

# 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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Presenter:

Nathan Valentine, Applications Manager



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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.



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# 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**



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# 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  $\leq$  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**



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# 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?



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# 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)**



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