Headspace Technology for GC and GC/MS: Features, benefits & applications

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Oct 2015

Why use Headspace?

- Very Simple –no to minimum sample prep
- Robust – enhance uptime
- Non-detectable carry-over
- Inert sample path
- Enhance accuracy and repeatability
- Excellent repeatability
- Investigating volatiles in many matrices
  - Avoid extraction
  - Eliminate losses
  - Prevent non-volatiles from entering chromatographic system
- Enables aggressive detection limits
  - Concentrator
  - 1mL, 2mL entire volume.

… enhance productivity and efficiency - saves time and money

Enables the Analysis of Volatiles In Matrices
Which Cannot Be Directly Injected

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Advantages of using HeadSpace technology…

- Maintenance: is there any?
  - No Septum to change
  - No Liner to change
  - No Glass Wool required (no active sites)
  - No Syringe to clean

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Advantages of using HeadSpace technology…

- Saves Time
  - Not changing the above (or forgetting to change them)
  - Analysis time - Shorter runs - analyzing
  - Volatiles not Matrix

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Advantages of using HeadSpace technology…

- Saves Money
  - Increase productivity
  - Minimal consumables
  - Extends Column Live

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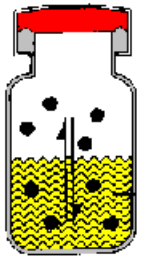
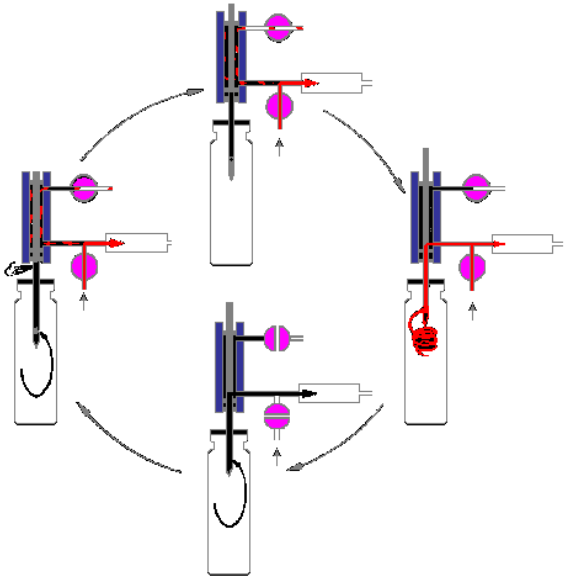
Three sampling methods

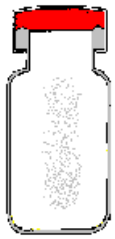
- Static (equilibrium) Headspa



- Multiple Headspace Extraction (MH



- Total Evaporation



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Static or Equilibrium Headspace

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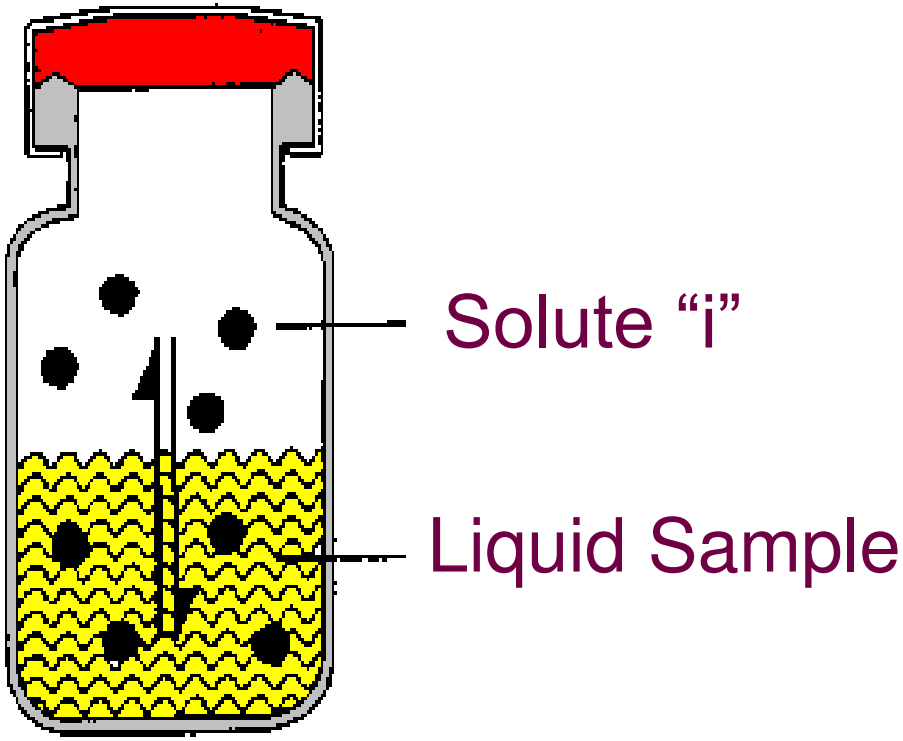
Partition equilibrium of analyte “i” between liquid and gas phase

Consider:

Time
Temperature



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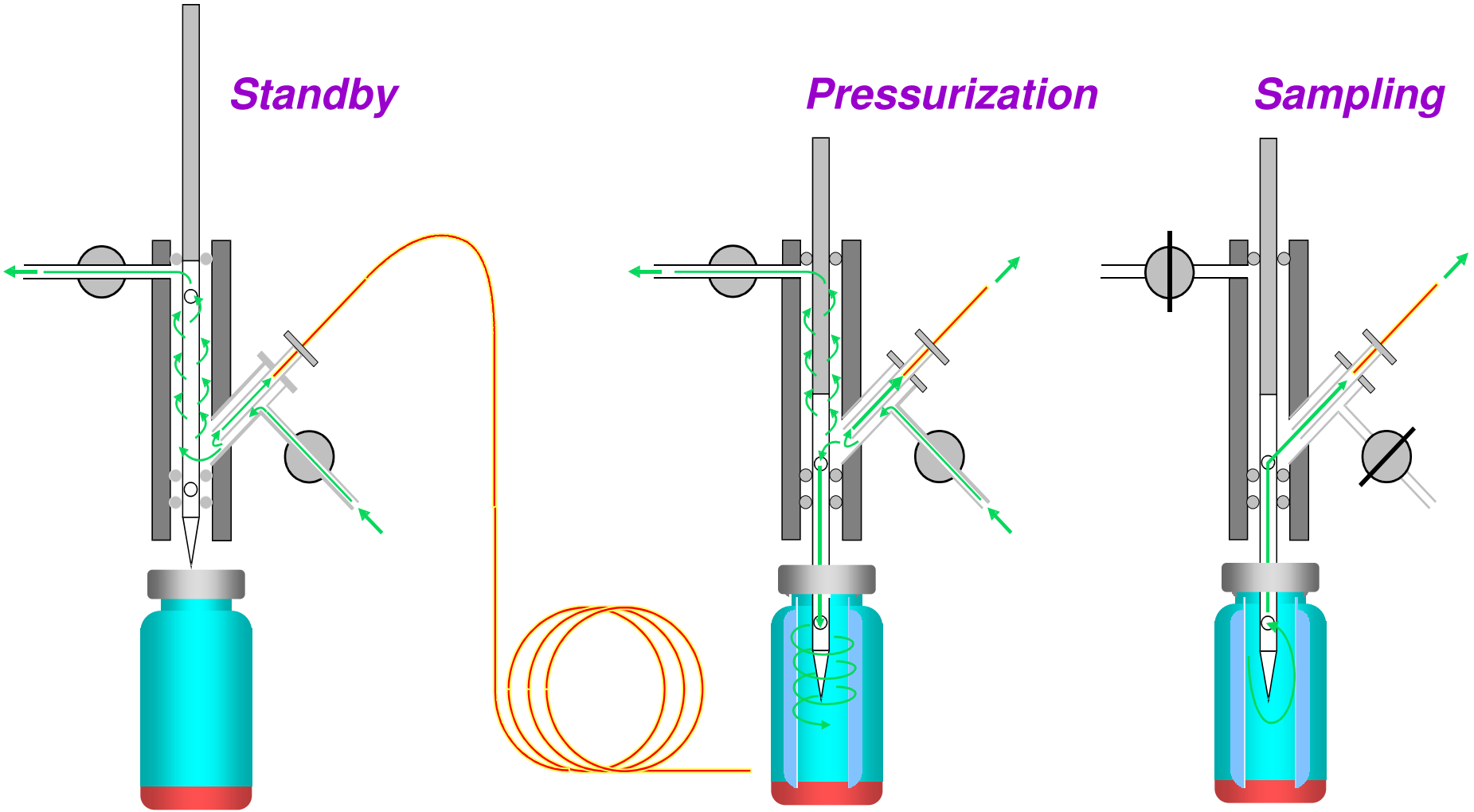
Balanced – Pressure Sampling



