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Natural Gas from Shale: the Resource of Our Time

Focus on the analysis of gasses in Water

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Outline

- Introduction
  - “fracking” info
- Analyzing Methane and other gases
  - Headspace Theory and Operation
  - Method parameters and results

The opportunity that lies ahead. . .

- "The United States is in the midst of a 21st century gold rush—a natural gas boom, driven in large part by the discovery of vast amounts of gas in unconventional plays. The spotlight is on the practice of fracking, which is quickly becoming one of the most highly visible and controversial environmental issues of the day..."*

* FrackingInsider.com, Kelley Drye & Warren LLP, last read August 10, 2011

PerkinElmer can play a significant role in facilitating the environmental efficacy of the process – we have the know-how; the neutrality; the measurement tools to make people effective - making the process and results safe and profitable.

Natural Gas from Shale . . .

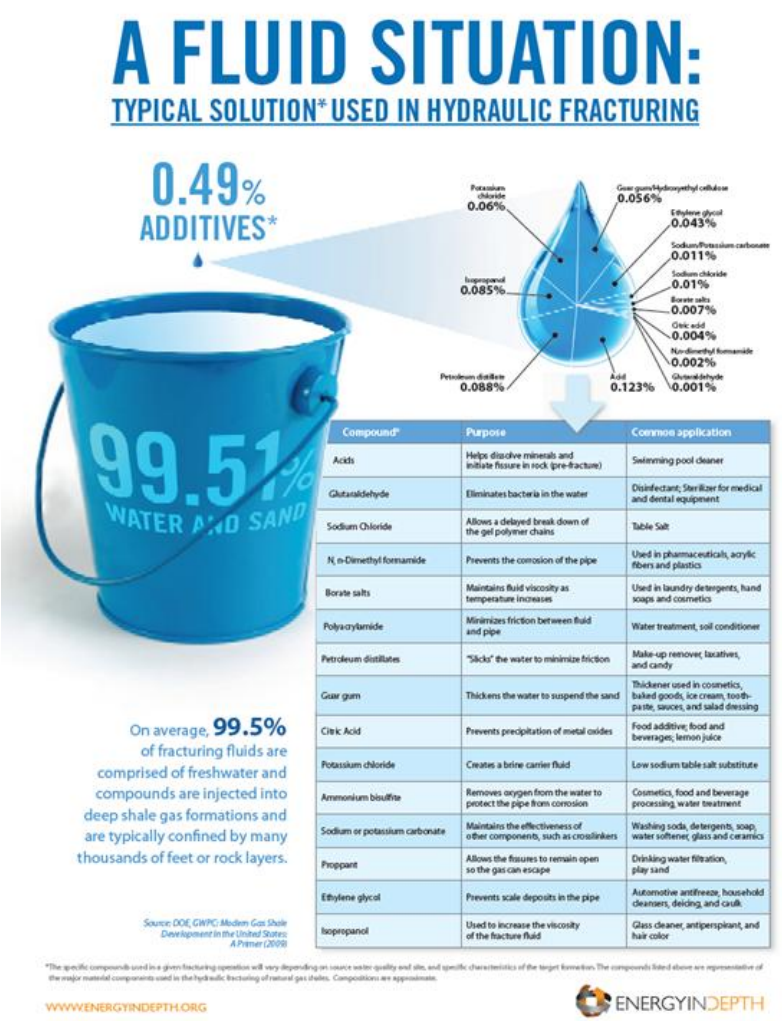
- Gas in shale lies deep in the earth
  - Typical wells are 5000-10000 ft deep
  - Shale is impervious, the gas is tightly held
- Horizontally drilled wells are required
  - Well is vertical until it nears the “pay zone”
  - Drilling is turned to horizontal – well understood process - ~50 years old
  - Continues through the deposit up to 1 mile.

Shale Gas Opportunities

Environmental concerns linked to ‘fracking’ . . .

