

pennsylvania
DEPARTMENT OF ENVIRONMENTAL PROTECTION

Bureau of Laboratories

Sample Preparation and Method Development for Analysis of Unique Environmental Matrices Associated with Gas Drilling Activities

Dr. Pamela J. Higgins

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APHL National Meeting

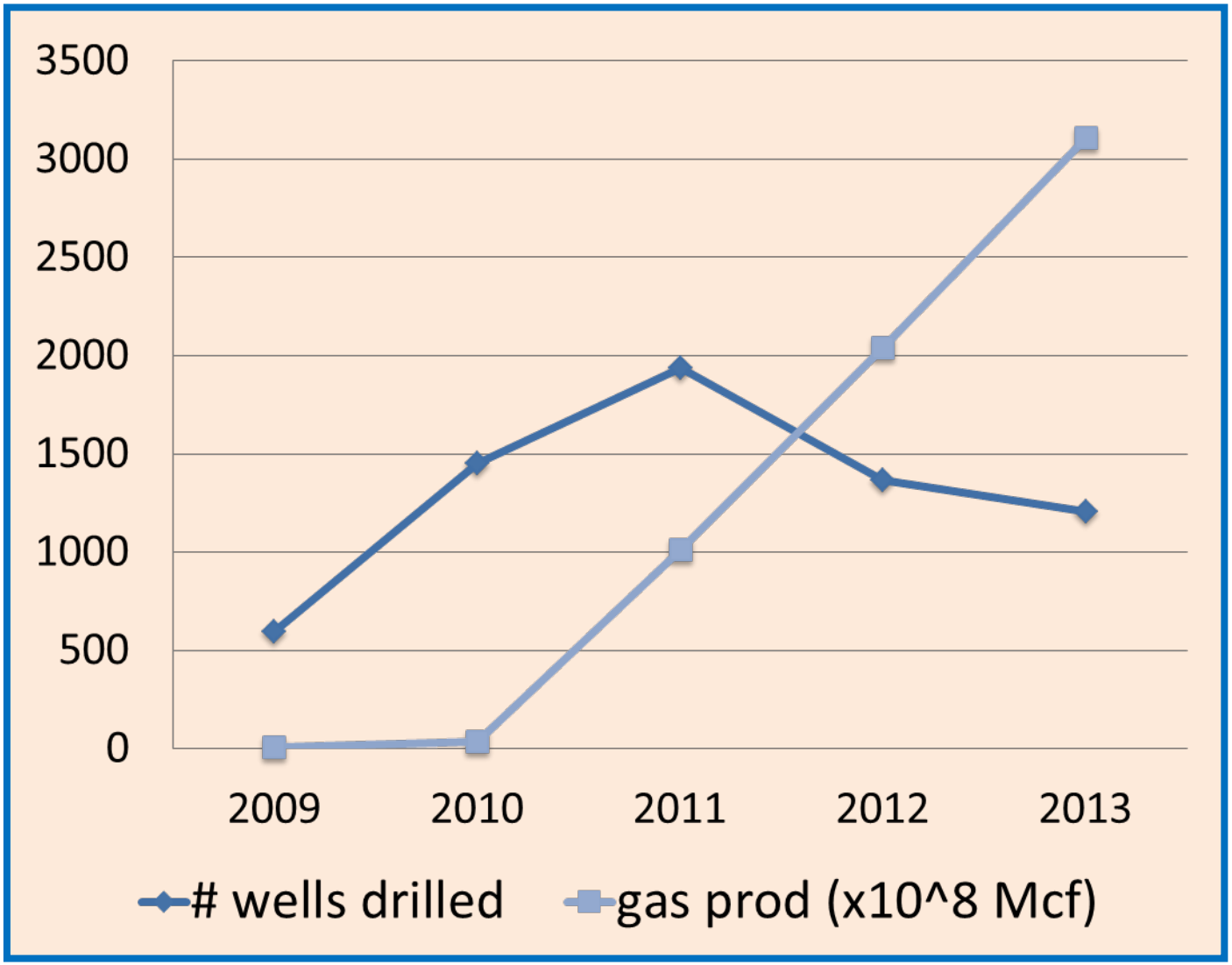
Overview

1) Stages of gas drilling: associated solids and fluids

2) Preparation of TENORM sample matrices

3) Method/sample preparation adaptations for analysis of other gas drilling analytes

PA Marcellus Shale Activity Trends



What comes up……..

The fluids and solids coming to the surface have been exposed to shale formation chemistry !

