

Sampling CO₂

Why all the fuss?

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Technologists

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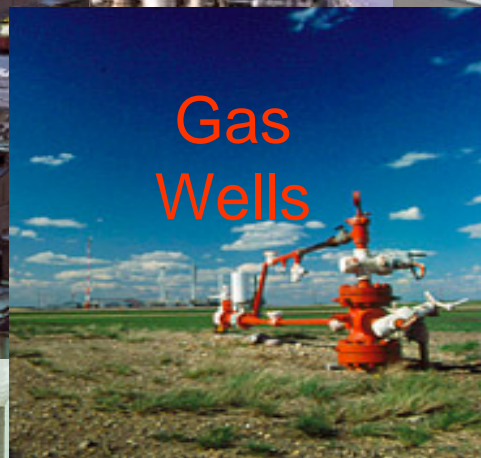
Introduction



Ammonia Plants



Power Plants



Gas Wells



HyCO/
Syngas



Refineries



Distilleries

Introduction

According to the US EPA Emission Inventory from 2004, the listed sources produced the following materials in their waste streams:

Fluorine, Nickel, Naphthalene, Formaldehyde, Indeno(1,2,3-cd)pyrene, Lead, Manganese, Mercury, 3-Methylcholanthrene, N-Hexane, Nitrogen oxides (NO_x), Copper, Carbon monoxide, Chromium, Formaldehyde, Cobalt, Formaldehyde, Dibenzo(a,h) anthracene, Dichlorobenzene, mixed isomers, Dimethylbenz(a)anthracene, Ethane, Fluoranthene, Nitrogen oxides (NO_x), Chrysene, PM₁₀, primary, Volatile organic compounds (VOC), Vanadium, Carbon dioxide, Zinc, Total organic compounds (TOC), 2-Methyl Naphthalene, N-Pentane, Total organic compounds (TOC), Toluene, Sulfur dioxide, Selenium, Pyrene, Propane, PM, condensable, Nitrogen oxides (NO_x), Nitrous oxide, PM_{2.5}, primary, Phenanthrene, PM_{2.5}, filterable, PM₁₀, filterable, Volatile organic compounds (VOC), Nitrous oxide, Acenaphthylene, Molybdenum, Cadmium, Acenaphthene, Ammonia, Anthracene, Arsenic, Benzo (k) fluoranthene, Benzene, Benzo (a) anthracene, Benzo (a) pyrene, Benzo (b) fluoranthene, Benzo (g,h,i) perylene, Beryllium, n-Butane, Barium

Introduction

- Increased public awareness of ingredients and health risks make QA/QC of CO₂ paramount to maintaining your brand
- Improper analysis of of these feed streams can lead to “Out of Specification” product.

Topics of Discussion

- The easiest part of CO₂ analysis is analyzing
 - ◆ Significant improvements have been made to the operability and detection limits of analytical instrumentation
- The hardest part is sampling
 - ◆ Physical and Chemical characteristics makes this molecule quite challenging.
 - ◆ Design considerations must be made for
 - ★ The properties of the contaminants of interest
 - ★ The materials of construction
 - ★ Operational physics of the sample system

Topics of Discussion

- This presentation will focus primarily on sampling considerations surrounding:
 - ◆ Non-Aromatic Hydrocarbons
 - ◆ Sulfur Compounds
 - ◆ Aromatic Hydrocarbons
 - ◆ Particles/Metals/NVOR's
- These are the principle contaminants in the ISBT Beverage Specification

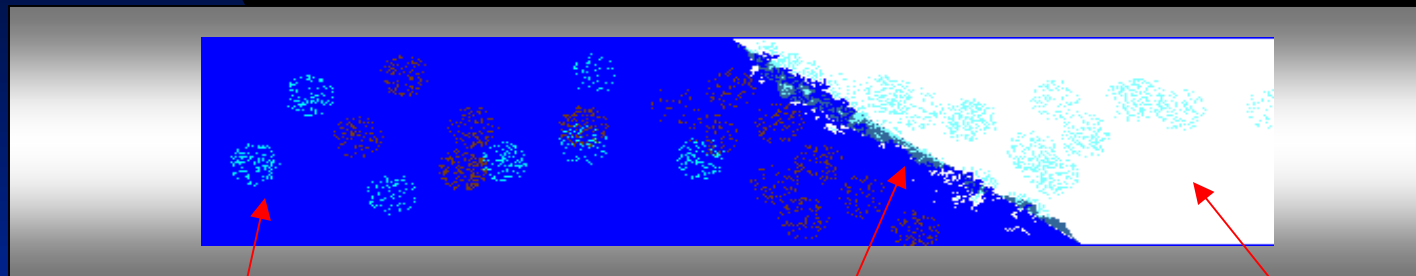
Sampling Considerations:

Consider the Contaminant

Sampling Considerations: Consider the Contaminant

- When we analyze carbon dioxide, we analyze the gas phase.
- Carbon dioxide has a very strong *Partitioning Coefficient*.
 - ◆ *At any given pressure or temperature, certain components will (preferentially) exist in the gas phase, while others prefer the liquid phase.*
- This effect is most pronounced in light (non-condensable) and heavy (condensable) hydrocarbons

