Gas Chromatograph Maintenance (Understanding GC Fundamentals)

by Don Ford

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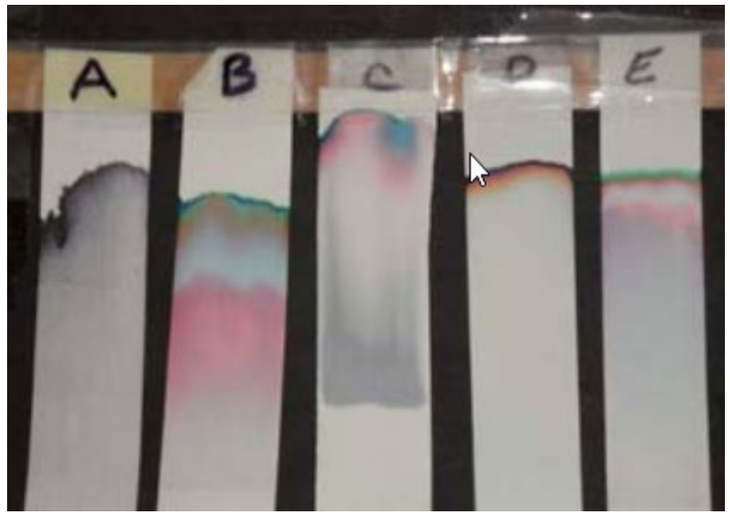
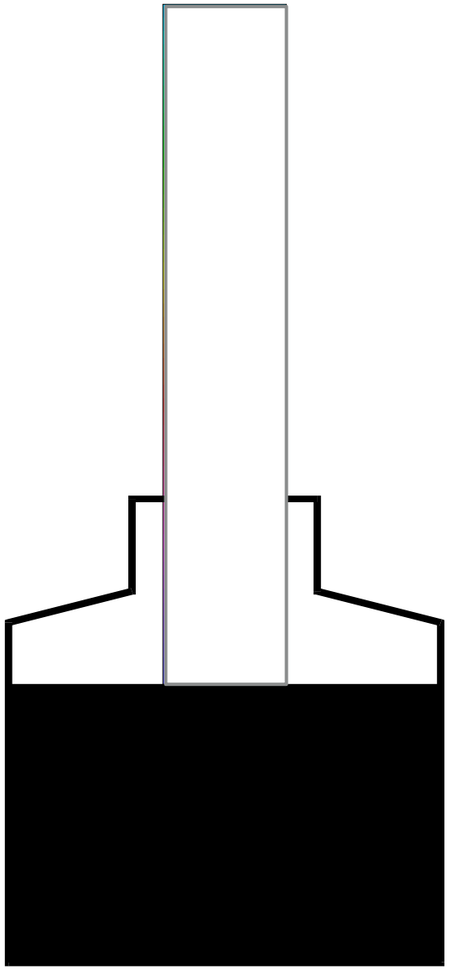
EMERSON

Fundamental Chromatography
(Greek: Chromatography – color writing)

- Dipped a piece of absorbent paper into Black Ink
- Capillary action draws liquid through the paper
- The color bands formed from various pigments in the ink absorbing onto the paper at different rates
- This showed that a mixture of compounds could be separated by differences in how fast they moved through the media

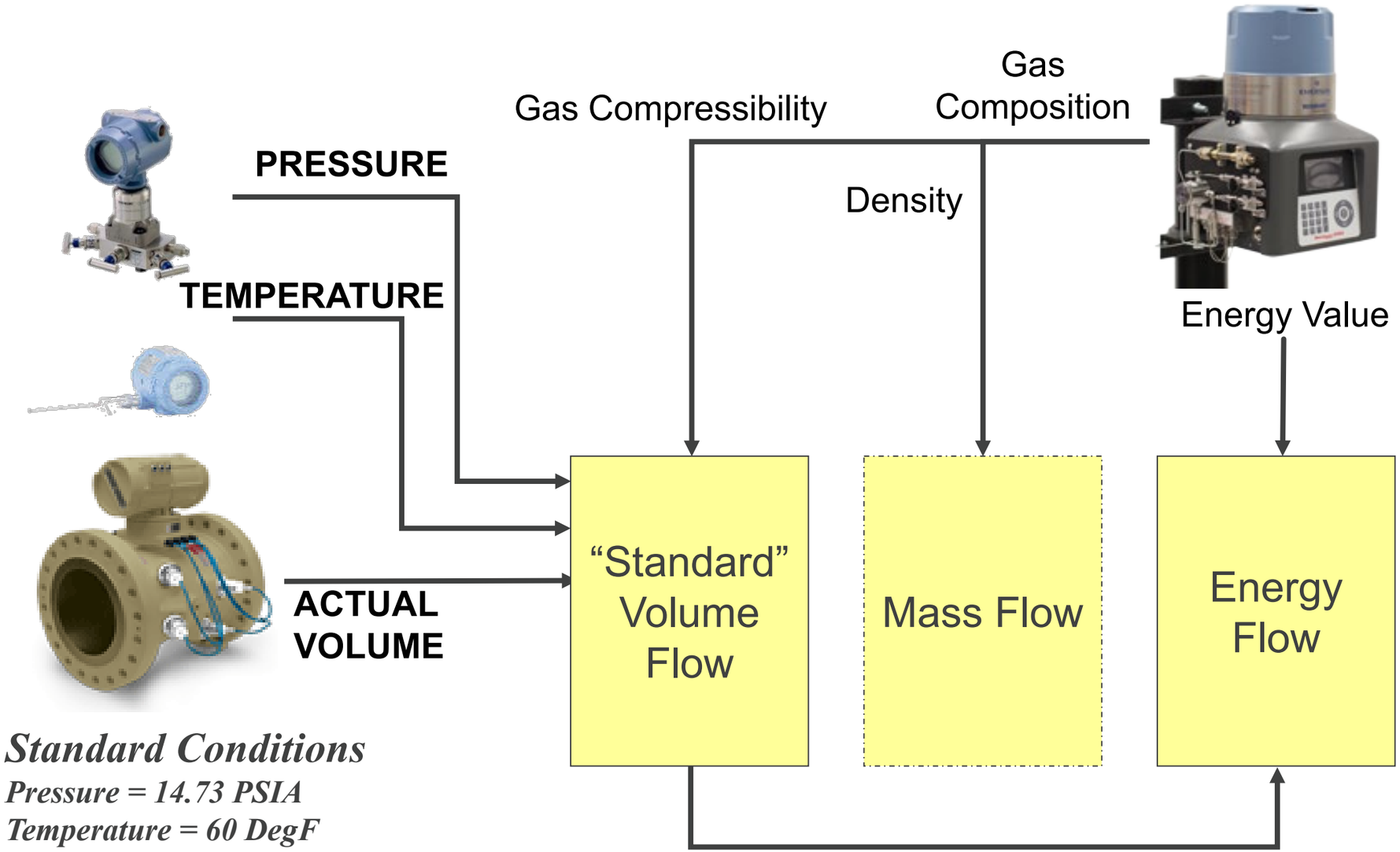




Purpose of Gas Chromatograph

- Gas Chromatography is used in the Oil and Gas industry to:
- Determine the quality of the product and compare against the required tariff specifications
- Calculate physical properties of the product
  - **Heating Value (BTU) – using GPA 2172 or ISO 6976 (metric)**
  - **Specific Gravity – using AGA 8**
  - **Compressibility – using AGA 8**
  - Wobbe Index (Heating value/Square Root (Specific Gravity)

