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Demystifying the Process of Calibrating your Thermal Desorption Gas Chromatography System using Compressed Gas Standards.

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What will be Covered

- What is Thermal Desorption
- Air Concentration Units
- Overview of the tube spiking technique we've been using with compressed gas standards.

Liquid Calibration Standards
µg/mL of solvent e.g. Methanol

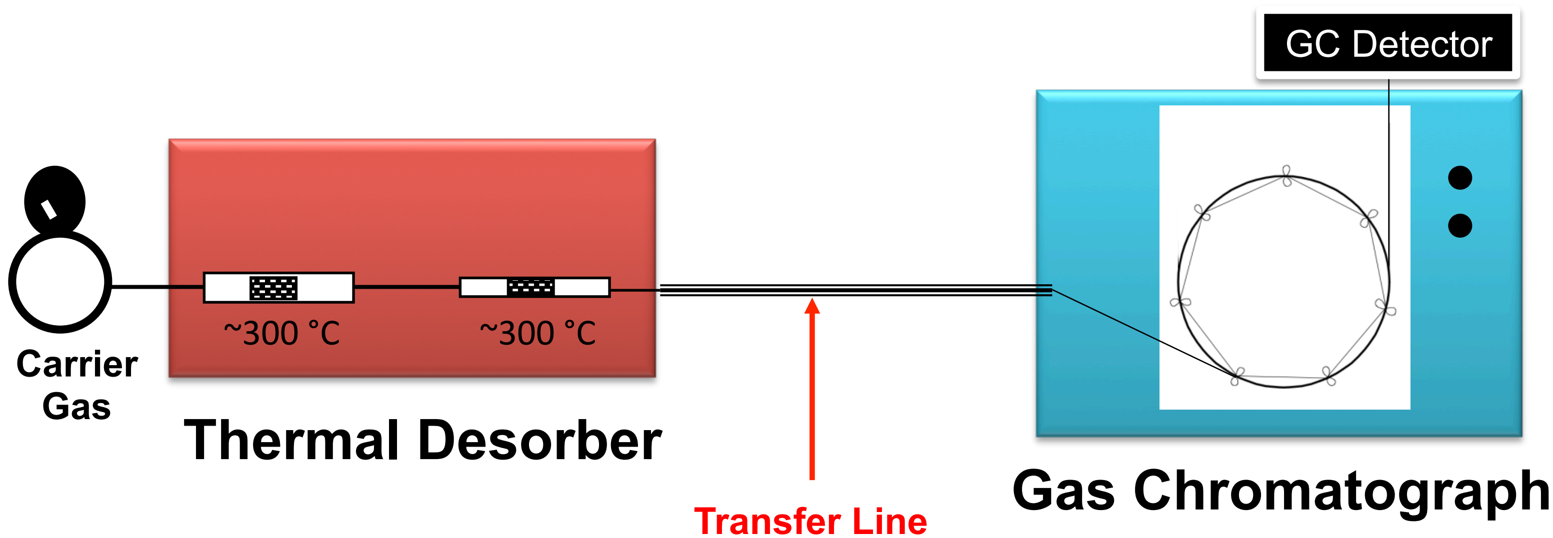
Compressed Gas Calibration Standards
PPBv by (volume or by mole)

What is Thermal Desorption?

A sample preparation technique for gas chromatography.

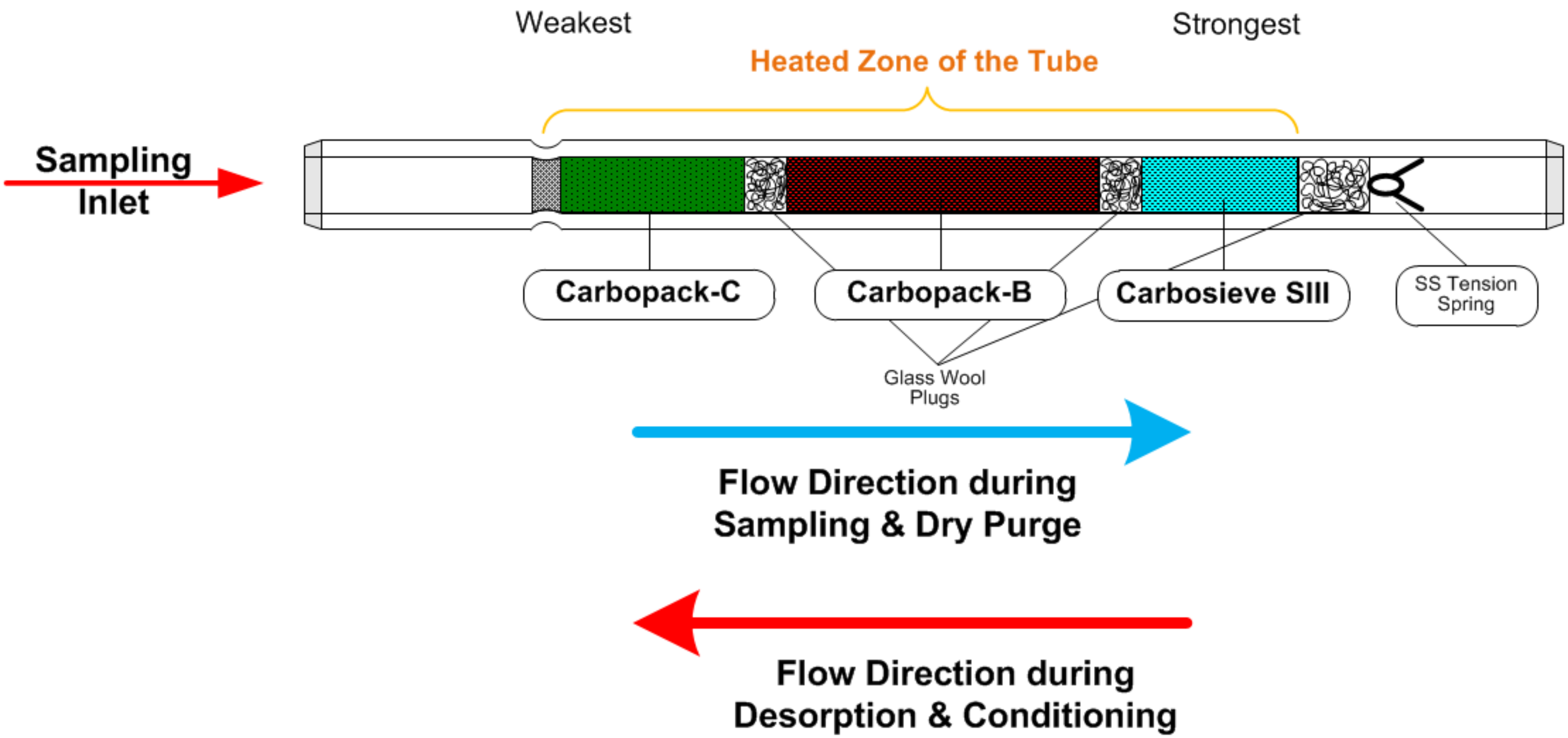
- The sample is collected onto an adsorbent packed glass or stainless steel tube. *The sample is concentrated on the adsorbents.*

