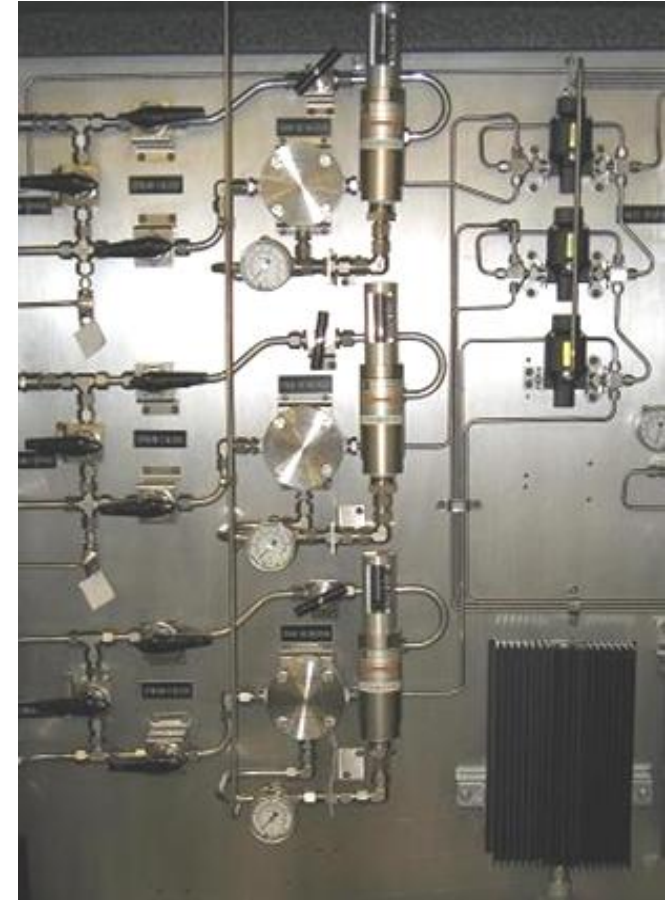


# Gas Analysis

## Sample Handling

### Gas Sample Handling Systems

- What we try to achieve
- Some ways we do it
- Problems of time delay
- Problems of representation

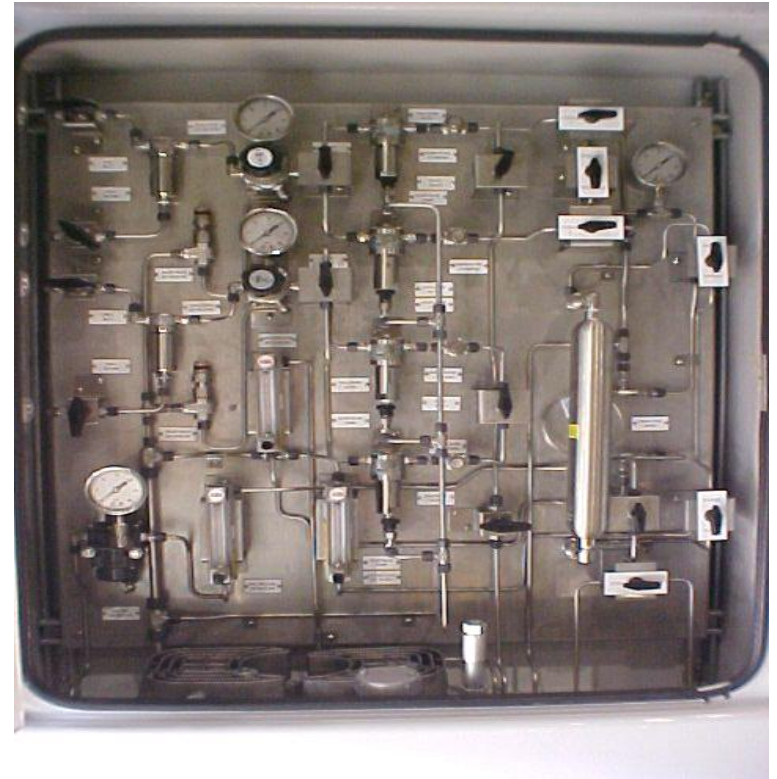


# Introduction

## Sampling Criteria

Samples for analysis must be:

- Compatible
- Timely
- Representative



# Goal #1: Compatible Sample

## Definition

A compatible sample will not harm the analyzer nor prevent it from producing a reliable analytical result.