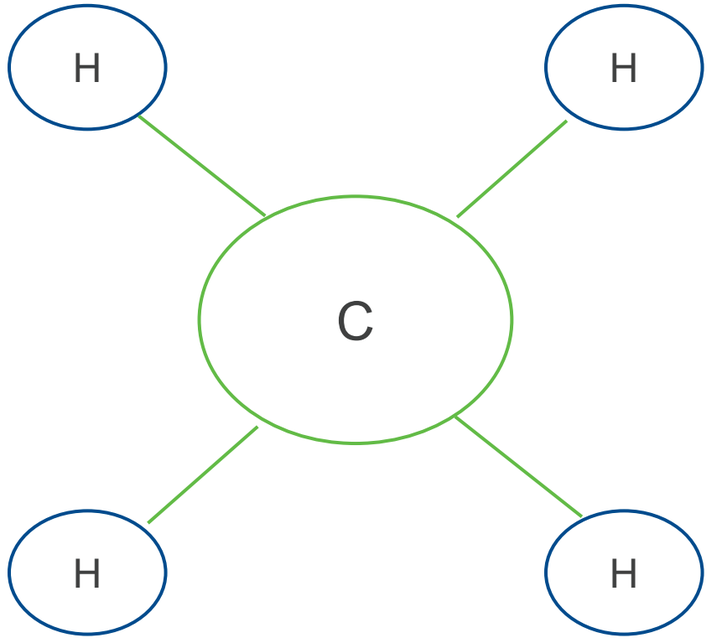
Gas Chromatographs in Custody Transfer



What is Natural Gas?

A mixture of Hydrocarbons that are molecules made up of Carbon and Hydrogen atoms

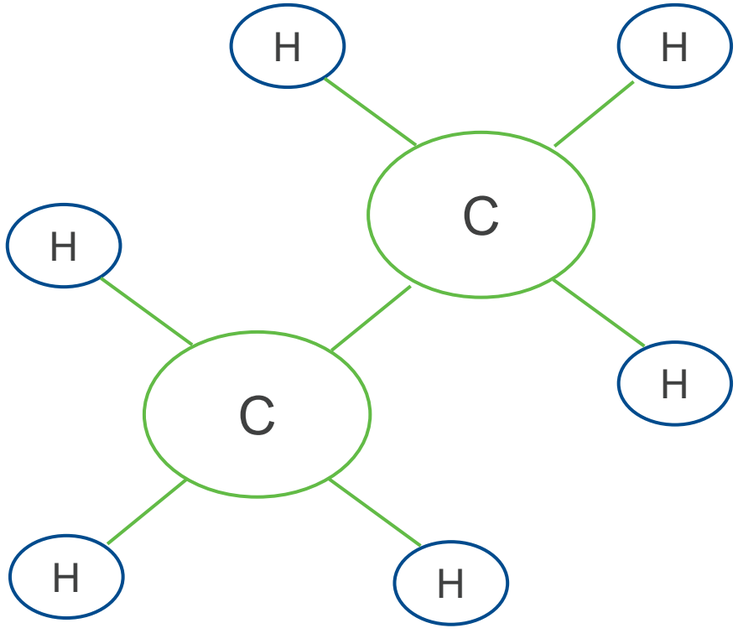
- The simplest hydrocarbon molecule contains one carbon atom and four hydrogen atoms
- The chemical formula is CH4, known commonly as Methane, which is the principle component of Natural Gas



Methane (CH_4)

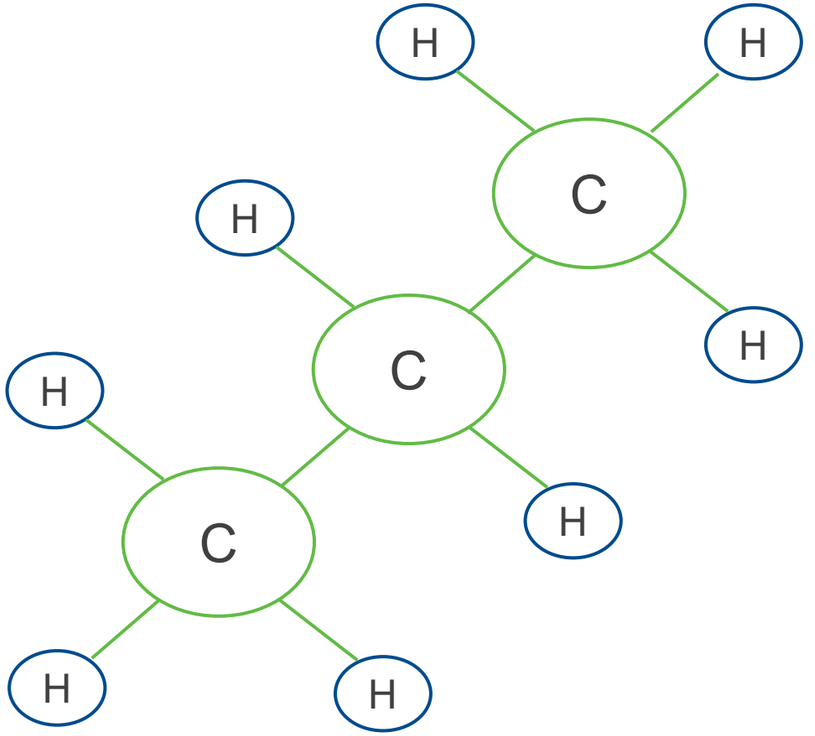
What is Natural Gas?