- The packed tube is heated (Thermal) and the compounds are released into the carrier gas (Desorption) where they are swept onto the GC column and analyzed by the gas chromatograph.



Multi-Bed Thermal Desorption Tube

3-Bed Tube (Carbotrap® 300)



Wrong Assumptions of Air Concentration Units

µg/L is equivalent to ppbv - this is false

µg/m^3 is equivalent to ppbv - this is false

The M.W. of the compound, the temperature, and barometric pressure are needed to convert between the units

Using a Molar Volume 24.46 L/mole gets me close enough - this is false

(This value only applies when your at the beach)

Calibration Process Using Liquid Standards

- Typically the data handling system is setup to calculate the **mass** of contaminate(s) found on the tube (e.g. ng/tube, or µg/tube).
- (Online or Offline) –The **sample volume** that passed through the tube is divided by the mass found on tube to calculate the air concentration in mass per volume units. (e.g. ng/L, or µg/m^3)
- If spike tubes using liquid standards the process is straight forward, since the mass of all the compounds are at the **same mass concentration** (e.g. 2000 µg per mL of solvent).
- Simple dilutions of the liquid standard allow us to make the multi-point calibration curves.

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Calibration Process Using Gas Standards

- Most compressed gas standards are produced so the compounds are at **the same ppmv, or ppbv conc.** But, the mass of each compound will be different for each compound due to it's molecular weight.

- <u>Creating a curve based on units of Mass (e.g. ng/tube):</u>

  Requires the user to manually enter the mass concentration for each compound in the data handling system while creating the curve.

OR,

- <u>Creating a curve based on units of Concentration (e.g. ppbv):</u>

  Only a single value is required for each level of the curve.

But for a ppbv curve to calculate the correct concentration, the sample volume must be accounted for by using scaling factors in the data handling system prior to analysis.

Creating Calibrations Curves the Hard Way

To create calibration curves using gas standards often times users develop elaborate processes to dilute the gas mix using mass flow controllers etc., or create complex dilutions using a series of air sampling bags to spike their tubes.

There is an an easier way……

By simply removing a series of **representative** syringe volumes direct from the gas cylinder without any dilution.

Advantage of Compressed Gas Standards

- Methods like EPA TO-17 require the calibration curve to bracket a range of 0.5 to 25ppbv. Using gas standards makes this easy, since the compounds are in the same units.

- This task is not so easy when using liquid standards, since the ppbv concentration for each compound will be different *related to air.*

Spiking Tubes by EPA Methods

- EPA TO-17, and the new proposed Method 325B – discusses the option of using either gas or liquid phase standards.
- Section 6.5 of Method 325B talks about using a GC injection unit, or suitable device that has the means of controlling a carrier gas flow through the tube when spiking calibration standards.

How to use Gas Standards to meet the Methods

How Much of the Gas Mix Do I Need ?

$$V\ \text{syringe} = \frac{C\ \text{expected}}{C\ \text{gas mix}} \times V\ \text{sample}$$

V syringe = Syringe Volume needed in (Liters)
C expected = Concentration Expected in the Field (ppbv)
C gas mix = Concentration of the Gas Mix (ppbv)
V Sample = Sample Volume to be collected on the TD Tubes

The amount in the syringe will contain the appropriate mass of each compound, as if you sampled this specific sample volume.

$C_1V_1 = C_2V_2$

Example of Creating a Curve

Desired Calibration Curve Range: 0.5 to 25 parts per billion (ppbv)

Sample Volume to be collected is 4-Liters

Concentration of the gas mix: 1000 ppbv

Curve	Syringe Volume Required
0.5 ppb	2 mL
1 ppb	4 mL
2.5 ppb	10mL
5 ppb	20 mL
10 ppb	40 mL
25 ppb	100 mL

Gas-tight syringes with on/off valve

Converting the Gas Mix from ppbv to ng/L

Step 1

$$\frac{\text{ppbv} \times \text{M.W.}}{24.46\ \text{L/mole}} = \text{ng/L}$$

Use the Molar Volume based on the Temp & Pressure of your lab

Step 2

ng/L x Syringe Volume (L) = ng in syringe

How to Calculate Molar Volume for my Location?

Equipment Required:

- Thermometer
- Barometer

$$\text{Molar Volume} = \frac{\text{Lab Temp}\,(^{\circ}\text{C}) + 273.15}{\text{Lab Pressure}\,(\text{mmHg}) \times 62.36}$$

Universal Gas Constant Values for Different Pressure Units:

- atm: 0.08205
- kPa: 8.315
- mm Hg or (torr): 62.36
- Inch Hg: 2.246

Mass per Tube Based on a 4-Liter Sample

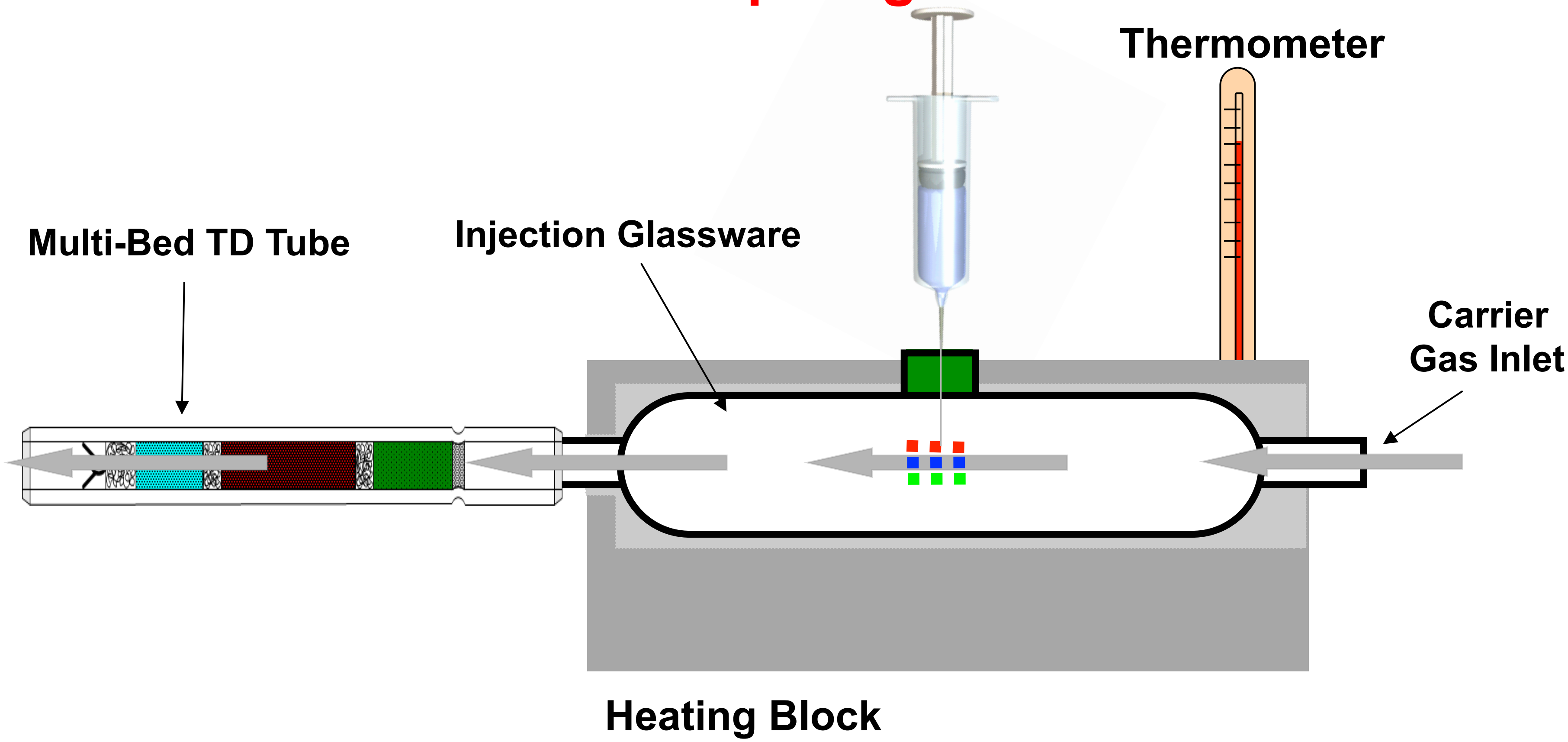
Temperature (°C)	Pressure (mmHg)	Molar Volume		0.5ppb	1ppb	2.5ppb	5ppb	10ppb	25ppb
23	735	25.11		Syringe Volume (Liters)					
		Actual Values from Cylinder Certificate	Mass Conc. from Cylinder	0.002	0.004	0.010	0.020	0.040	0.100
Compound	**M.W.**	**ACTUAL (ppbv)**	**ng/Liter**	**ng in syringe**					
Vinyl chloride	62.5	1050	2613	**5**	**10**	**26**	**52**	**105**	**261**
1,3-Butadiene	54.1	1050	2262	**5**	**9**	**23**	**45**	**90**	**226**
Acrylonitrile	53.1	1070	2261	**5**	**9**	**23**	**45**	**90**	**226**
Methylene chloride	84.9	1040	3517	**7**	**14**	**35**	**70**	**141**	**352**
Chloroform	119.4	1050	4992	**10**	**20**	**50**	**100**	**200**	**499**
1,2-Dichloroethane	99.0	1050	4138	**8**	**17**	**41**	**83**	**166**	**414**
Benzene	78.1	1050	3266	**7**	**13**	**33**	**65**	**131**	**327**
Trichloroethene	131.4	1050	5494	**11**	**22**	**55**	**110**	**220**	**549**
Tetrachloroethene	165.8	1050	6934	**14**	**28**	**69**	**139**	**277**	**693**

How Much Benzene is contained in 10mL Syringe
@ different Laboratory Temperatures & Pressures

Concentration of the Gas Mix = 1000ppbv

	Lab in Denver, CO (5000 ft)	My Lab Bellefonte, PA (1000 ft)	STP Sea Level (0 ft)
Temp	23°	23°C	25°C
Station Pressure	626 mm of Hg	735 mm of Hg	760 mm of Hg
Molar Volume	**29.5 L/Mole**	**25.1 L/Mole**	**24.5 L/Mole**
Mass Contained in the 10mL syringe	**26.5ng**	**31.1ng**	**31.9ng**
% diff from STP	21%	3%	0%

The Tube Spiking Process



---- Small M.W. Chloromethane

---- Mid M.W. Benzene

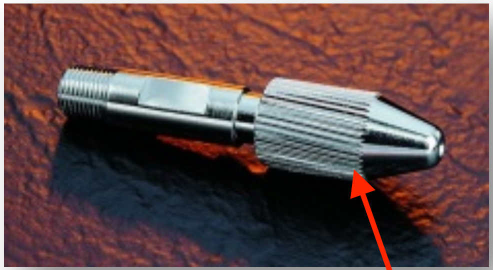
---- High M.W. Dichlorobenzene

Getting the Gas out of the Cylinder

Using a syringe adapter makes filling the syringe simple.

Set the pressure regulator to ~10 psig when working with glass syringes.