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How Sampling works
HS Trap

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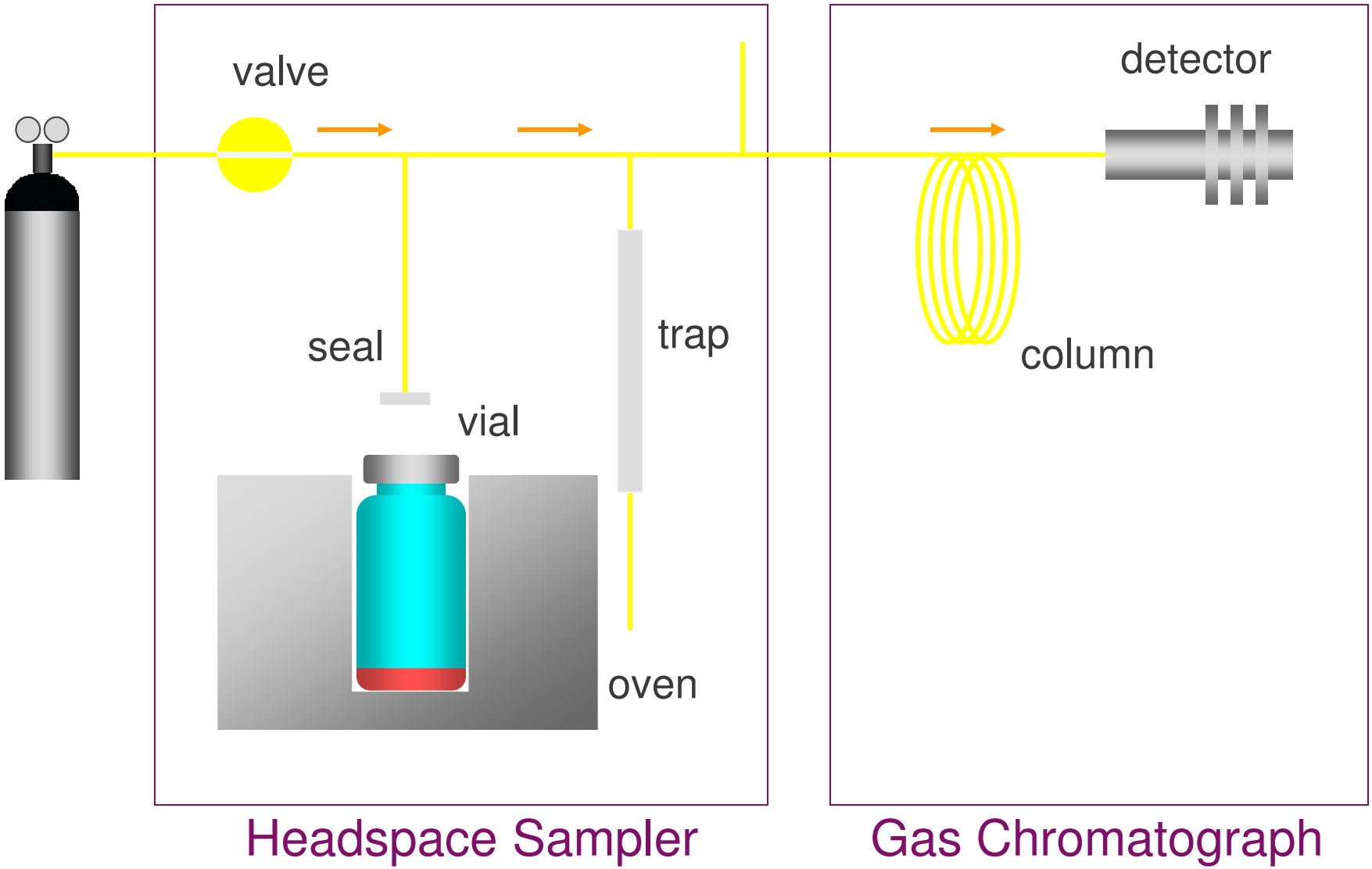
Why use Headspace Trap (HS Trap) instead of conventional HS

- Enhance Detection Limits by at least 50
  - Enables injection of entire HS vapor plus more with multiple injections of same vial focusing on a trap
- Dry Purge – remove water excellent water management
- Removes Oxygen
- Enables the use of Narrow Bore Short columns for Fast GC

Sample Vial Thermal Equilibration



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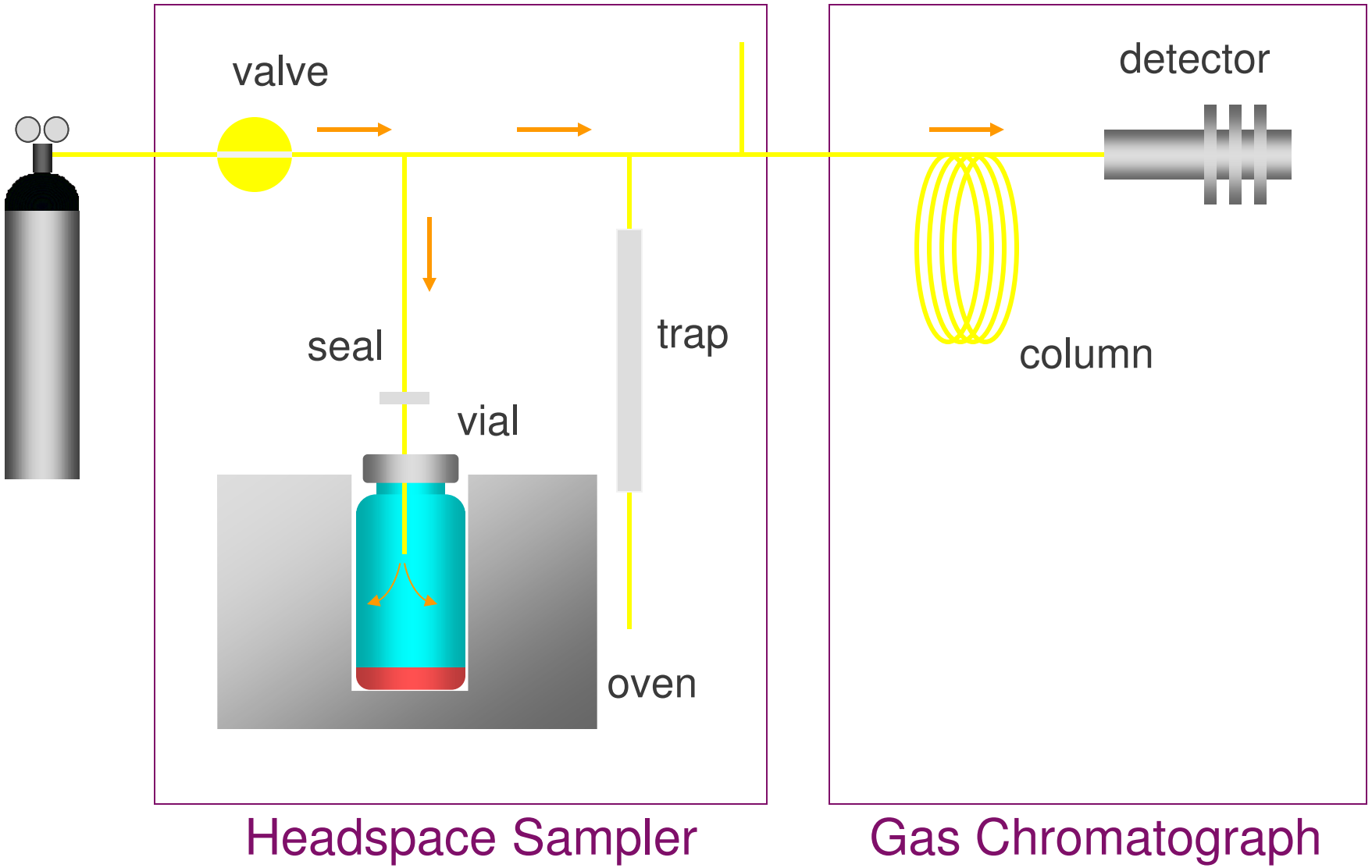
Vial Pressurization



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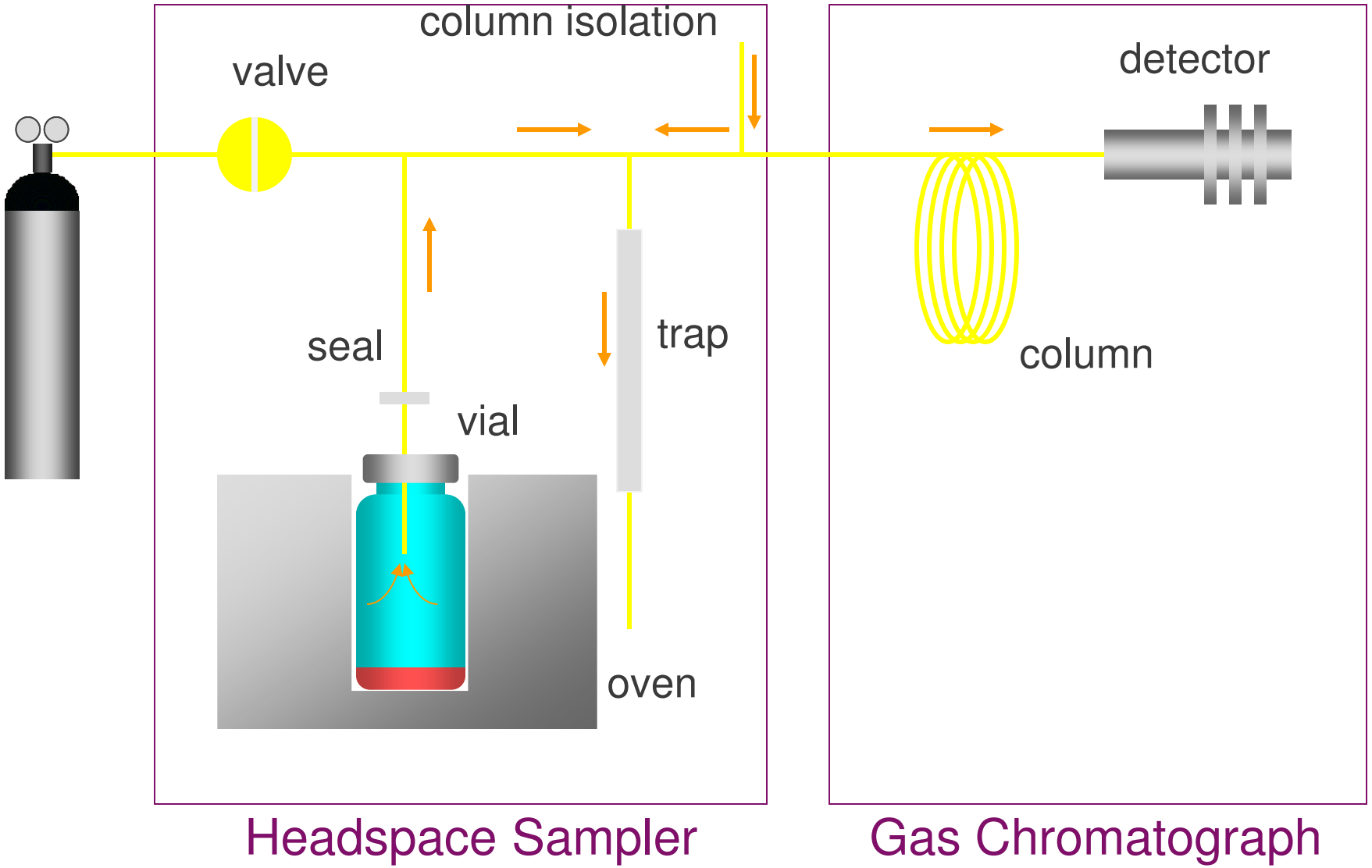
Trap Load