Marcellus Shale formation

-rich in methane gas, little CO_2, N_2 or H_2S contaminants

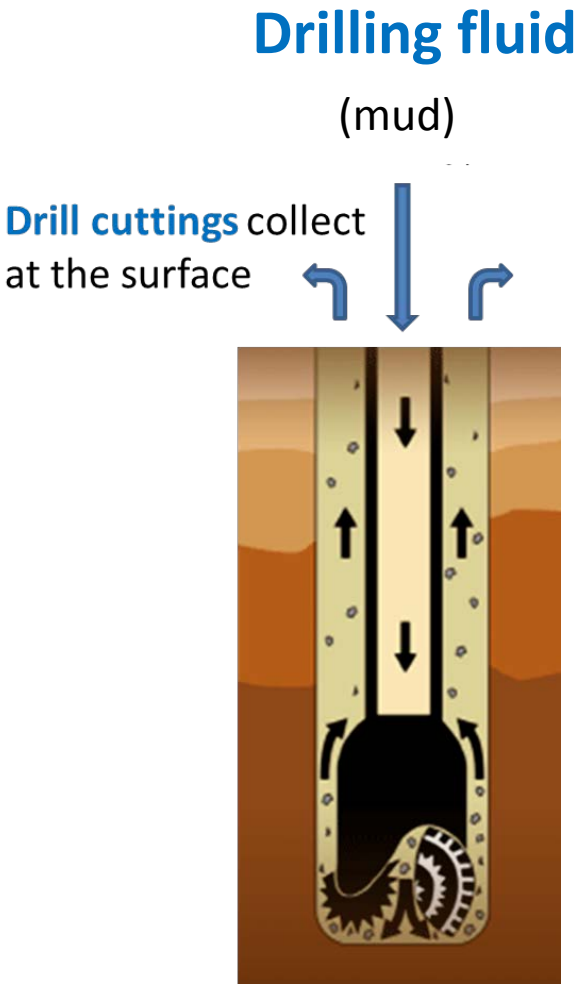
-very high levels of solids (dissolved/suspended) and chloride ion

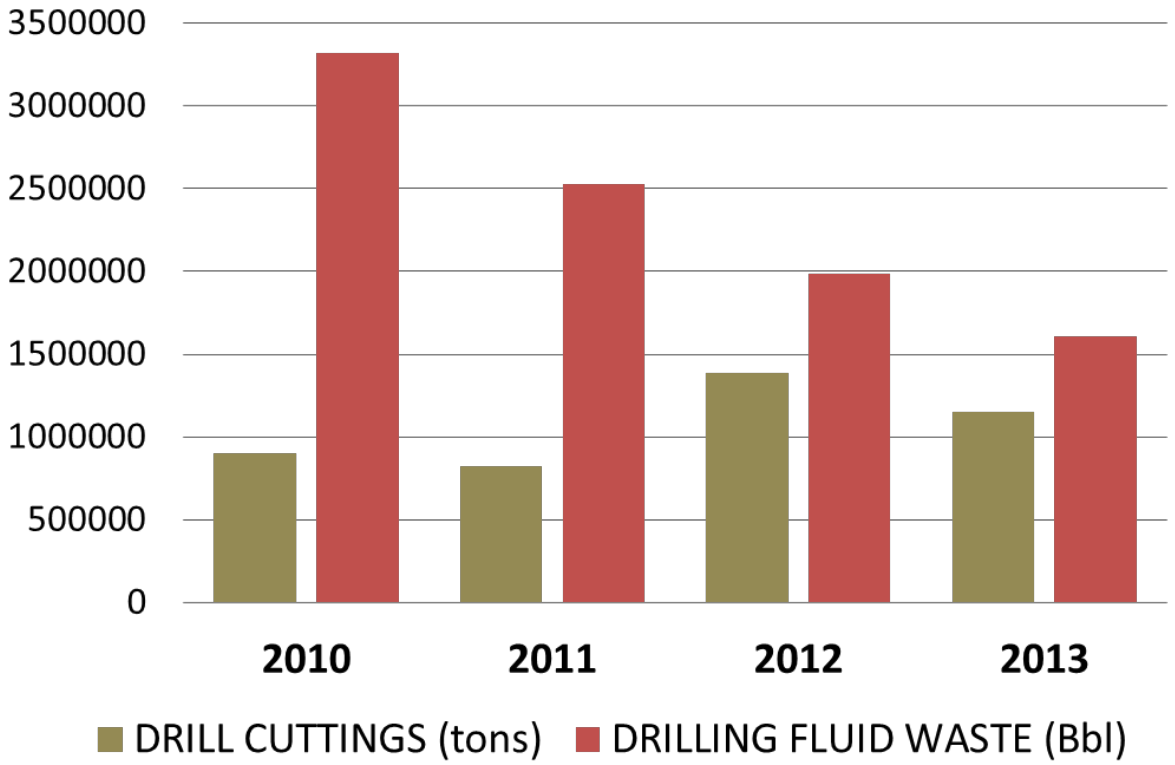
OTHERS:

- hydrocarbons
- divalent cations (Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+})
- heavy metals, Br-
- uranium, thorium, and decay products (TE/NORMs)

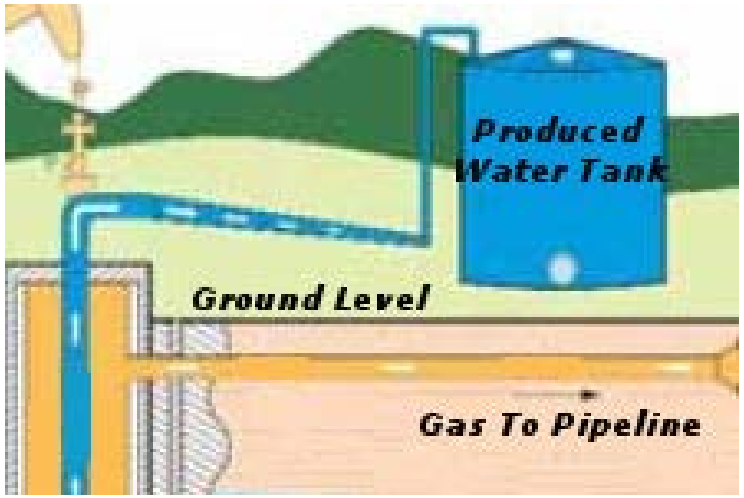
Well Drilling

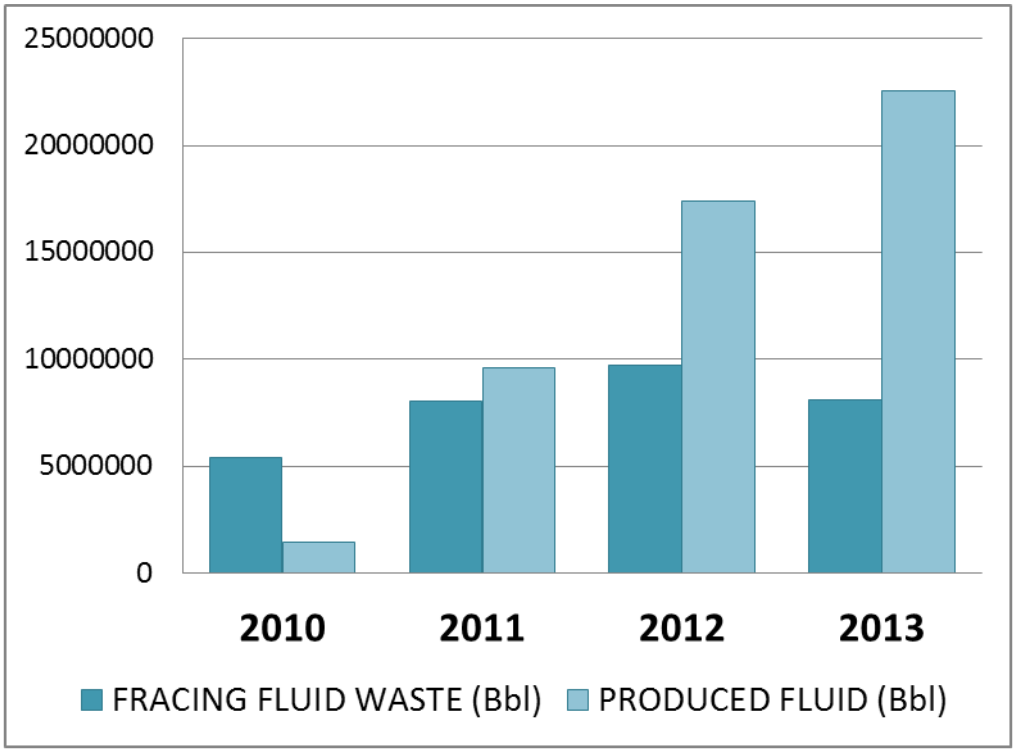
Cuttings / fluid (sludge) : more difficult to assess, leach non-uniform in nature





Well Production





Produced fluids

- separated off from shale gas during collection

Flowback and produced fluids: high concentrations of solids/brine causes interference with sample preparation and analysis

Waste Perspective

2013 Totals	PA Gas Drilling Waste	PA Municipal Waste
Waste solids (million tons/year)	1.3 (cuttings/sand)	21.5* (30 % imported)
Waste fluids (million barrels)	7.7 per year	5 - 7 per **DAY**!

