Odorant Systems

Lisa Mazur

Energy Nexus | Annual Technical Conference

Fuelling the Future

Course overview

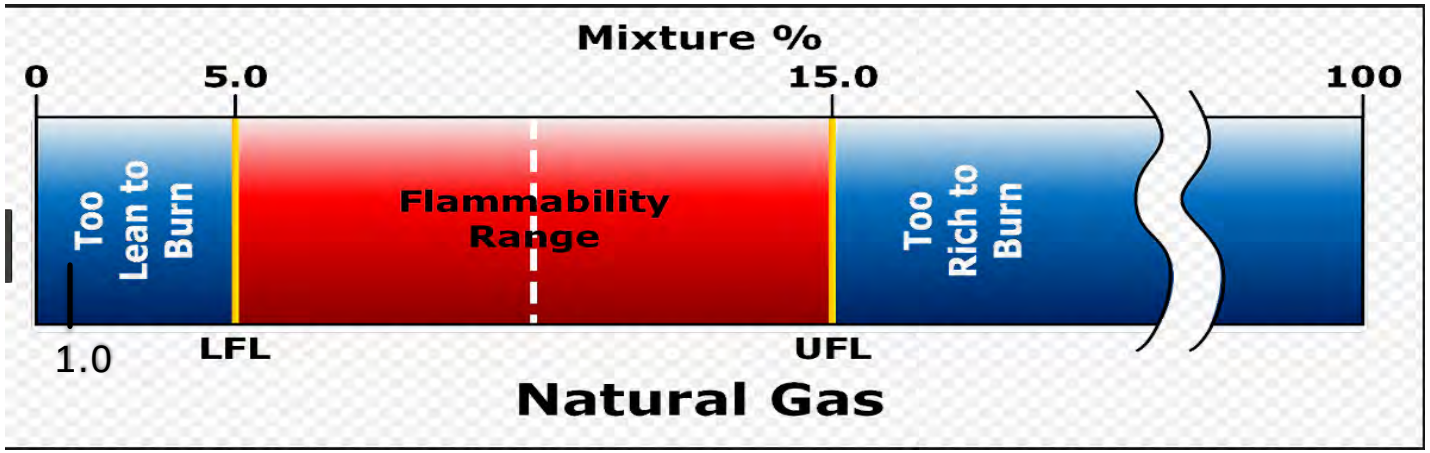
- Legislation around odorization
- Characteristics of Mercaptan
- Various Mercaptan blends
- Odorant systems and their function
- Ways to ensure odorization thresholds have been met
- Constraints/ limitations of use of Mercaptan odorant systems

Industry standards

Natural gas explosive limits

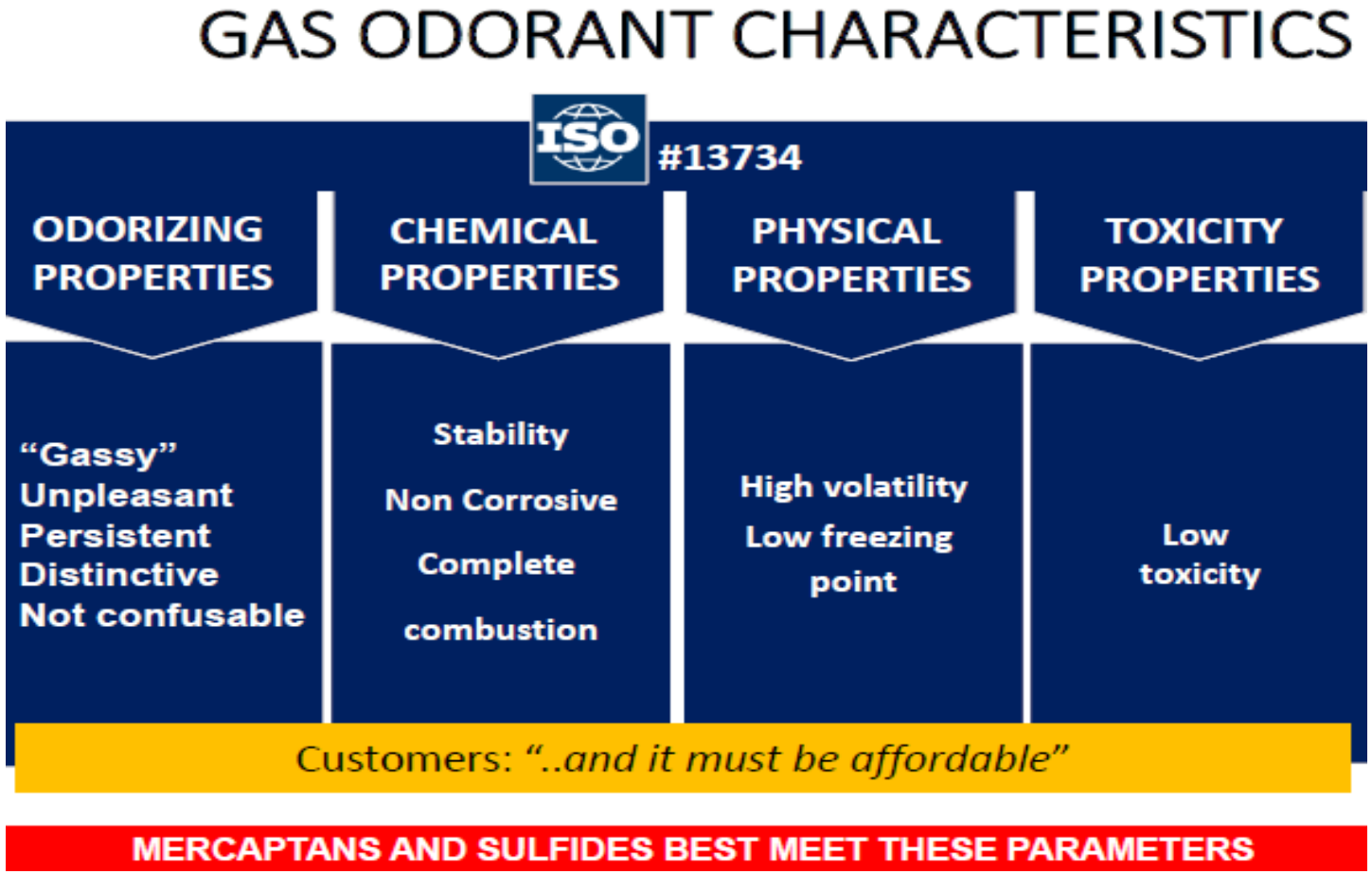
The Lower Explosion Limit (LEL) = 5% Gas in Air

The Upper Explosion Limit (UEL) = 15% Gas in Air



- The Canadian Standards Association (CSA) Z662 4.21 defines the standards for odorization.
- Gas is to be readily detectable at concentrations not less than 1/5th of the LEL = 1% Gas in Air (GIA)

Liquid odorant for natural gas



- Clear, Potent smelling liquid
- Mineral oil like consistency
- 1 Drop will clear this room
- Very volatile (low vapor pressure)
- UN Number 3336- Mercaptans, Liquid, Flammable

Mercaptans are also found in Nature (skunks) and daily household items like essential oils