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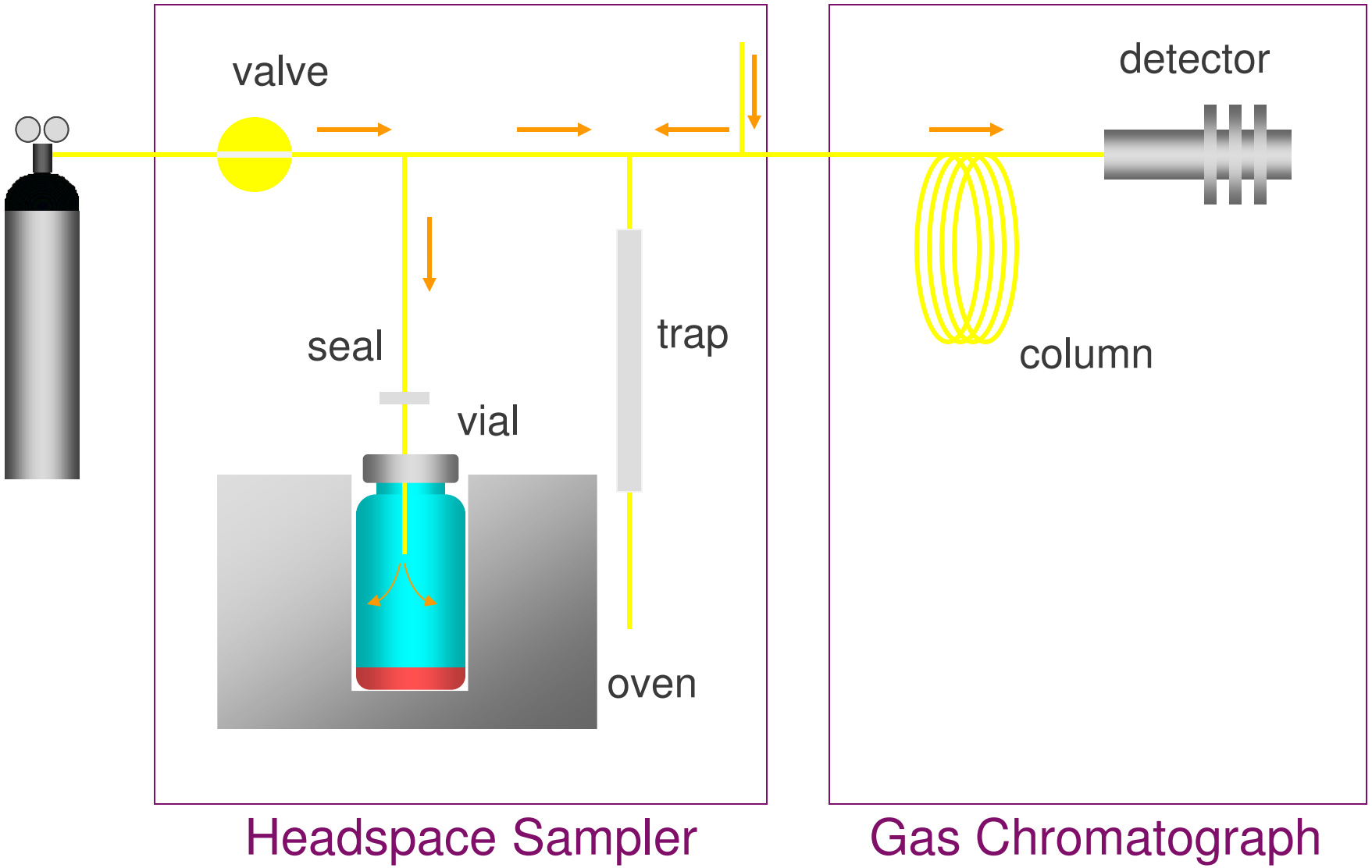
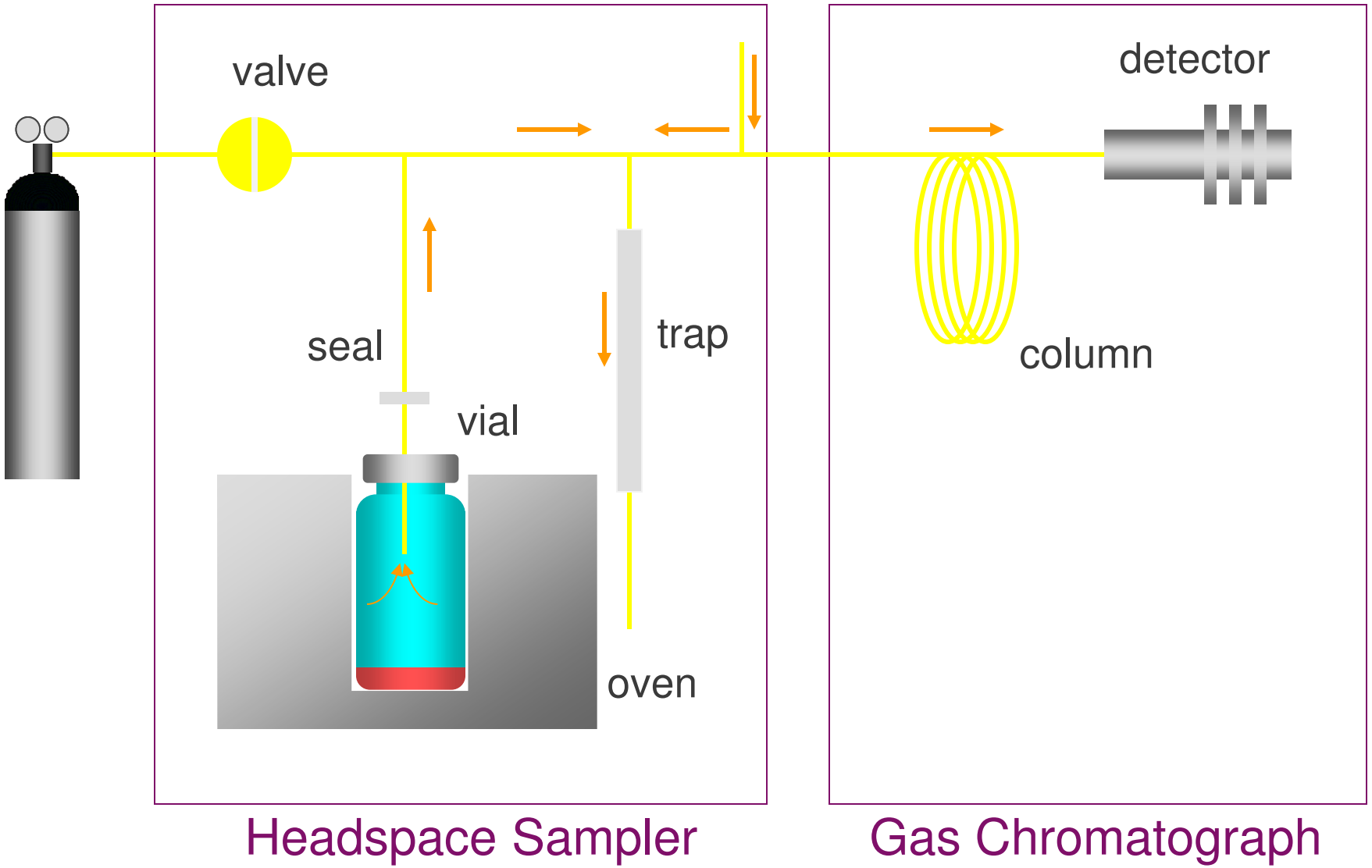
Vial Re-Pressurization



Trap Re-Load



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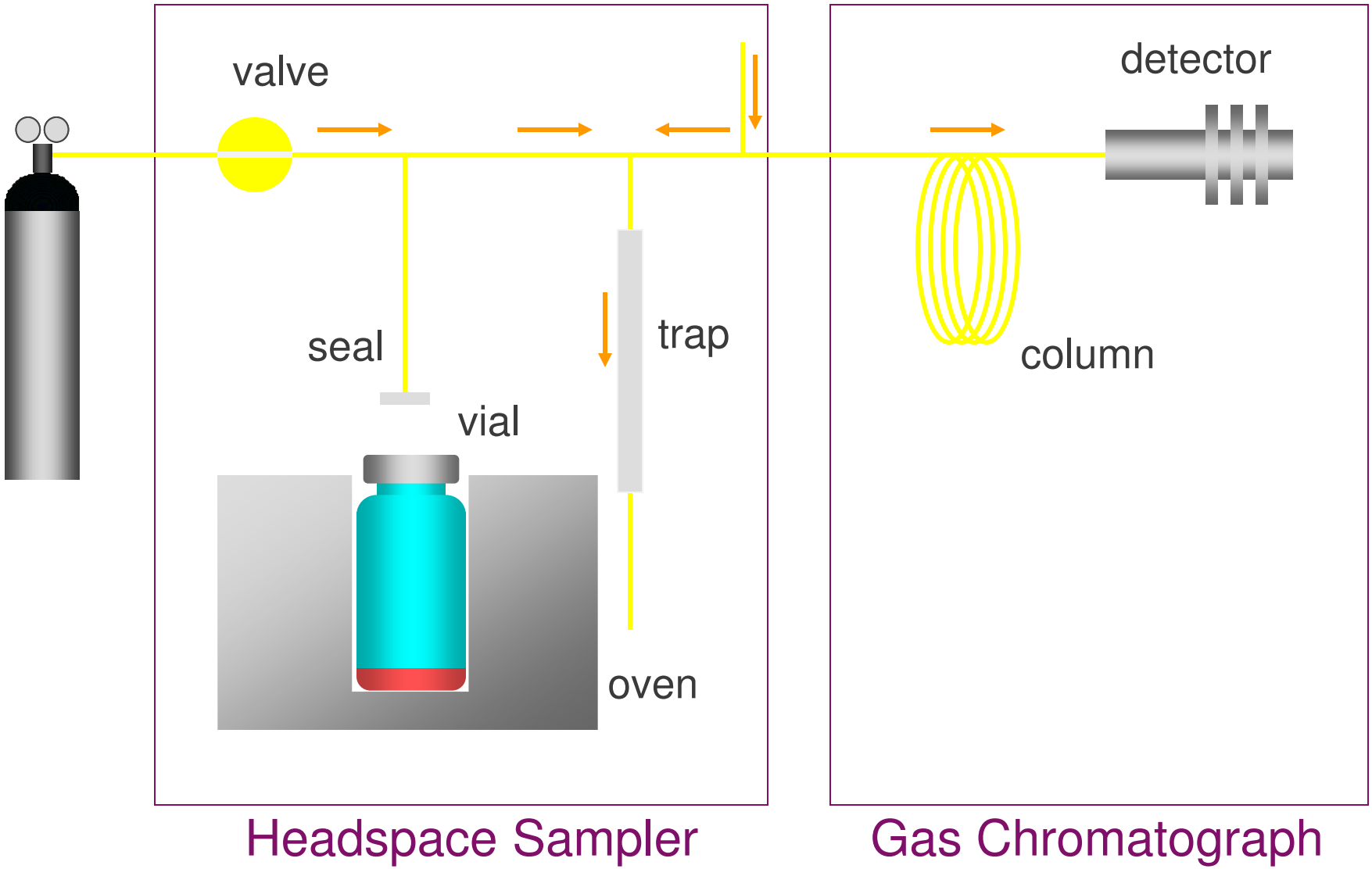
Dry Purge



