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Optimizing RSK 175 for the analysis of Methane, Ethylene, Acetylene and Ethane in Water by Headspace-Gas Chromatography (HS-GC) with Flame Ionization Detection (FID)

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Outline

- Introduction

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- Headspace Theory and Operation

- Method parameters and results

Air Sampling Applications

- The rapid development of natural gas from unconventional sources in North America has created an energy “gold rush”. The advent of horizontal drilling technologies and hydraulic fracturing has made this production economical and presents an energy source of sufficient magnitude that could last 100 years.

- The technology presents a number of analytical challenges. The wells are drilled vertically through aquifers on their way to the deep shale deposits thousands of feet under the surface. In the process of drilling the wells and preparing them for production (including “fracking” to optimize production), opportunities arise for contamination of the clean drinking water aquifers with methane and other low molecular weight organics (e.g., propane and ethane).

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Theory and Operation

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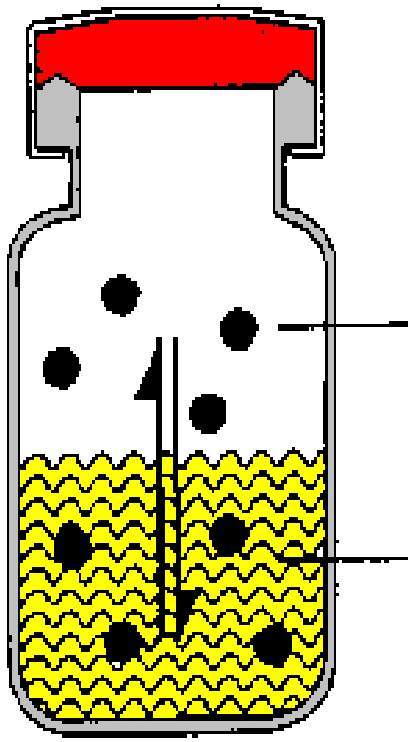
Partition Equilibrium Headspace

Consider:

Time
Temperature



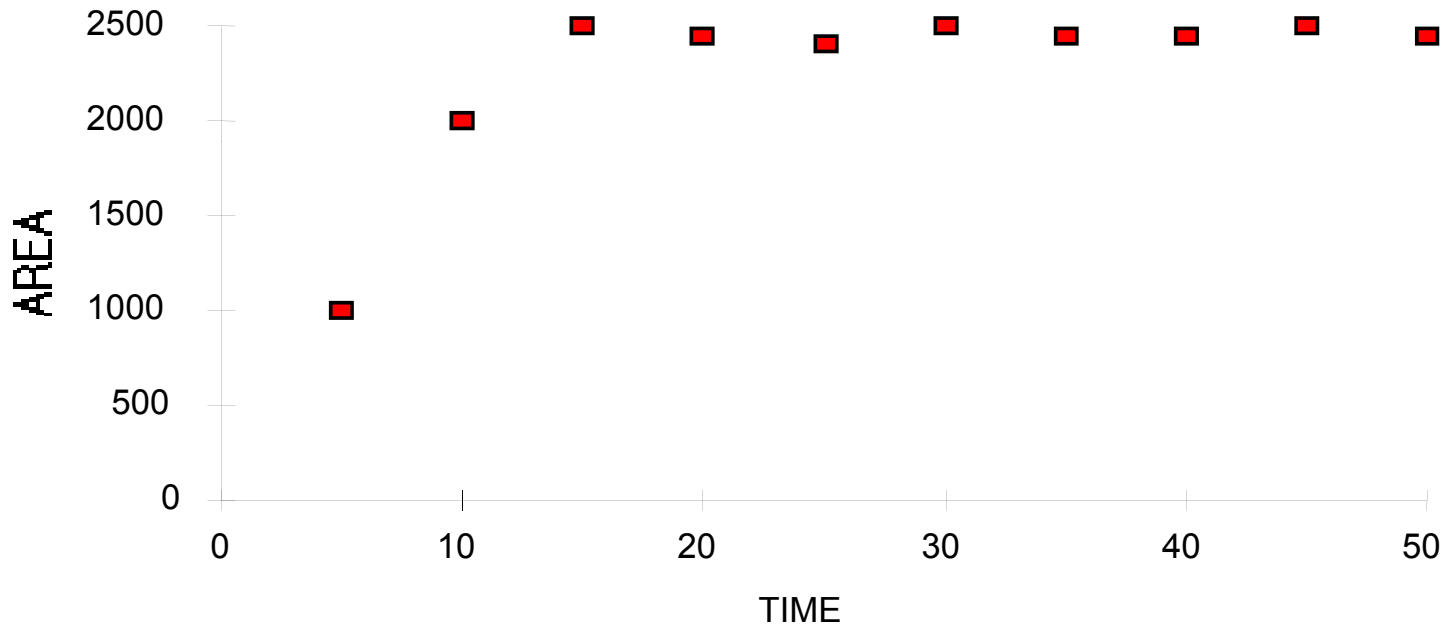
Solute “i”