- Ethane is the second most common hydrocarbon and contains two carbon atoms



Ethane (C_2H_6)

- Propane is the third most common hydrocarbon and contains three carbon atoms

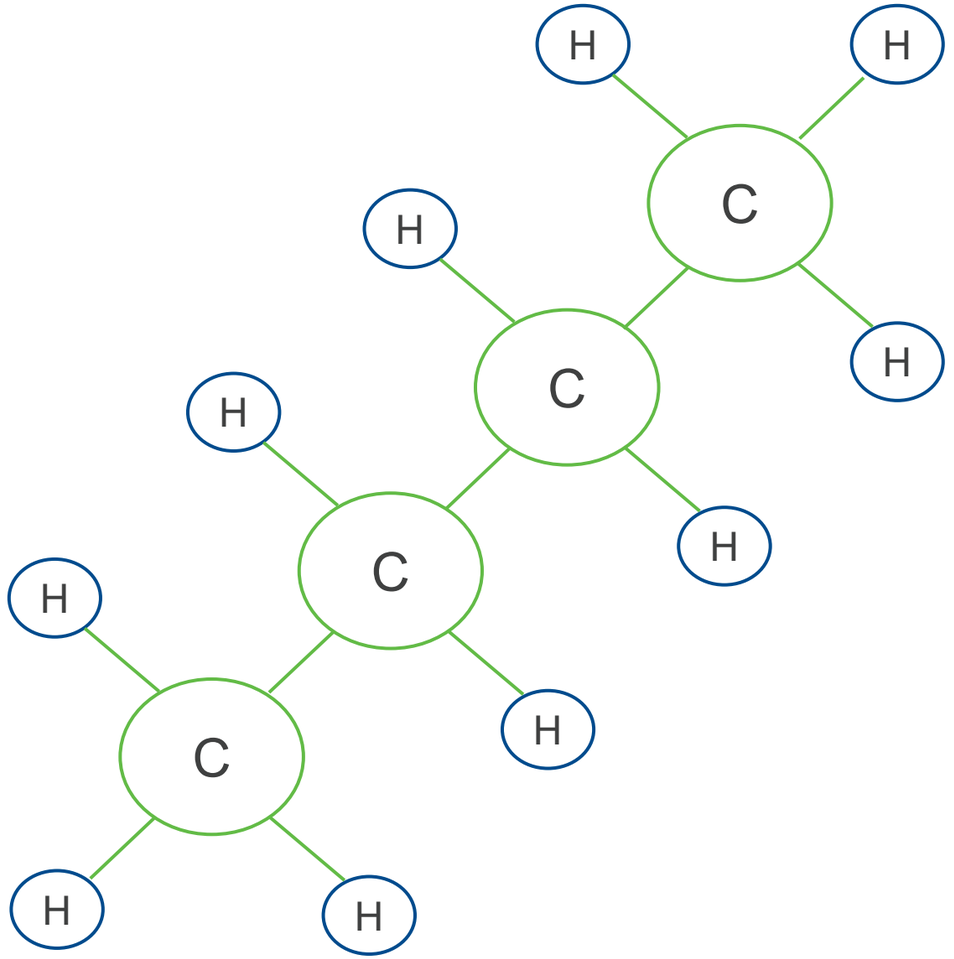


Propane (C_3H_8)

What is Natural Gas?

- Butane has 4 carbon atoms, and 10 Hydrogen atoms
- However, Butane can exist in more than one configuration with the same chemical formula
- These different types of the same compound are known as:

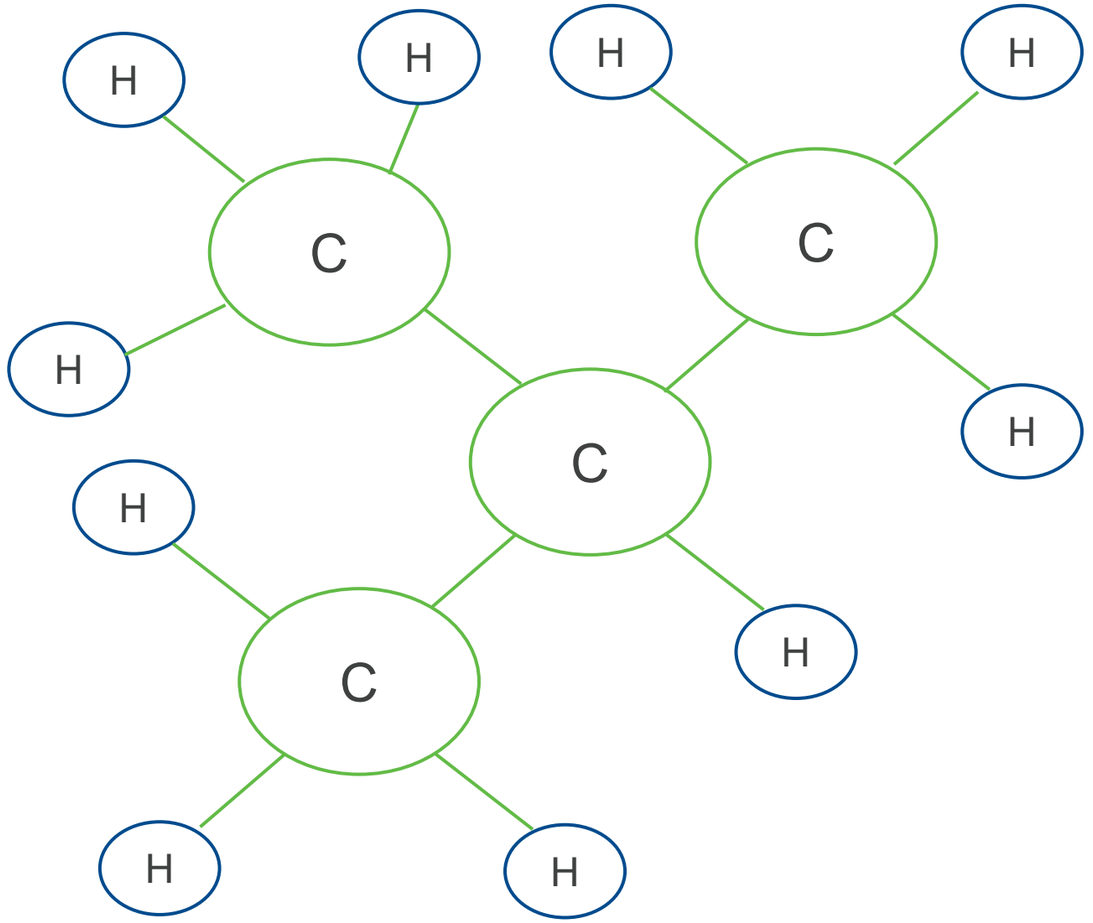
ISOMERS



Normal-Butane (n -C_4)

What is Natural Gas?