- Testing is
  - Inorganic
  - Anions
  - Methane in Water
  - Radioactivity
  - Little (yet) organic needs

Some of what goes into the well:



Compound*	Purpose	Common application
Acids	Helps dissolve minerals and initiate fissure in rock (pre-fracture)	Swimming pool cleaner
Glutaraldehyde	Eliminates bacteria in the water	Disinfectant; Sterilizer for medical and dental equipment
Sodium Chloride	Allows a delayed break down of the gel polymer chains	Table Salt
N, n-Dimethyl formamide	Prevents the corrosion of the pipe	Used in pharmaceuticals, acrylic fibers and plastics
Borate salts	Maintains fluid viscosity as temperature increases	Used in laundry detergents, hand soaps and cosmetics
Polyacrylamide	Minimizes friction between fluid and pipe	Water treatment, soil conditioner
Petroleum distillates	"Slicks" the water to minimize friction	Make-up remover, laxatives, and candy
Guar gum	Thickens the water to suspend the sand	Thickener used in cosmetics, baked goods, ice cream, tooth-paste, sauces, and salad dressing
Citric Acid	Prevents precipitation of metal oxides	Food additive; food and beverages; lemon juice
Potassium chloride	Creates a brine carrier fluid	Low sodium table salt substitute
Ammonium bisulfite	Removes oxygen from the water to protect the pipe from corrosion	Cosmetics, food and beverage processing, water treatment
Sodium or potassium carbonate	Maintains the effectiveness of other components, such as crosslinkers	Washing soda, detergents, soap, water softener, glass and ceramics
Proppant	Allows the fissures to remain open so the gas can escape	Drinking water filtration, play sand
Ethylene glycol	Prevents scale deposits in the pipe	Automotive antifreeze, household cleansers, deicing, and caulk
Isopropanol	Used to increase the viscosity of the fracture fluid	Glass cleaner, antiperspirant, and hair color

*The specific compounds used in a given fracturing operation will vary depending on source water quality and site, and specific characteristics of the target formation. The compounds listed above are representative of the major material components used in the hydraulic fracturing of natural gas shales. Compositions are approximate.

Additive volume = 25,000 gal in typical well

The TurboMatrix Headspace

and the Clarus 680 Gas Chromatograph

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The Analysis of Methane and other gases in water using Headspace/ Gas Chromatography Optimizing RSK 175