## Sample Conditioning

We make samples compatible by sample conditioning.

We modify and control the condition of the sample to ensure that it is always acceptable to the analyzer:

- Maintain a constant flow rate, temperature, and pressure
- Remove most of the solids
- Get a single phase sample – gas only, no liquid!
- Avoid corrosion

Most gas samples are not difficult to condition.

# Goal #2: Timely Sample

## Definition

A timely sample is one that provides an analysis with an acceptable delay from real time. Some delay is inevitable!

## Sample Motion

The sample fluid has to move:

- from its point of origin inside the process
- to the point of measurement inside the analyzer



To reach the analyzer the sample gas has to pass through process piping, sample tubing, and conditioning devices.

It all takes time!

# Noticing It

## Typical Symptoms

It's often difficult to detect a time delay problem because the symptoms are invisible!

- the measurement is too stable or varies without reason
- process control is unstable or ineffective
- the lab sample gives a different result
- operators have no confidence in analyzer

Process operators know there is something wrong but they may just call for “calibration”.

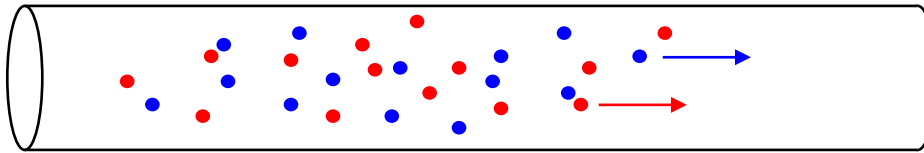
The classic symptom is:

- *the analyzer doesn't follow the process!*

# Line Delays

## Tubes & Pipes

This is very simple. We assume that all the molecules move down the line at the same speed.



Thus the time delay is just the time it takes to purge all of the old fluid out of the line.

$$\text{Lag Time} = \frac{\text{Volume of Line (L)}}{\text{Flow Rate (L/min)}} \times \frac{\text{Pressure in Line}}{\text{Pressure in Flowmeter}}$$

The “standard” for transport time is one minute.

# Capacity Lag

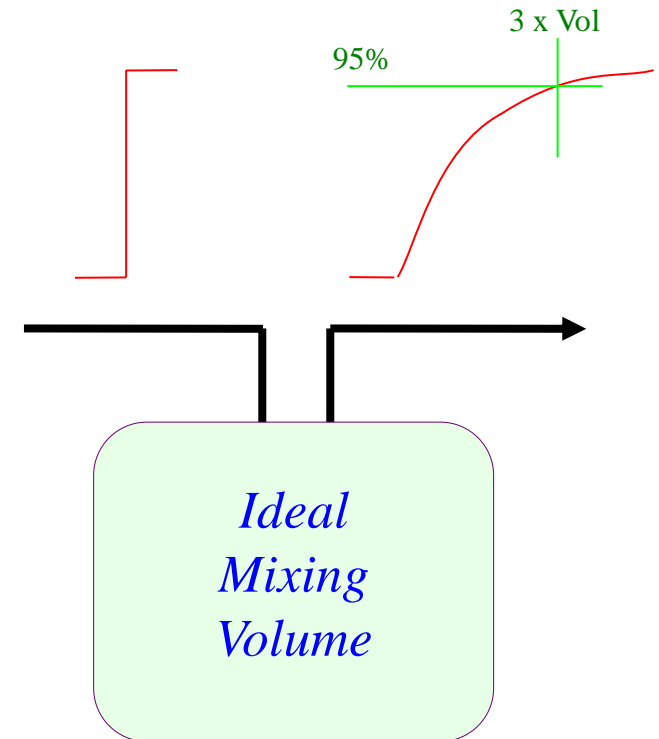
## Mixing Volume

This kind of delay is caused by new sample mixing with old sample in a mixing volume.

For the ideal case, delay is counted as the time to purge the internal volume three times.