Syringe Adapter

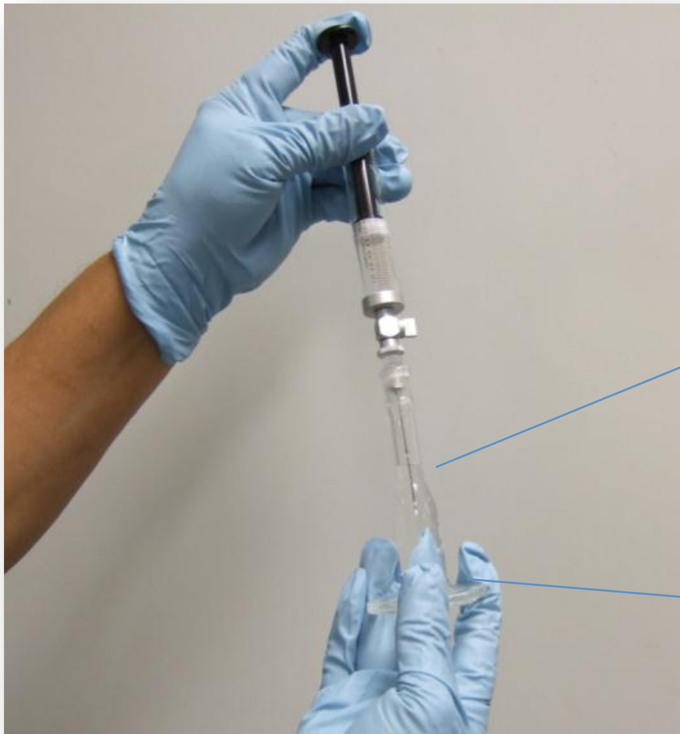


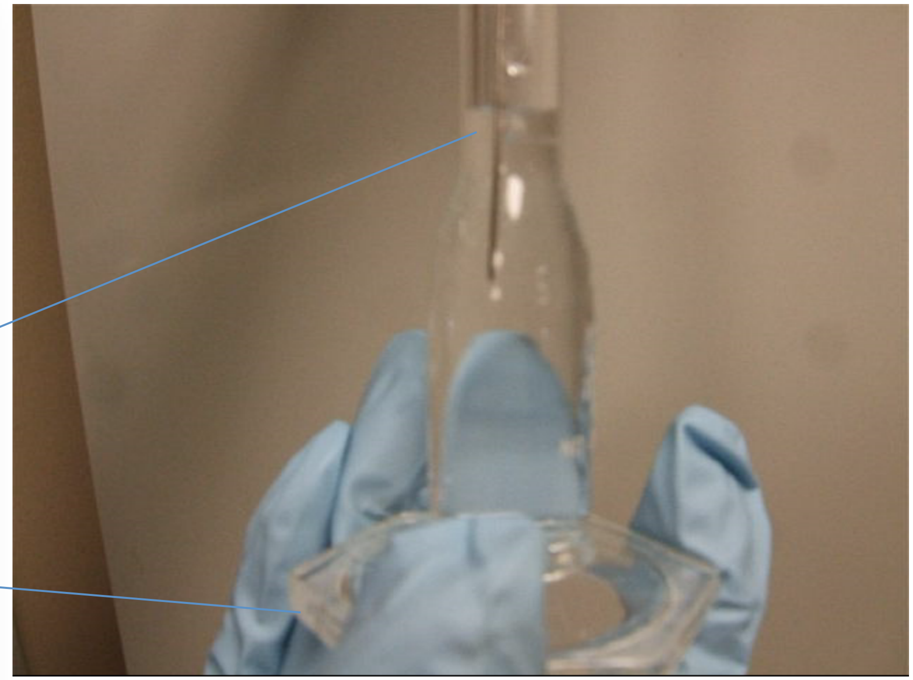
Septum Inside

Details of Spiking Tubes with a Gas Standard

1. Set the regulator pressure to ~10 psig
2. Insert the needle into syringe adapter
3. Open valve on the syringe
4. Fill syringe to the desired volume
5. Close valve on the syringe, and remove it from adapter
6. Insert needle into a small vial of de-ionized water
7. Open syringe valve to equalize the pressure in the syringe.
8. Close the valve, and remove the syringe from the vial of water.
9. Insert needle of the syringe into a Tube Injector. (carrier gas ~50mL/min)
10. Slowly inject the contents of the syringe. (2-3 second per mL)
11. Remove the syringe & wait 2 to 5 minutes before removing the tube.

How to Equalize to Atmospheric Pressure



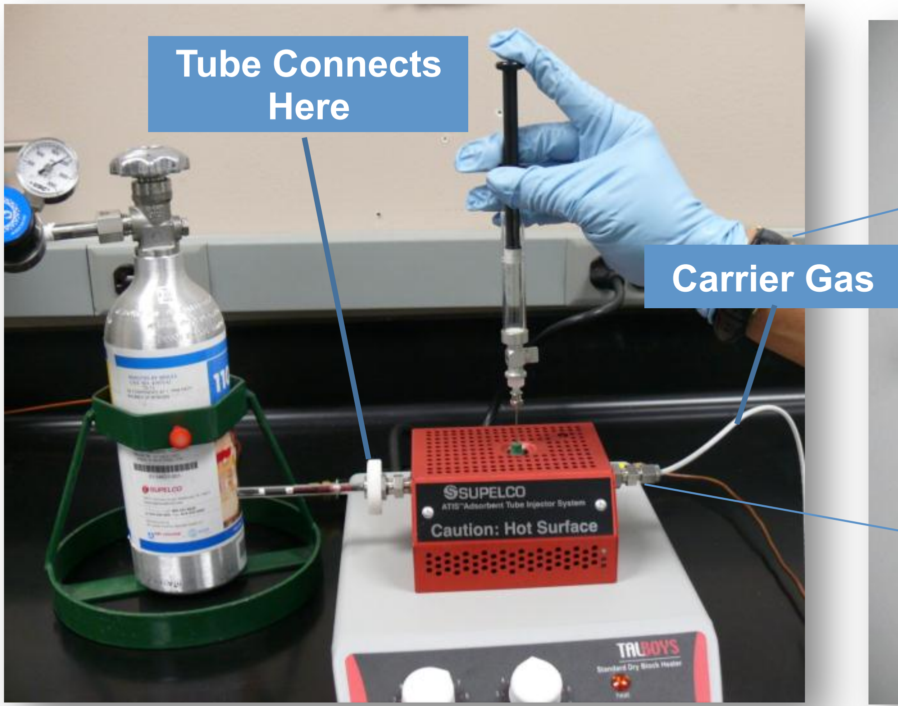


Once the gas is at atmospheric pressure - it's easy to calculate the mass of the each compound contained in the syringe.