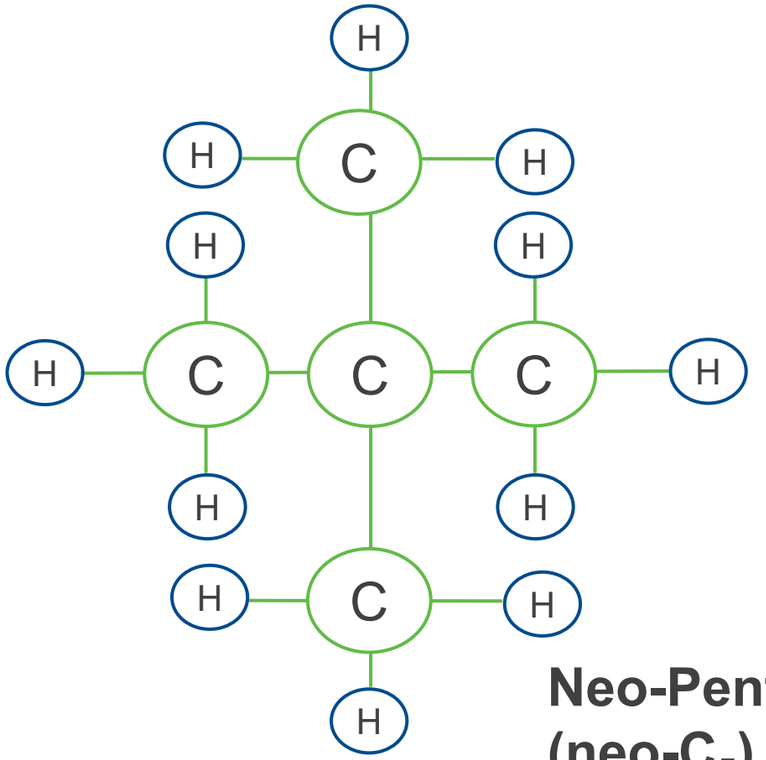
- Isomers have slightly different physical and chemical properties
- Calorific values and densities are almost identical
- **Boiling points are different (branching decreases boiling point)**
- Butane has one Isomer, called Iso-Butane



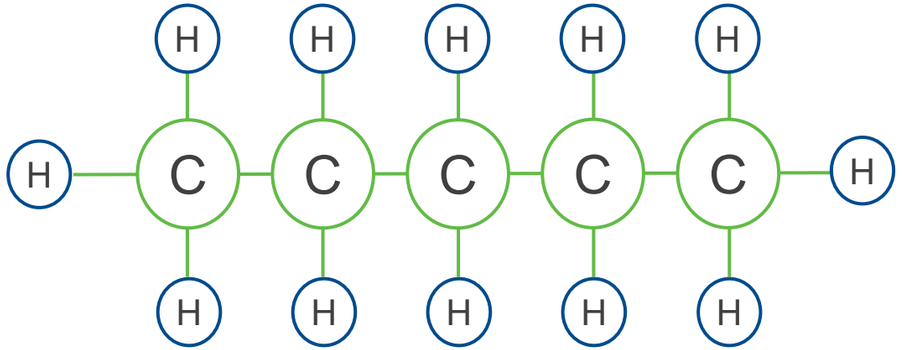
Iso-Butane (i -C_4)

What is Natural Gas?

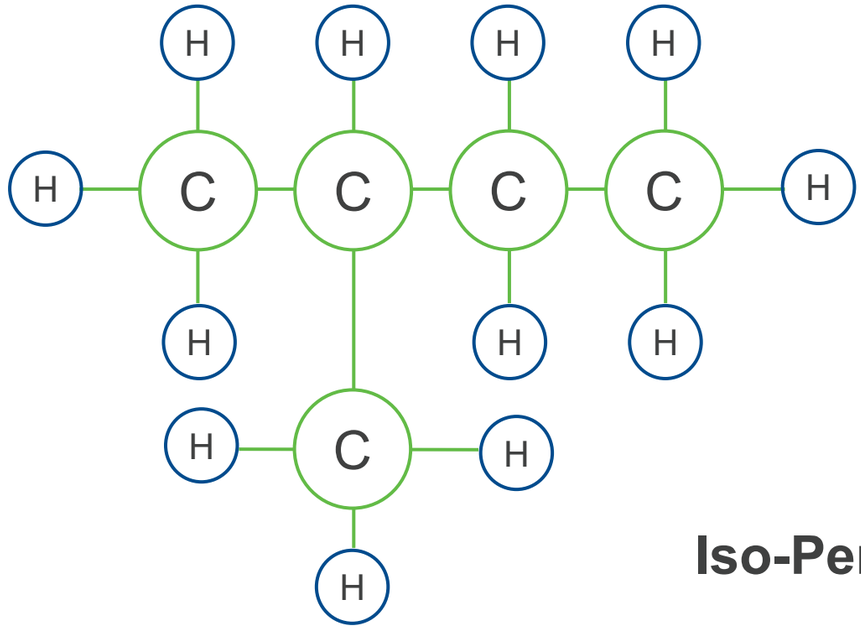
- Higher Carbon number hydrocarbons have more Isomers



Neo-Pentane (neo-C_5)



