Alternative Methods to RSK 175 Using Purge and Trap Concentration and Automated Headspace for the Analysis of Dissolved Gases in Drinking Water

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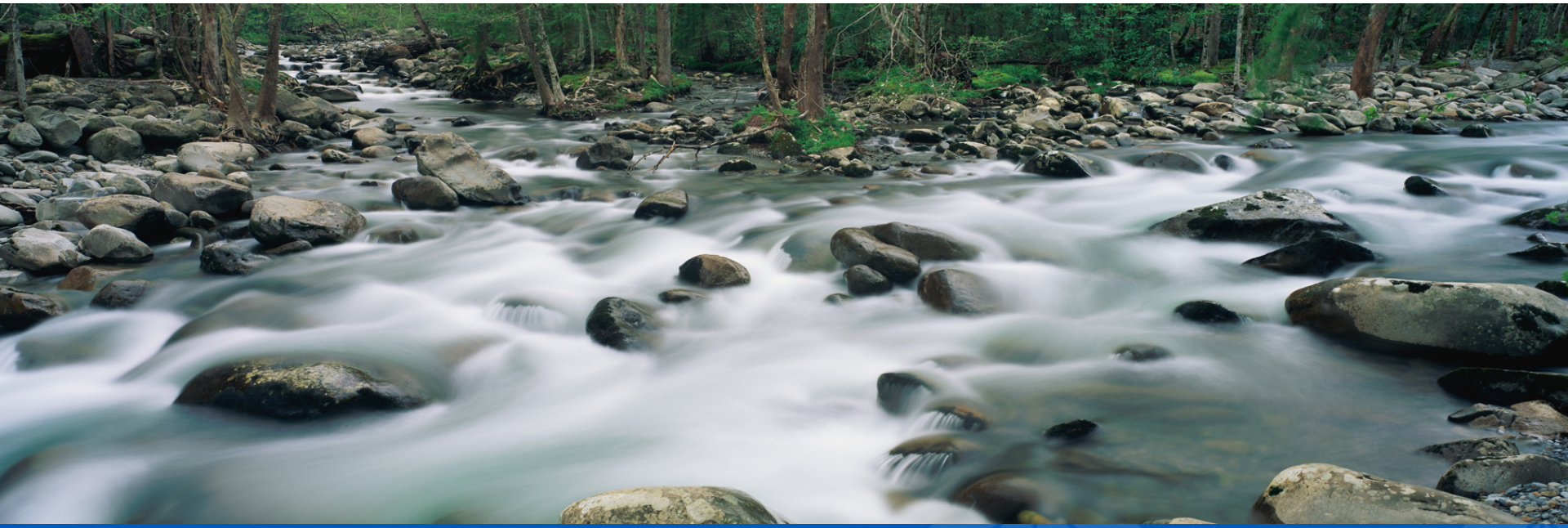
Due to increased concern over the hydraulic fracturing process and the release of methane and other chemicals into the local drinking water, a need has developed for fast and accurate analysis of dissolved gasses in water.



SOP RSK-175

“Sample Preparation and Calculations for Dissolved Gas Analysis in Water Samples Using a GC Headspace Equilibration Technique”

Not an official EPA-approved Method

Analytes: hydrogen, methane, ethylene, ethane, propane, butane, acetylene, nitrogen, nitrous oxide and oxygen

No standard calibration prep method – varies lab to lab

RSK 175 has been employed for analysis of light hydrocarbons in drinking water surrounding hydraulic fracturing well sites

BOL 6019 (PA-DEP 3686)

Modified method, developed by the Pennsylvania Department of Environmental Protection (PADEP), and helps to simplify and standardize the sample preparation associated with dissolved gas analysis

- **Automated headspace analysis**
- **Liquid calibrations using saturated solutions**
- **Requires sample handling – VOA => HS vial**

Calibration Requirements: %RSD ≤ 20% or $r^2 \geq 0.995$

Still requires sample manipulation for each analysis

Limited by equilibration time and platen positions of headspace analyzer

RESULTS

Compound	Calibration Range	Linearity (r^2)		MDL	
		HT3	Versa	HT3	Versa
Methane	20 ppb to 24 ppm	0.998	0.996	2 ppb	2 ppb
Ethene	141 ppb to 169 ppm	0.998	0.997	25 ppb	19 ppb
Ethane	66 ppb to 79 ppm	0.999	0.999	5 ppb	7 ppb
Propane	74 ppb to 88 ppm	0.999	0.999	6 ppb	4 ppb

CONCLUSIONS

Both the HT3 and Versa Headspace Analyzers automate the RSK 175 analysis, allowing for higher efficiency and throughput

- **HT3 multi-position platen allows for continuous sample prep**

Decreases potential variability associated with manual GC injections

Met all method performance criteria for all constituents

Standardization to liquid calibrations provides apples to apples comparison to real world samples

CAN WE USE PURGE AND TRAP FOR RSK 175?

Trapping Material – Can we trap light gases?

Dynamic Range – low ppb to ppm levels

Purge and Trap Parameters

- Sample Volume
- Purge Volume – Time and Flow

Autosampler

- Sample Temperature
- Carryover

GC Considerations

- Column
- Oven Program
- Split?

RESULTS

Compound	Calibration Range	Linearity (r^2)	%RSD	MDL	% Carryover
Methane	7.92 ppb to 19.8 ppm	1.000	2.0	0.4 ppb	0.04%
Ethene	56.2 ppb to 281 ppm	0.9995	4.5	31 ppb	0.03%
Ethane	26.4 ppb to 132 ppm	0.9998	13.9	21 ppb	0.04%
Propane	29.4 ppb to 147 ppm	0.9999	12.0	18 ppb	0.04%

CONCLUSIONS

Utilizes existing P&T instrumentation with limited modifications

- **Trap, column, and recirculating bath are all that is required**

Same advantages to running automated headspace, but also self-contained in 40 mL VOA vials

- **No need to manipulate the samples**

Potential for fastest run times and highest throughput of all available RSK 175 testing methods since there is no equilibration time

- **GC cycle is the limiting factor: too fast = coelutions**

New Method: PA-DEP 9423 (October 2012)