* Landfill/incinerator disposal

PA DEP TENORM Study

Year long comprehensive survey of TENORM concentration in gas drilling related samples across the state:

Well pads

Centralized WTF

Landfill

-solids

-leachates

Publicly owned TP

Zero Liquid TP

Drill Cuttings / Mud Analyses

Gamma Spectroscopy (on HPGe)

U-238, Th-232 and progeny (Ra-226/228)

K-40 (not in above decay chains)

-requires transfer to 0.5 L Marinelli

Raw sample

-sludge, sometimes oily

-non-homgeneous

-rocks/roots

Drill Cuttings / Mud Preparation

1) Dry sample at 100 °C

2) Pulverize in coal grinder

-easily transferrable and homogeneous

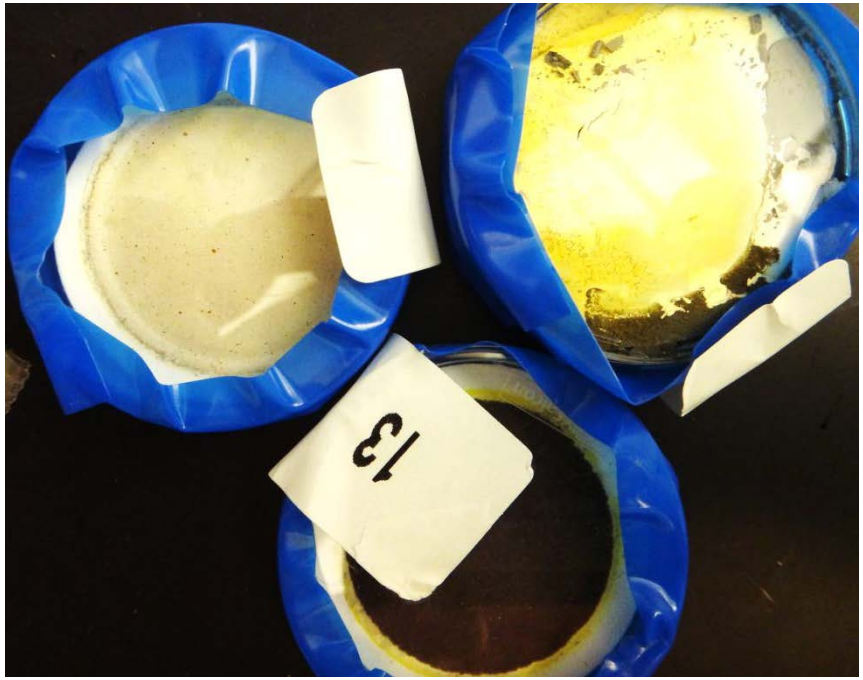
-report results by actual mass transferred to the Marinelli

Well Pad / Treatment Plant Fluids

Gamma Spectroscopy

Pass sample through 0.45 micron filter

-high solids content can impair flow



Filtrate – Marinelli

Filter cake – Petri dish

Gross alpha/beta Spectroscopy

Routine environmental samples:

Evaporate ≈ 100 mL of sample onto shallow metal planchets

-careful application of small aliquots of sample to obtain a **thin layer of solids (< 100 mg)**

-allows **low detection** capability of these two radiation particles (500 min count on GPC)

Planchet Sample Problems

Thick oily and crusty residues from **waste fluids**:

Consistently negative values for gross alpha radiation !

Planchet Sample Solutions

Smaller volumes: 1 mL **waste fluid** + 10 mL nitric acid
Evaporate to 5 mL, planchet