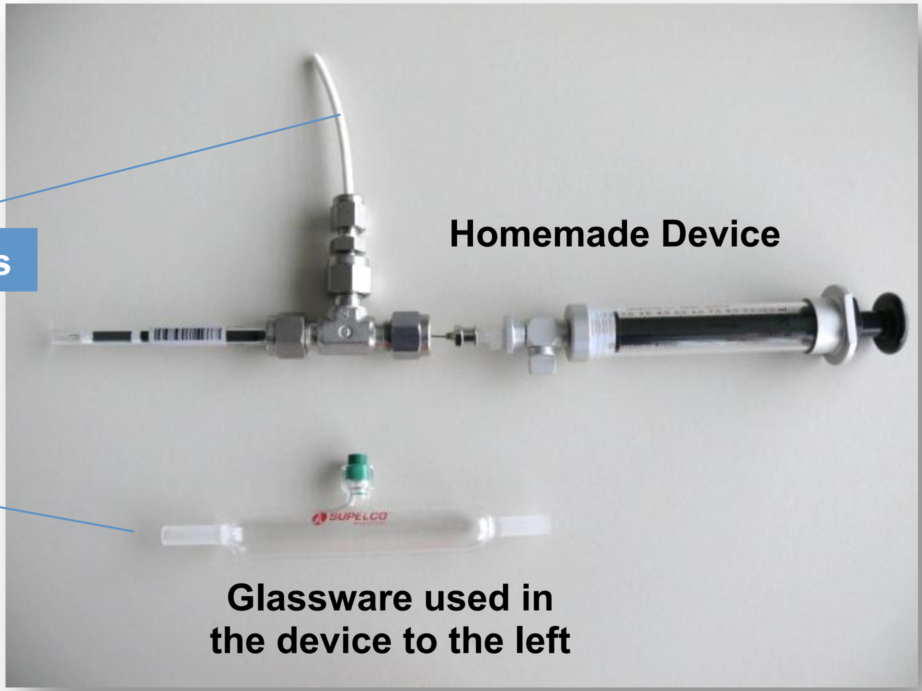
1. The water provides a visual - to when the pressure is equalized.

2. It prevents any additional gas from escaping until we close the syringe valve.

Using a Tube Injector (Commercially Available, or Homemade)



Commercially Available



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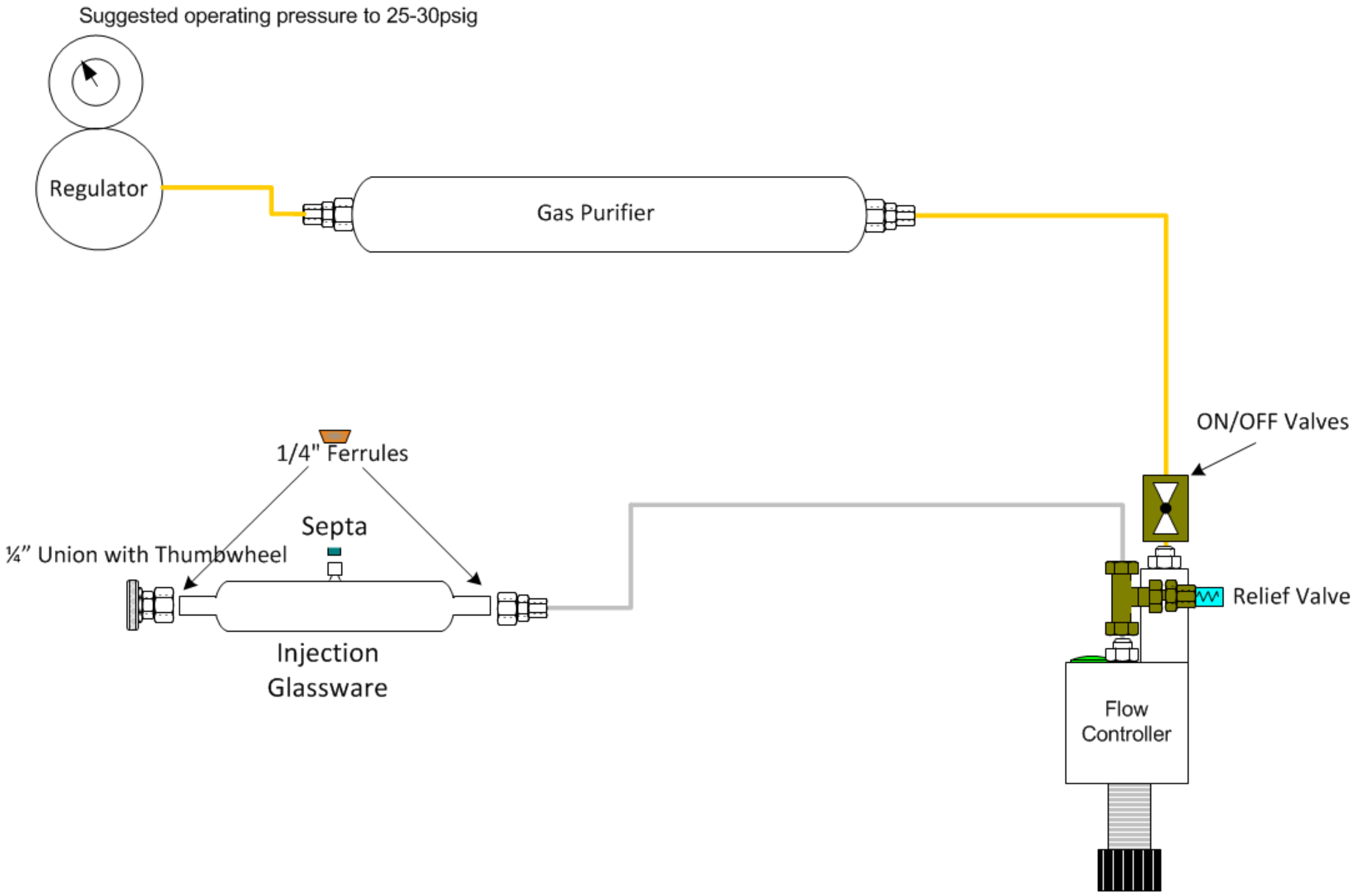
Tube Injector- Dry Carrier Gas