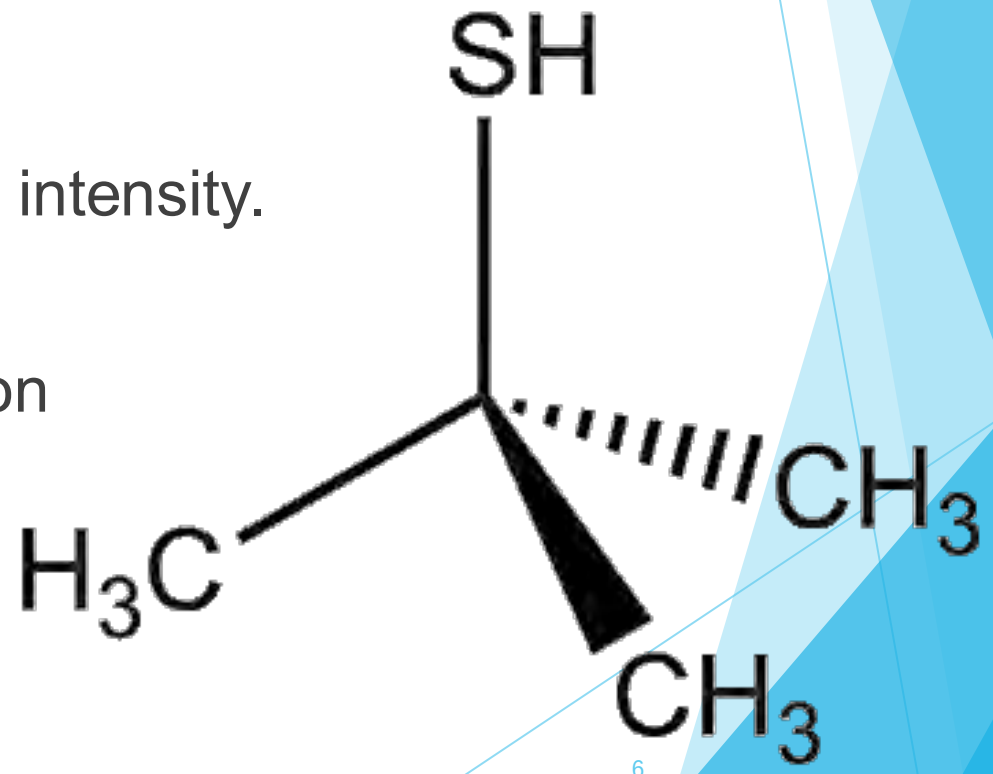
COMMON GAS ODOURANTS BLENDS

Mercaptans					Sulfides			Injection type		Density at 60F (15.5C) in lbs/Gal	Cloud point
TBM	IPM	NPM	SBM	Ethyl Mercaptan	DMS	MES	THT	Vapor	liquid		
79%	18%	3%						■	■	6.76	
80%						20%		■	■	6.79	
75%					25%				■	6.80	
10%	70%	10%			10%				■	6.87	≤ -50°F -46°C
50%						50%		■	■	6.88	
80%					20%				■	6.80	
50%							50%		■	7.46	
30%							70%		■	7.84	
							100%	■	■	8.36	
				> 99%					■	7.05	≤-20°F [-29°C]
1 °C 34 °F	-130 °C -202 °F	-113 °C -171 °F	-140 °C -220 °F	-148 °C -234 °F	-98 °C -144 °F	-106 °C -159 °F	-96 °C -141 °F				

Mercaptans

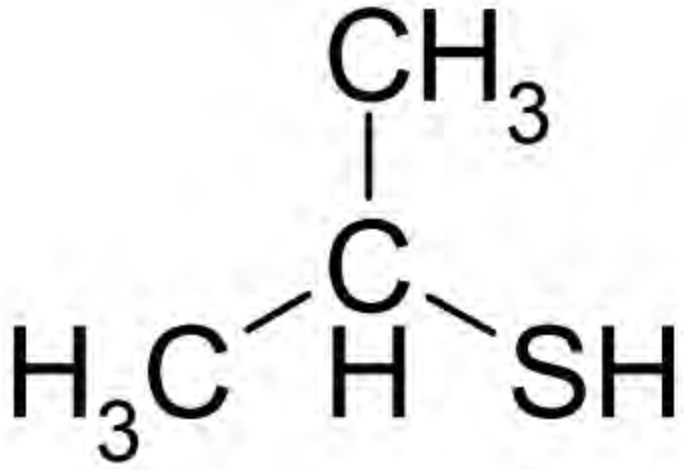
Tertiary Butyl Mercaptan (TBM)

- Typical gassy odor with very high intensity. (THE STINK)
- The highest resistance to oxidation
- High freezing point (1°C,34°F)
- Easily masked and faded



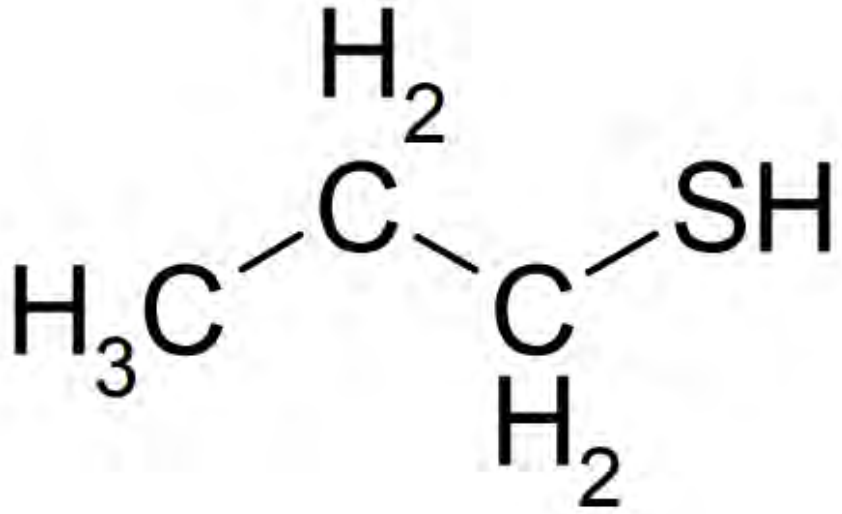
Mercaptans

Iso-Propyl Mercaptan (IPM)



- 2nd most resistant to oxidation
- Low freezing point (-130°C,-202°F)

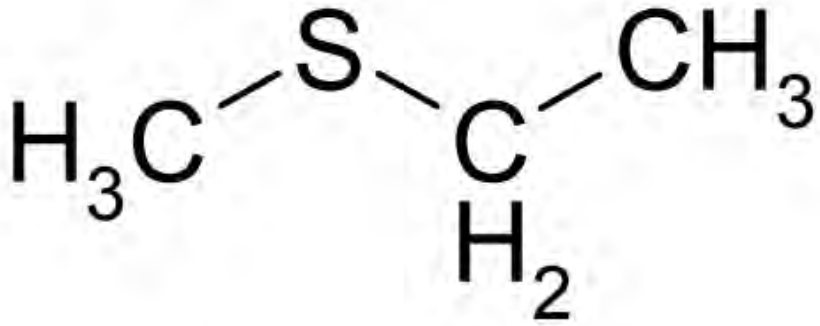
N-Propyl Mercaptan (NPM)



- Easily oxidized
- Low freezing point (-113°C,-171°F)