Theory and Operation

Gas Chromatography

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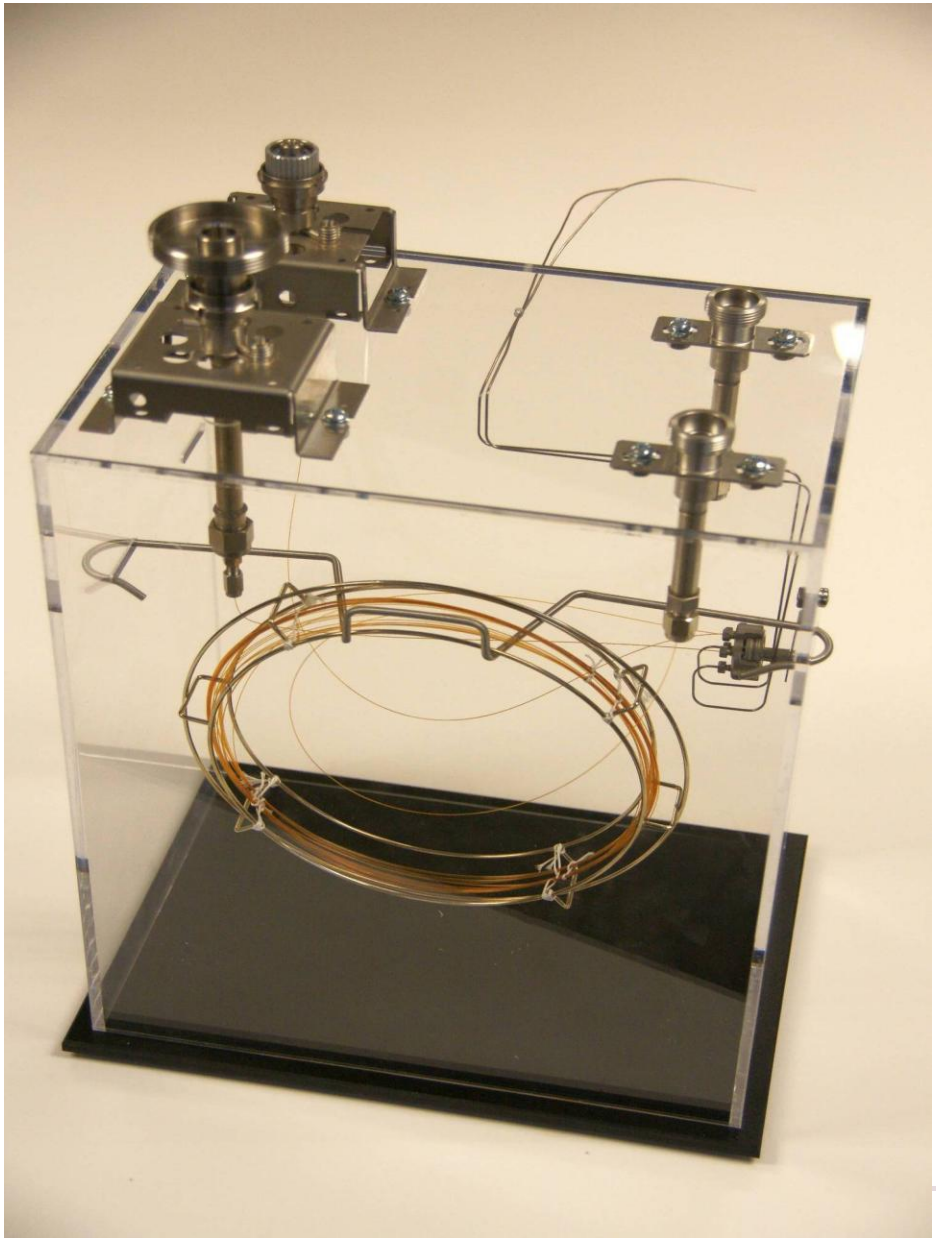
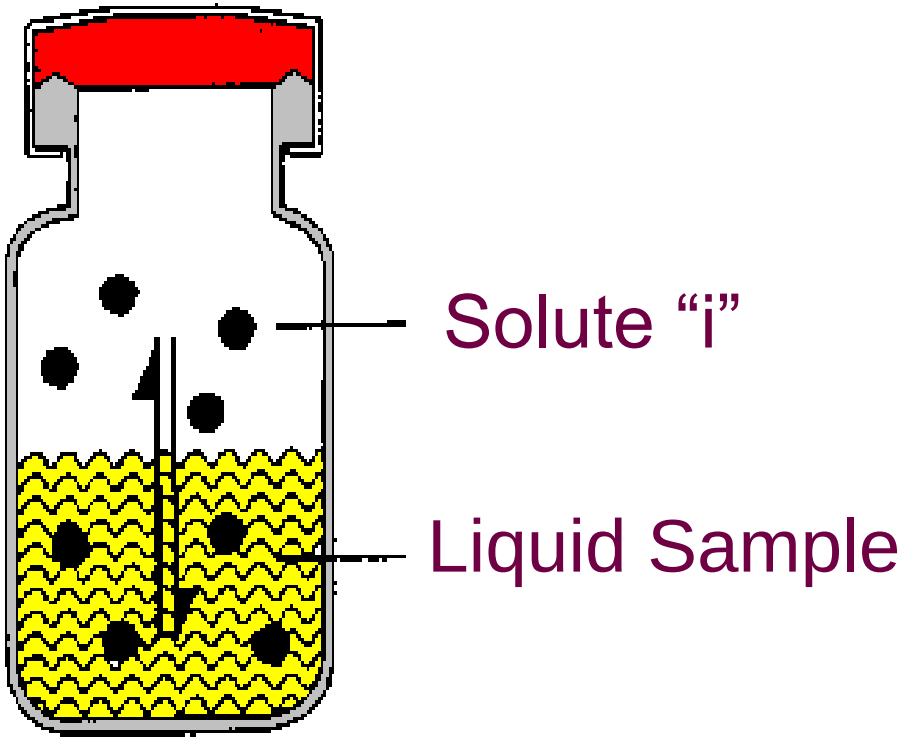


Headspace: The sample Introduction System

Consider:

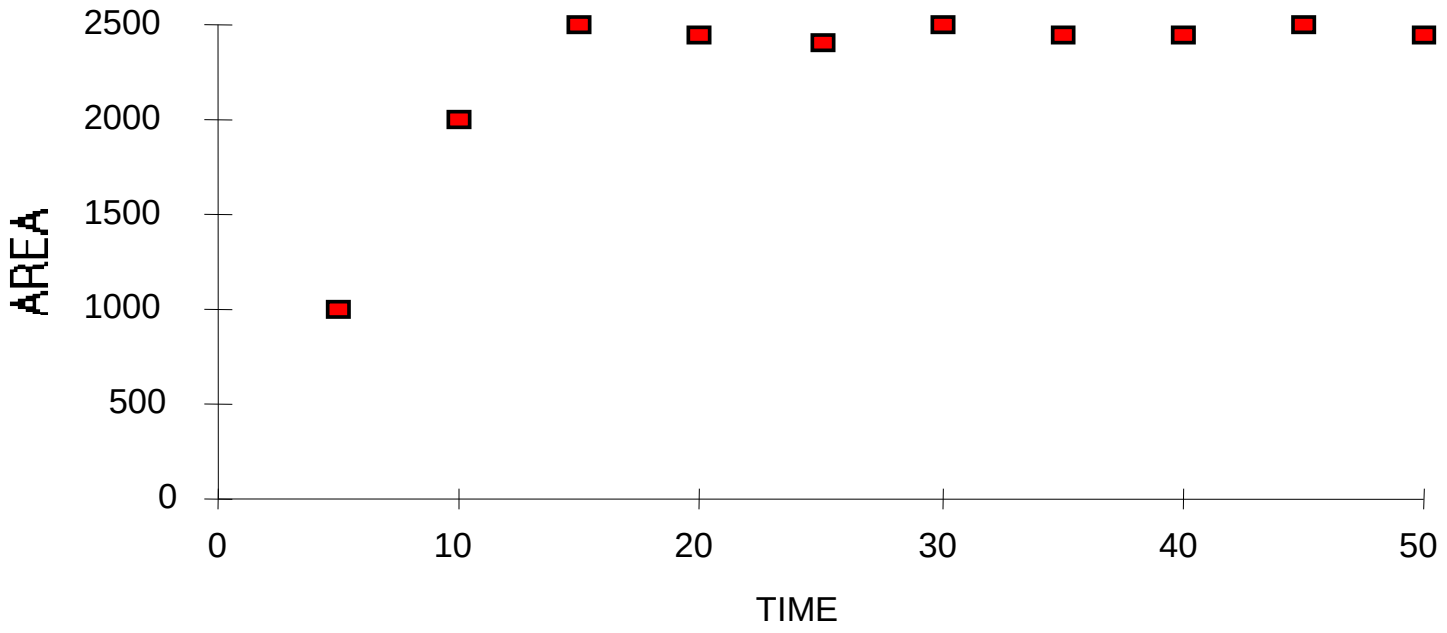
Time
Temperature



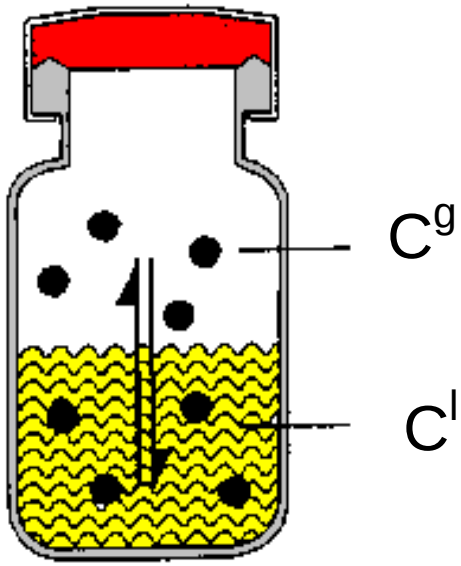
Optimizing two Parameters

- Equilibration time must be long enough for each analyte to be in equilibrium
- Matrix effect – the partition coefficient is matrix dependent therefore the partition for each analyte in the standard and the sample must be the same