Liquid Sample

Enabling quantitative Static Headspace

- 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
- Low (dilute) vapor phase – Activity Coefficient must remain constant
- Sample must represent a partitioned system

Determining Equilibration Time



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Partition Coefficient

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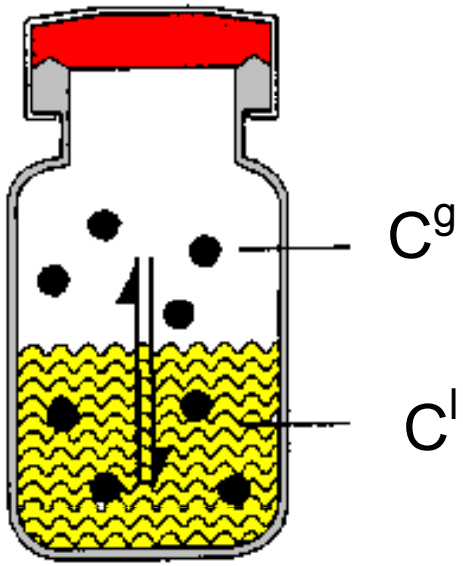
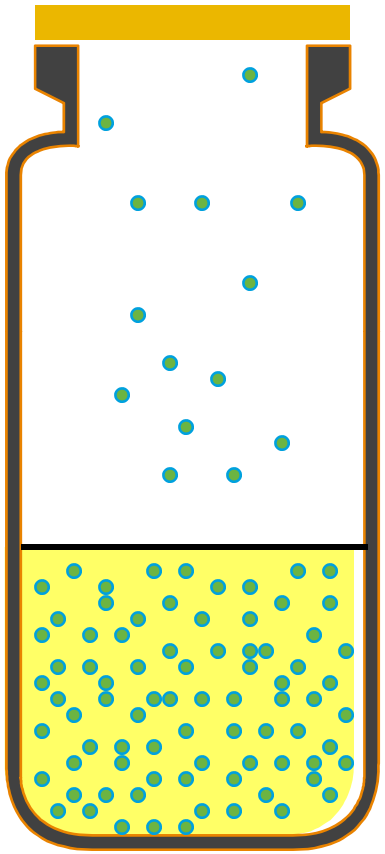
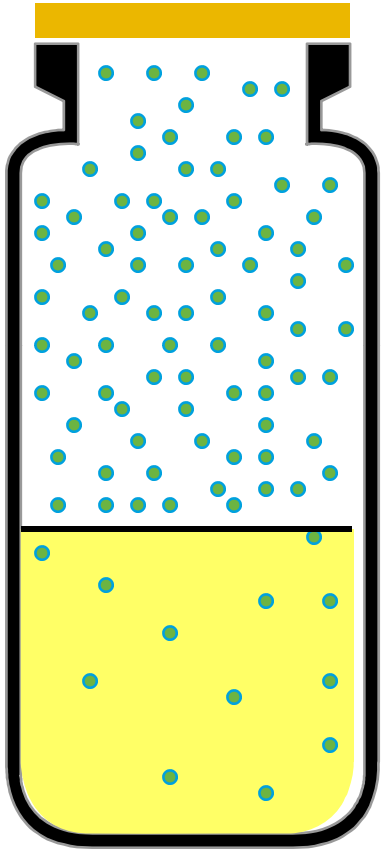