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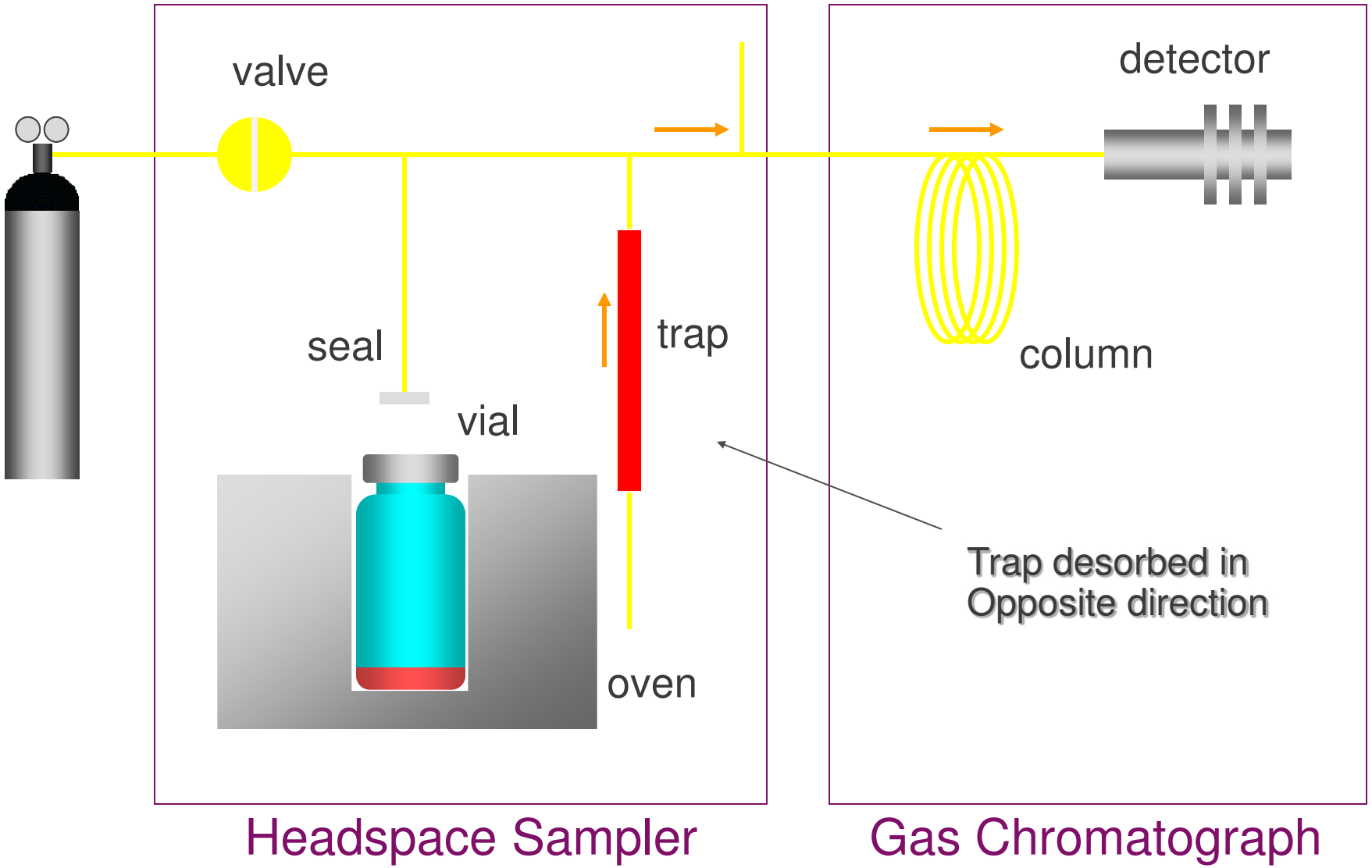
Trap Desorption



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Applications

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New USP Residual Solvent Test by Static Headspace Technique

Class 1 Residual Solvents

1,2-Dichloroethane
1,1,1-Trichloroethane
Carbon Tetrachloride
Benzene
1,1-Dichloroethene

Class 2 - Mixture A Residual Solvents

Acetonitrile
Chlorobenzene
Cyclohexane
c-1,2-Dichloroethene
t-1,2-Dichloroethene
Methylene Chloride
1,4-Dioxane
Methanol
Methylcyclohexane
Tetrahydrofuran (THF)
Toluene
Ethyl Benzene
m-Xylene
p-Xylene
o-Xylene

Class 2 - Mixture B Residual Solvents

Chloroform
1,2-Dimethyoxyethane
Hexane
Methylbutylketone
Nitromethane
Pyridine
Tetralin
Trichloroethylene

Class 3 Residual Solvents

Acetic Acid
Acetone
Anisole
1-Butanol
2-Butanol
Butyl Acetate
t-Butylmethyl ether
Cumene
Dimethyl sulfoxide
Ethanol
Ethyl Acetate
Ethyl Ether

Class 3 Residual Solvents (continued)

Heptane
Isobutyl Acetate
Isopropyl Acetate
Methyl Acetate
3-Methyl-1-Butanol
Methylethylketone
Methylisobutylketone
2-Methyl-1-propanol
Pentane
1-Pentanol
1-Propanol
2-Propanol

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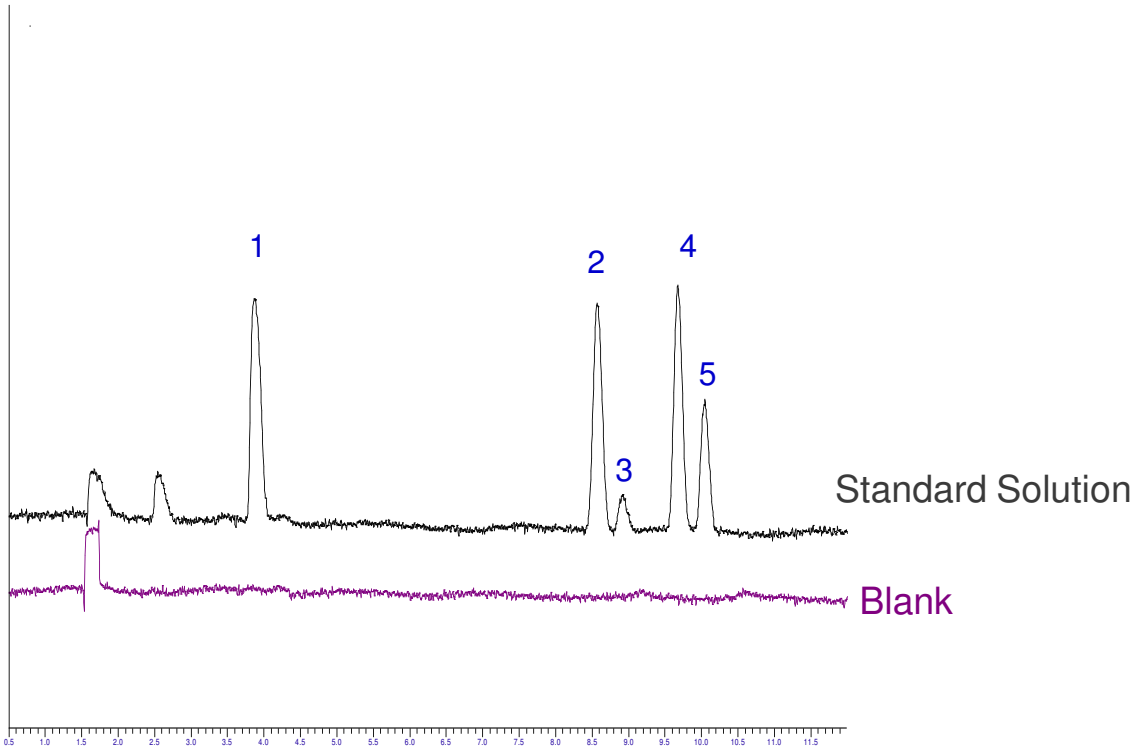
Blank (bottom) / Class 1 Standard Solution (top)



- HS Conditions
  - Eq. Temp: 80°C
  - Eq. Time: 15min
  - Inj Volume: 1mL
  - Needle Temp: 110°C
  - T Line Temp: 130°C
  - Injector Temp: 140°C

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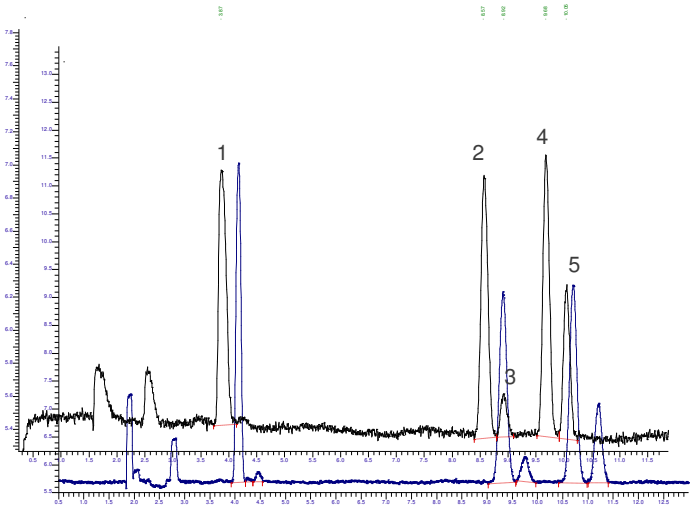
Class 1: Comparing results on 0.32 id column to 0.53 id column