Determining Equilibration Time

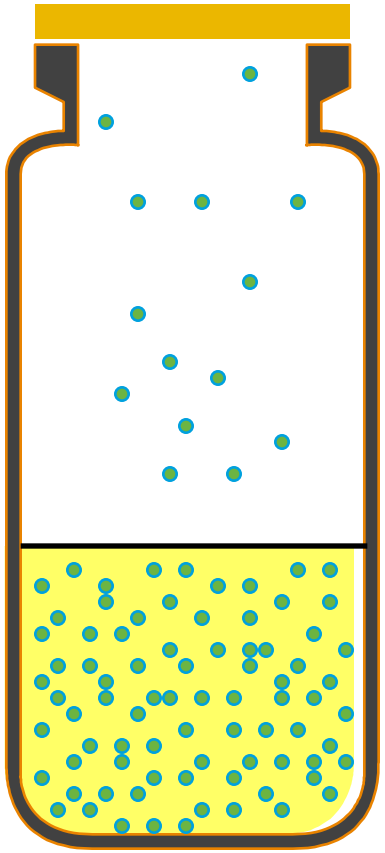


Partition Coefficient

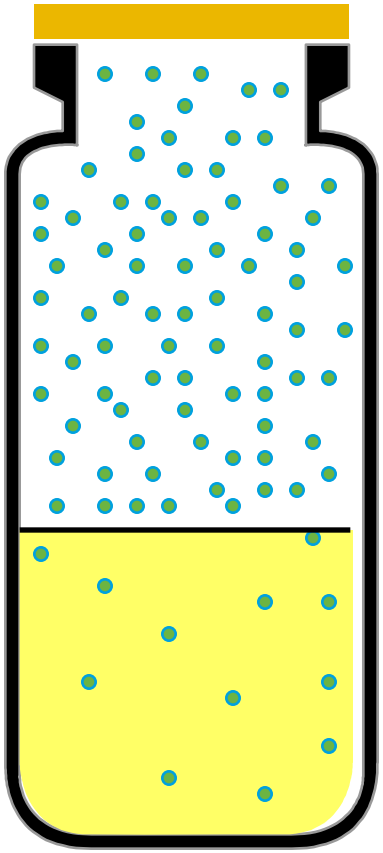


$$K = C^l/C^g$$

K = Partition coefficient of a volatile
C^l = Concentration in the liquid phase
C^g = Concentration in the gas phase