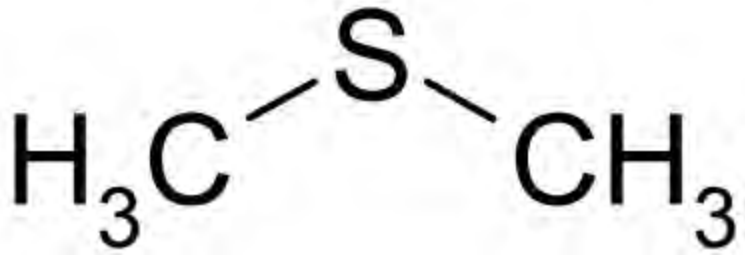
Sulfides

Methyl Ethyl Sulfide (MES)



- Low freezing point (-106°C,-159°F)
- Won’t oxidize in the presence of rust
- Good gassy odor
- Suitable for injection or vaporization type odorizers

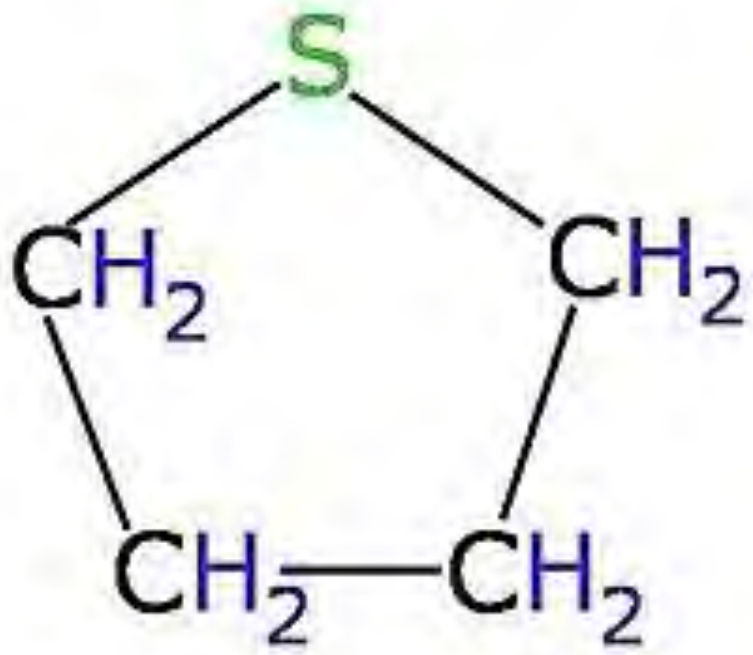
Dimethyl Sulfide (DMS)



- Low freezing point (-98°C,-144°F)
- Won’t oxidize in the presence of rust
- No gassy odor

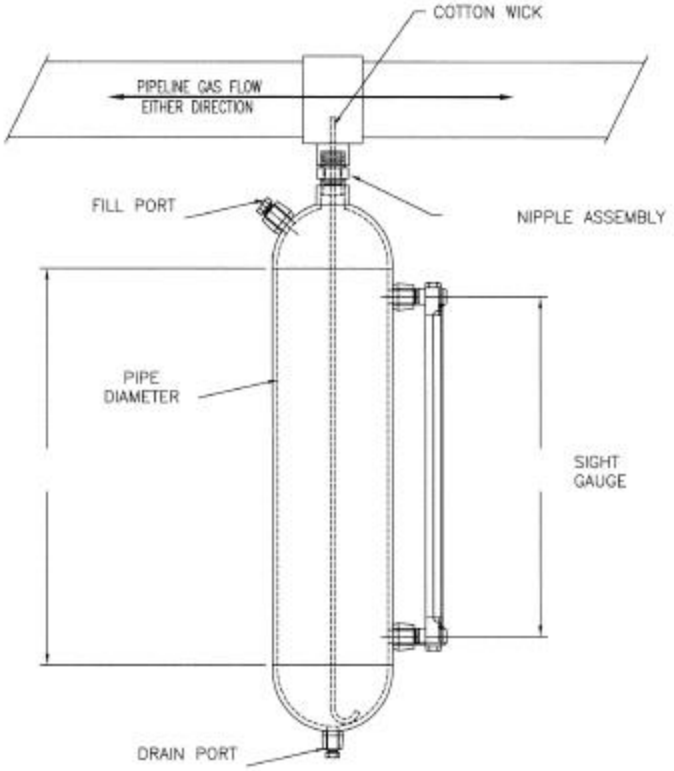
Sulfides

Tetrahydrothiophene (THT)



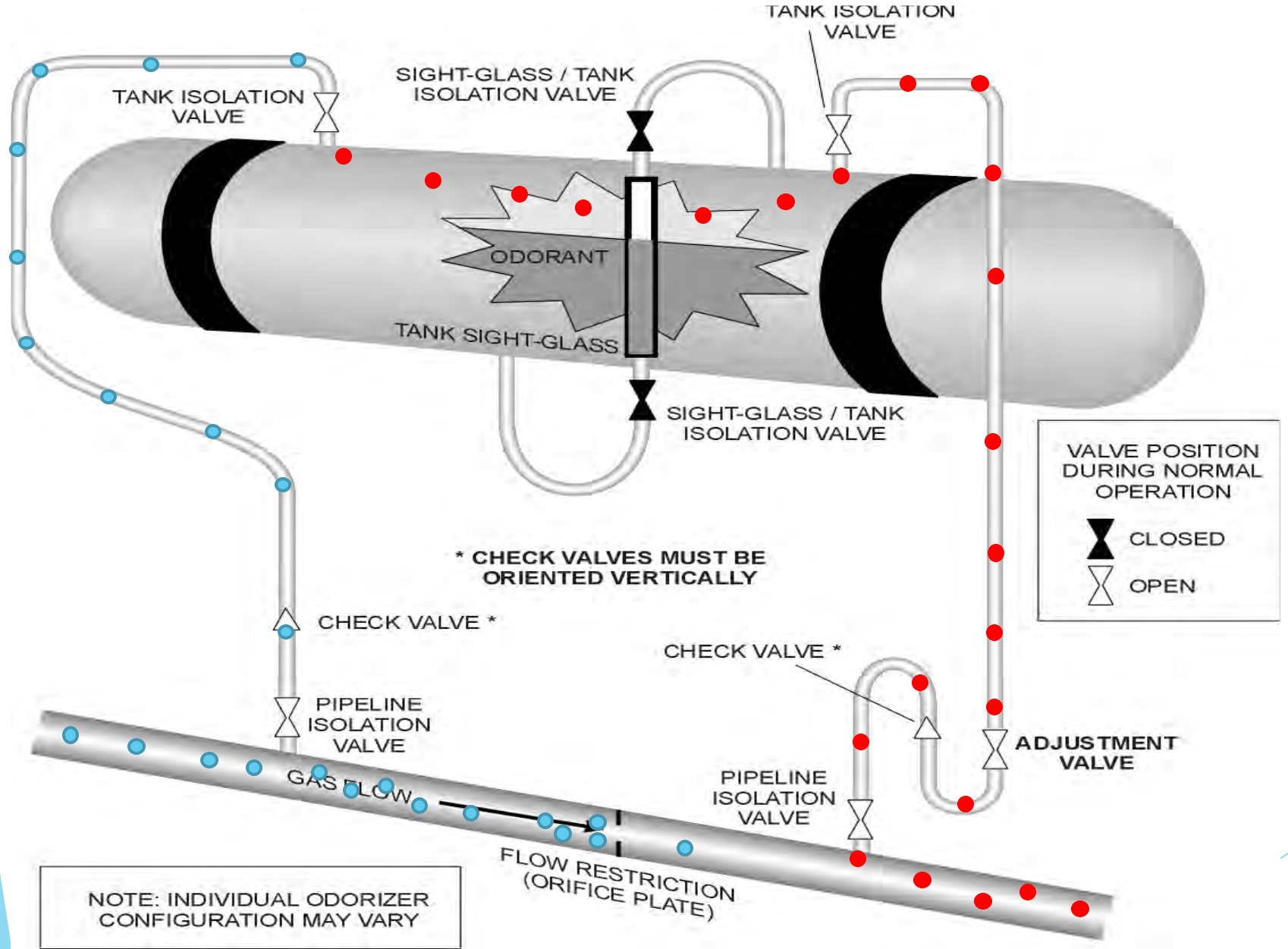
- Gassy odor
- Resistant to pipeline & soil oxidation
- Used in pure form or as part of TBM blend