To compute; divide three times the volume by the flow rate and apply the pressure correction:

$$\text{Lag Time} = \frac{3 \times \text{Volume of Line (L)}}{\text{Flow Rate (L/min)}} \times \frac{\text{Pressure in Line}}{\text{Pressure in Flowmeter}}$$



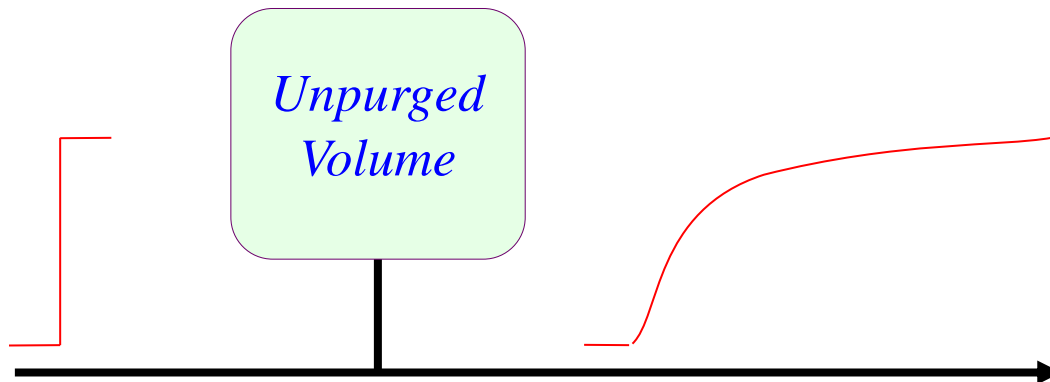
# Dead Legs

## Tube Tees

At a pressure gauge, valve manifold, relief valve, etc.

A *dead leg* is an unpurged volume that allows molecules to diffuse into and out of the flowing sample – causing

- First, a slow initial response
- Then, a continuous contamination!



The time delay in a dead leg cannot be calculated exactly.

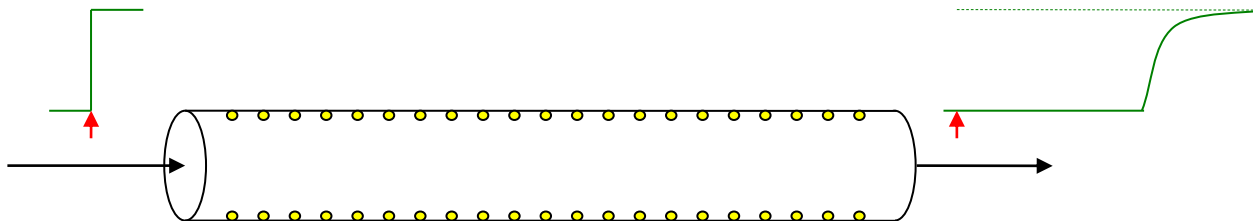
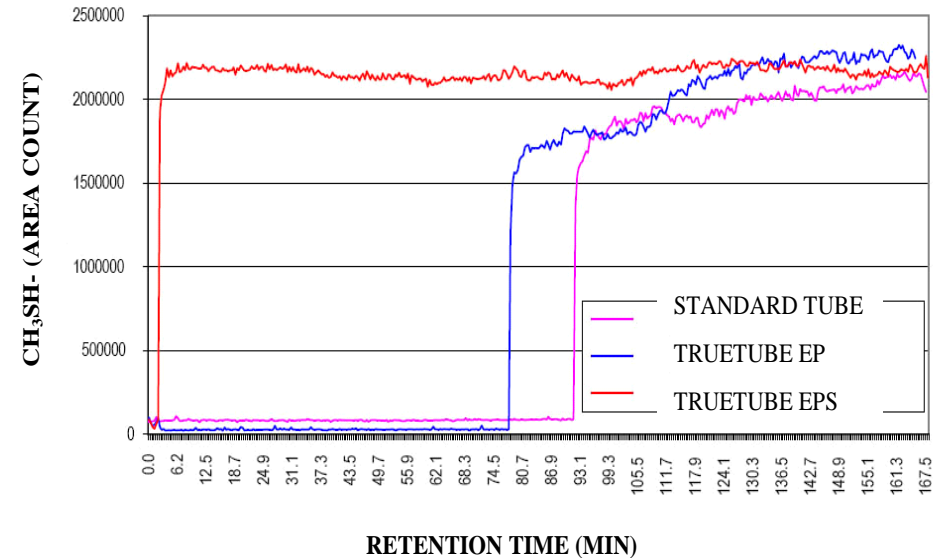