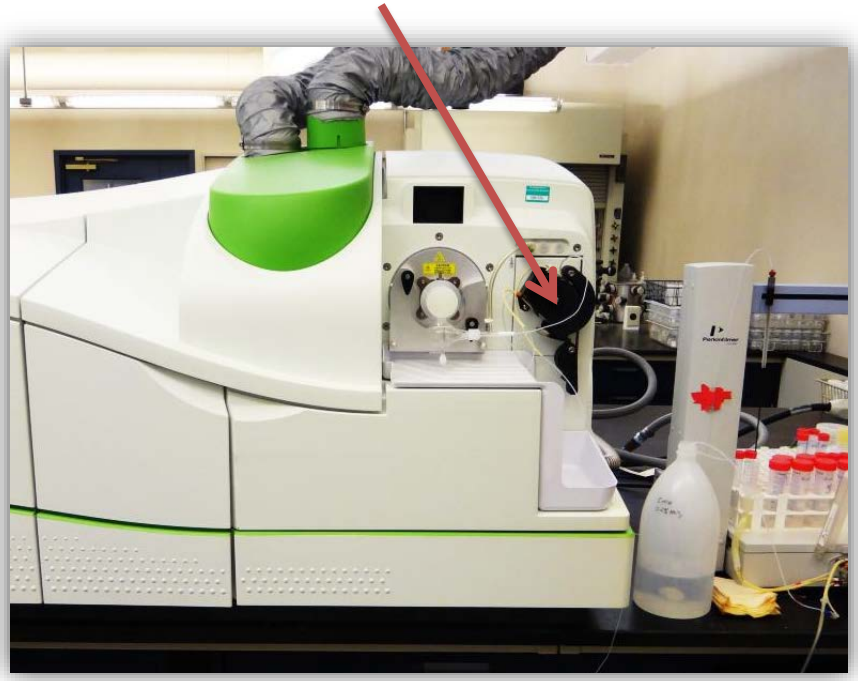
Apply the heat: Drive off salt hydrates

Over flame

On hotplate

Total Metal Analyses

Samples clog thin aspirators



ICP-MS ☒

Samples in small cup container

X-Ray Fluorescence ☑

XRF Data for Fluid Blank Sample

Z	Symbol	Element	Concentration	
11	Na	Sodium	1564	ppm
12	Mg	Magnesium	156.4	ppm
13	Al	Aluminum	130.7	ppm
14	Si	Silicon	209.2	ppm
15	P	Phosphorus	12.7	ppm
16	S	Sulfur	38.5	ppm
17	Cl	Chlorine	240.9	ppm
19	K	Potassium	57.0	ppm
20	Ca	Calcium	16.6	ppm
22	Ti	Titanium	3.6	ppm
23	V	Vanadium	0.7	ppm
24	Cr	Chromium	2.3	ppm
25	Mn	Manganese	1.7	ppm
26	Fe	Iron	24.5	ppm
27	Co	Cobalt	< 2.6	ppm
28	Ni	Nickel	2.3	ppm
29	Cu	Copper	0.8	ppm
30	Zn	Zinc	1.4	ppm
31	Ga	Gallium	0.2	ppm
32	Ge	Germanium	< 0.5	ppm
33	As	Arsenic	< 0.5	ppm
34	Se	Selenium	< 0.5	ppm
35	Br	Bromine	0.2	ppm
37	Rb	Rubidium	0.4	ppm
38	Sr	Strontium	0.3	ppm
39	Y	Yttrium	1.5	ppm
40	Zr	Zirconium	< 0.4	ppm
41	Nb	Niobium	< 1.0	ppm
42	Mo	Molybden	1.4	ppm
47	Ag	Silver	< 2.0	ppm
48	Cd	Cadmium	< 2.0	ppm
50	Sn	Tin	< 3.0	ppm
51	Sb	Antimony	< 3.0	ppm
52	Te	Tellurium	< 3.0	ppm
53	I	Iodine	< 3.0	ppm
55	Cs	Cesium	< 4.0	ppm
56	Ba	Barium	< 2.0	ppm
57	La	Lanthanur	< 2.0	ppm
58	Ce	Cerium	< 2.0	ppm
72	Hf	Hafnium	2.1	ppm
73	Ta	Tantalum	12.7	ppm
74	W	Tungsten	0.4	ppm
80	Hg	Mercury	< 0.2	ppm
81	Tl	Thallium	0.8	ppm
82	Pb	Lead	0.9	ppm
83	Bi	Bismuth	< 1.0	ppm
90	Th	Thorium	1.0	ppm
92	U	Uranium	1.0	ppm