Sampling Considerations: Consider the Contaminant



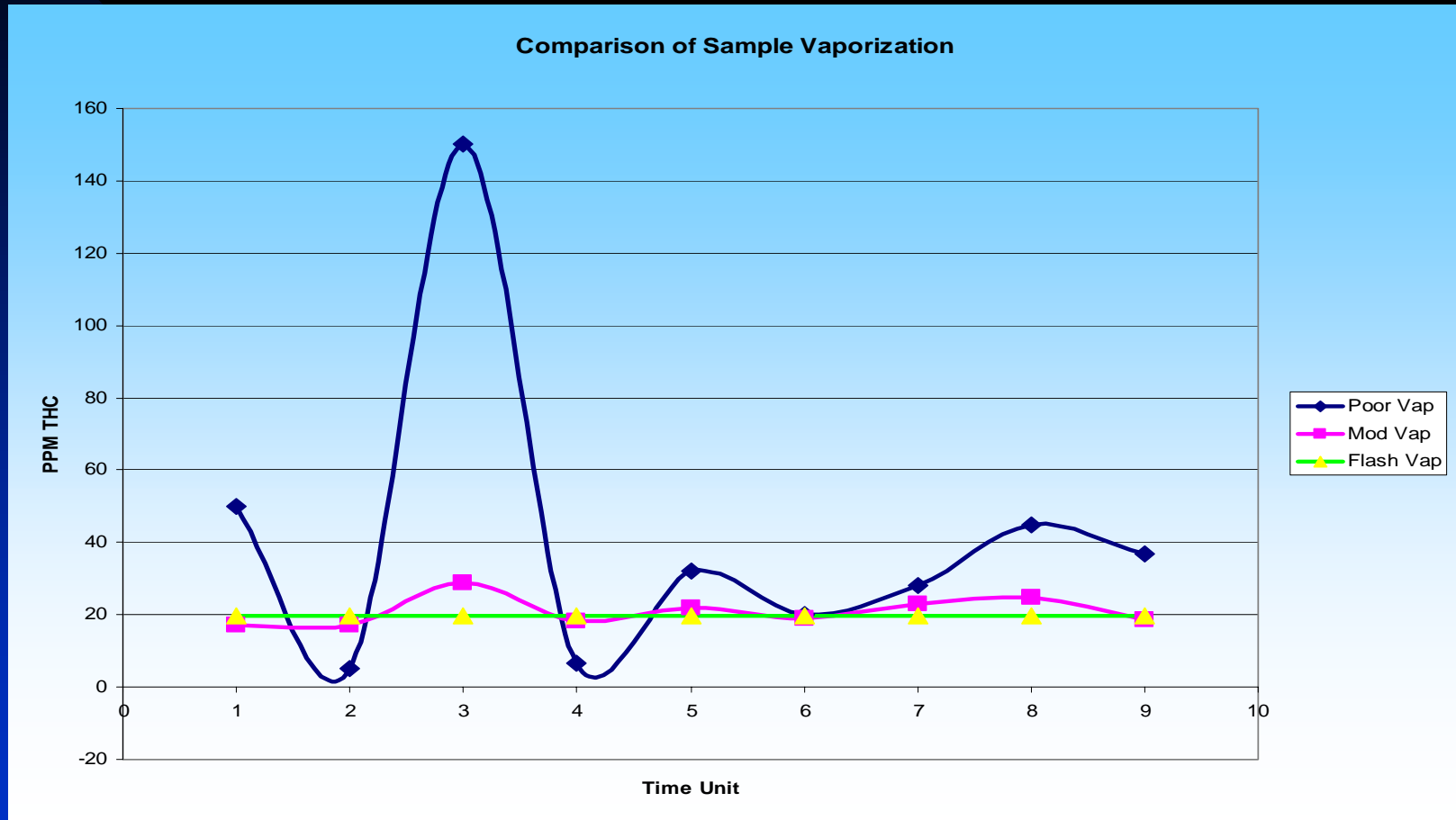
Liquid CO₂ + Partitioned
Methane + Partitioned NMHC

Boiling Front

Gaseous CO₂ + High levels
of Methane + Low or No
NMHC

So what does this look like in real life?

Sampling Considerations: Consider the Contaminant



Methane Readings in Liquid and Vaporized CO₂

Sampling Considerations: Consider the Contaminant

Take Home Message:

- *Proper Design and Operation of your sample system will keep your sample*
 - ◆ *Homogenous*
 - ◆ *Representative*
- *Improper application will lead to erroneous results*

Sampling Considerations:

Consider the Materials of Construction

Sampling Considerations: Materials of Construction

- Sample system materials fall into 2 major categories
 - ◆ Soft/Flexible
 - ★ Teflon
 - ◆ Rigid
 - ★ Stainless Steel
 - ★ High Performance Coated Stainless Steel
 - ◆ Depending on the contaminants and operational characteristics, some materials are superior to others.

