. Magni, S. Pelagatti

Thermo Fisher Scientific, Milan, Italy

Overview

Purpose: Exploring the possibility to perform a quantitative determination of dissolved gases in water in a reliable and accurate way

Methods: The quantification of dissolved gases is performed by building a calibration curve spiking blank water samples with increasing quantities of saturated water followed by headspace sampling and GC/ FID analysis.

Results: The results show good correlation factors and limit of quantification lower than 10 ppb for the four gases analyzed.

Introduction

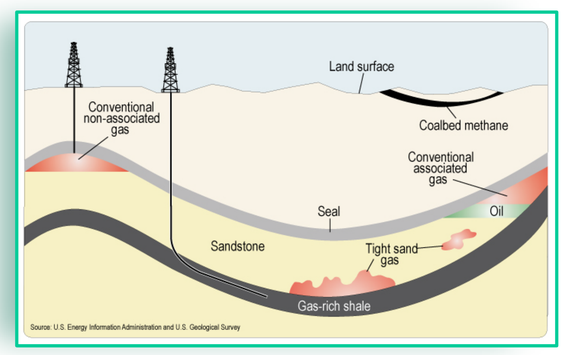
Hydraulic fracturing or fracking is a technique that consists of pumping water into a wellbore to create small fractures into which fluids can migrate and be collected into the drilling well (Figure 1). Fracking facilitates the extraction of natural gas from shale plays in which it is unreachable with conventional technologies. The importance of this technique is increasing with the depletion of “traditional” gas fields offering the possibility to access a new energetic source.

With the spreading of fracking, concern is raising about its safety and sustainability for the environment, in particular for air and water quality. Fracking processes can impact the quality of groundwater by leakage of gas, exposure to chemicals used during the drilling and mobilization of salts and metals from the subsurface.

For various chemicals, official methods, S.O.Ps and protocols do exist that offer guidelines for their analysis in water. However, there is not yet a formal method for the analysis of dissolved gas into ground or drinking water.

The analysis is not particularly challenging from a chromatographic standpoint, and the main issue involves the preparation and storing of samples and standards.
To date, regulatory agencies ,such as the EPA and state public health labs have not developed a validated method, although some US states have adopted legislation and regulations for the *baseline monitoring* of methane.

FIGURE 1. Fracking process.



Methods

The most widespread method for monitoring gases in water is the RSK-175 SOP, developed by Robert S. Kerr, that tests for dissolved gases through static headspace gas chromatography and then calculates the results according to Henry’s Law.

RSK-175 is not an official EPA -approved method, but is widely applied in environmental laboratories and dictates all necessary steps to collect , prepare, and store samples. The method validation is currently being submitted as a work item to the ASTM D19.09 subcommittee on hydraulic fracturing.

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Standard preparation and sample chain of custody can be considered the most delicate parts of the Work Item.

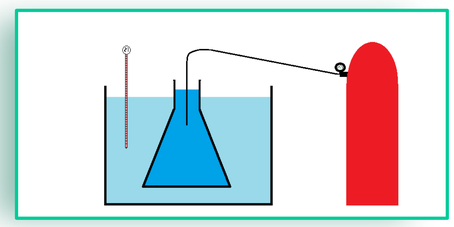
In this work, we focus on the analysis of methane, ethylene, ethane and propane in water following **ASTM Work Item WK43267** to prepare the samples.
The gas content was quantified by building a calibration curve obtained by spiking deionized water with increasing amounts of water previously saturated with those gases.

Standards Preparation

The following materials were used:

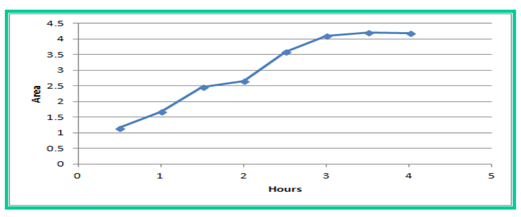
- Gas standards for methane, ethane, ethylene, propane
- 500 mL glass flask, for deionized water
- Water bath, with temperature control
- Luer lock syringes with shut off valve to transfer saturated water volumes
- The 500 mL flask is placed into the water bath maintained at 20 °C
- Standard gas is bubbled from the cylinder directly into the flask for three hours with a flow of 12 mL/min circa (Figure 2).
- A 20 mL headspace vial is filled up with the saturated water and capped immediately without leaving headspace into the vial
- Water aliquots are taken from this vial with the valve syringe and used to build the calibration curve.

FIGURE 2. Schematics of standard preparation apparatus.



The optimal saturation time has been calculated collecting samples every 30 minutes (Figure 3). Employing apparatuses different from the ones here described could lead to different saturation times.

FIGURE 3. Ethane saturation cinetics.



Sample Preparation

Ideally, samples should be collected in HS-compatible vials to avoid sample mishandling. Samples are usually collected in 20 mL or 40 mL vials without leaving headspace and, whenever possible, water should be carefully removed leaving 10 mL of sample into the vial for the headspace analysis.

To remove water samples without affecting the headspace, nitrogen can be pushed into the vial while water is withdrawn with the syringe. Samples should be stored in refrigerator if not immediately analyzed.

FIGURE 4. Thermo Scientific™ TriPlus™ 300 HS Autosampler and TRACE™ 1310 GC.