$$K = C^l/C^g$$

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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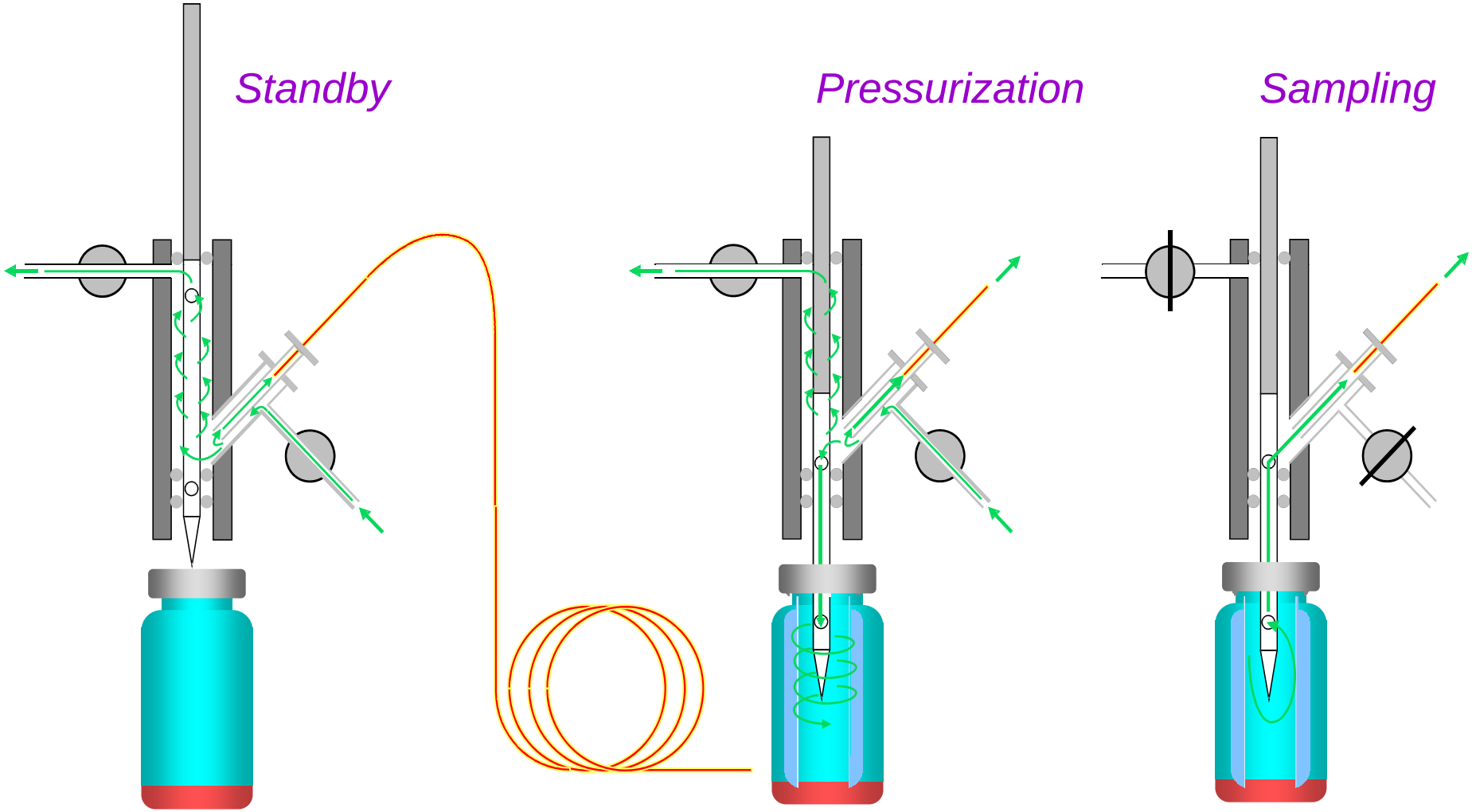

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Method Parameters and Results