How to we add odorant to our system?



Wick odorizers

Bypass/mini-bypass odorizer



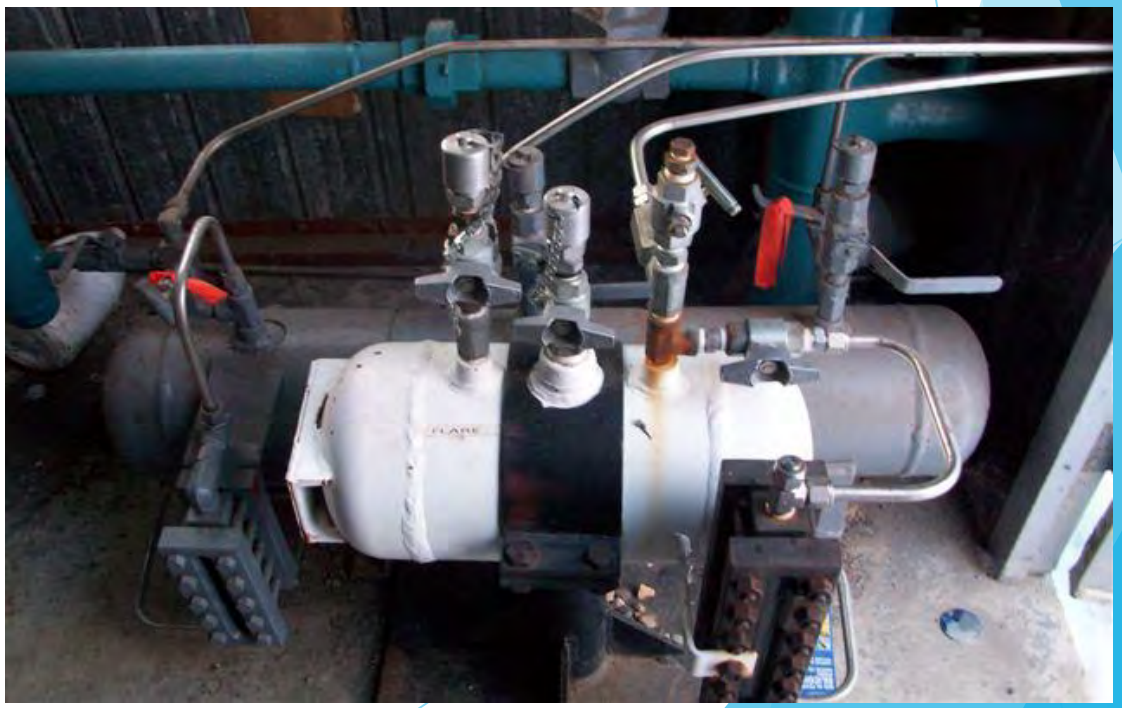
Orifice plate creates *pressure differential*

High pressure upstream

Low pressure downstream

Causes gas to find path of least resistance into and out of the odorizer.