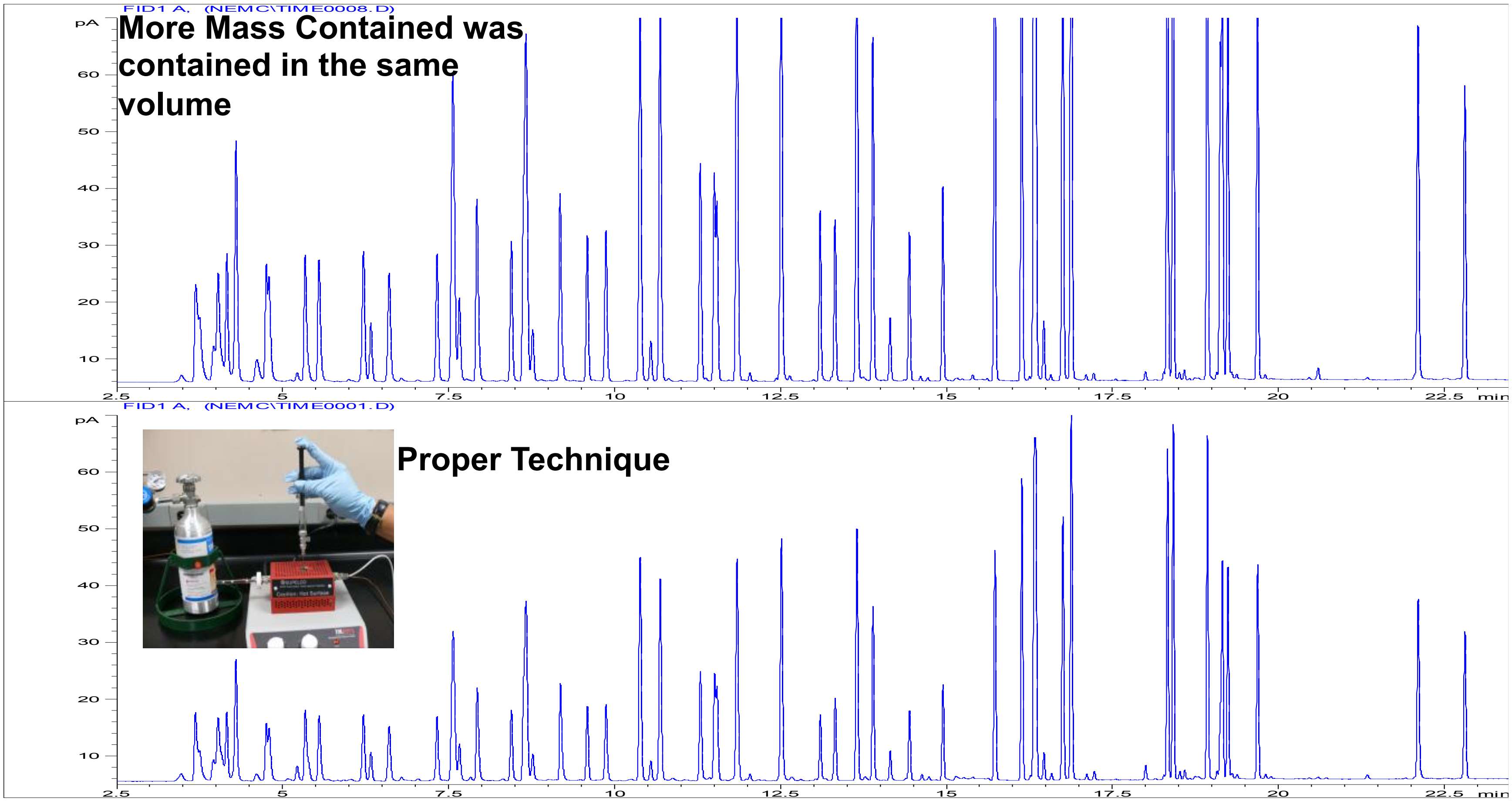


Examples of How Things Can Go Wrong

Details about the gas mix used for these examples:

- 43-Compound Gas Mix at *1000ppbv (Many of them are suitable for TO-17 and Method 325B)*
- Range: (Chloromethane 52 M.W. to Hexachlorobutadiene 261 M.W.
- Gas Mix is contained in small cylinder (12" high) pressurized to 1800 psig.
- The cylinder contains 110 Liters of gas. *(<1000 injections can be made if using 100mL syringe).*