# Adsorption Delays

## Sticky Molecules

Polar molecules, like hydrogen sulphide  $\text{H}_2\text{S}$  and water  $\text{H}_2\text{O}$ , are strongly attracted to a surface and are difficult to wash off:

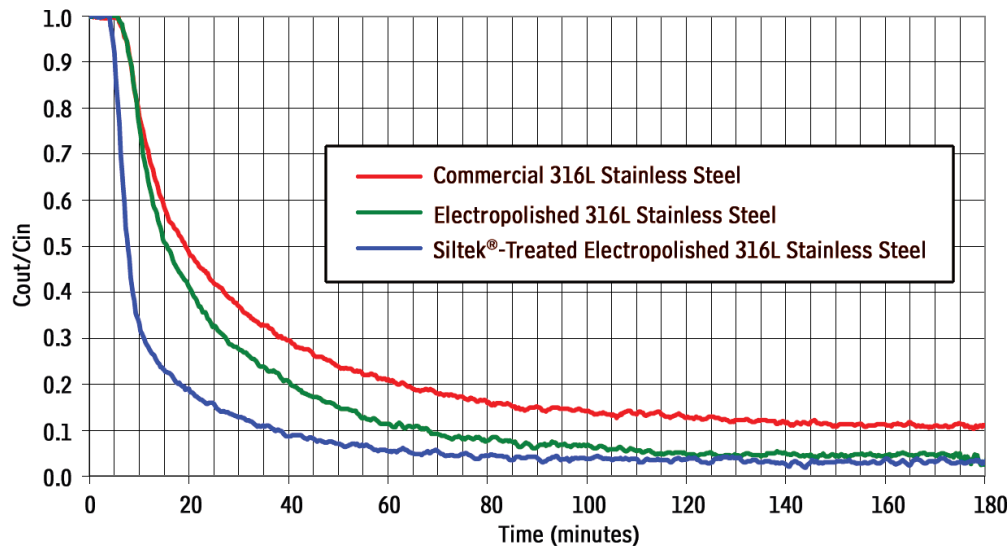
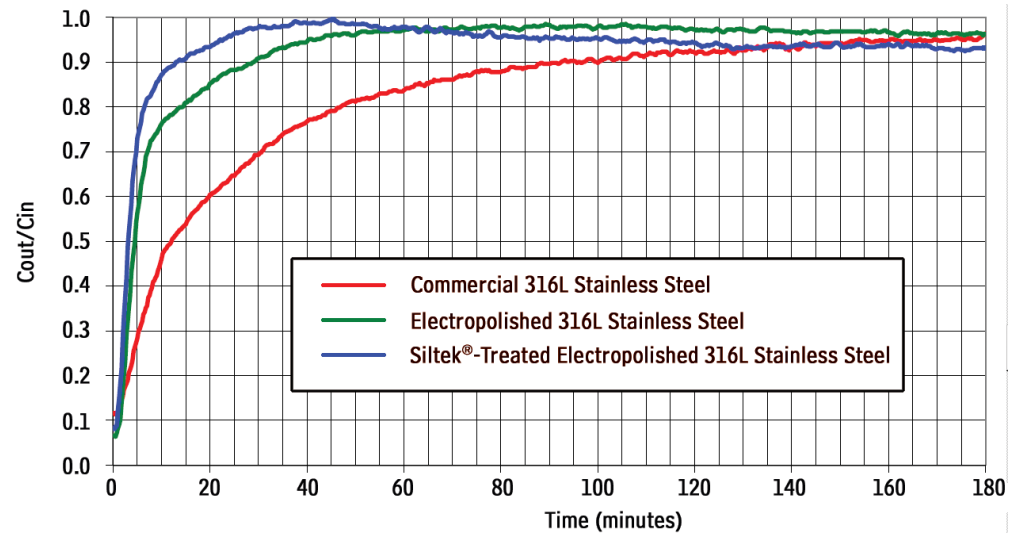
- adsorption of polar molecules causes an unpredictable delay
- or even complete removal of the analyzed molecules!