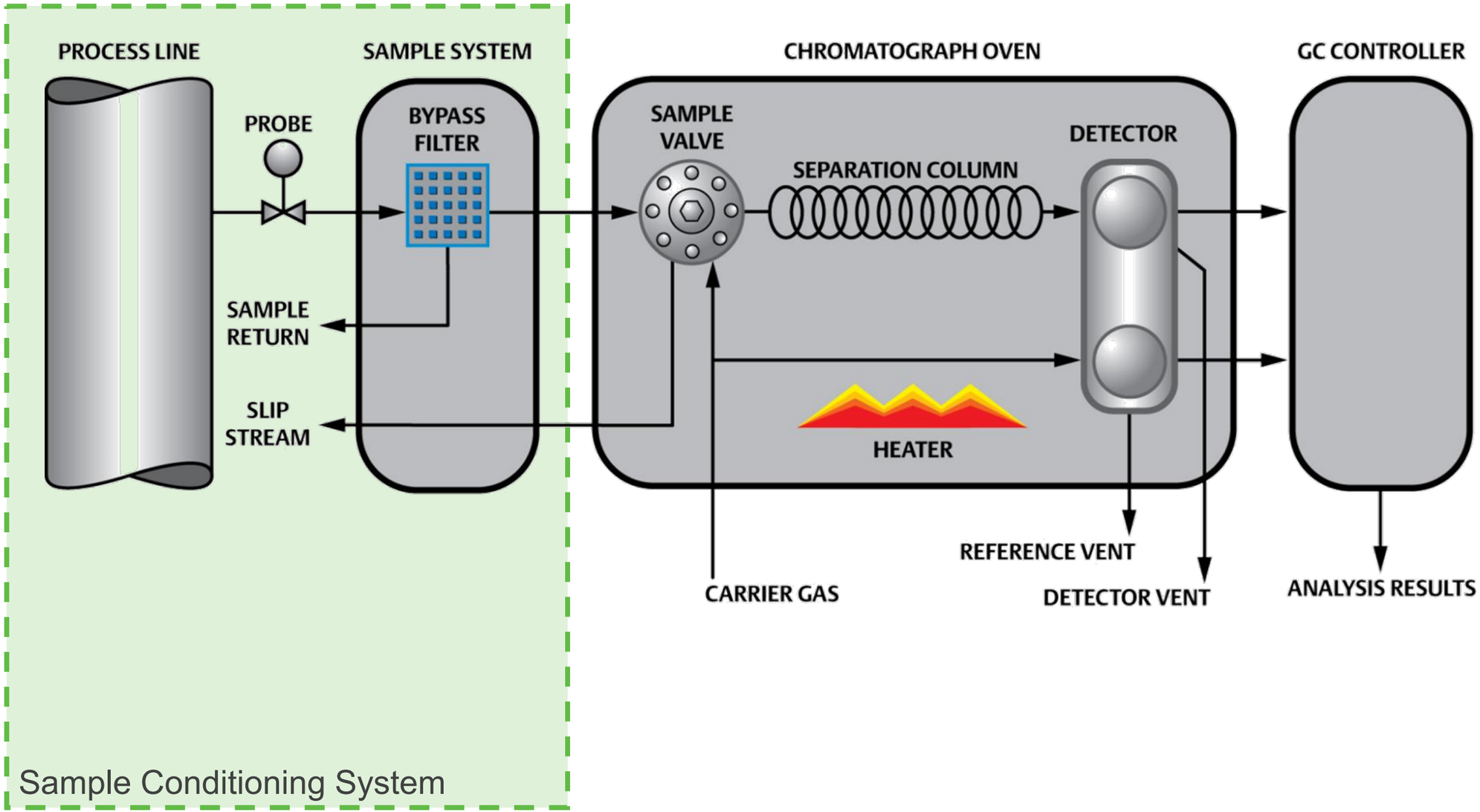
Normal Pentane (n-C_5)



Iso-Pentane (i-C_5)

Sample Handling System

Sample Handling System

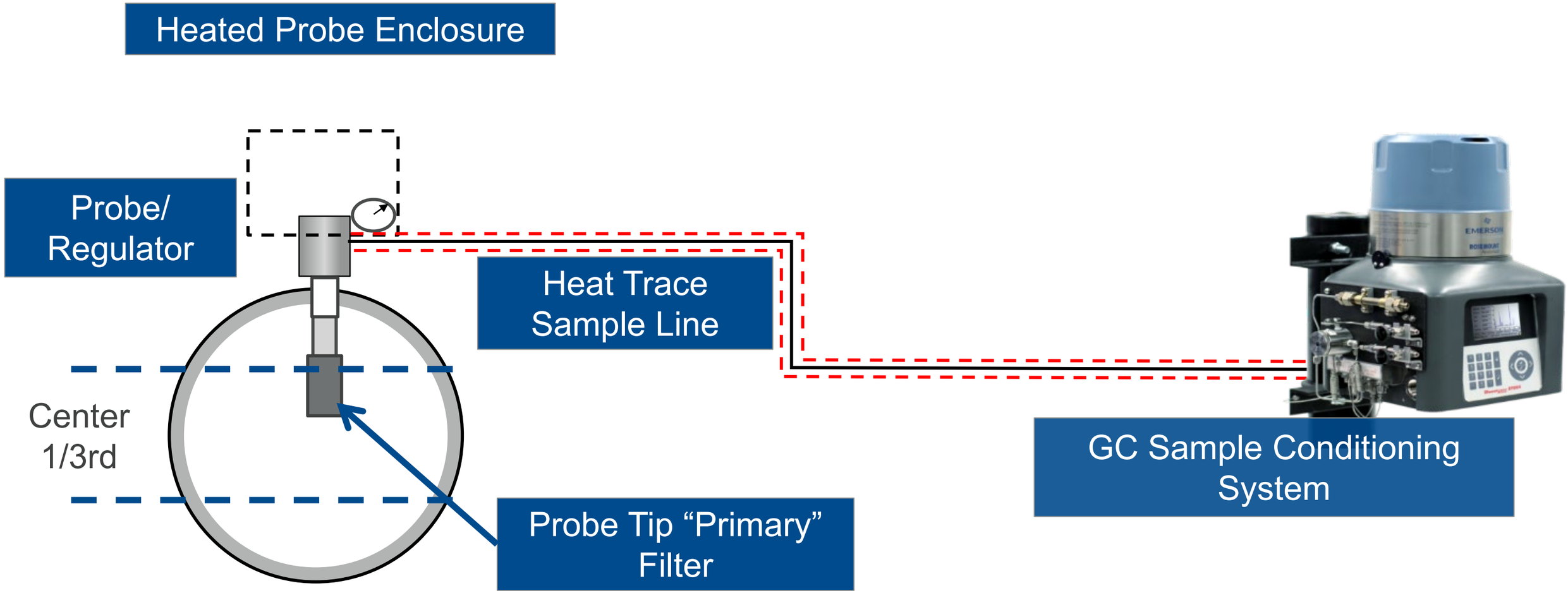


Sample Conditioning Directly Impacts The Performance of the Analyzer

- Sample System is critical for the reliable and accurate operation of the analyzer
- Sample System must perform the following:
  - Take a representative sample
  - Maintain the composition of the sample
  - Remove solid particles to at least 5 micron
  - Remove any free liquid (Water or Liquid Hydrocarbons)
  - Reduce/control the pressure of the sample