Organic Analyses of Drilling Associated Samples

1) Methane

-primarily tested for in well water

2) Semi/Volatile compounds

-primarily tested for in waste fluids

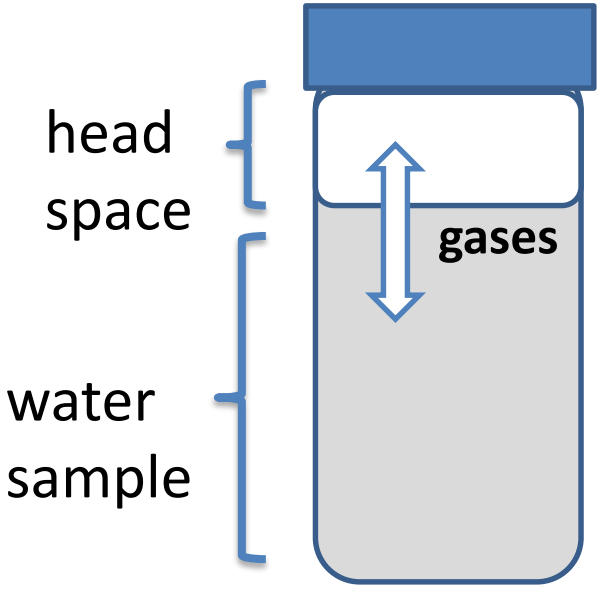
Dissolved Methane Sampling Techniques

Headspace sampling

-shake sample vial and heat to a constant temperature; allow the dissolved gases to equilibrate between headspace / water sample

-obtain sample of the headspace gases

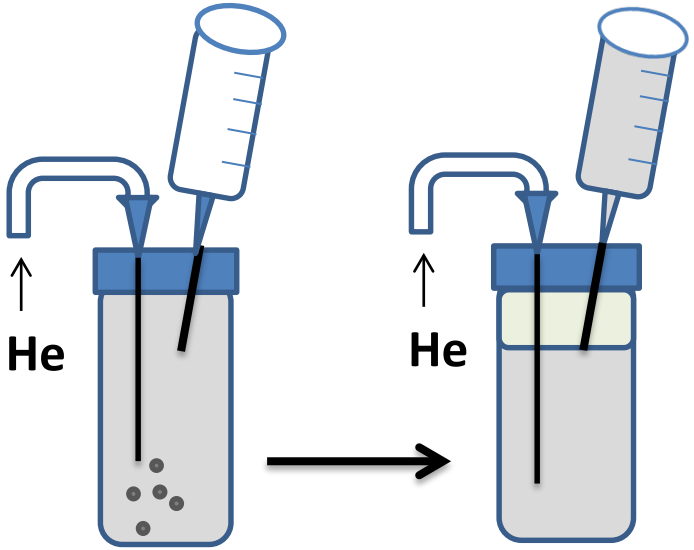
-gas chromatography (GC) analysis



Dissolved Methane Sampling Techniques

EPA RSKSOP-175

-create 10 % (v/v) headspace in **unopened sample vial**

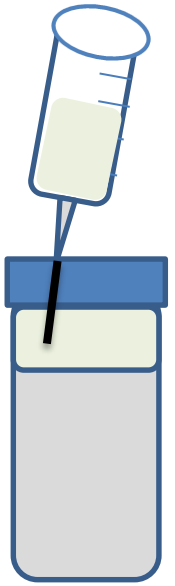


Quantitation:

Manually inject gas standards

Determine [gas] in headspace

Indirect determination of the dissolved gas in water using ideal gas law calculations



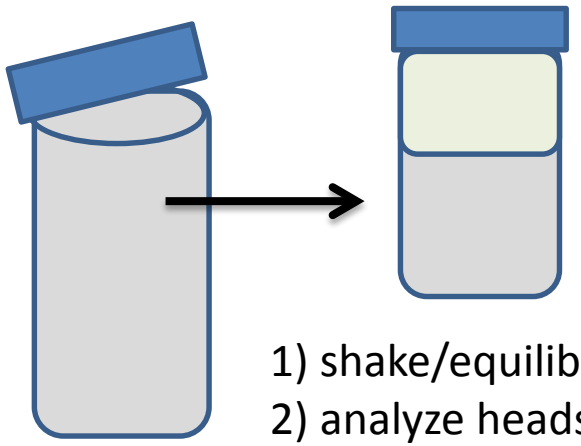
1) shake, equilibrate

2) analyze headspace

Dissolved Methane Sampling Techniques

PA-DEP 3686

-chill, then **open sample vial** for quick transfer to GC headspace vial

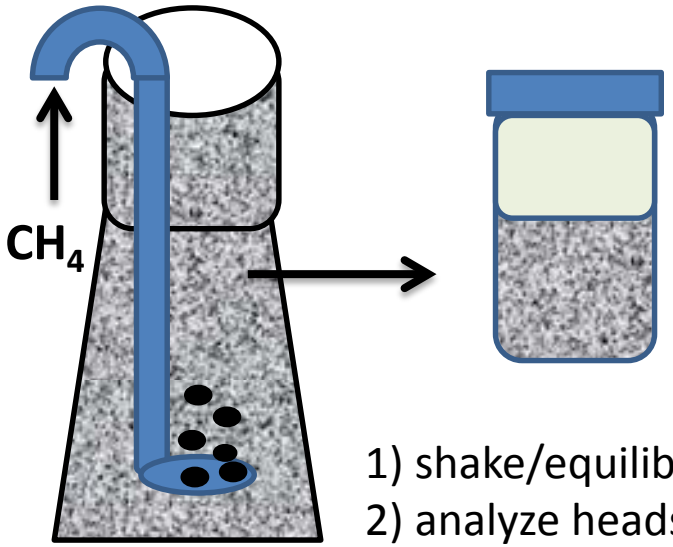


1) shake/equilibrate
2) analyze headspace

Quantitation:

Sparge methane into water to **known saturation**
-aliquot / dilute into vial

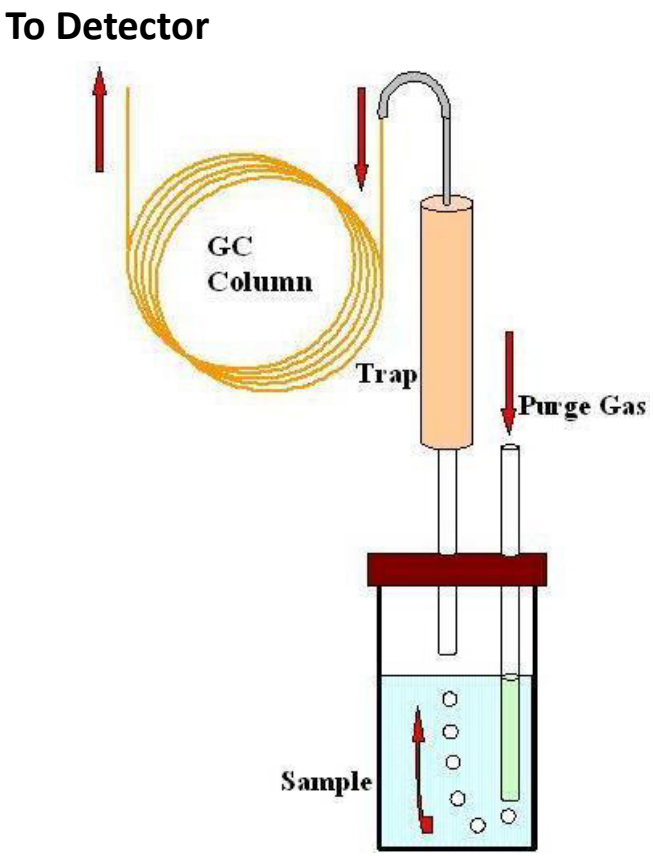
Direct determination of the dissolved methane in water correlated to [headspace gas]