# Slow Response

## Moisture Adsorption

Shows the slow response to moisture measurement in untreated tubing and improvement using silica-coated tubing.



Barone, G., M. Higgins, T. Neeme, and D. Smith. 2008. "Study of Chemical and Physical Adsorption Properties of Moisture, Sulfur, and Mercury Streams Through a Variety of Tubing Substrates." In *Proceedings of ISA Analysis Division Symposium 2008*. Paper #S05.1.

# Goal #3: Representative Sample

## Definition

A representative sample is one that provides a meaningful analytical measurement useful for its intended purpose.

A result can be “representative” without being accurate.

## Not so easy!

What do we want the sample to represent?

- Just the gas phase – ignoring any liquid present?
- Or the entire process gas + liquid?

When liquid is present in the process gas, it's vitally important to decide what you want to measure.

- the choice of measurement makes a big difference to the sampling system!
- be careful what you ask for ...  
you might not like the result!

# Dry Gas Sample

## Stop Condensation!

If starting with a dry gas sample, don't let the gas contact any metal surface cooler than its dew point temperature.

- All gas lines must be dry!
  - may need to heat the process line!
  - can separate liquid that doesn't dissolve analyte
- In many cases, heating is essential:
  - use heated pressure regulator, then heat line
  - insulation alone won't keep a gas warm
  - set tracing temperature to 20 °C above dew point
- It's surprisingly difficult to avoid cold spots:
  - allow no unheated sections (even line joints)
  - continue to heat line inside analyzer house
  - ensure analyzer is heated above dew point
  - heat vent pipe too!

# Joule-Thomson Effect

## Adiabatic Cooling

A pressure drop will tend to vaporize aerosol liquids – but it also cools the gas!

The cooling may cause condensation and composition change; need heated regulator.

The temperature drop is:

- Same at any flow rate
  - but harder to reheat at high flow
- Proportional to pressure drop.  
Table gives
  - temperature drop at 25°C
  - heating power with 5 NL/min
- Less cooling at higher temperature
- Hydrogen warms up!

Gas	Cooling Effect	Heating Power
	C° / bar	mW / bar
Helium	-0.10	n/a
Hydrogen	-0.02	n/a
Nitrogen	0.25	25
Air	0.26	26
Methane	0.40	49
Ethane	0.72	130
Ethylene	0.74	110
Propane	0.89	230
Carbon Monoxide	0.38	28
Carbon Dioxide	0.67	88
Sulfur Dioxide	1.25	170
Nitric Oxide	0.30	31
Ammonia	0.82	110
Hydrogen Chloride	0.89	90
Methyl Chloride	1.3	190
Chlorine	1.4	170

# Separating Liquids

## Careful!

Only separate liquids that don't dissolve the analyzed gases.

- OK to remove:
  - water when measuring  $H_2S$  in sour gas
  - polymer oil when measuring butadiene
- Not OK to remove:
  - water when measuring hydrogen chloride
  - hexane when measuring butane & pentane
- Coalescer for Gas Sample Conditioning:
  - a vortex cooler provides chilled air as coolant
  - process gas passes through cooled tubes
  - water and heavy hydrocarbons condense & run down tubes into bottom
  - gas continues upwards through a coalescer to remove liquid mist before analysis