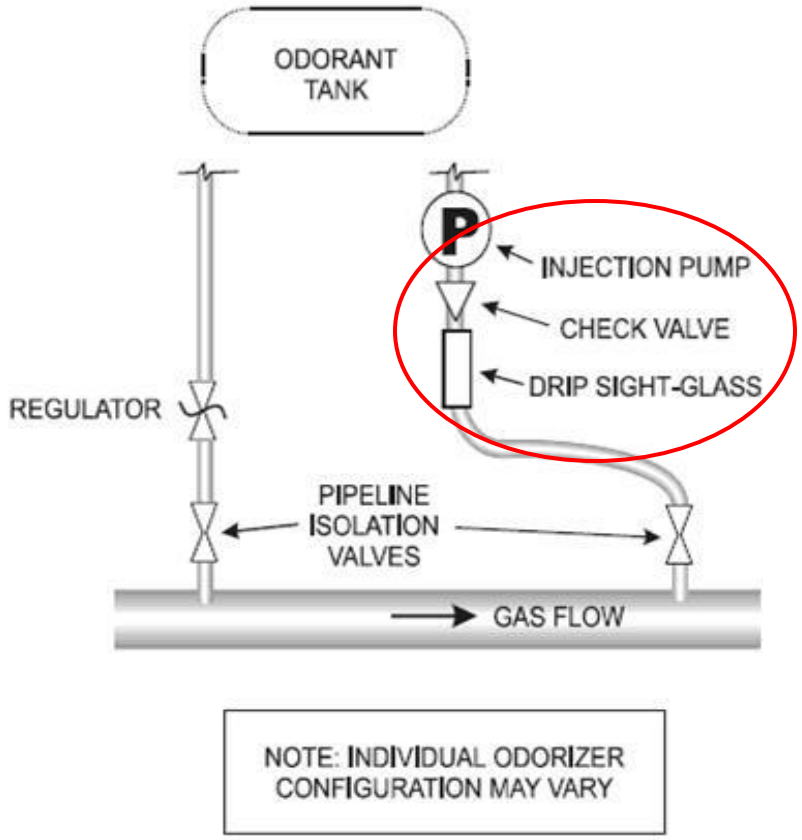
Bypass/ mini-bypass odorizers



Drip and injection odorizers

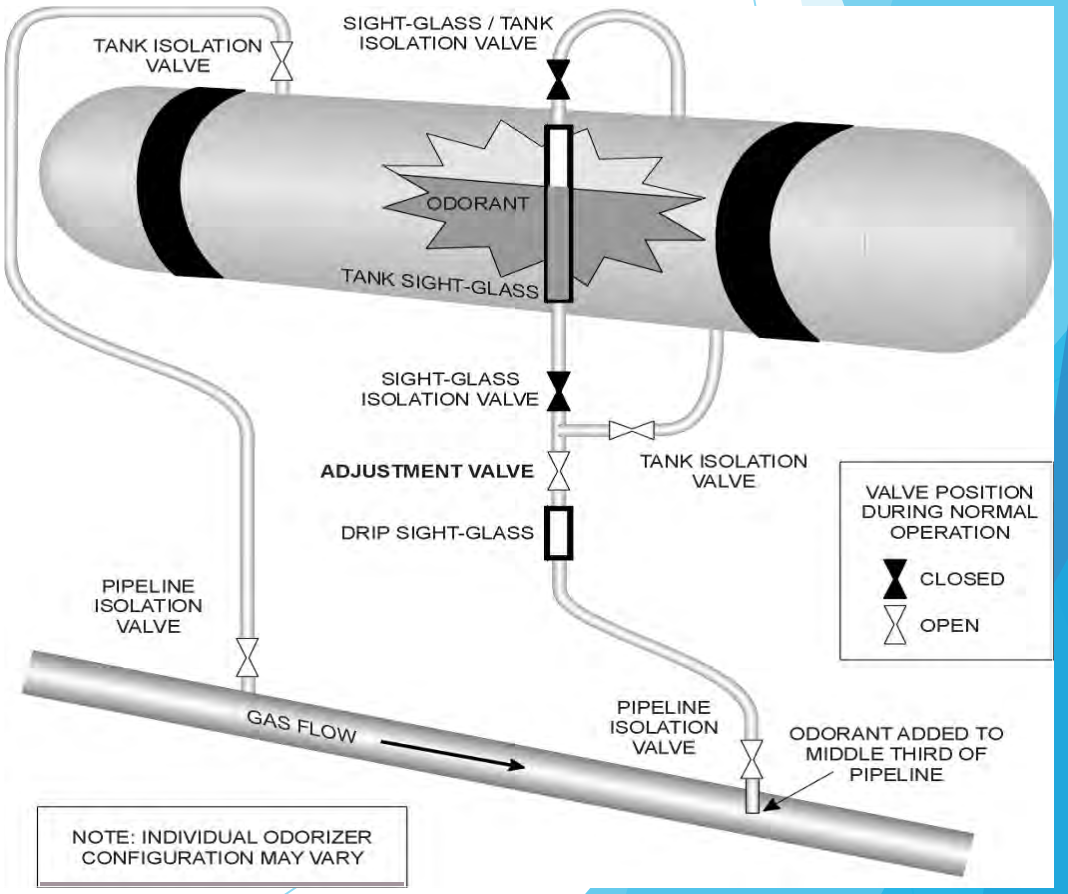
INJECTION

- Computer monitors the flow and adjusts the drip rate automatically
- More accurate



DRIP

- Manual drip rate change(Labour intensive)
- Difficult to adjust accurately



Injection odorizer

- Monitored by SCADA type systems for cc/stroke and flow rates
- Large system option, larger volume odorant tanks on site
- Typical rates of injection are 1lb/mmcf which is equal to 16mg/m^3 Total odorant (TBM/MES)

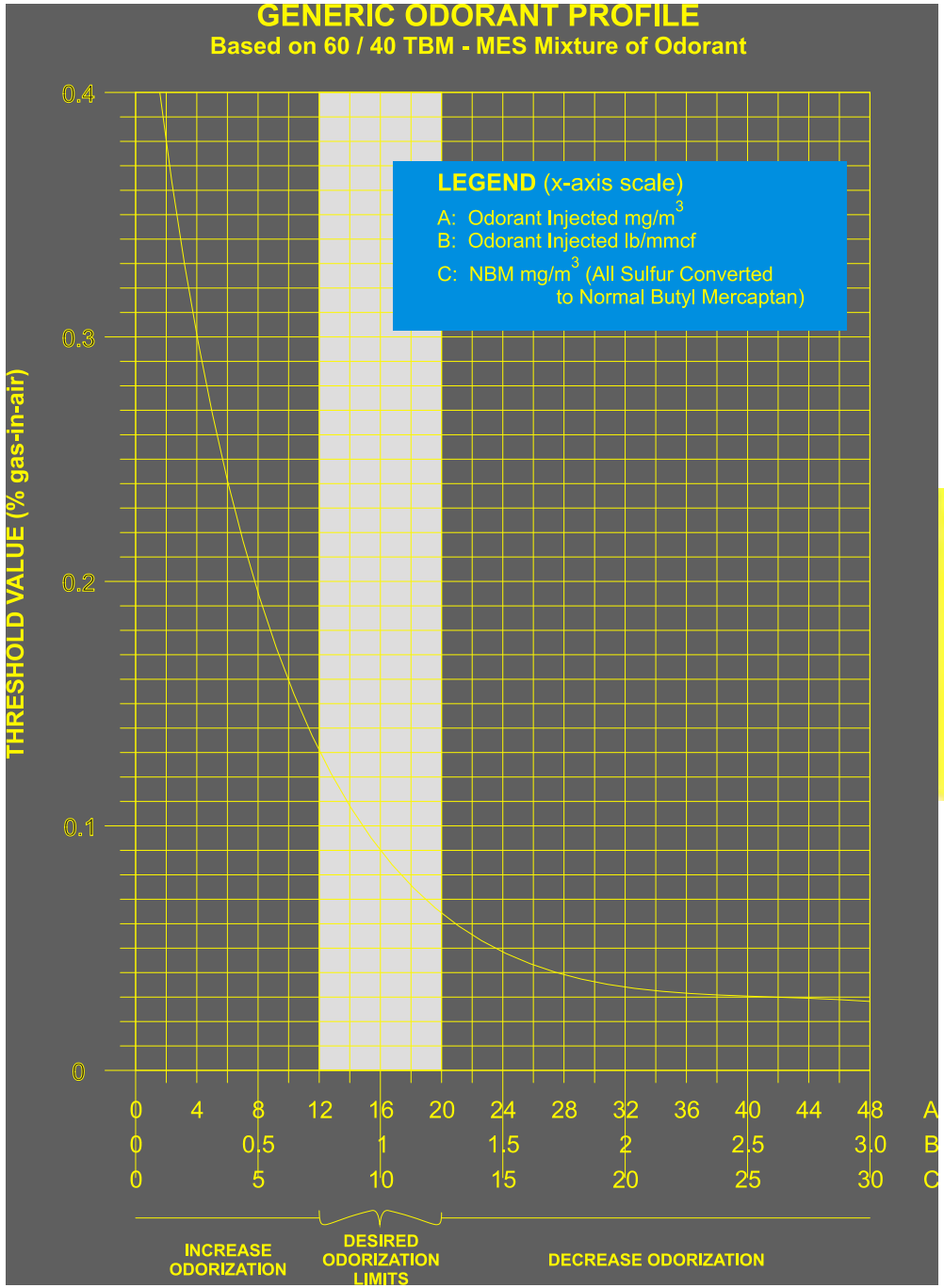
Low Volume Injection odorizer

How do we ensure odorant thresholds are met

Odorometers

- These units provide a known mixture of Gas in Air (GIA) for testing, meeting the 1% GIA CSA Z662 requirement
- Units also provide safe test environment for employees only exposing them to 1% GIA