When K is large



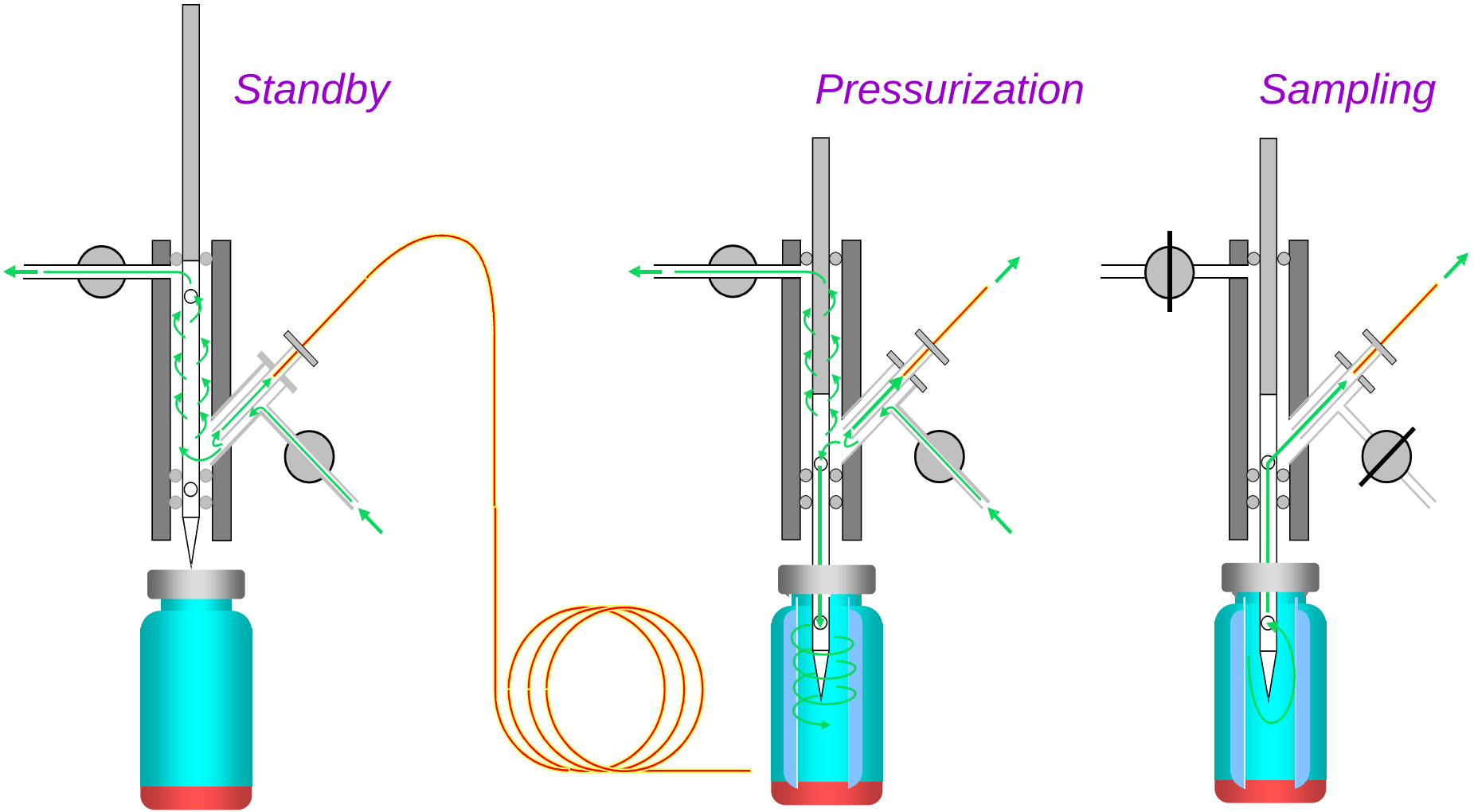
When K is small

Affects of Partition Coefficient on Response

$$A = \frac{C^o}{K + \beta}$$

- A = Peak Area or Response
- C^o = Concentration of analyte in sample
- K = Partition Coefficient
- β = Phase Ratio = Vg/Vs
- Vg = Volume of the gas phase
- Vs = Sample Volume