# Phase Diagram

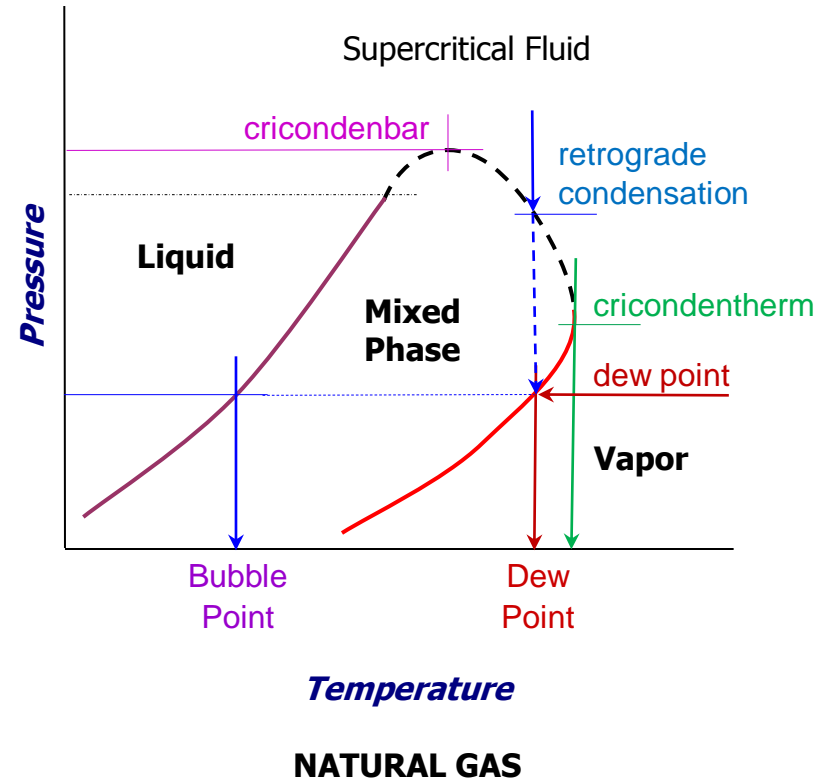
## Natural Gas

For a mixture, the phase diagram will show a region where both liquid and vapor coexist. In this diagram:

- The purple line is the bubble point or initial boiling point of the liquid
- The red line is the dew point temperature of the vapor
- At any condition between these two lines, a two-phase mixture of liquid and vapor will be present

Notice that a gas at high pressure can retro-condense when its pressure is reduced – then revaporize again!

A gas heated above its cricondenthem can't condense at any pressure.



# Composition Diagram

## Condensation

Consider a gas sample of 80 vol.% pentane and 20 vol.% hexane at 2 bara and 85 °C.