All method criteria are achieved



PE Elite 624 – 30m x 0.32mm x 1.8um

	Component	PPB	Area	S/N
1	1,1-Dichloroethene	64.7	14685	34 : 1
2	1,1,1-Trichloroethane	83.3	14097	35 : 1
3	Carbon Tetrachloride	33.0	2185	6 : 1
4	Benzene	17.0	14116	35 : 1
5	1,2-Dichloroethane	42.2	7546	17 : 1

PE Elite 1301 – 30m x 0.53mm x 3.0um

	Component	PPB	Area	S/N
1	1,1-Dichloroethene	64.7	38361	143 : 1
2	1,1,1-Trichloroethane	83.3	36551	86 : 1
3	Carbon Tetrachloride	33.0	4658	11 : 1
4	Benzene	17.0	36528	89 : 1
5	1,2-Dichloroethane	42.2	14349	36 : 1

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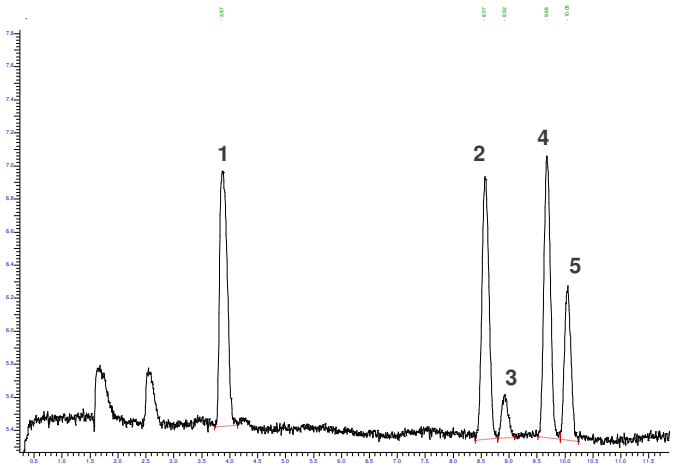
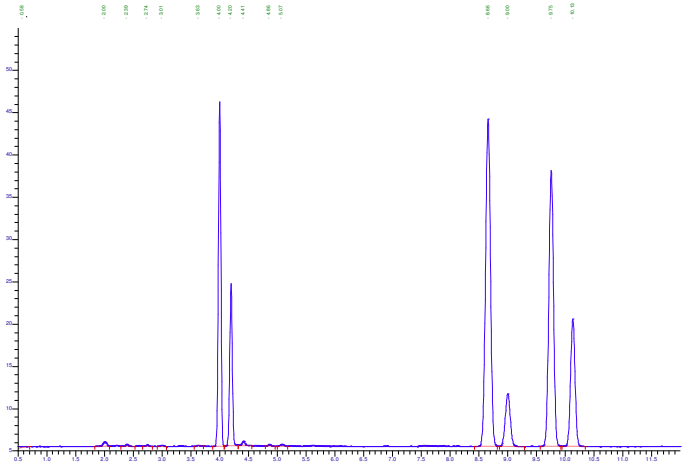
Headspace vs Headspace Trap



Residual Solvents Class 1
Conventional Headspace

	Component	PPB	Area	S/N
1	1,1-Dichloroethene	64.7	14685	34 : 1
2	1,1,1-Trichloroethane	83.3	14097	35 : 1
3	Carbon Tetrachloride	33.0	2185	6 : 1
4	Benzene	17.0	14116	35 : 1
5	1,2-Dichloroethane	42.2	7546	17 : 1



Residual Solvents Class 1
Headspace Trap

	Component	PPB	Area	S/N
1	1,1-Dichloroethene	64.7	123689	1021: 1
2	1,1,1-Trichloroethane	83.3	230364	969 : 1
3	Carbon Tetrachloride	33.0	38202	156 : 1
4	Benzene	17.0	184737	816 : 1
5	1,2-Dichloroethane	42.2	81162	377 : 1

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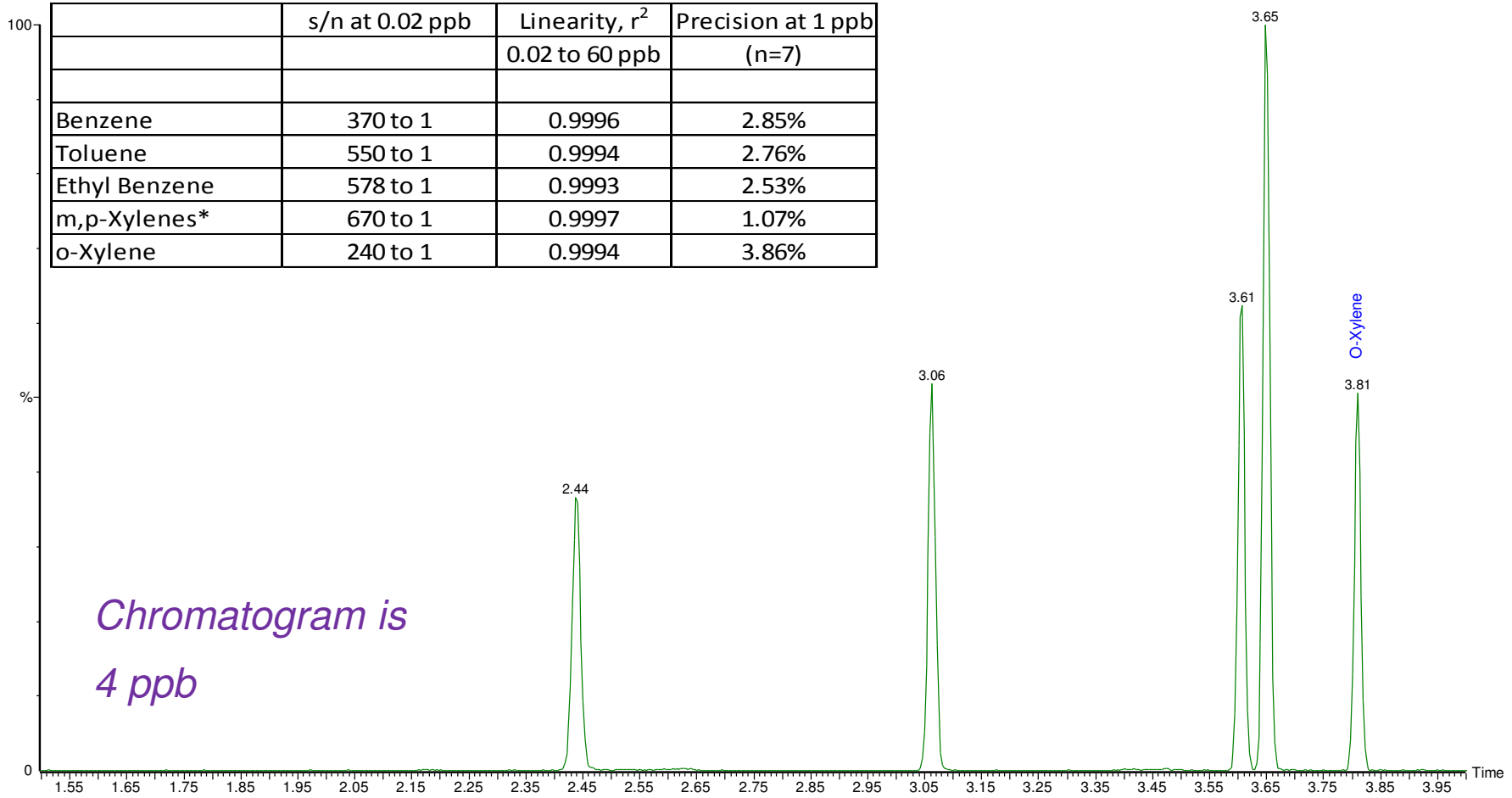
Analytical Performance of BTEX acquiring in Full Scan

	s/n at 0.02 ppb	Linearity, r^2	Precision at 1 ppb
		0.02 to 60 ppb	(n=7)
Benzene	370 to 1	0.9996	2.85%
Toluene	550 to 1	0.9994	2.76%
Ethyl Benzene	578 to 1	0.9993	2.53%
m,p-Xylenes*	670 to 1	0.9997	1.07%
o-Xylene	240 to 1	0.9994	3.86%



Chromatogram is 4 ppb

- …Under four minutes

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Amount of Ethanol in Glycerin Soap via Headspace GC

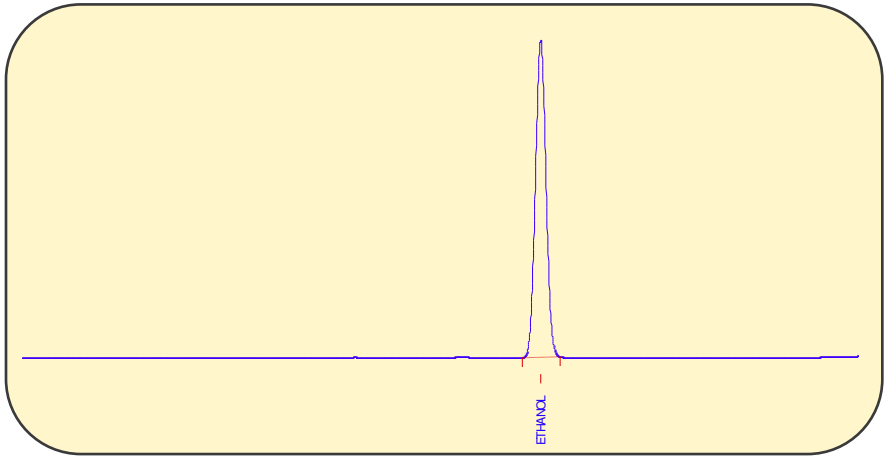
This test was performed via equilibrium HS and total evaporation techniques.

Received same results with both techniques 3% ethanol in soap

3% is a lot of material so dilution and/or using total evaporation works well

Since total evaporation is easier, this would be the recommended technique (both are described)

Soap is a matrix that cannot be directly injected into a GC inlet and extraction is laborious. Headspace provided a quick, precise, accurate means of determining the amount of ethanol in soap while significantly reducing labor time and costs.