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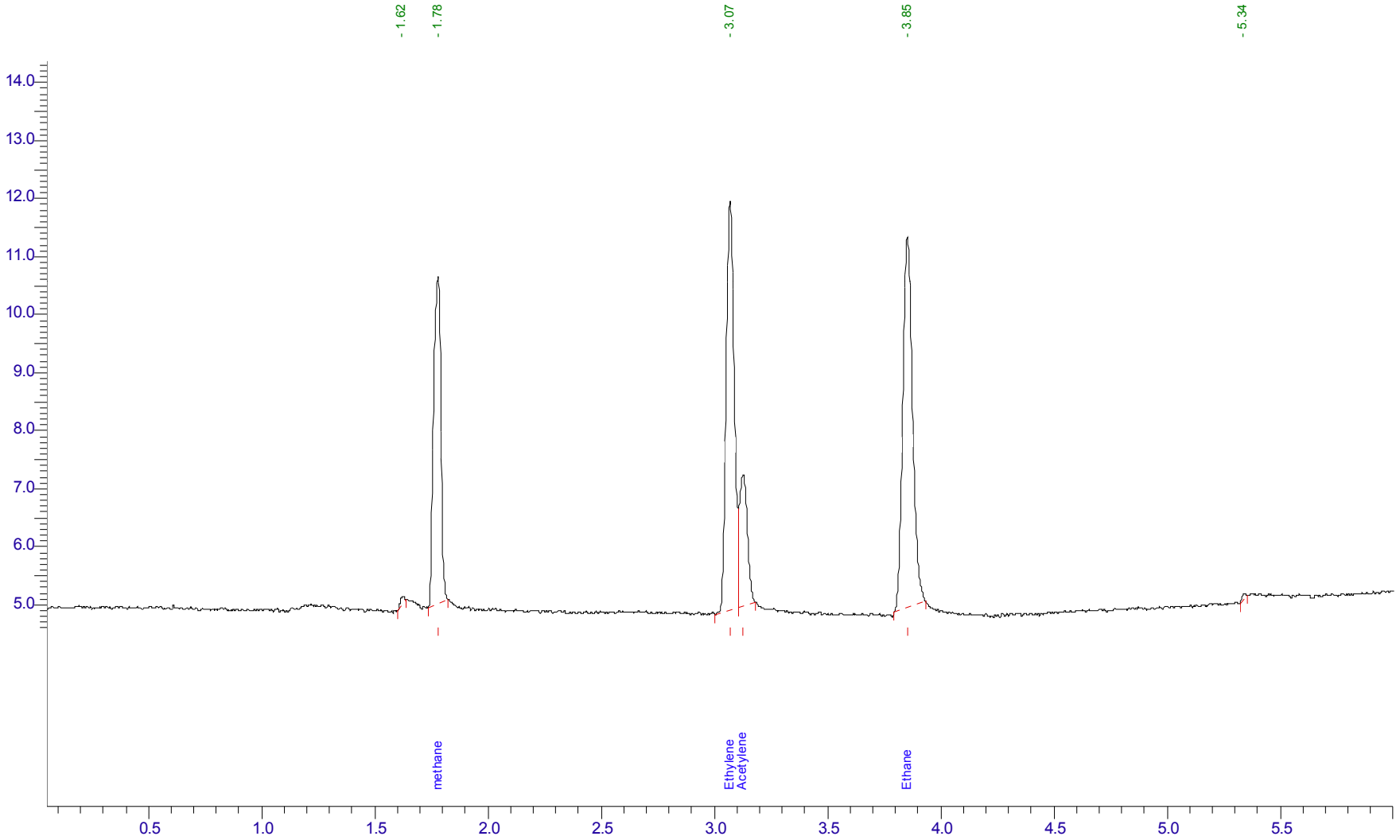
HS and GC Parameters

HS Conditions:	
Sample Temp:	90°C
Equilibration time:	10 min
Needle Temp:	110°C
Transfer Line Temp:	120°C
Inject Time:	0.06 min
Withdrawal Time:	0.4 min
Pressurization Time:	1.0 min
HS Mode:	Constant
HS pressure:	20 psi

GC Conditions:	
Oven Temp:	
Initial Temp:	40°C
Initial Hold:	4.5 min
Ramp	40°/min
Final Temp:	205°C
Final Hold:	1 min
Detector (FID):	
Detector Temp:	240°C
Air Flow	400 mL/min
Hydrogen Flow	40 mL/min
Range	1
Attenuation	-6 (or 1)