1. Suppose gas cools to 65° C and condensate is removed by a catchpot:

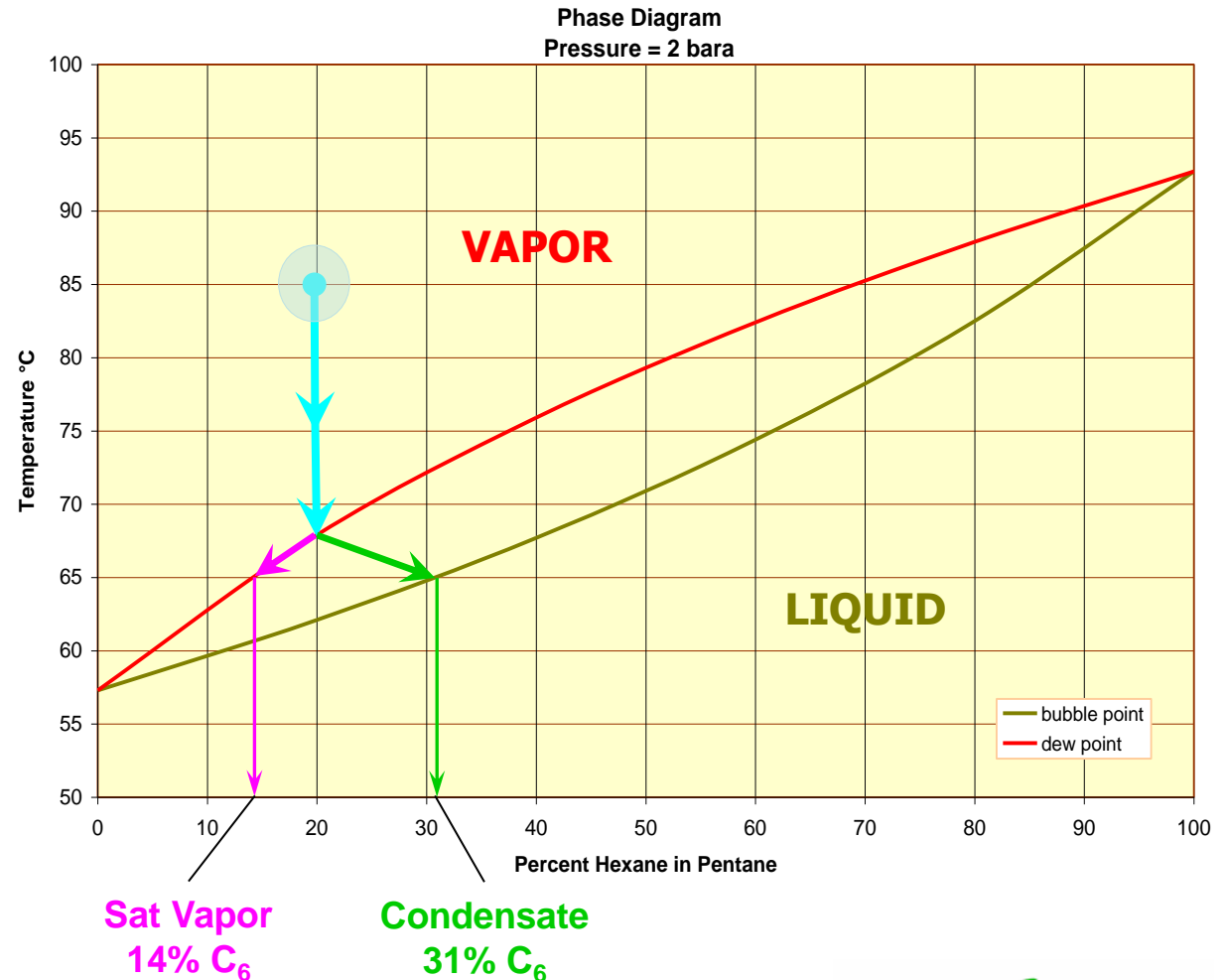
➤ What does the gas analyzer measure?

2. Suppose the process gas changes to 25 % C<sub>6</sub>

➤ What does the gas analyzer measure?

3. Suppose the pipeline temperature changes:

➤ What does the gas analyzer measure?





# Sampling Vapor Only

## Difficult

We see from the phase composition diagram that:

- The liquid & gas compositions are very different
- Both compositions change with line temperature

If you take a sample of the gas phase only:

- The sample composition is fixed by line temperature
- The analyzer becomes an expensive thermometer!

It's very difficult to get a gas sample only:

- If liquid enters the probe or sample line it will vaporize and dramatically change sample composition
- Must separate liquid at exactly line conditions
- Best to separate liquid inside the probe – in the pipe!

Mayeaux, D. P. 2000. "Sampling and Conditioning of a Gas Containing Liquids in Droplet or Aerosol Form." In *Proceedings of ISA Annual Analysis Division Symposium 2000*:247-254.

# Sampling Gas & Liquid

## Maybe Impossible

It's very difficult to get a representative sample:

- The liquid content varies in different places in the process pipe
- Any sample taken cannot be representative of the whole process stream
- A “vaporizing regulator” is not the answer!

Even an isokinetic probe will sample only the local aerosol and will omit the liquid running along the walls of the pipe.

- Grab sampling methods are used to sample gas and liquid separately and combine analyses, but the gas/liquid ratio is never accurately known
- Perhaps a simple solution is to install a process heat exchanger that vaporizes all the liquid!

# Summary

## Gas Sampling is Easy

If the process gas contains no liquid:

- Yet many systems fail because they allow condensation to occur – easy to prevent!
- Some symptoms of liquid present are noisy measurements, wet lines, and blocked filters

## Gas Sampling is Difficult

If the process gas contains liquid, even as aerosol:

- Can try to sample only the gas phase, but there's little value gained – results will follow pipeline temperature!
- Vaporizing the liquid content is not a good idea!
- A successful outcome is unlikely

**Thank you!**

Questions?

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