Nose profiles



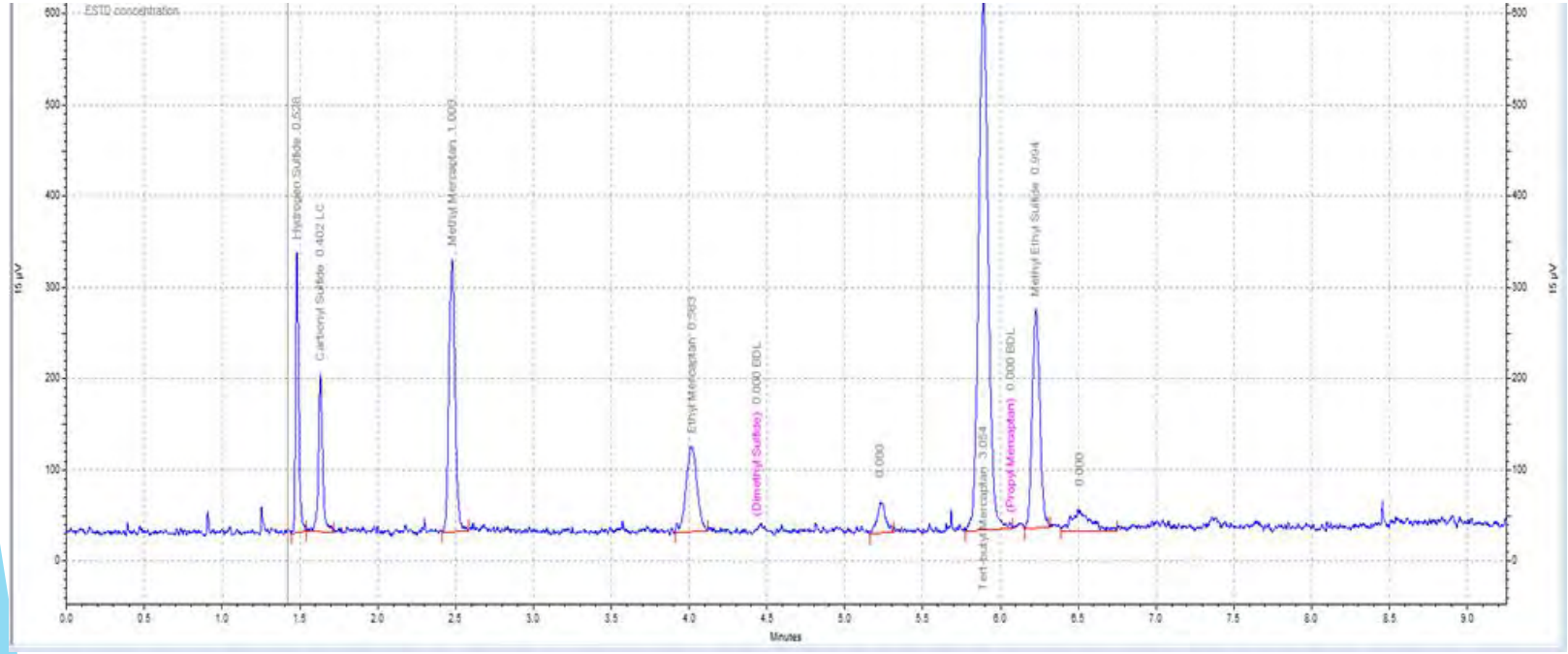
Odorant Tank Level (cm): _____ Odorometer Serial #: _____ Resample ☐

Print Name & Sign	Threshold Detection Level % Gas in Air	Readily Detectable Level % Gas in Air	Odorant Intensity @ 0.5% Gas in Air	Odorant Odor Intensity Legend
				0 - Absent 1 - Faint 2 - Readily detectable 3 - Strong 4 - Very Strong

Comments:

0119-0038-0214

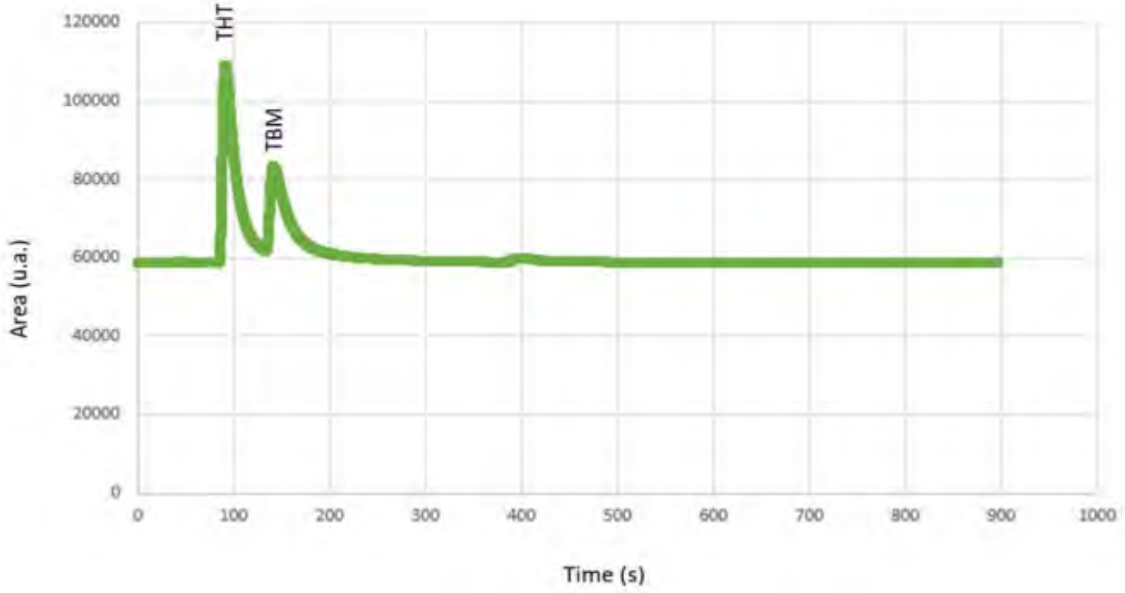
Laboratory analysis



Analysis is done using a Gas chromatograph (GC) equipped with a sulfur Chemiluminescence detector (SCD) or flame photometric detector (FPD).

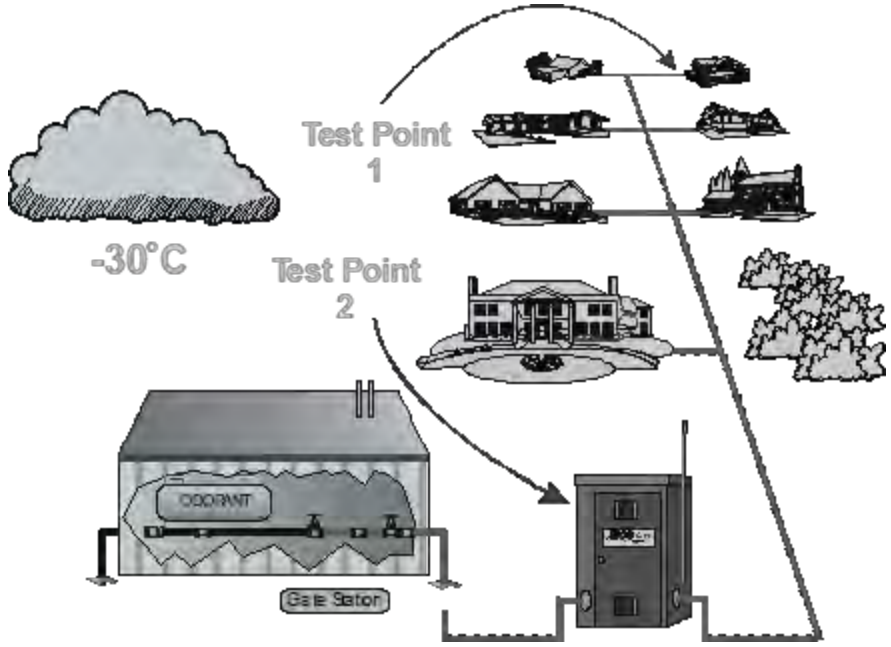
Online and hand-held devices

Compounds	Permeation rate	External permeation oven T°C	Concentration
THT	311 ng/min	60 °C	0.778 ppm
TBM	424 ng/min	60 °C	1.04 ppm



Where do we sample?