10 ppb Chromatogram



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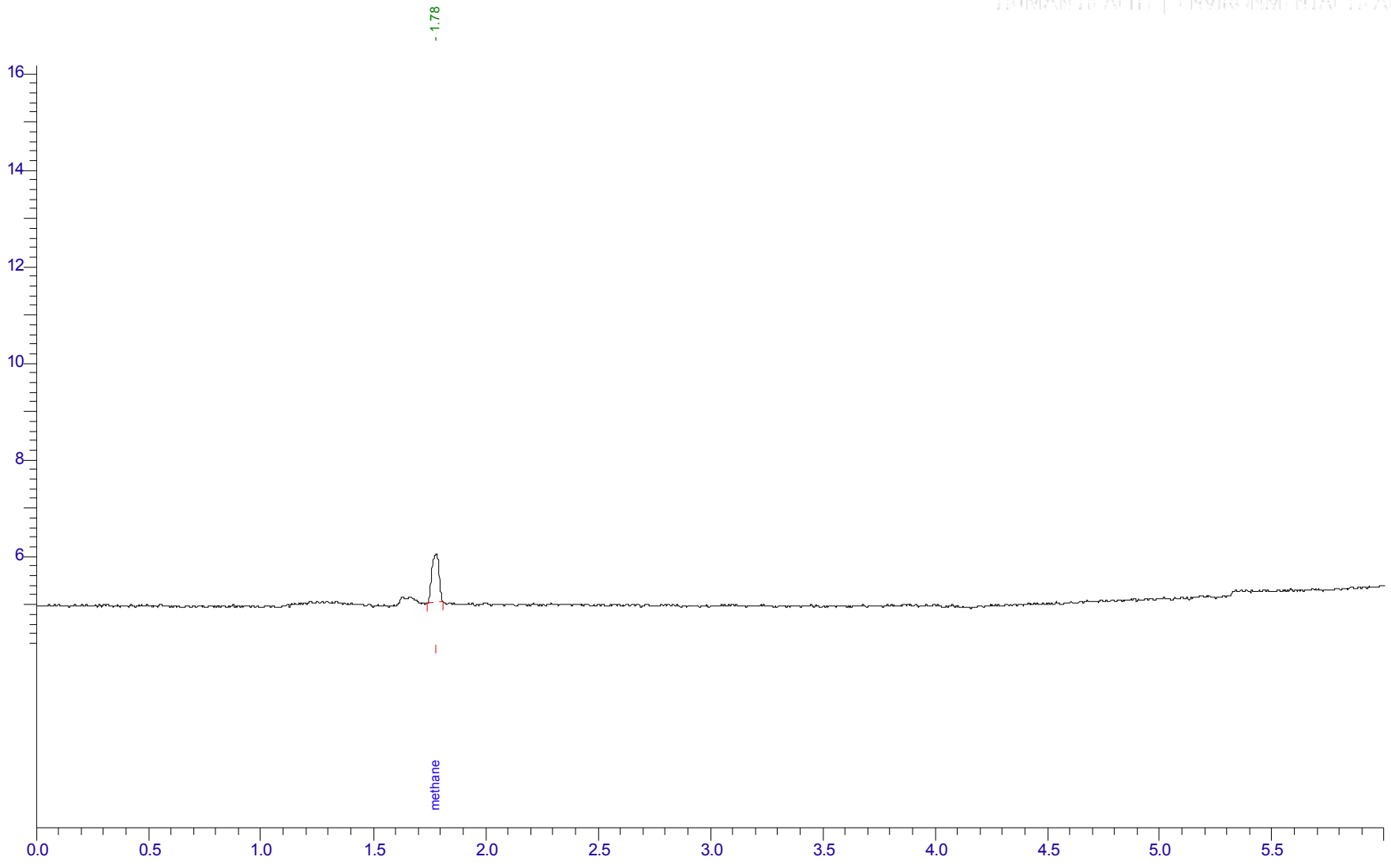