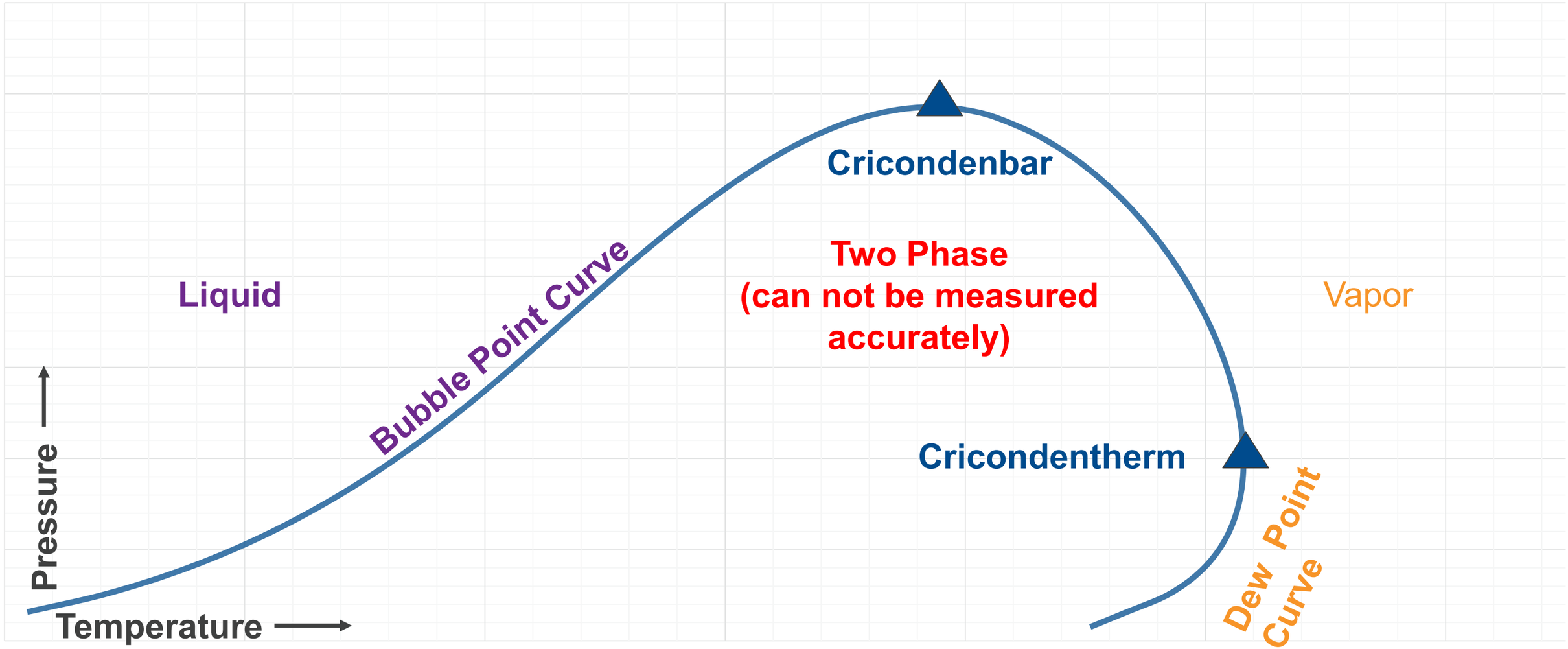
Refer to API 14.1 – Collecting and Handling of Natural Gas Samples for Custody Transfer (6th edition, Feb. 2006)

The “Typical” Gas Sample Handling System



* Location of probe based on vapor sample, horizontal pipe

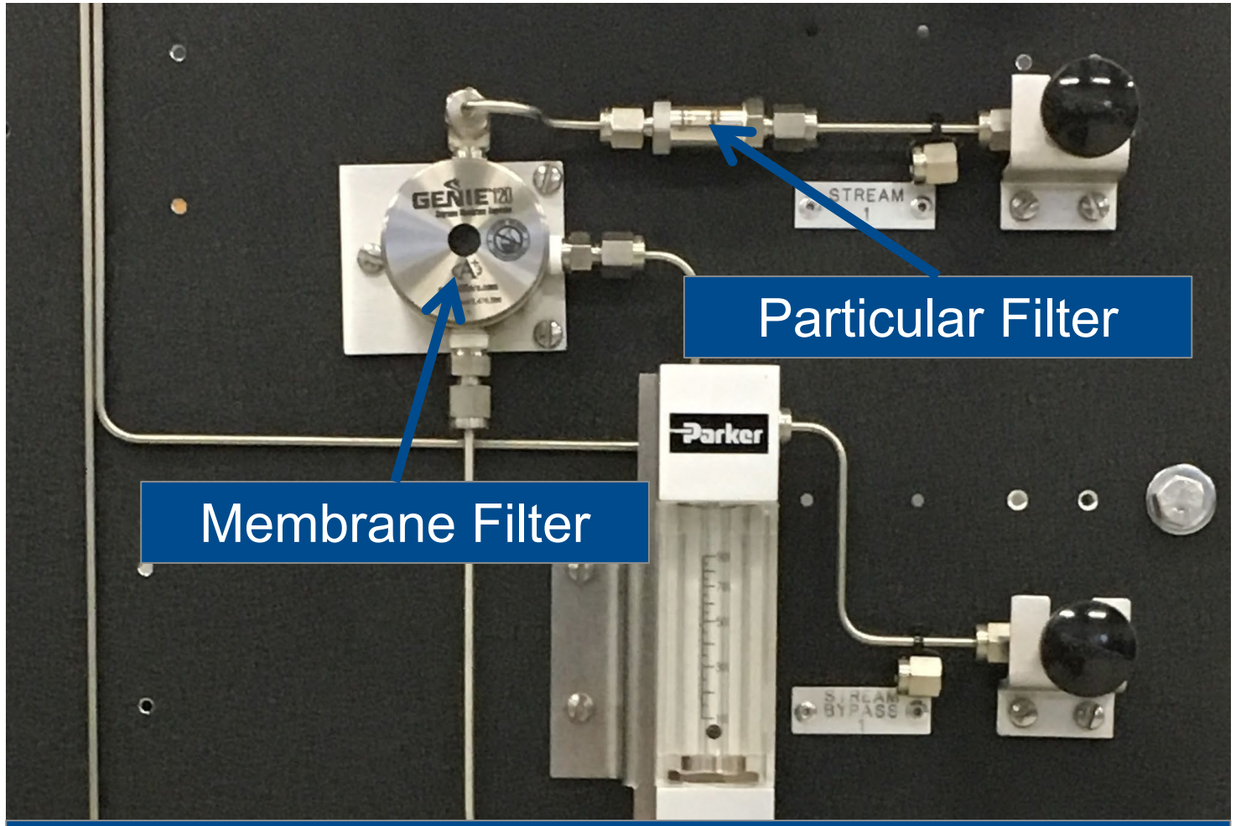
Phase Diagram – Know Where the Dew Point Is



Need to watch the JT Effect – 7 °F drop in temperature for every 100 psig drop in pressure

Sample System – Filtration Best Practices

- Particulates should be removed to at least 5 microns
- Filters should not be coalescing type to avoid large volumes in the sample system
- Liquids should be removed using Membrane technology
- Sample Probes which provide solids filtration inside the line are highly recommended



Typical Basic Sample System. This is the “last line of defense”