# of Customers	Min # of Sample Point Locations	Odorizer Sampling Frequencies
1 to 500	1	3-6 months (± 2 weeks- depending on reliability of odorizer)
501 to 5,000	2	2 months (± 2 weeks)
5,001 to 20,000	3	1 month (± 1 week)
> 20,000	4	2 weeks (± 1 week)



- Ideally near the end of the scheme
- Every odorizer in a system needs to be monitored to ensure customer safety
- More flow and more customers = more testing to minimize risk

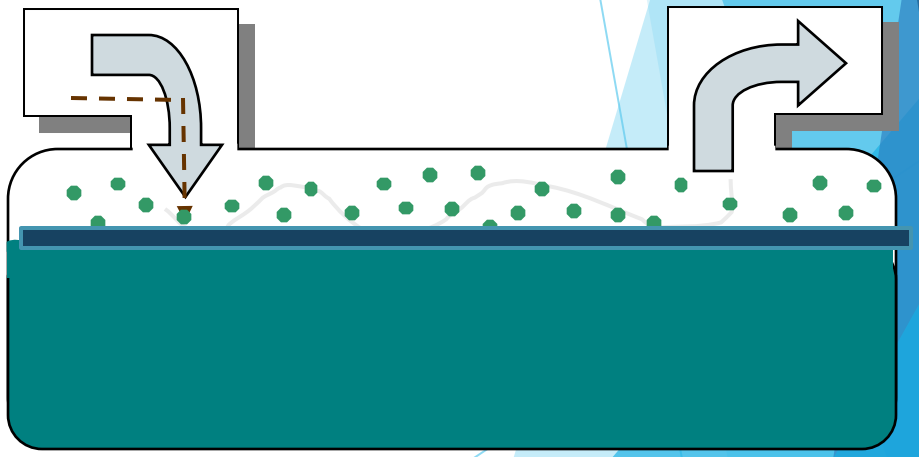
Working with odorant

- Don’t wear clothes you like!!!!!
- Odorant has an affinity for metals, leather, hair.
- Wear your PPE
  - Gloves
  - Safety glasses
  - RPE (respiratory protective equipment)
  - Grounded Safety footwear
  - FR clothing

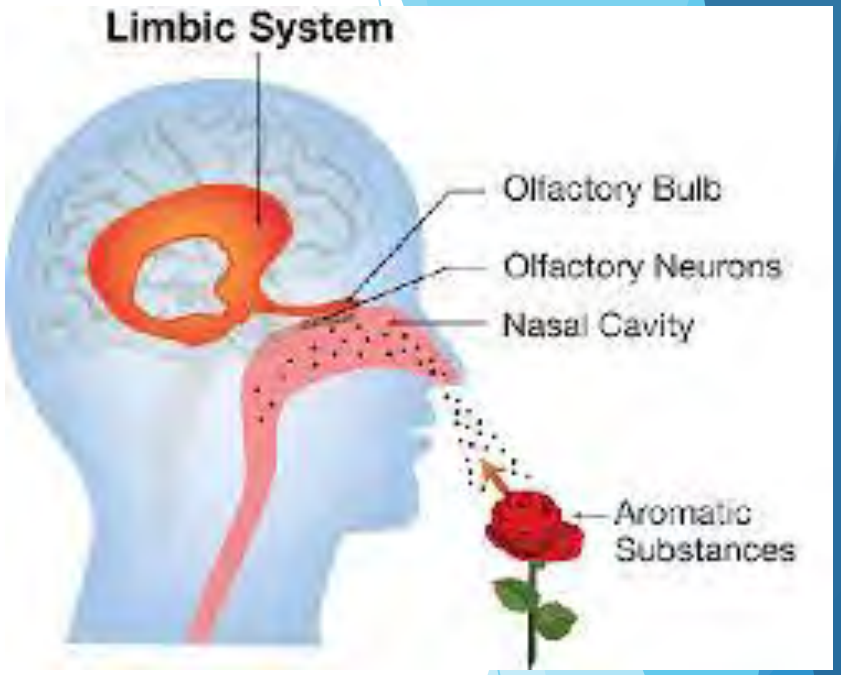
Constraints/ Interferences within Mercaptan Odorant Systems

Odorizer constraints

- Depending on selected odorant blend will determine acceptable odorizer choices
- For bypass odorizers:
  - Hydrocarbons can collect in the pot, creating an oily layer on top of the odorant which will inhibit the gas from interacting with the odorant vapour

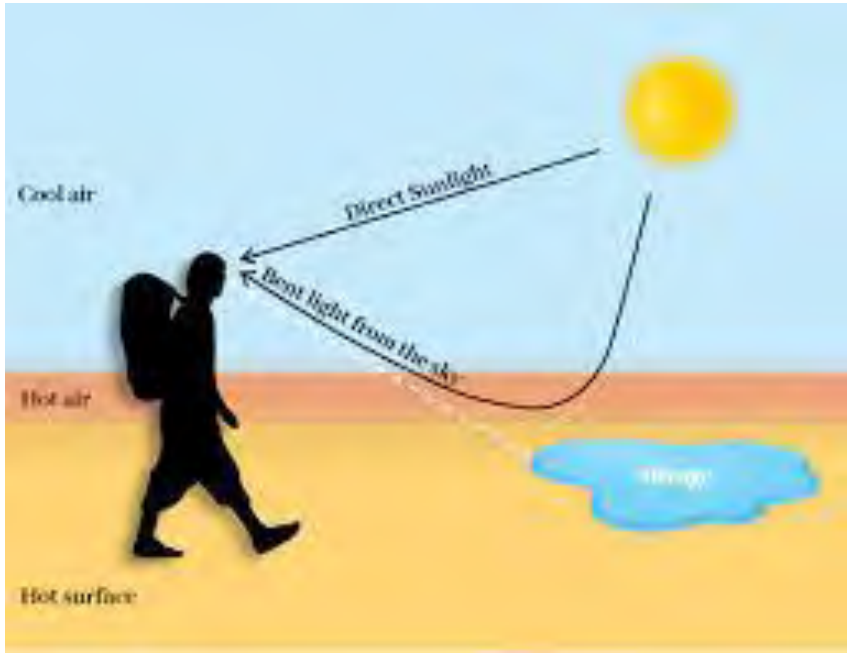


Human Interferences



- Olfactory Fatigue

"is the temporary, normal inability to distinguish a particular odor after a prolonged exposure to that airborne compound" (*Odors chapter, Fundamentals volume of the ASHRAE Handbook, ASHRAE, Inc., Atlanta, GA, 2005*)