Sampling Considerations: Materials of Construction

- Carbon Dioxide contaminants of interest fall into two very critical categories:
 - ◆ “Sticky”- affected by the process of physical adsorption. Examples:
 - ★ Moisture (water vapor)
 - ★ Benzene
 - ◆ “Reactive”- affected by the process of chemical adsorption Examples:
 - ★ Hydrogen Sulfide
 - ★ Ammonia

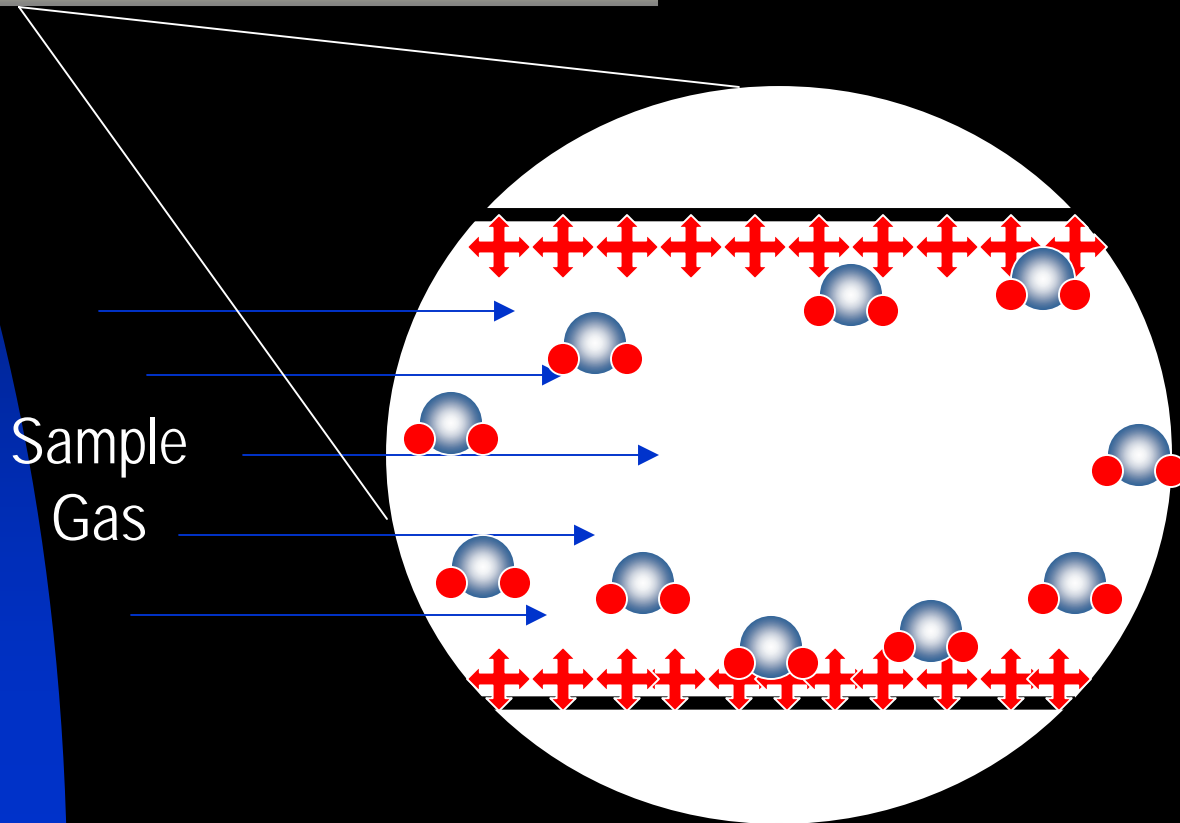
Sampling Considerations: Materials of Construction

- “Sticky” Effects are primarily based on Sample Energy (pressure/velocity/temperature), while
- “Reactive” Effects are primarily based on Chemical Energy (such as covalent bonding and catalysis)

Which means:

Sampling Considerations: Materials of Construction

Lets take a look at our sample line again with a “Sticky” molecule:

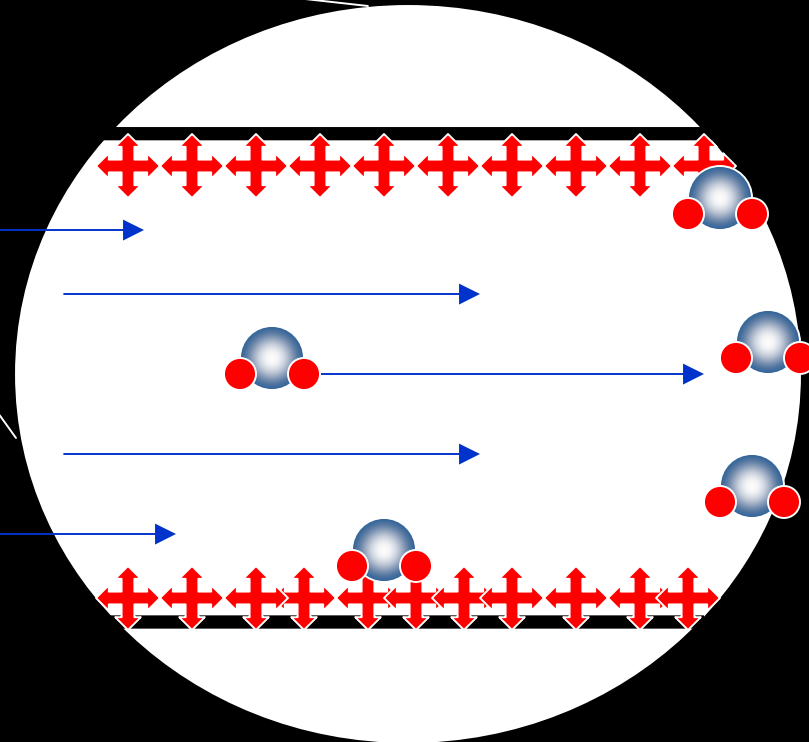


Sample Gas +
Moisture at **low**
velocity, high rate
of adsorption

Sample
Gas

Sampling Considerations: Materials of Construction

Lets take a look at our sample line again with a “Sticky” molecule:



Sample Gas +
Moisture at **high**
velocity, low rate
of adsorption

Sample
Gas

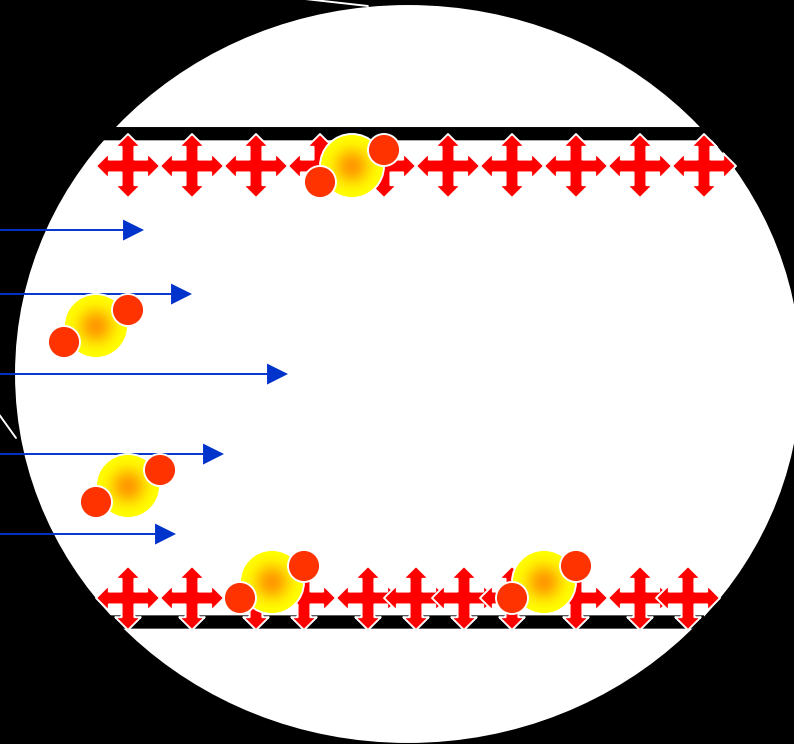
Sampling Considerations: Materials of Construction

Lets take a look at our sample line again with a “Reactive” molecule :



Sample Gas + Hydrogen Sulfide at **low** velocity, active sites are passivated slower, contaminant not seen at analyzer

Sample Gas



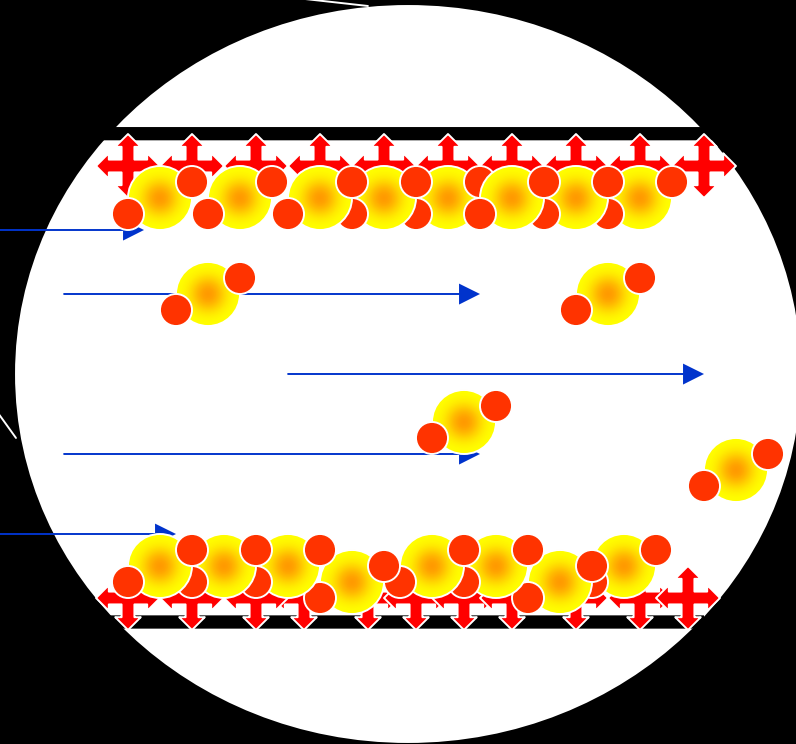
Sampling Considerations: Materials of Construction

Lets take a look at our sample line again with a “Reactive” molecule :



Sample Gas + Hydrogen Sulfide at **high** velocity, active sites are passivated faster, readings stabilize quicker