Balanced – Pressure Sampling



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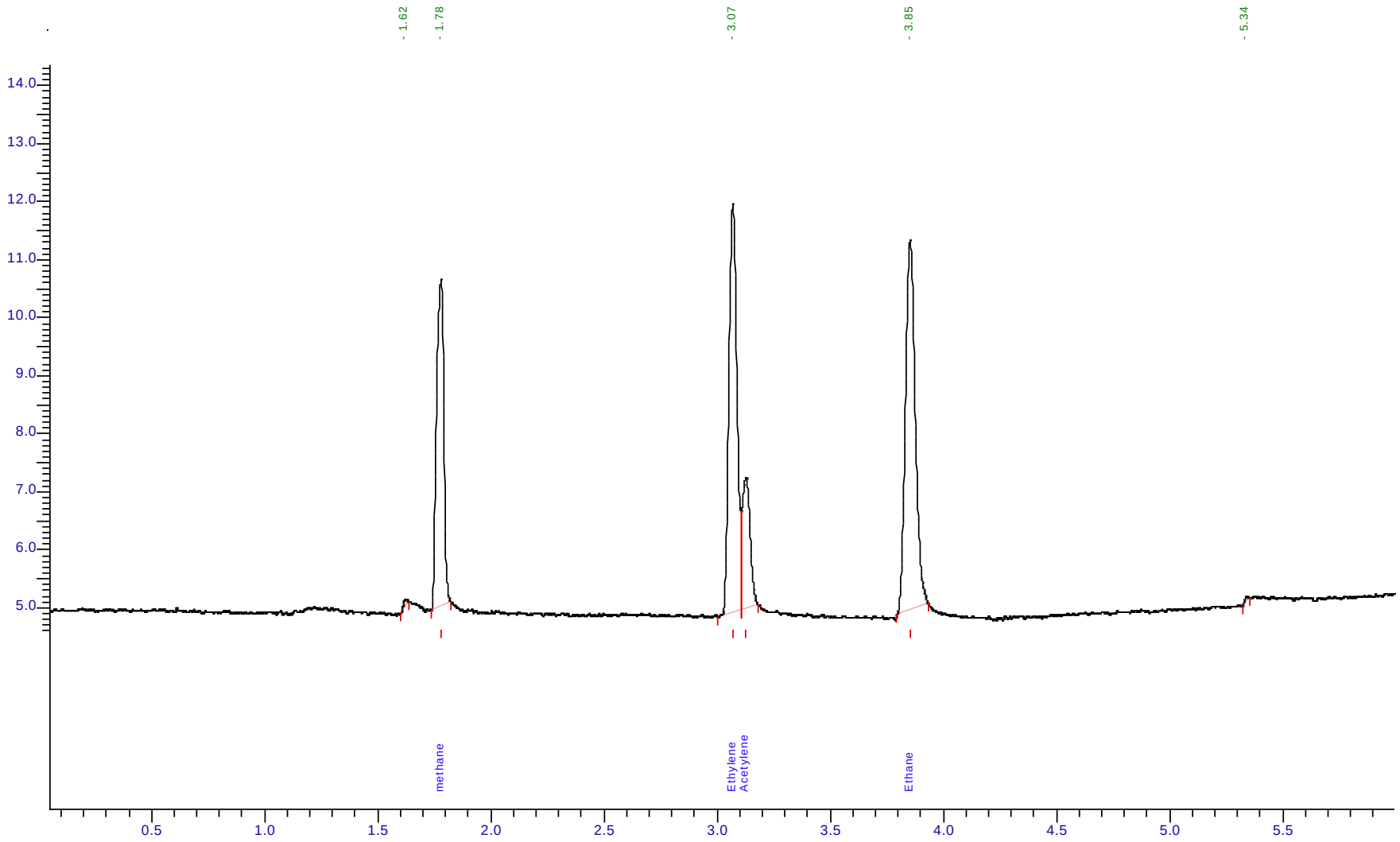
Method Parameters and Results

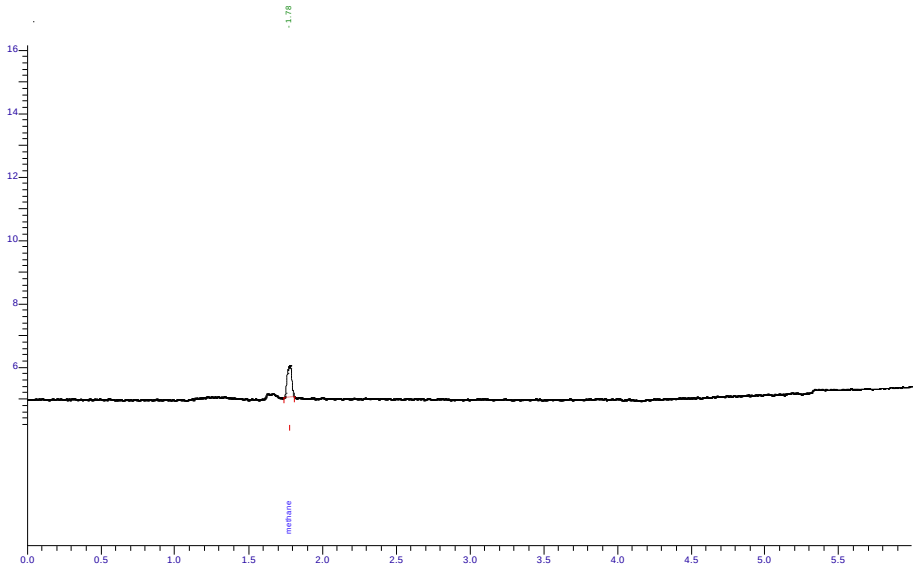
10 ppb Chromatogram



Dealing with Methane in Ambient Air

Sample Name	Area (Methane)
15mL Water Blank	2093.5
15mL Water Blank	2163.7
15mL Water Blank	2337.4
15mL Water Blank	2124.3
Average	2179.7
%RSD	5%