Pressure Not Released from the Syringe



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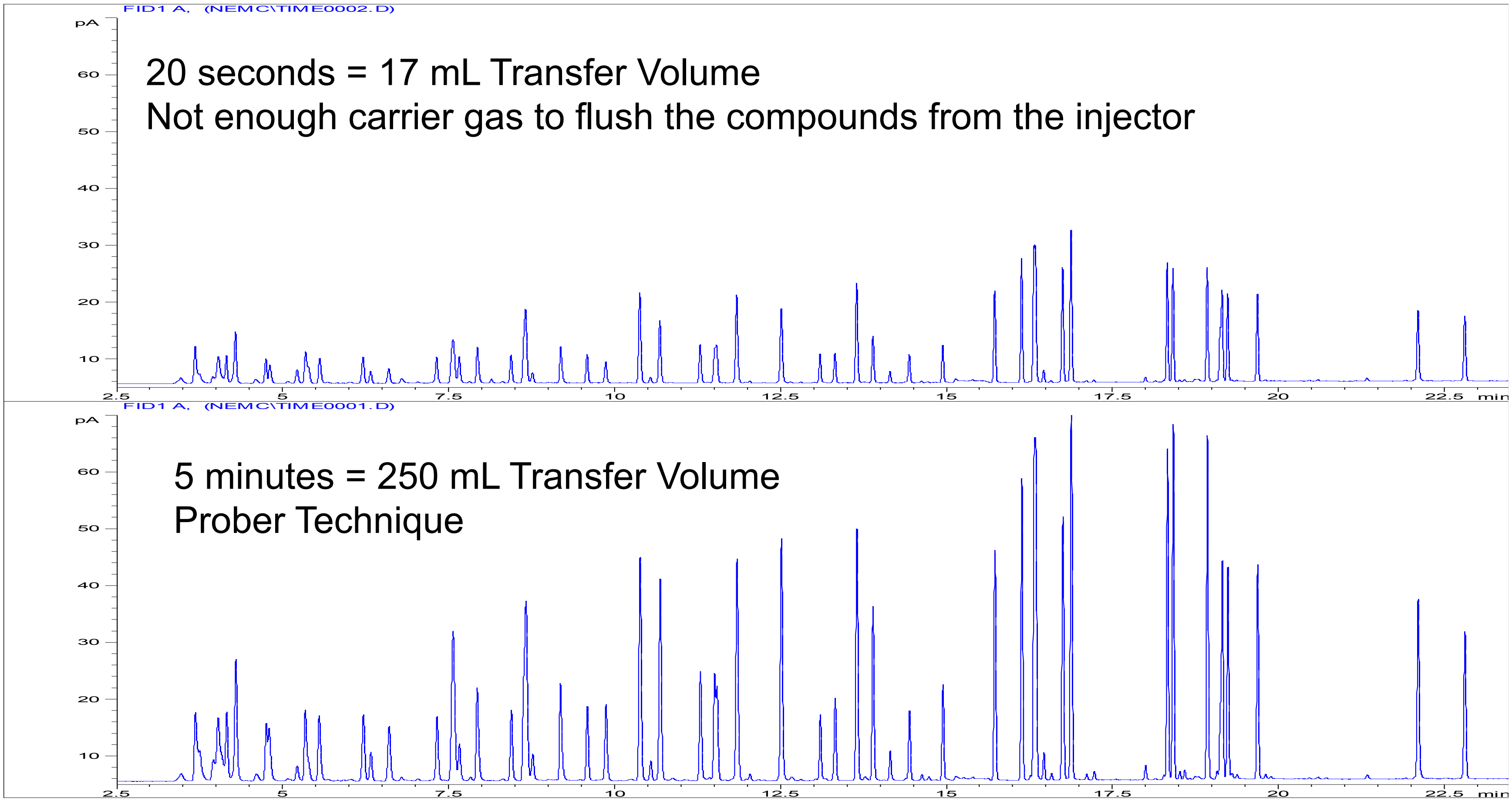
Not Enough Carrier Gas



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Recent Calibrations Done in Our Lab

Tube Injector Parameters

Carrier Gas	Nitrogen
Flow Rate	50 mL/min
Block Temp	65° C
Gas-Tight Syringes*	10 mL & 50 mL
Range of the Curve	0.5, 1, 2.5, 5, 10, 25ppbv @ 4-Liters
Gas Mix and Concentration	9-compound mix at 1000ppbv

* 10 mL used for the 2,4, and 10mL injections
* 50 mL used for the 20, 40 & 100mL injection (2qty 50mL injections)

Analytical Parameters

- Thermal Desorber: PerkinElmer TurboMatrix
- Tube Desorb: 330°C for 5 min.   (Primary Tube: Carbotrap-300)
- Trap Desorb: 330°C for 5 min.   (Trap: Carbopack-B & Carboxen-1000)
- Valve & Transfer Line: 175°C
- Desorb Flow: 30 mL/min
- Inlet Split: 5 mL/min
- Outlet Split: 5 mL/min

- Column: Equity-1 60 m x 0.25 mm ID x 1.0 µm film (28050-U)
- Flow Rate: 2.5mL/min

- 40°C for 5min,10°C/min hold for 0min 15°C/min/ to 225°C hold for 5min.
- GC/FID: H_2 40 mL/min, Air 400 mL/min, Makeup (N_2) 40 mL/min

6-point Calibration Curve using Dry Nitrogen as the Carrier Gas

Linear Regression - *Origin Ignored*

Compounds	Slope	Intercept	Corr
Vinyl chloride	21.720	8.375	0.99918
1,3-Butadiene	50.390	-3.293	0.99999
Acrylonitrile	17.078	0.043	0.99942
Methylene chloride	10.805	-1.182	0.99999
Chloroform	8.949	-0.787	0.99999
1,2-Dichloroethane	23.489	-4.048	0.99997
Benzene	69.435	-7.103	0.99998
Trichloroethene	24.880	-4.323	0.99993
Tetrachloroethene	25.843	-6.419	0.99985

Average Response Factor

Compounds	Average	Stdev	%RSD
Vinyl chloride	24.171	1.296	5%
1,3-Butadiene	49.287	0.894	2%
Acrylonitrile	16.147	1.593	10%
Methylene chloride	10.224	0.524	5%
Chloroform	8.513	0.430	5%
1,2-Dichloroethane	21.510	1.809	8%
Benzene	66.424	2.696	4%
Trichloroethene	23.040	1.530	7%
Tetrachloroethene	23.000	2.442	11%

Range of the Curve	0.5, 1, 2.5, 5, 10, 25ppbv @ 4-Liters

Humidity

Humidity Can Cause Problems

Problems During Sampling:

- Water vapor can be retained by the adsorbent
- Can mask the available sites of the adsorbent
- Can in (some cases) displace the compounds

Problems During Analysis:

- Water vapor can alter split flow ratios during desorption
- Can create chromatographic separation issues
- Can blow out the FID flame
- Reduces the vacuum of an MS detector

Water Vapor Retained by Adsorbents

- Silica gel is hydrophilic and will retain ~40% of its own weight in water.

  Reason why silica gel is not typically used for thermal desorption applications.

- Some adsorbents are more hydrophobic than others.

  Porous Polymers & Graphitized Carbons are very hydrophobic and virtually no water will be retained on them while sampling in humid conditions.

- Carbon Molecular Sieves are still classified as hydrophobic.

  At high humidity some water is retained, but the bond to the water is weak. It can be driven off at ambient temperatures using a dry purge prior to analysis.

Should We Be Spiking Tubes Using Humidified Carrier Gas?