Sample Gas



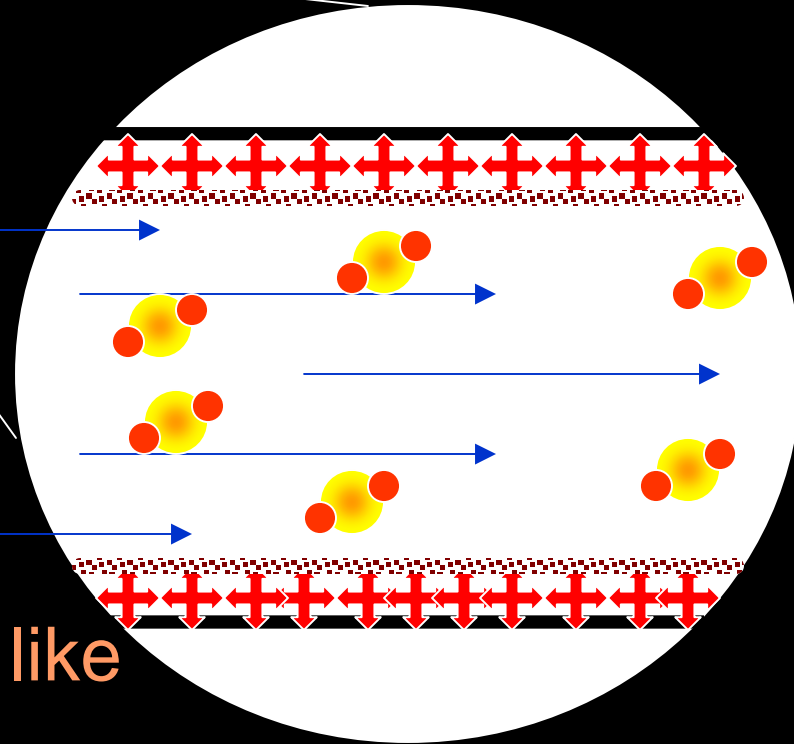
Sampling Considerations: Materials of Construction

Lets take a look at our coated sample line again with a "Reactive" molecule:



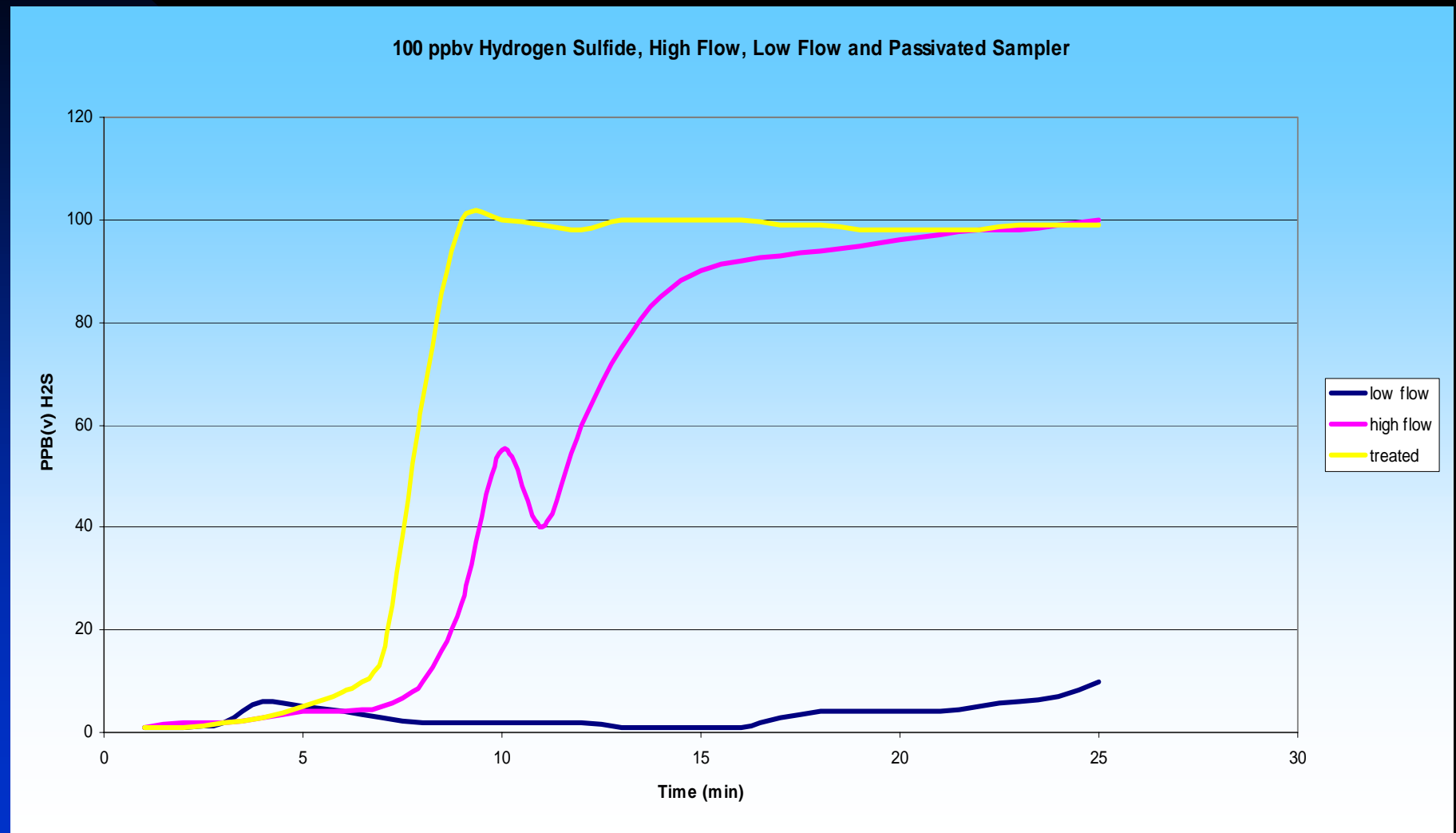
Sample Gas + Hydrogen Sulfide regardless of velocity, coating occupies active sites on steel, side reactions reduced and readings stabilize quickly.