Dealing with Methane in Ambient Air

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 subtracts this value from the calibration

Standard Preparation

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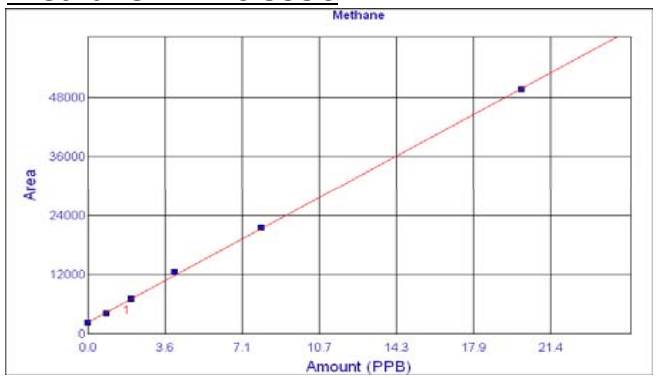
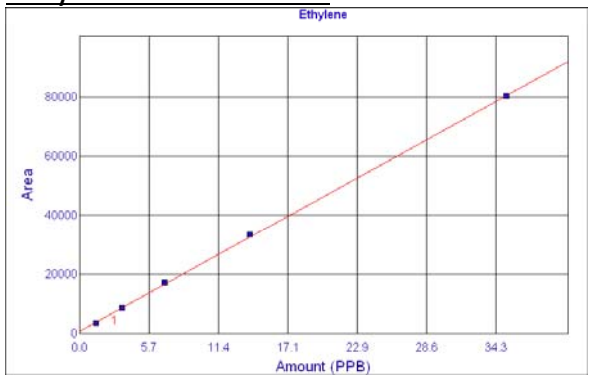
Level #	Methane	Ethylene	Acetylene	Ethane
Level 1	0.80	1.40	1.30	1.50
Level 2	2.00	3.50	3.25	3.75
Level 3	4.00	7.00	6.50	7.50
Level 4	8.00	14.00	13.00	15.00
Level 5	20.00	35.00	32.50	37.50

Results of Calibration

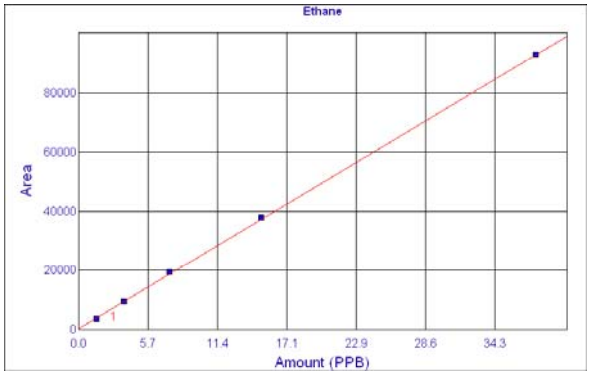
Methane: $r^2 = 0.9996$



Ethylene: $r^2 = 0.9998$



Ethane: $r^2 = 0.9999$



Quality Control Results

Methane				Ethylene		
Actual Amount	Calc Amount	% Dev		Actual Amount	Calc Amount	% Dev
2.00	2.05	2.50		3.50	3.43	-2.00
10.00	10.72	7.20		17.50	18.68	6.74
14.00	15.19	8.50		24.50	26.40	7.76
20.00	20.69	3.45		35.00	36.44	4.11

Acetylene				Ethane		
Actual Amount	Calc Amount	% Dev		Actual Amount	Calc Amount	% Dev
3.25	3.24	-0.31		3.75	3.59	-4.27
16.25	18.27	12.43		18.75	19.91	6.19
22.75	24.31	6.86		26.25	28.43	8.30
32.50	35.55	9.38		37.50	39.14	4.37

Precision (n=5)

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Sample Name	Methane Area	Ethylene Area	Acetylene Area	Ethane Area
40 uL	43180	70067	25773	80441
40 uL	44330	70199	25430	81390
40 uL	43421	67911	23123	79164
40 uL	44331	71017	24700	82016
40 uL	42184	66722	23495	76234
Average	43489	69183	24504	79849
% RSD	**2.1**	**2.6**	**4.8**	**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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