- Equlibrium Headspace
- Sample
  - Weigh 0.20g of soap into vial
  - Fill vial with 5mL of water
  - Cap vial and place on autosampler
- Standard
  - Prepare a standard of known concentrations in water
  - Add 5mL aliquot of this standard to HS vial
  - Cap vial and place on autosampler and run
- Software calculates results (Std amt and sample weight is entered into appropriate places in software)
  - For single level calibration
  - (response unknown/response std)*std conc.=amount of unknown
- Total Evaporation
  - Sample
    - Weigh 0.2g of soap into vial
    - Cap vial and place on autosampler
    - Thermostat sample at temp that will volatilize ethanol from matrix leaving most matrix in vial
  - Standard
    - Prepare a known standard in a volatile solvent
    - Add 20uL into HS vial. The amount of ethanol into vial is known
  - Software calculates results

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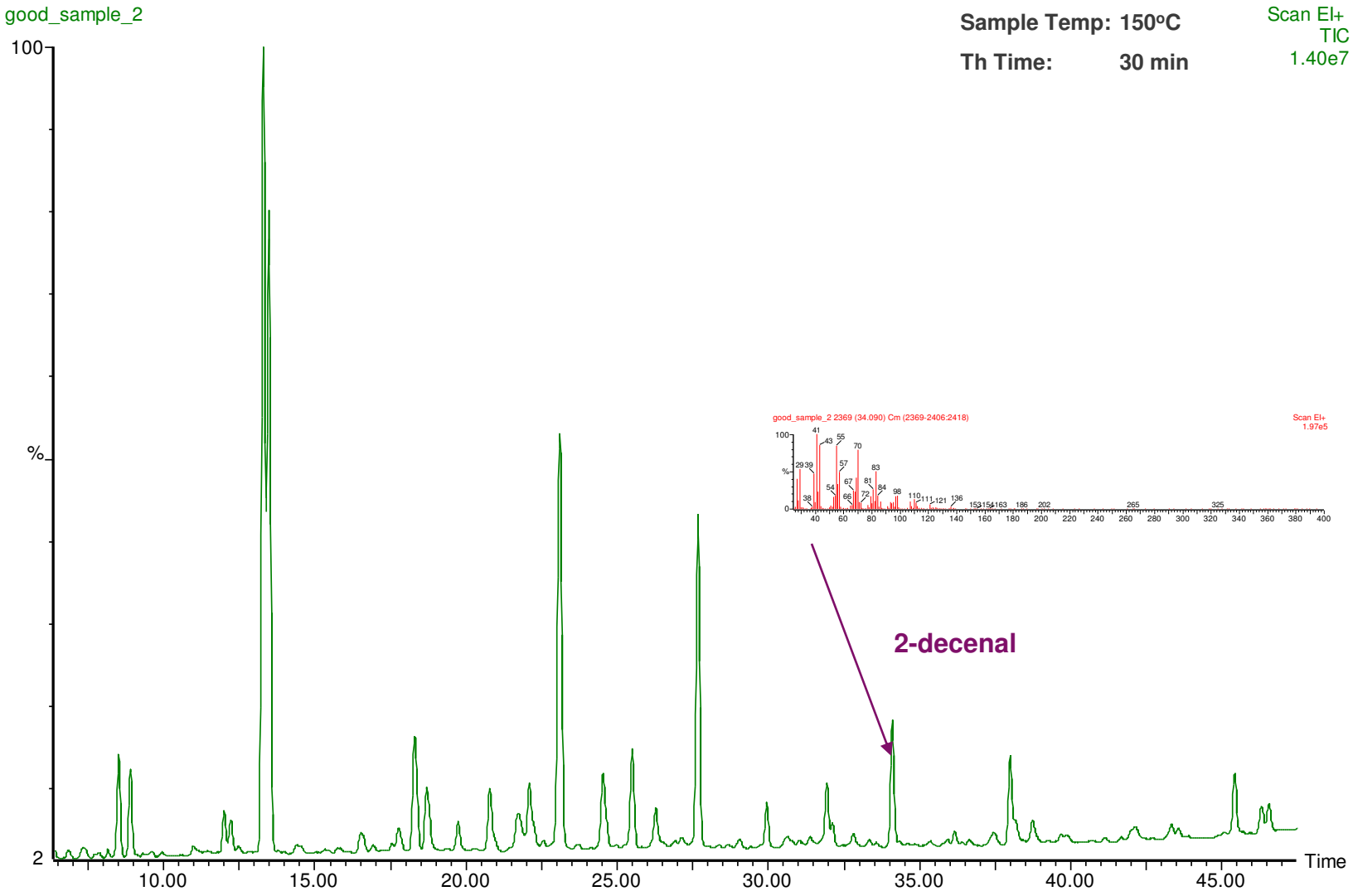
Analytes in Paper - Headspace - GC / MS (5g paper)



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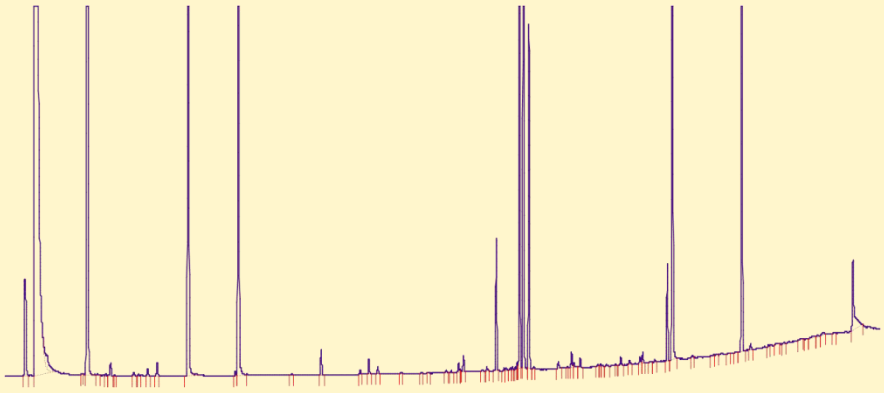
Determination of amount of Fragrance in a polymer sphere by Headspace

- Sample Matrix: Fragrance is suspended in a polymeric sphere. The amount of fragrance in this matrix needs to be known for QC purposes. Injecting polymer directly into GC, would have resulted in time consuming maintenance. Extracting fragrance, would have been time consuming and expensive. In addition, the extraction recoveries could be poor and also selective depending upon analyte.
- With Headspace:
  - Easy, fast sample prep.
  - Extremely low maintenance
  - Precise, accurate results
- Sample Preparation: 0.06 g sample in 1mL THF
- Volume in HS vial: 20 uL aliquot in HS vial…cap vial
- Standard Preparation: Prepare fragrance at known concentration in THF
- Volume of Std in vial: 20uL of standard in HS vial…cap vial
- Sample Temp: 120°C (this temperature was enough to completely volatilize the fragrance but not the matrix
- Required detection limits and accurate results were attained. The fragrance amount calculated at 15% which was the expected amount
- Using HS resulted in reduced costs and time



Chromatogram of fragrance in a matrix by HS/GC

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“Beer”

Analyzing Beer

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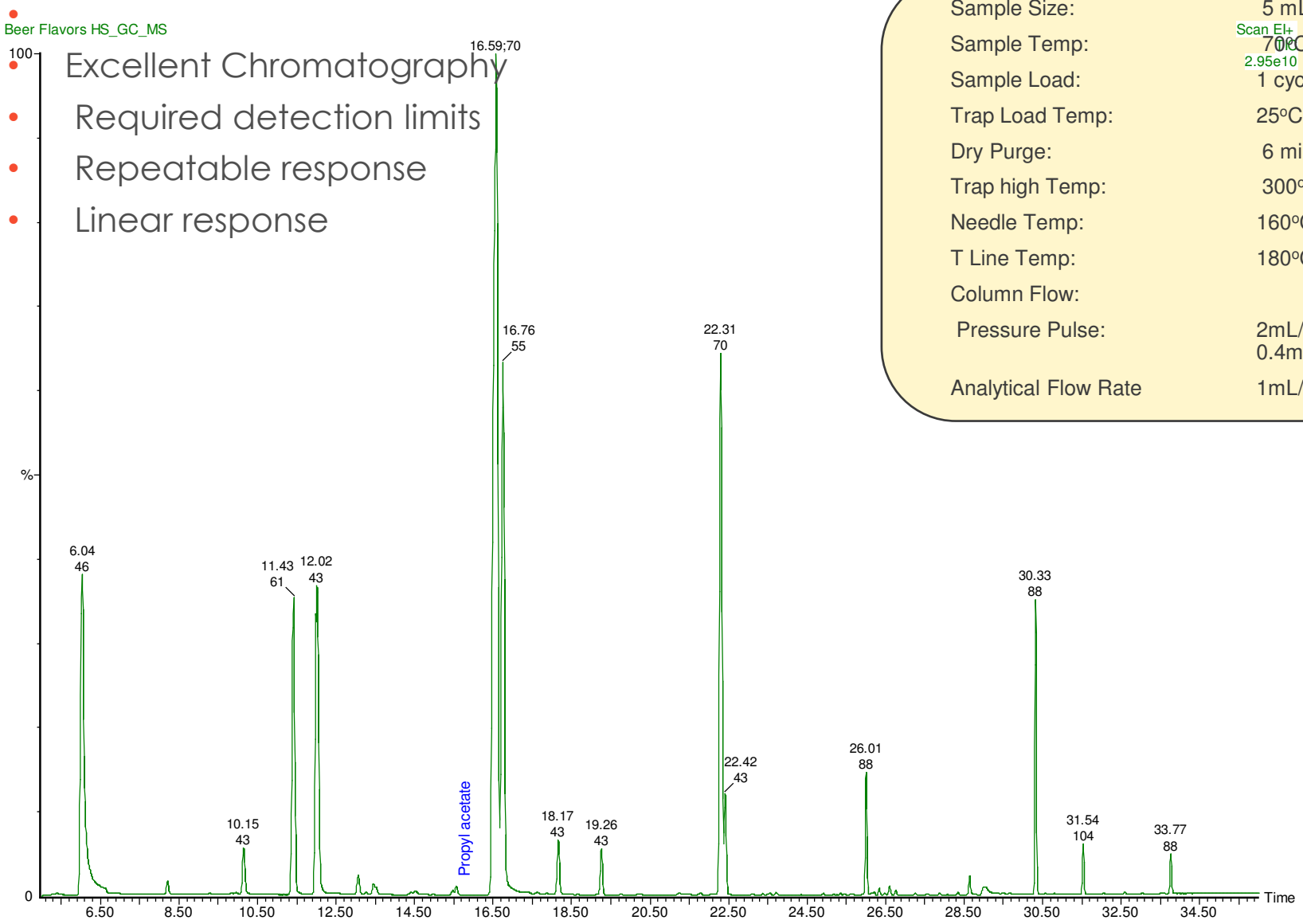
Characterizing Flavors in Beer and starting products: HSTrap/GC/MS