Sample Gas



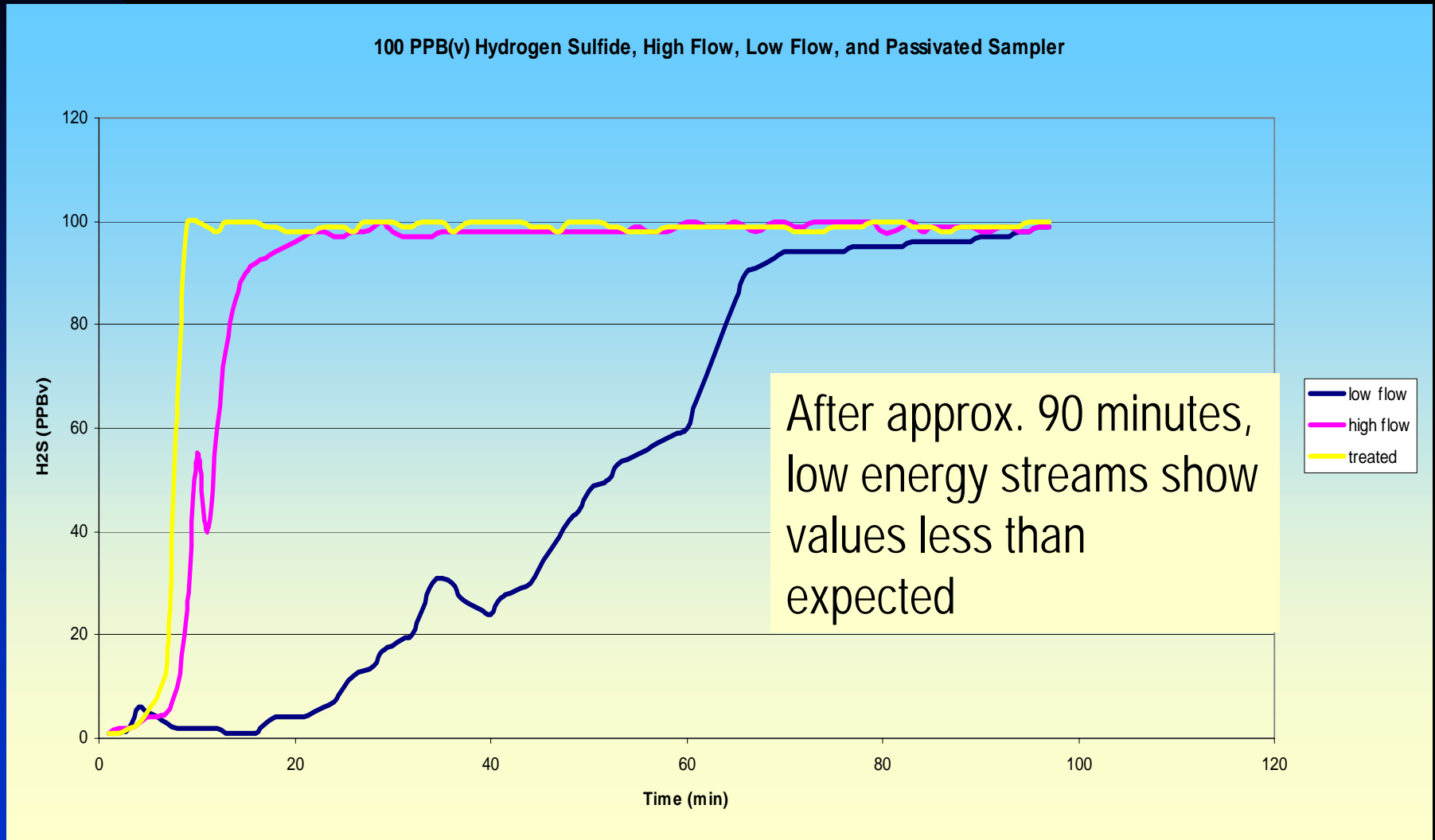
So, what does it look like in real life?