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Effects of Liquids

- If liquids (such as compressor oil or glycol) enter the chromatograph oven, the valves and columns will become contaminated, resulting in a failure of the analyzer
- If liquids are to be analyzed, then they will be vaporized into a gas first

Liquid Contaminated Valve

Heated Vaporized Stream SHS

Calibration Gas System

- All Chromatograph systems are a **comparative measurement**, where the analysis is actually a comparison to a known “Standard”
- The Calibration Gas system is a part of the sample handling system, and is also critical to the accuracy of the analysis
  - The GC is only as accurate as the Calibration Gas
- The Calibration Gas must be stored and installed so that:
  - The composition is maintained
  - There is no contamination to the Calibration Gas

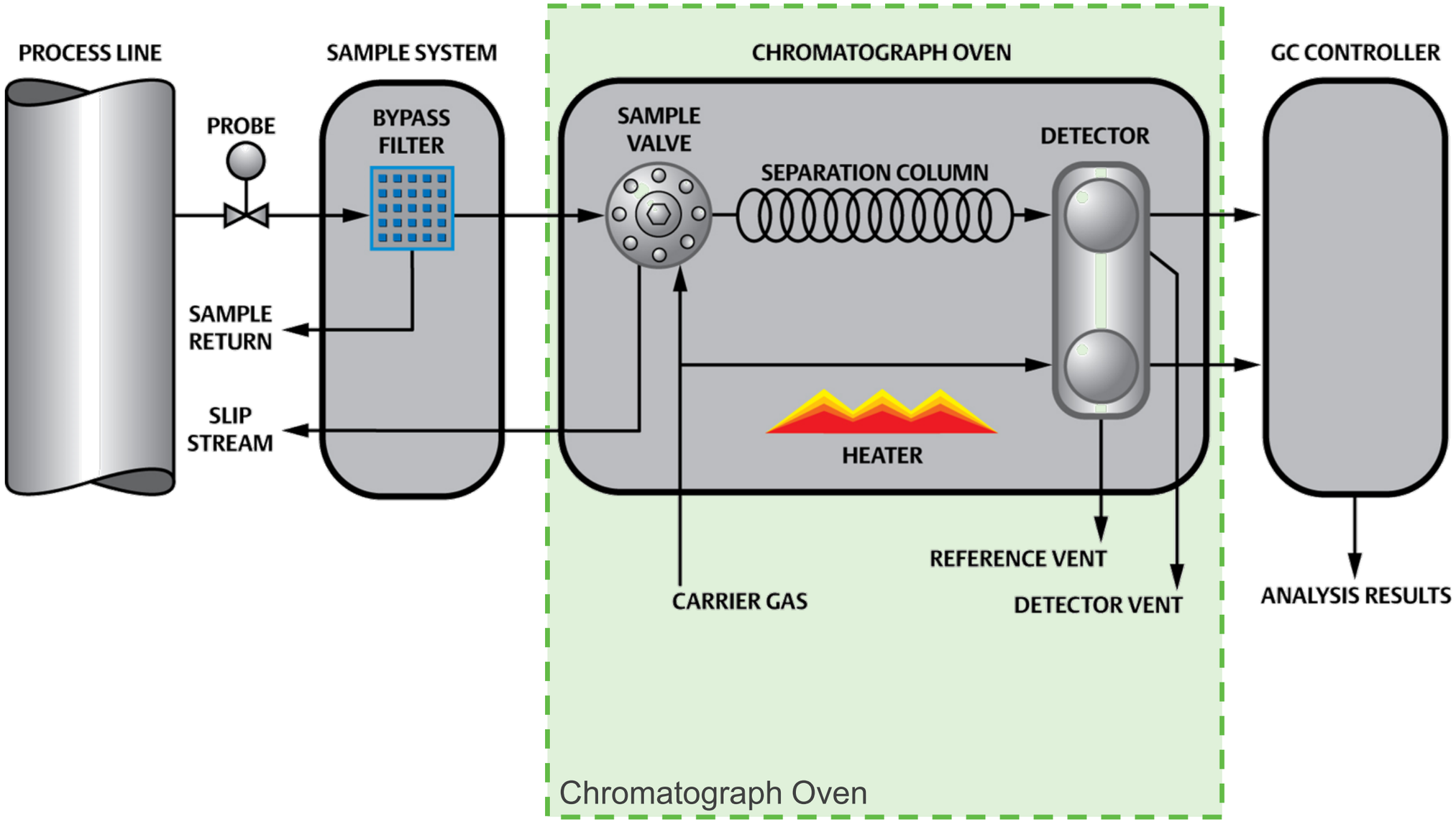
The GC Compares Stream Gas Analysis to Calibration Gas Analysis

Summary - Gas Chromatograph Conditioning Systems

- Take a representative sample
- Transport the sample to the analytical oven in a controlled manner
- Condition the sample for optimum analysis
- Provide sample stream switching and calibration
- Accommodate sample return or venting systems
- Accomplish above without excessive maintenance and service attention