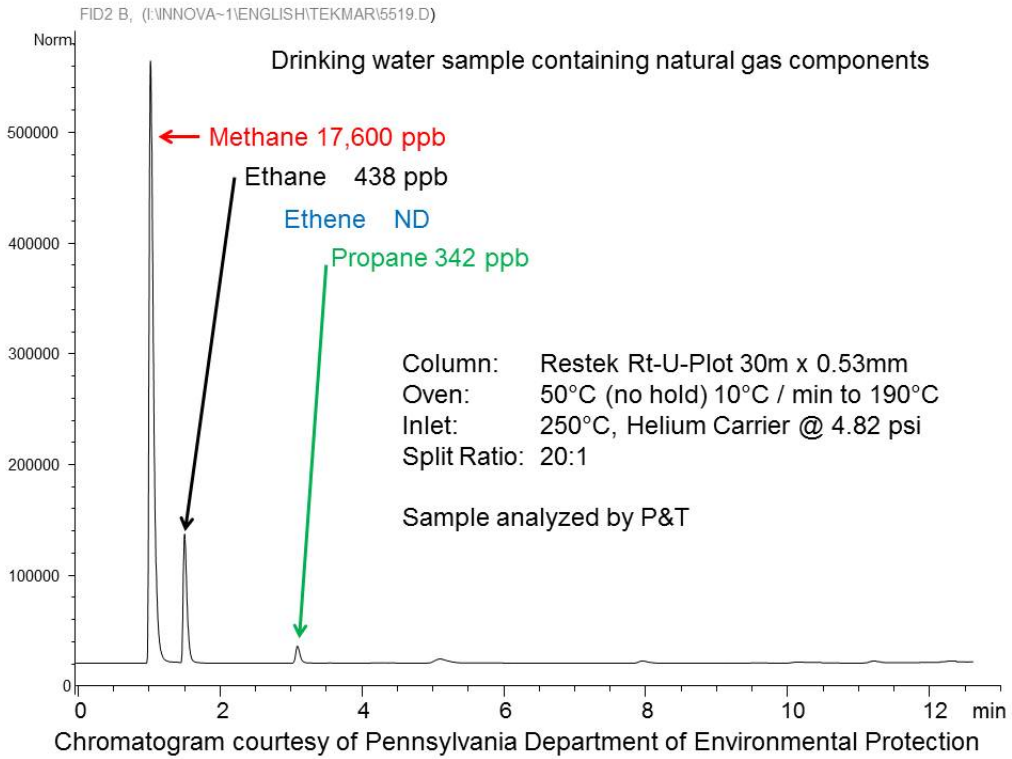


1) shake/equilibrate
2) analyze headspace

Dissolved Methane Sampling Techniques

Purge and Trap Sampling (PA-DEP 9243)





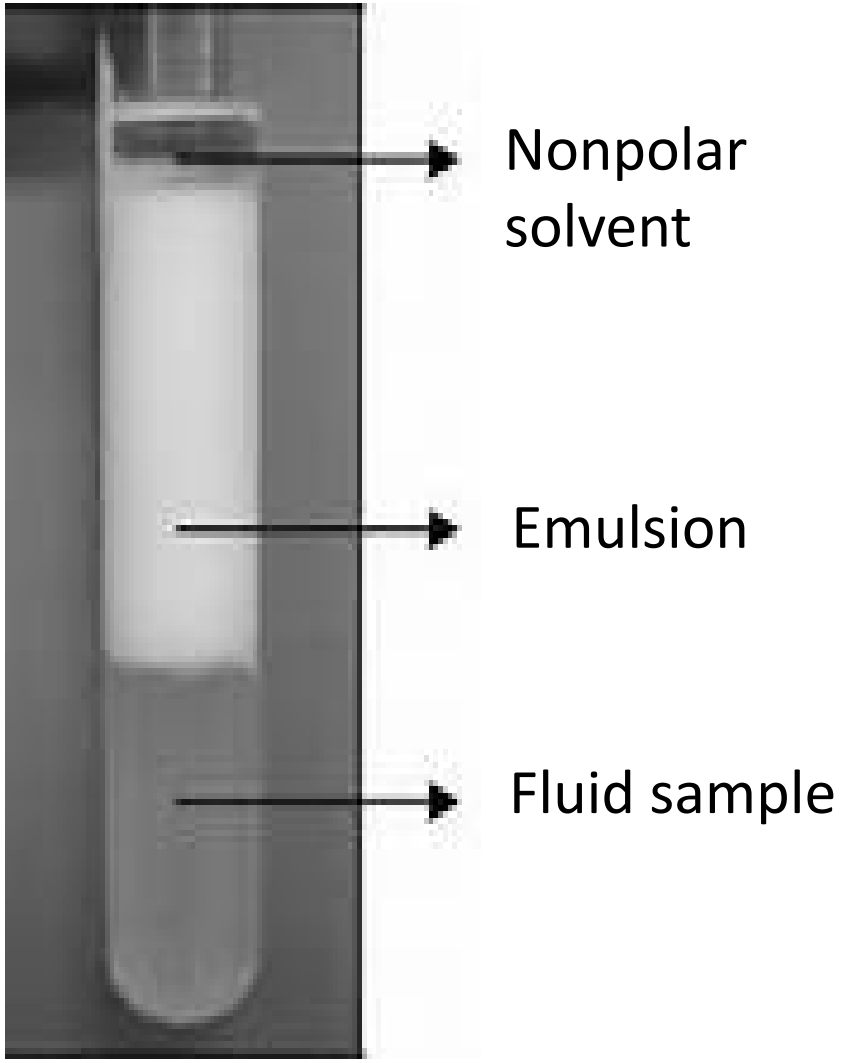
DEP method collaboration with Teledyne Tekmar

-more common lab apparatus, results similar to headspace

Extraction of Semi/Volatile Compounds

Emulsion formation during extraction of organic analytes using nonpolar solvents

Increased concentration of **surfactants** and **stabilizers** in waste and impoundment fluids



Summary

1) Matrices surfacing after shale contact during gas drilling (waste fluid/solids) are more complex than those introduced into the shale .

2) TENORM matrices from gas drilling activities required additional sample preparation steps before analysis.

3) Method development for monitoring gas drilling related analytes is an evolving process.


Questions? Contact us:

PA DEP Bureau of Laboratories
(717)-346-7200

Martina Q. Mcgarvey, D.M.
Director
mmacgarvey@pa.gov

Pamela J. Higgins, Ph.D.
Special Assistant for Laboratory Operations
pahiggins@pa.gov