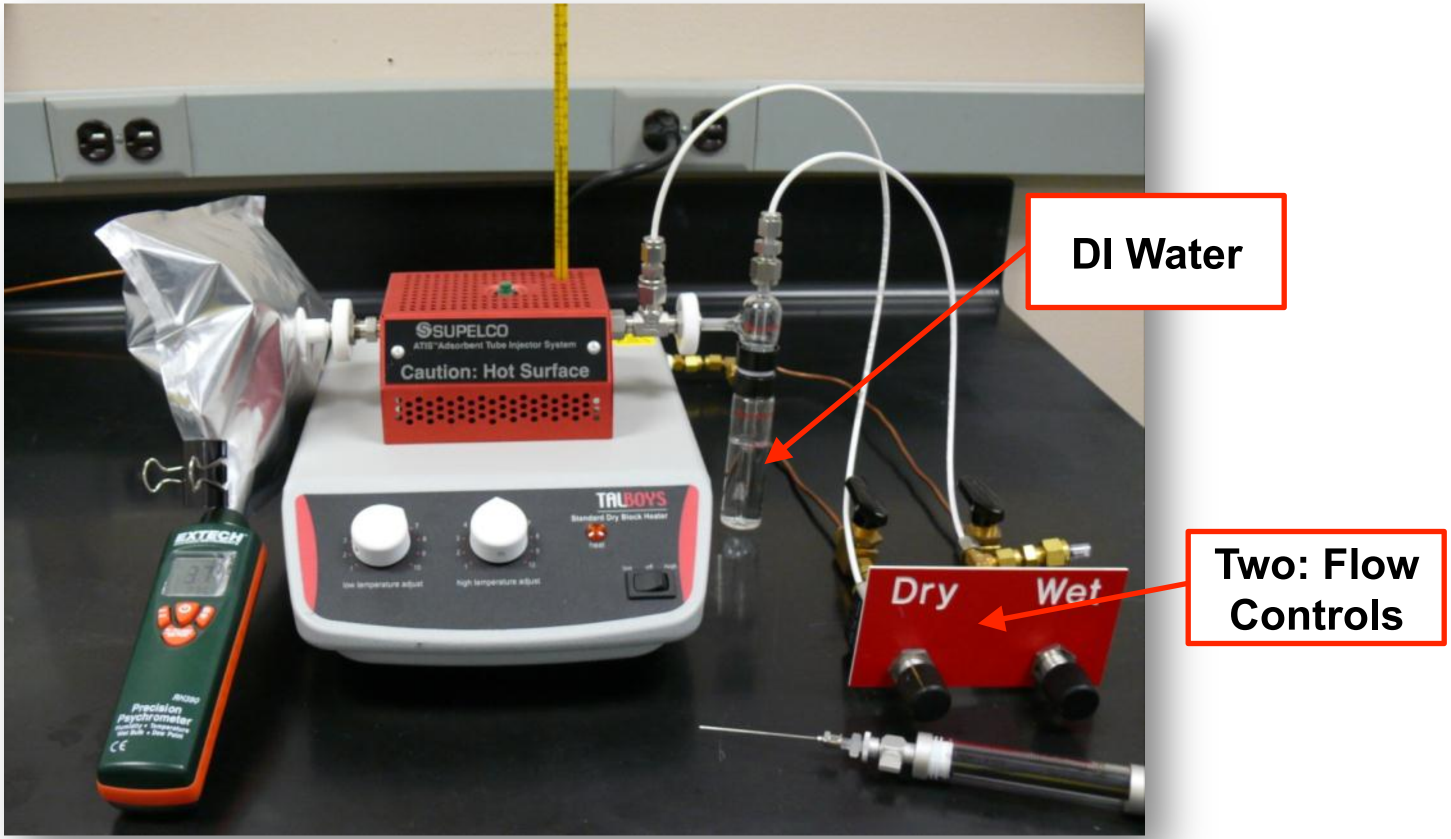
It depends on how you interpret the specific method.

Both EPA TO-17 and the proposed 325B describe using humidified gas when testing tube performance, but during calibration it's vague.

With all of the problems humidity can cause, maybe we should spike our tubes using a humidified gas stream?

If so - It's easy to do….

Device For Spiking Using Humidified Carrier Gas



6-point Calibration Curve using Humidified Carrier Gas 50% RH
(A dry purge volume of 0.5 Liters was needed)

Linear Regression - *Origin Ignored*

Compounds	Slope	Intercept	Corr
Vinyl chloride	22.338	8.401	0.99940
1,3-Butadiene	46.004	-6.094	0.99984
Acrylonitrile	16.437	-1.847	0.99969
Methylene chloride	10.820	-1.249	0.99992
Chloroform	9.121	-0.655	0.99990
1,2-Dichloroethane	24.040	-3.548	0.99989
Benzene	71.178	-4.402	0.99989
Trichloroethene	25.632	-3.309	0.99988
Tetrachloroethene	26.341	-4.912	0.99988

Average Response Factor

Compounds	Average	Stdev	%RSD
Vinyl chloride	25.657	2.692	10%
1,3-Butadiene	44.428	0.847	2%
Acrylonitrile	15.568	1.764	11%
Methylene chloride	10.510	0.257	2%
Chloroform	8.953	0.227	3%
1,2-Dichloroethane	22.856	0.841	4%
Benzene	71.342	3.746	5%
Trichloroethene	24.802	0.779	3%
Tetrachloroethene	24.788	0.962	4%

Range of the Curve	0.5, 1, 2.5, 5, 10, 25ppbv @ 4-Liters

Conclusions

- Compressed Gas Standards offer an alternative to using Liquid Standards.
- A carrier gas is required to distribute the compounds to the adsorbent(s) in the Thermal Desorption Tube.
- Equalizing the pressure of the syringe to atmospheric pressure is required for representative curves.
- Spiking tubes with a humidified gas stream can make the calibration more representative of actual sampling conditions.

References

- EPA TO-17. *Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes.*
- Proposed EPA Method 325B. *Volatile Organic Compounds From Fugitive and Area Sources*, available from the Federal Register Vol. 79 No.125 June 30, 2014
- Dinardi, Salvatore. *Calculation Methods for Industrial Hygiene:* Van Nostrand, 1995. Print

Thank You for Attending !

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