- Excellent Chromatography
- Required detection limits
- Repeatable response
- Linear response



Sample Size:	5 mL
Sample Temp:	70°C
Sample Load:	1 cycle
Trap Load Temp:	25°C
Dry Purge:	6 min
Trap high Temp:	300°C
Needle Temp:	160°C
T Line Temp:	180°C
Column Flow:	
Pressure Pulse:	2mL/min for 0.4min
Analytical Flow Rate	1mL/min

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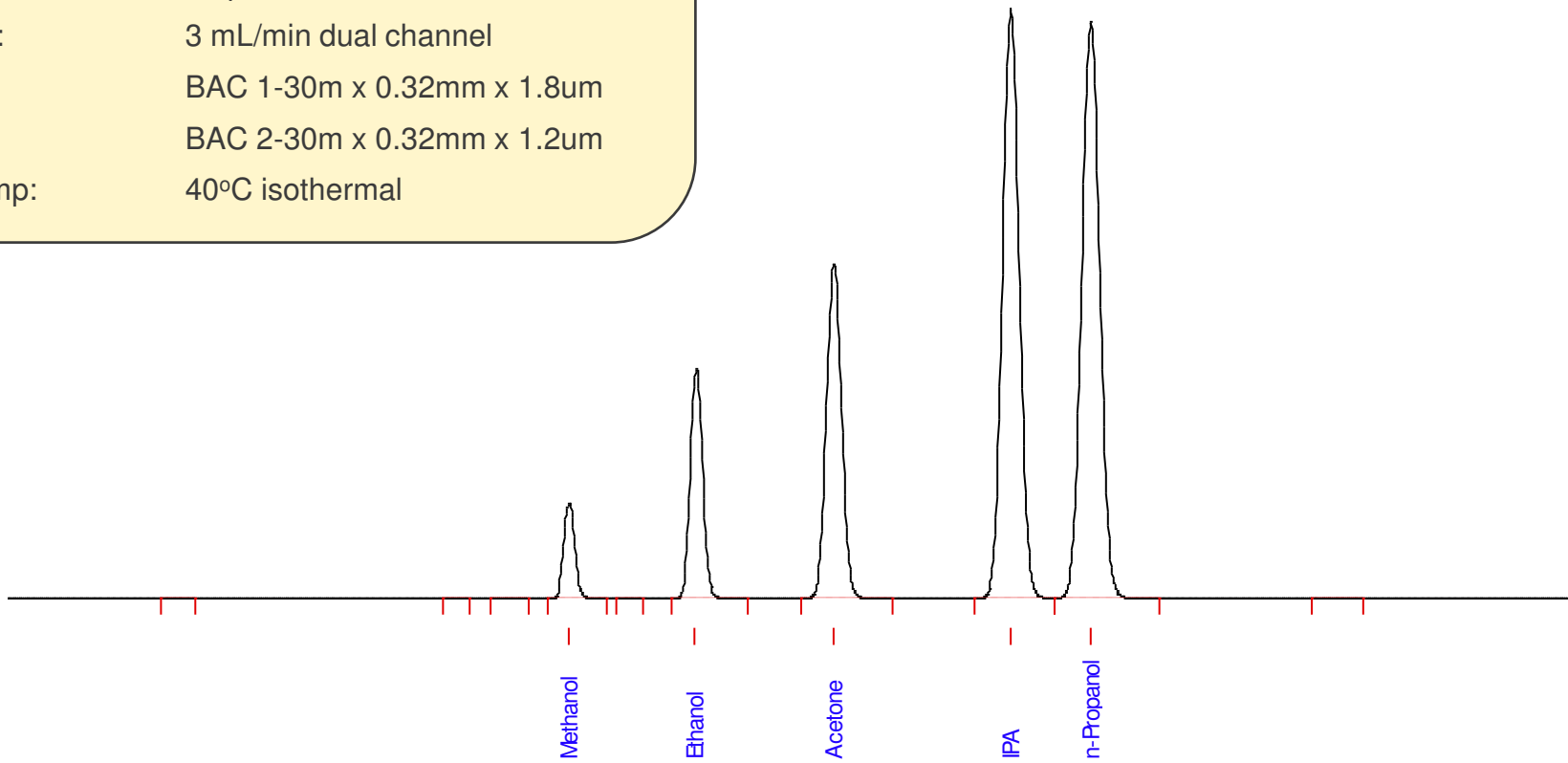
Blood Alcohol composite

Oven Temp:	70 °C
Needle Temp:	110 °C
T Line Temp:	120 °C
HS psi:	25 psi
Column psi:	21 psi
Column Flow:	3 mL/min dual channel
Columns:	BAC 1-30m x 0.32mm x 1.8um
	BAC 2-30m x 0.32mm x 1.2um
GC Oven Temp:	40°C isothermal



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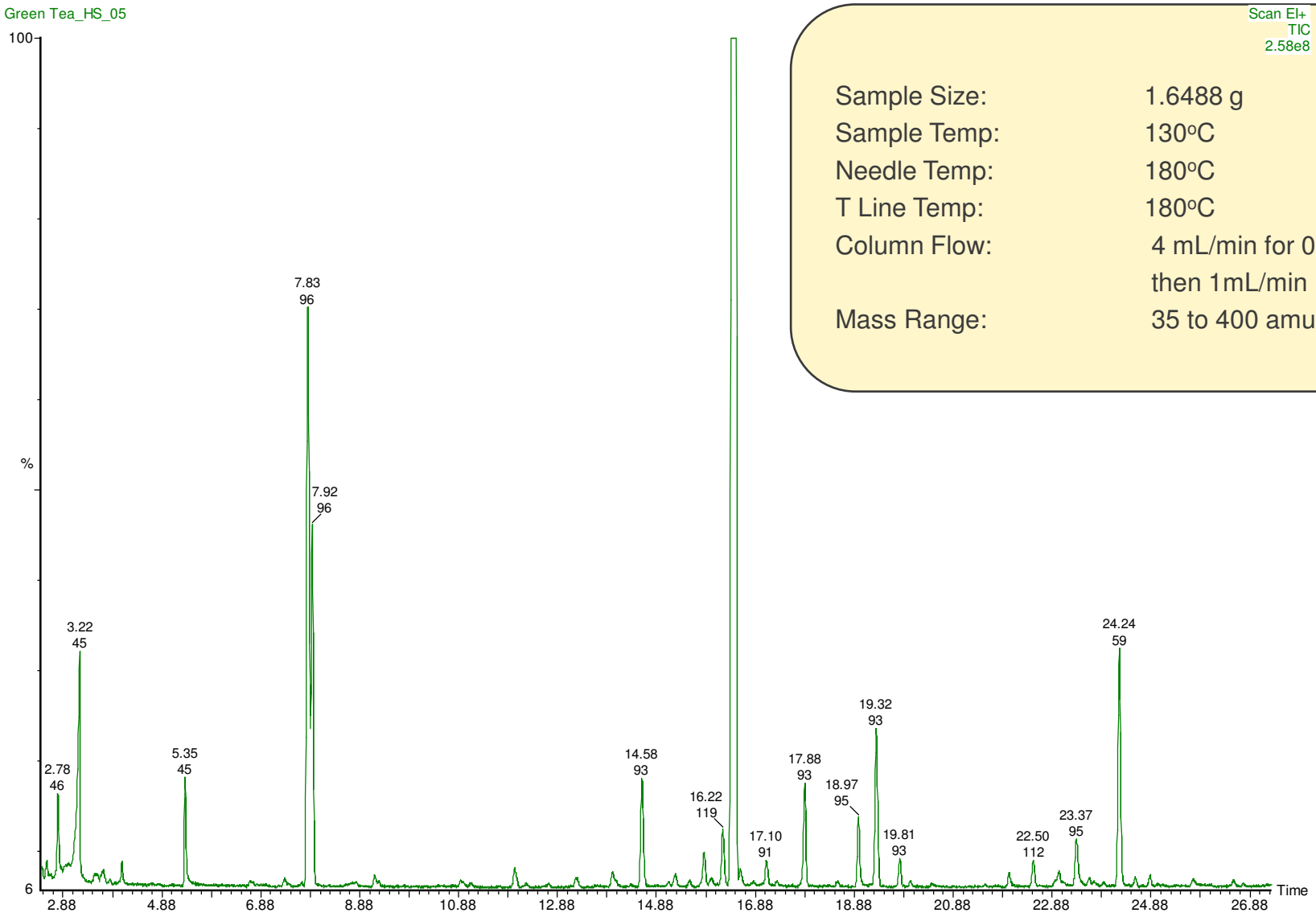
Flavors in Green Tea – HS/GC/MS



Sample Size:	1.6488 g
Sample Temp:	130°C
Needle Temp:	180°C
T Line Temp:	180°C
Column Flow:	4 mL/min for 0.2 min then 1mL/min
Mass Range:	35 to 400 amu