Sampling Considerations: Materials of Construction



**Analytical Science and Technologies Laboratory Results. Newton, NJ

Sampling Considerations: Materials of Construction



**Analytical Science and Technologies Laboratory Results. Newton, NJ

Sampling Considerations: Consider the Contaminant

Take Home Message:

- *Physical and Chemical Adsorption reactions result in similar analytical effects;*
- *Untreated Stainless Steel is OK, as long as the system is designed to maximize sample energy;*
- *Coated Steels are excellent options, when low energies or low/no flow conditions are expected;*
- *Teflon.....*

Sampling Considerations:

Consider the Physics of Sampling

Sampling Considerations: Consider the Physics of Sampling

- Particles, Metals and Residues are unique constituents to measure
 - ◆ Typically SAMPLED in the liquid phase, but MEASURED in the gas phase or dissolved from the sample matrix.
- Very little online or insitu measurement feasible or available.
- These materials are typically Big, Heavy, and Sticky!

Sampling Considerations: Consider the Physics of Sampling

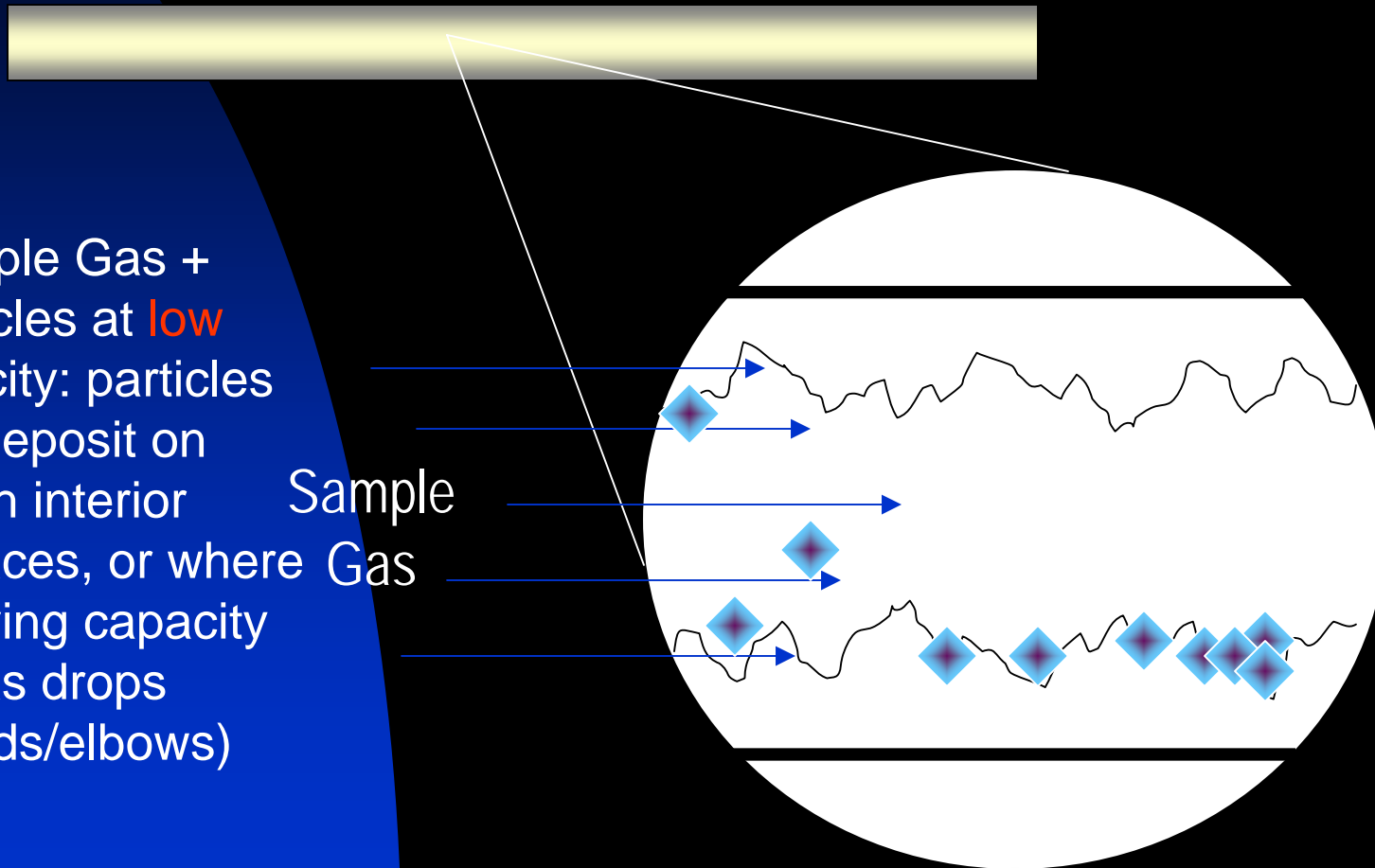
- So why is this a problem?
 - ◆ Low energy streams will deposit particles of interest in the sample vessel, rather than at the point of analysis
 - ◆ “Carrying Capacity” of the fluid stream is dependant upon
 - ★ Stream velocity (energy)
 - ★ Laminar/Turbulent flow
 - ★ Particle Size
 - ★ Particle Buoyancy
 - ★ Tubing Roughness (RA Factor)