Gas Chromatography

The headspace sampling and chromatographic analysis has been performed with Thermo Scientific™ TRIPLUS™ HS autosampler coupled with a Thermo Scientific™ TRACE™ 1310 Gas Chromatograph (Figure 4). The following conditions were used:

- TriPlus 300 Headspace Autosampler
  - Temperatures: oven 70°C, manifold and transfer line 80°C
  - Equilibration time: 15 min
  - Vial Pressurization mode : pressure, set to 1.5 bar
  - Loop Pressurization mode : pressure, set to 0.8 bar
- TRACE 1310 Gas Chromatograph
  - Oven: starting temperature 60 °C, raise to 200 at 20 °C/min, hold for 1 min
  - Injector: 200 °C, carrier gas Helium 5 mL/min, split ratio 5:1
  - FID Detector : 250 °C, with default gas settings.
- Column: Thermo Scientific™ TracePLOT TG-BOND Q 25 25 m, 0.53 mm.

Data Analysis
All data have been collected and processed with Thermo Scientific™ Dionex™ Chromeleon ™ 7.2 Chromatography Data System.

Results

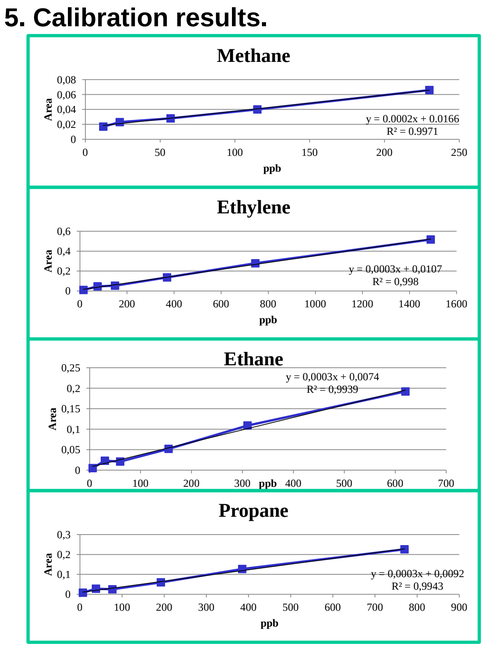
A six points calibration curve (Figure 5) has been built adding respectively 100, 50, 25, 10, 5 and 1 uL of saturated water to 20 mL HS vials containing 10 mL of deionized water. Since the solubility in water of the four gases at 20 °C is:

- Methane: 23.2 mg/L
- Ethane: 62 mg/L
- Ethylene: 149 mg/L
- Propane: 76.7 mg/L

The calibration levels for each gas were (in ppb):

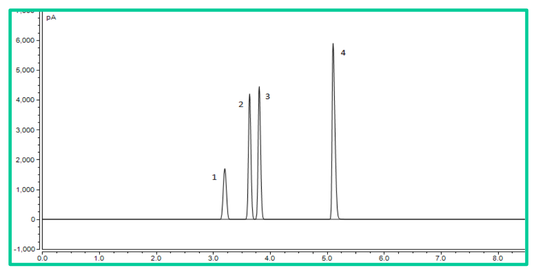
	Methane	Ethylene	Ethane	Propane
1	2.4	15	6	7
2	12	75	30	38
3	23	149	60	77
4	57	370	155	192
5	115	745	310	385
6	230	1490	620	770

FIGURE 5. Calibration results.



A full elution of the target analyzed is obtained in less than six minutes (Figure 6); the analysis time of ten miutes can be further shortened to increase lab productivity and is always overlapped with the incubation of the following samples into the high-capacity headspace oven.

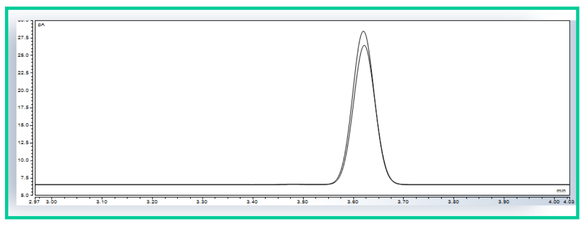
FIGURE 6. Chromatogram of a gas mix: 1.) Methane 2.) Ethylene 3.) Ethane 4.) Propane.



Standards Conservation

The vials containing standards can be refrigerated for up to 72 hours. This has been verified preparing and analyzing vials at different times after their collection (Figure 7).

FIGURE 7. The chromatograms represent two vials containing ethylene. One vial contains freshly saturated water, while the other vial has been kept in the refrigerator for 72 hours before the analysis. The difference is ~ 8%



Conclusion

The assessment of possible gas contamination of ground and drinking water is capital in areas interested by fracking procedures. The analysis can be performed following different methodologies and approaches.

We present a simple and convenient way to prepare and analyze samples using Static Headspace Sampling and FID detection, following ASTM Work Item WK43267.

The system, comprising the TriPlus 300 HS autosampler, TRACE 1310 GC, and Chromeleon 7.2 Data System, represents a valid and reliable option for the analysis of waters down to very low levels of contamination. The high sample capacity of TriPlus 300 HS autosampler is ideal for high-throughput laboratories in need of analyzing large quantities of water samples for their dissolved gases content.

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