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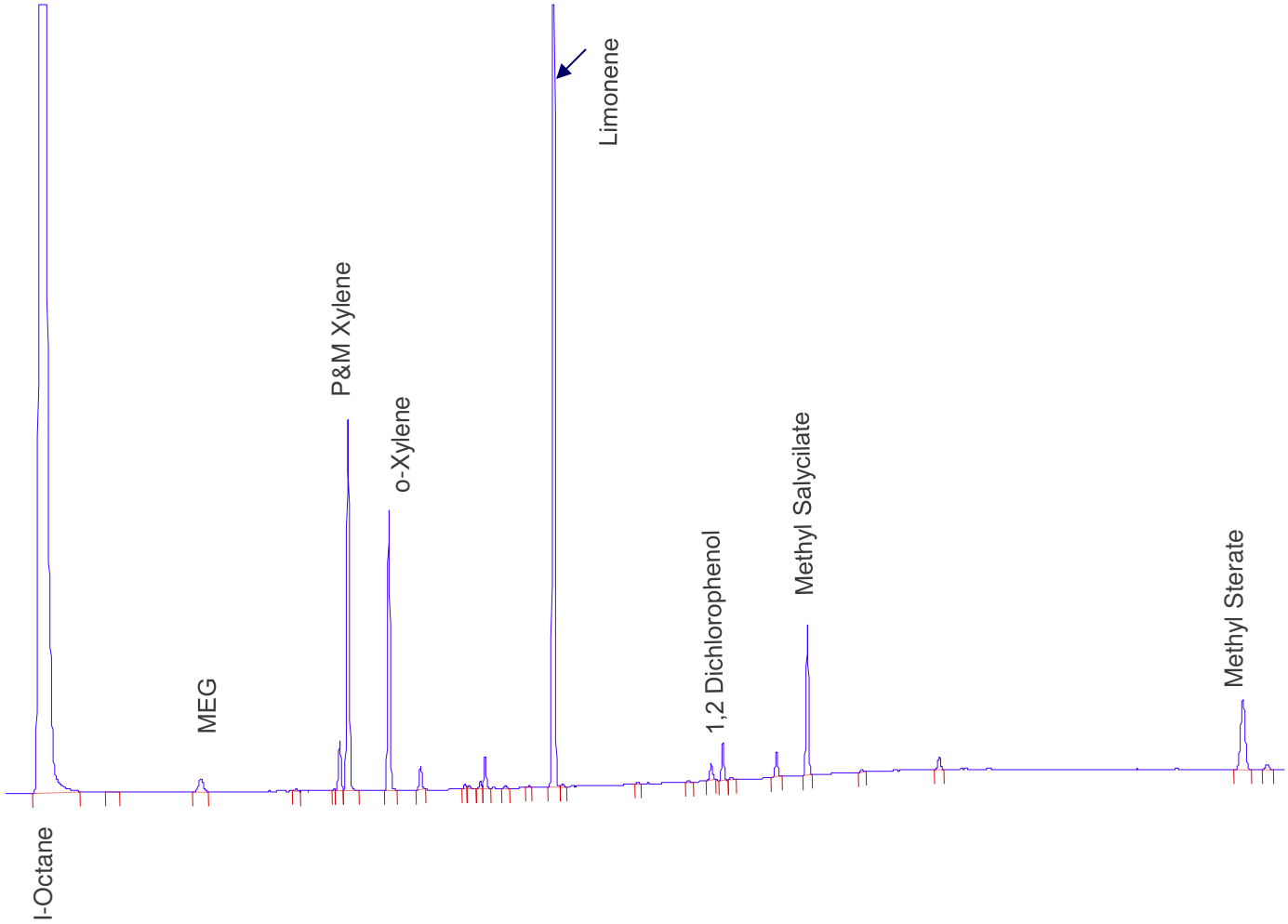
Volatiles and Semi-Volatiles in High Density Polyethylene



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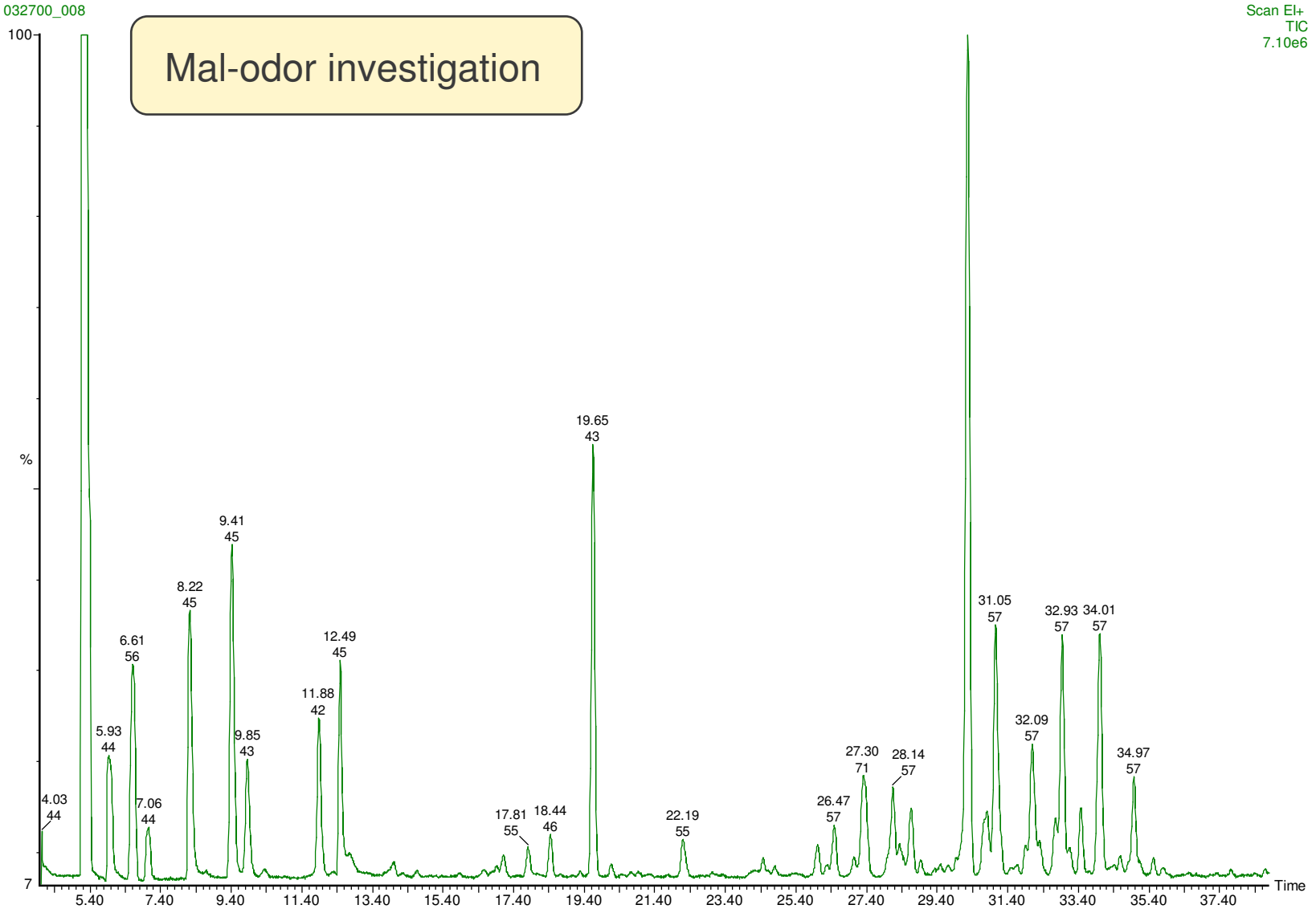
Off odors in Resin – 3.2g in vial – HS/GC/MS



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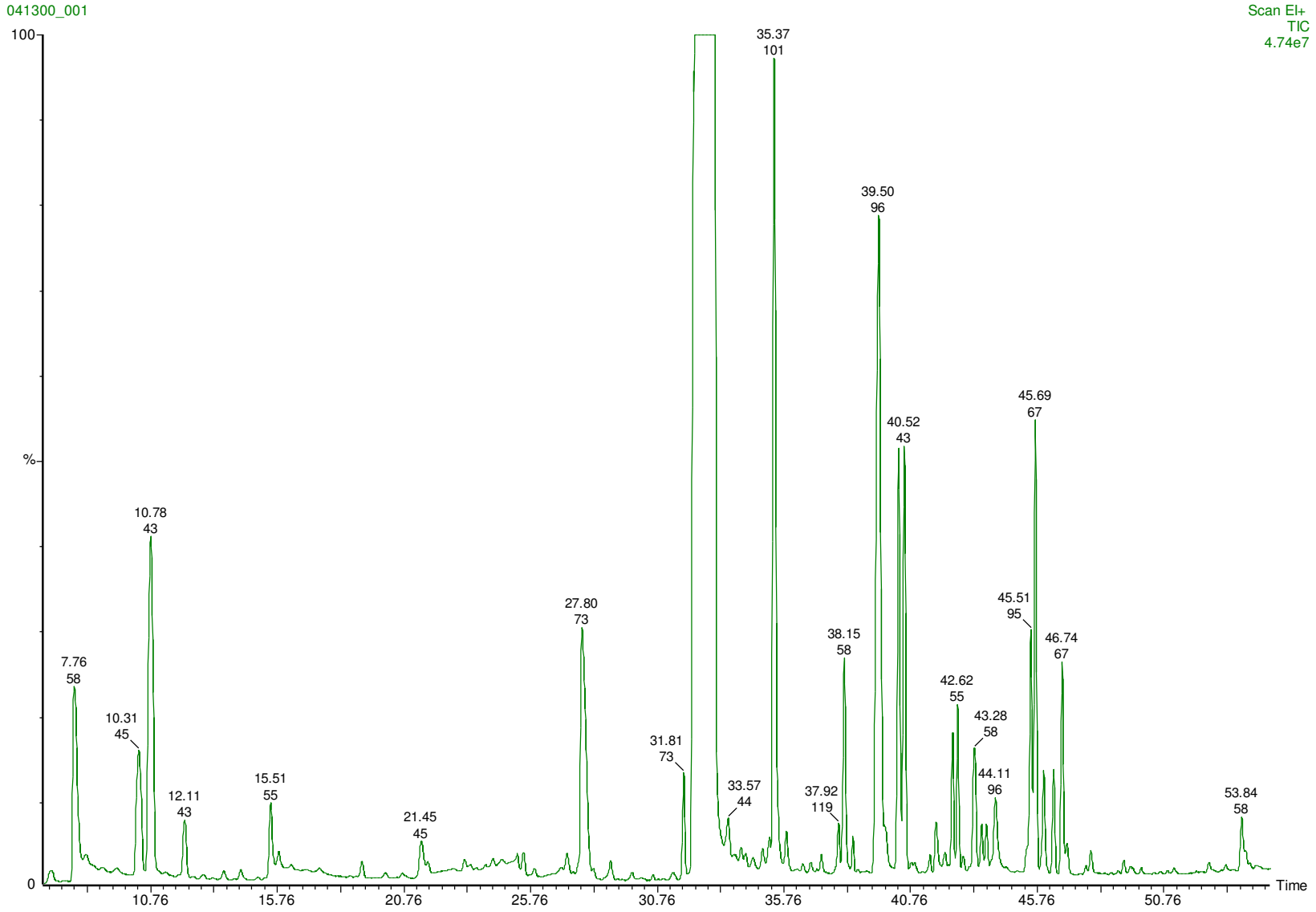
Off odors in Resin – 0.5g in vial – HS/GC/MS



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Summary – the optimum technique for analyzing residual solvents

- Robust and stable
- Inert
- Excellent analytical results
  - Precision
  - Accuracy
  - Detection Limits
- Minimal Maintenance
- User friendly interface
- Non-detectable carry-over
- Simple sample prep
- Enhance long term productivity and efficiency
- Enhance detection limits and repeatability with the HS Trap

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Karima Baudin

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