Sampling Considerations: Consider the Physics of Sampling

Lets take a look at our sample line again:

Sample Gas + particles at **low** velocity: particles will deposit on rough interior surfaces, or where carrying capacity of gas drops (bends/elbows)

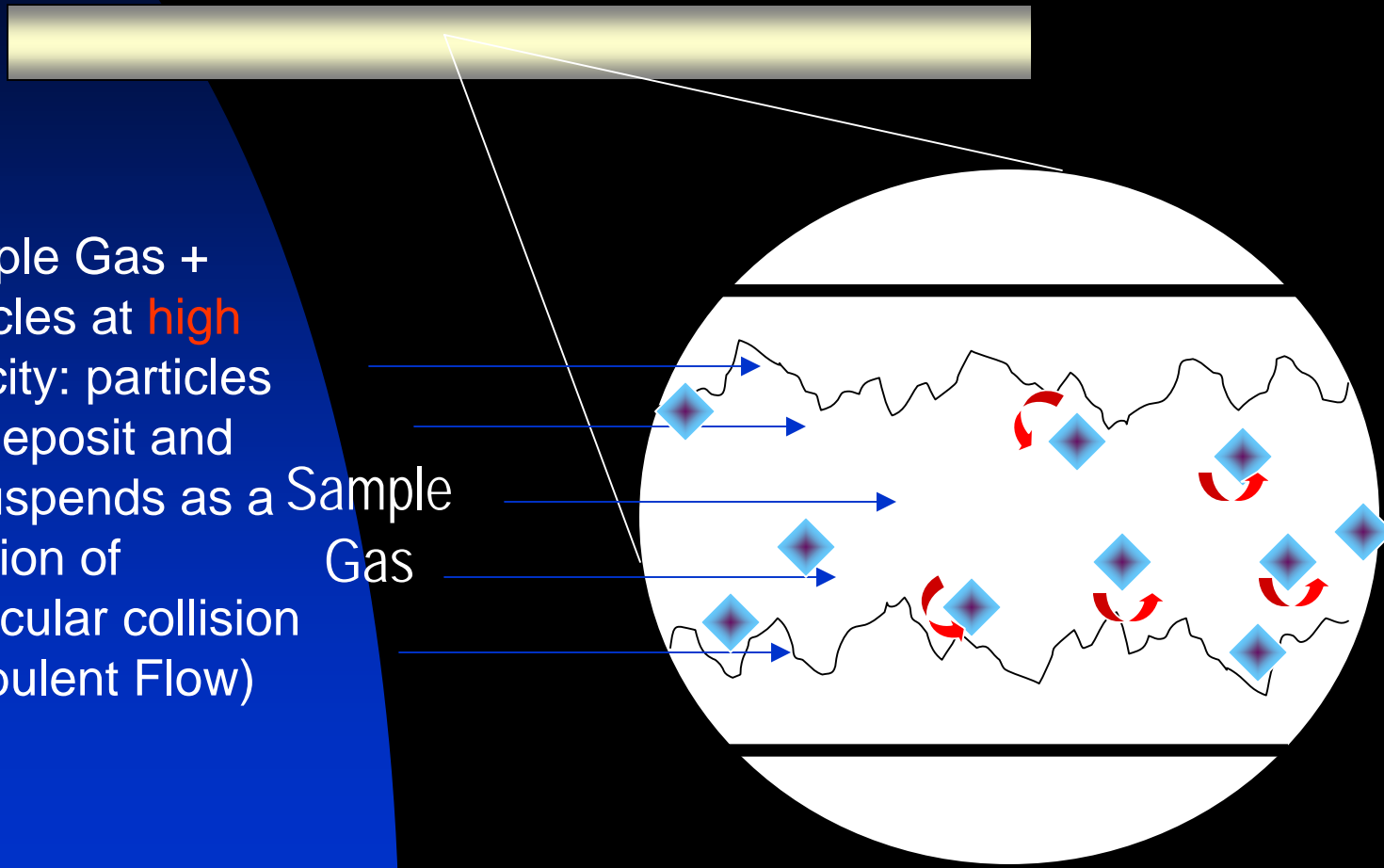
Sample Gas



Sampling Considerations: Consider the Physics of Sampling

Lets take a look at our sample line again at a higher velocity:

Sample Gas + particles at high velocity: particles will deposit and re-suspends as a function of molecular collision (Turbulent Flow)



Sampling Considerations: Consider the Physics of Sampling

Take Home Message:

- *Velocity is the big factor*
 - ◆ *Higher velocities impart energy to lift particles*
 - ◆ *Turbulent flow can be achieved and maintained*
- *When measuring for particulate, separate sample processes need to be used to conserve the kinetic profiles required for the contaminant of interest.*
- *Combining sampling processes will typically lead to low or no results*

Closing Comments:

- *Interest in the quality of Carbon Dioxide is at an all time high.*
- *A balance between the selection of component materials and operational qualities must be struck with the characteristics of CO₂ in mind.*
- *Improper sampling will lead to erroneous, potentially misleading results.*

A blue curved shape, resembling a quarter-circle or a similar arc, is positioned on the left side of a black background. The shape is solid blue and curves from the bottom-left towards the top-left.

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Technologies, LLC