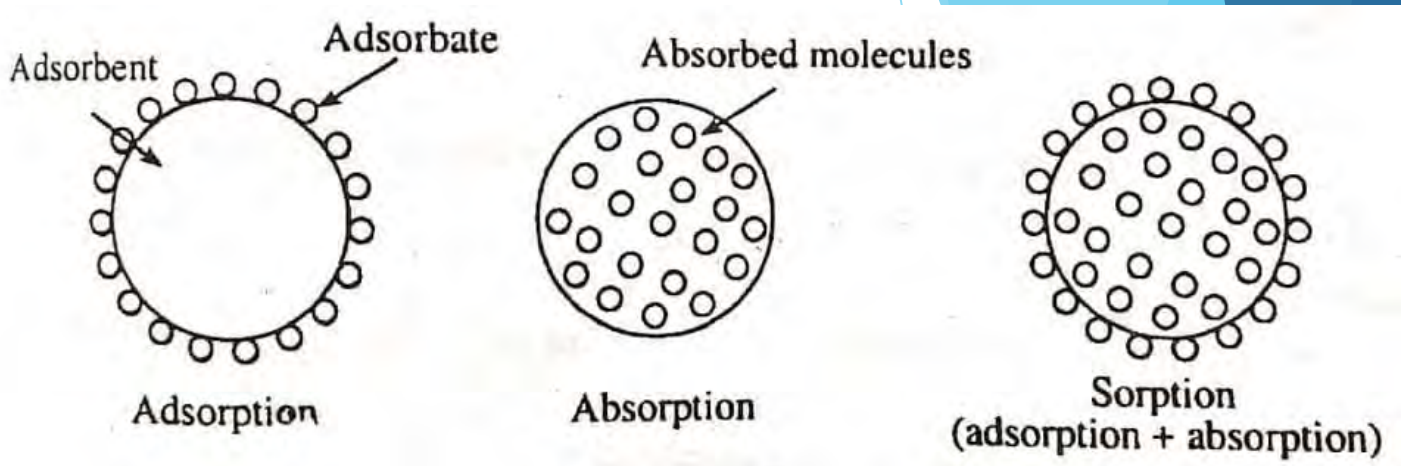


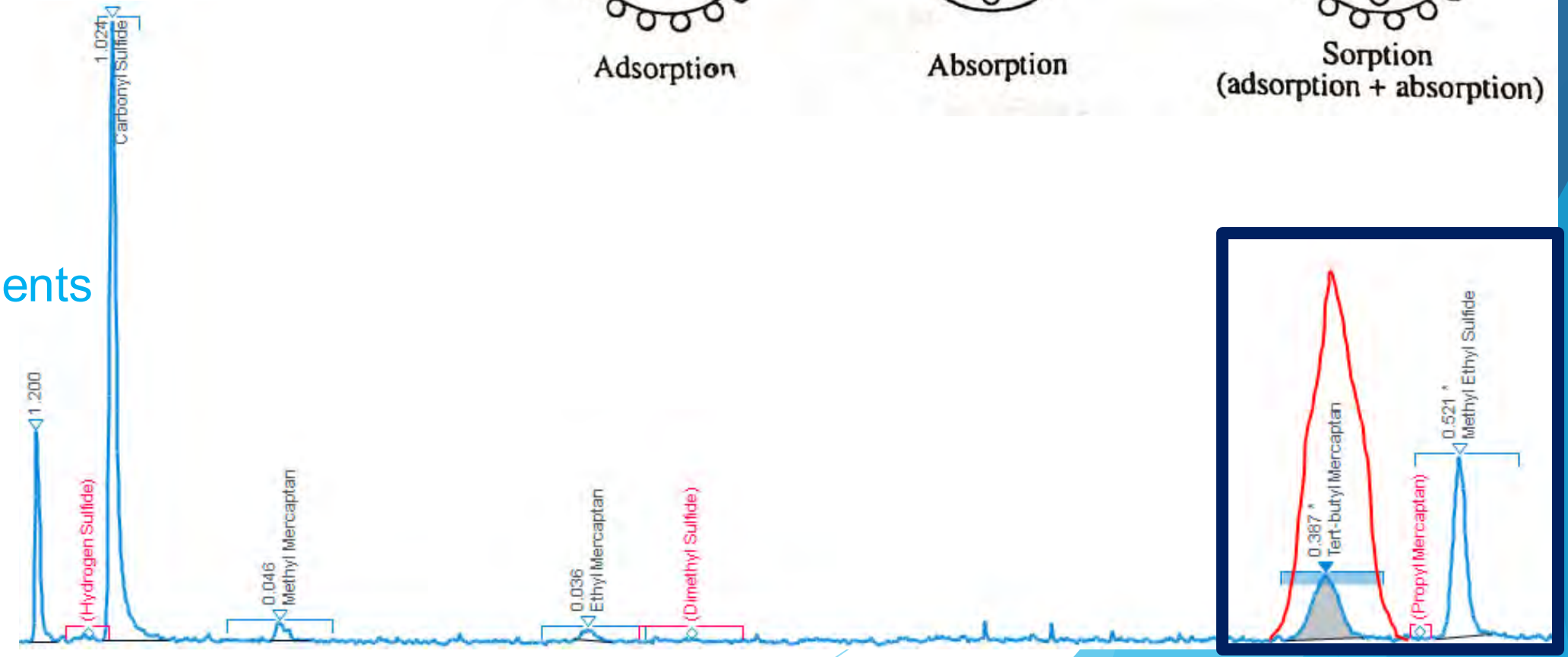
- Olfactory Mirage

Perception of an odor that isn't really there. Routine jobs with odor always present, could be a cause of this condition.(*AGA odorization manual 2017*)

Odorant interference

- Adsorption (Sticking Together)
- Absorption (Pulling Apart)
- Oxidation
- Masking Agents





QUESTIONS??

References

- AGA odorization manual 2017
- www.arkema.com
- https://naturalgasodorization.com
- www.cpchem.com
- CSA Z662-15
- ATCO odorant monitoring course training material
- Arkema odorization presentation
- https://www.gasdetectorsusa.com/gdusa/download/Natural_gas_odorization.pdf
- file:///C:/Users/ymvj/Downloads/tsp_m41_m42_energyMEDOR.pdf
- 2022 Natural gas odorization conference presentations
- SCD Manual.pdf

How does the SCD and FPD detectors work?

$$\text{Sulfur compound (analyte)} \rightarrow SO + H_2O + \text{other products}$$

$$SO + O_3 \rightarrow SO_2 + O_2 + h\eta\ (<300\text{–}400\ \text{nm})$$

Stinky Stories

- Close to 10 years ago Contractor delivering odorant to Southern Alberta was stopped just prior to reaching USA border to return to Texas. The reason for the stop was Odor Calls spanning from Calgary to the Border that matched the route the driver was expected to take. Filling hose valve was not shut properly dripping residual odorant along the highway until driver was stopped to correct the leak.

- Chronic odor calls in Edmonton region- primarily around the time that odorant was delivered to brand new storage facility. After months of not finding the leak it was discovered that a bolt holding the inspection plate onto the tank had been bent when installing a walkway in the station and the smallest of pressure was leaking from that bolt causing the odor calls when the pressure was highest after filling.