- Contribution is significantly below the reporting limit of 1ppb
- Incorporating this point on the curve as a “zero” amount incorporates a blank subtract

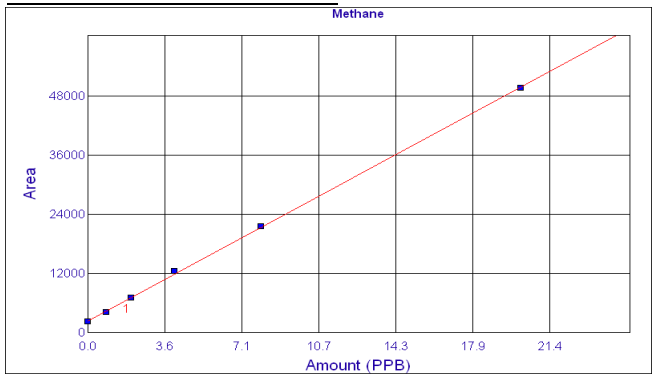


Standard Preparation

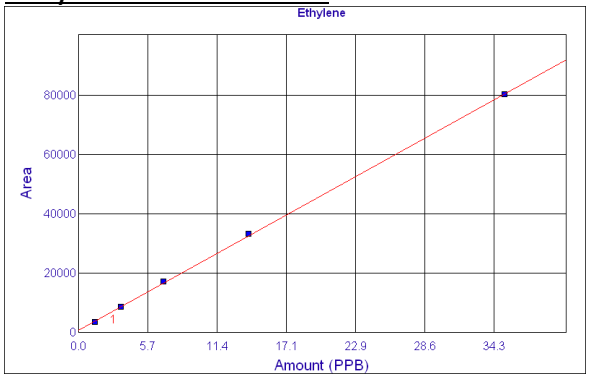
Level #	Methane	Ethylene	Ethane
Level 1	0.80	1.40	1.50
Level 2	2.00	3.50	3.75
Level 3	4.00	7.00	7.50
Level 4	8.00	14.00	15.00
Level 5	20.00	35.00	37.50

Results of Calibration

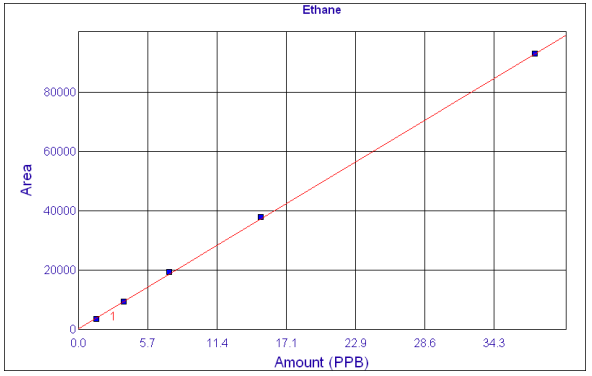
Methane: $r^2 = 0.9996$



Ethylene: $r^2 = 0.9998$



Ethane: $r^2 = 0.9999$



Quality Control Results

Methane		
Actual Amount	Calc Amount	% Dev
2.00	2.05	2.50
10.00	10.72	7.20
14.00	15.19	8.50
20.00	20.69	3.45

Ethylene		
Actual Amount	Calc Amount	% Dev
3.50	3.43	-2.00
17.50	18.68	6.74
24.50	26.40	7.76
35.00	36.44	4.11

Ethane		
Actual Amount	Calc Amount	% Dev
3.75	3.59	-4.27
18.75	19.91	6.19
26.25	28.43	8.30
37.50	39.14	4.37

Repeatability (n=5)

Concentration (ppb)	Methane Area	Ethylene Area	Ethane Area
8	43180	70067	80441
8	44330	70199	81390
8	43421	67911	79164
8	44331	71017	82016
8	42184	66722	76234
Average	43489	69183	79849
% RSD	**2.1**	**2.6**	**2.9**

Summary

- Fortunately, headspace/GC with Flame Ionization detection provides a very simple, fast, accurate and precise solution to this important analysis.

Thank you

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