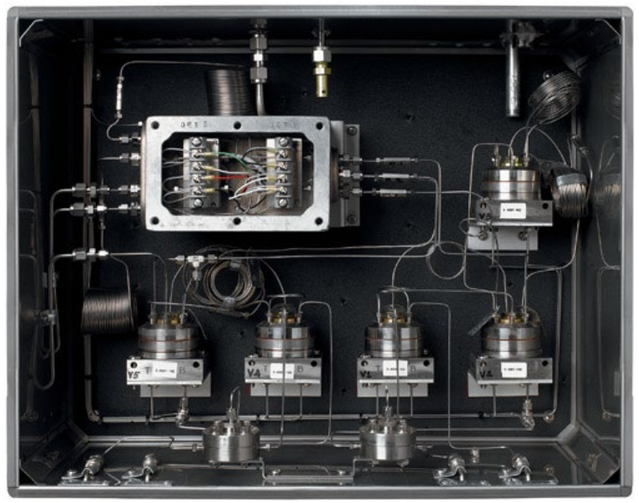
Chromatograph Oven

Basic Chromatograph System - Oven

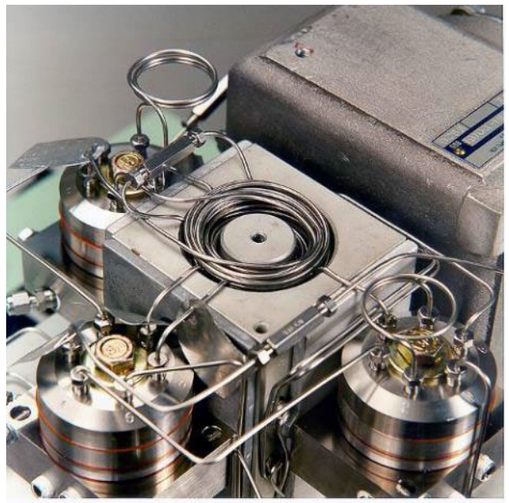


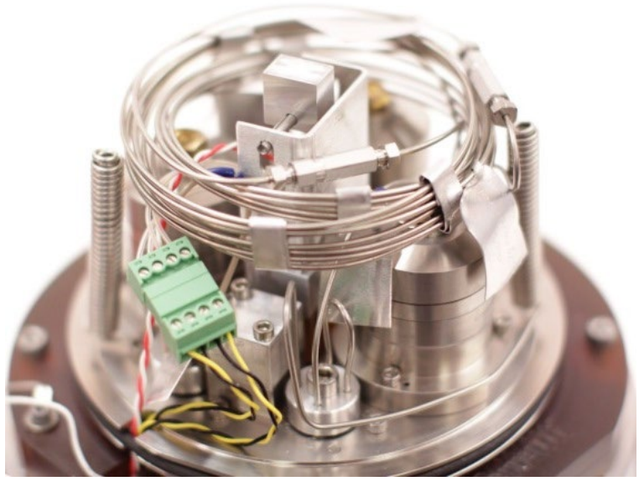
Functions Of The Chromatograph Oven

- Houses valves, columns and detectors
  - Valve injects a sample into the separation columns
  - Columns separate the sample into individual compounds
  - Detectors identify concentration of individual compounds



Air bath Oven





Air-less Heat Sink Ovens

Types Of Analytical Valves

- Sliding Plate
- Rotary Valve
- Diaphragm Valve
- Liquid Sample Injection Valve (LSIV)

6 port diaphragm valve

10 port diaphragm valve

LSIV

Rotary Valve

Different Types Separation Methods

- Separation by:
  - Boiling point differences
    - Individual components are separated, based on their different boiling points – usually related to number of hydrocarbons and their bonding arrangement.
  - Polarity differences
    - Components possessing the opposite charge of the column packing materials, are slowed down or held up
  - Molecular size
    - Works like a filter, allowing smaller particles to flow through quicker than larger ones.
- The purpose of any column is to separate the various components present in the sample stream.

Chromatographs Columns

A micro-packed column typically used in simple gas applications

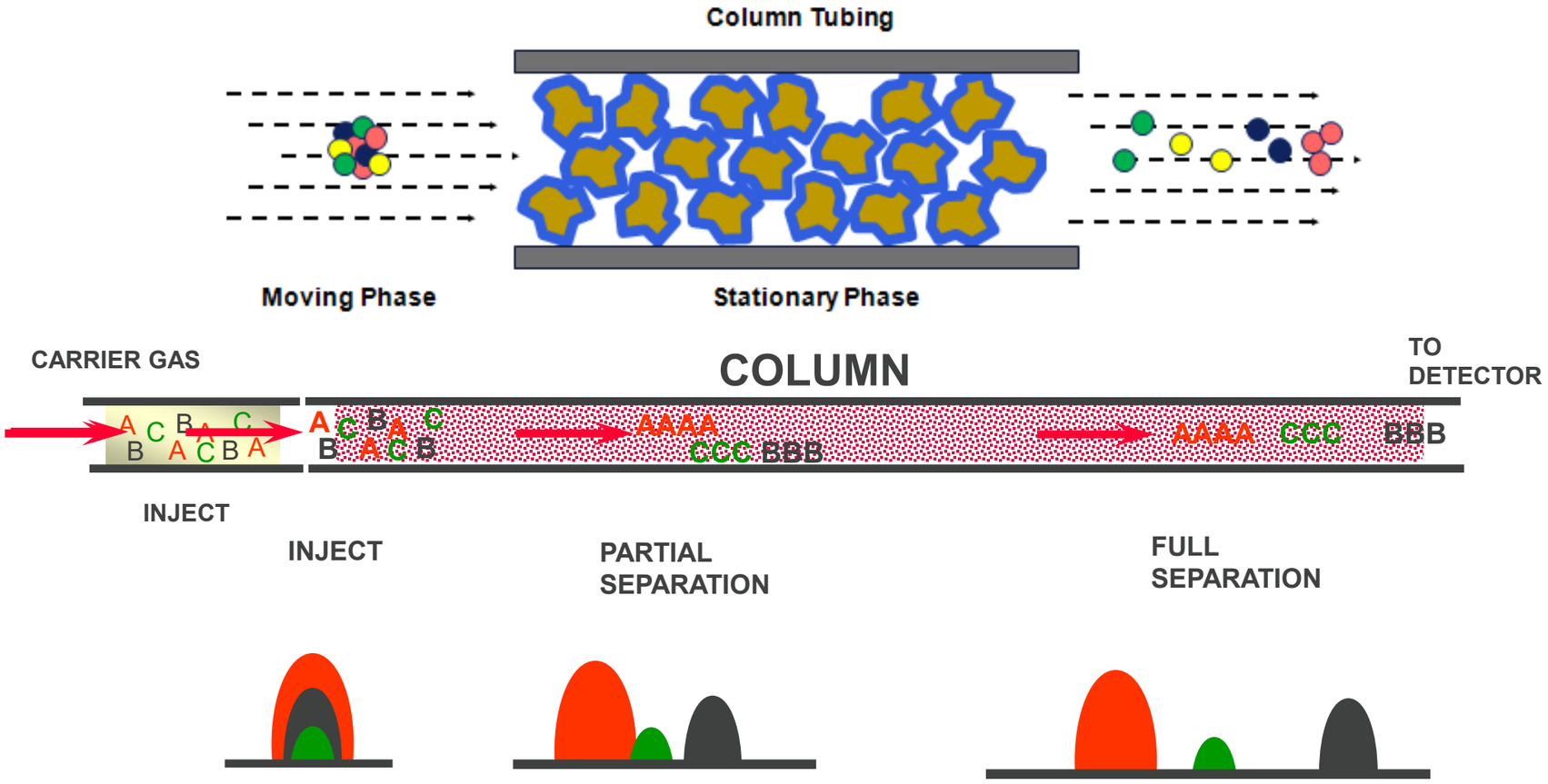
A capillary column typically used low concentration detection

Chromatograph columns separate the gas mixture into individual components

Types of columns include:

- Packed – 1/8” O.D.
- Micropacked - 1/16” O.D.
- PLOT - Porous Layer Open Tubular
- SCOT - Support Coated Open Tubular
- WCOT - Wall Coated Open Tubular
- FSOT - Fused Silica Open Tubular (Capillary)

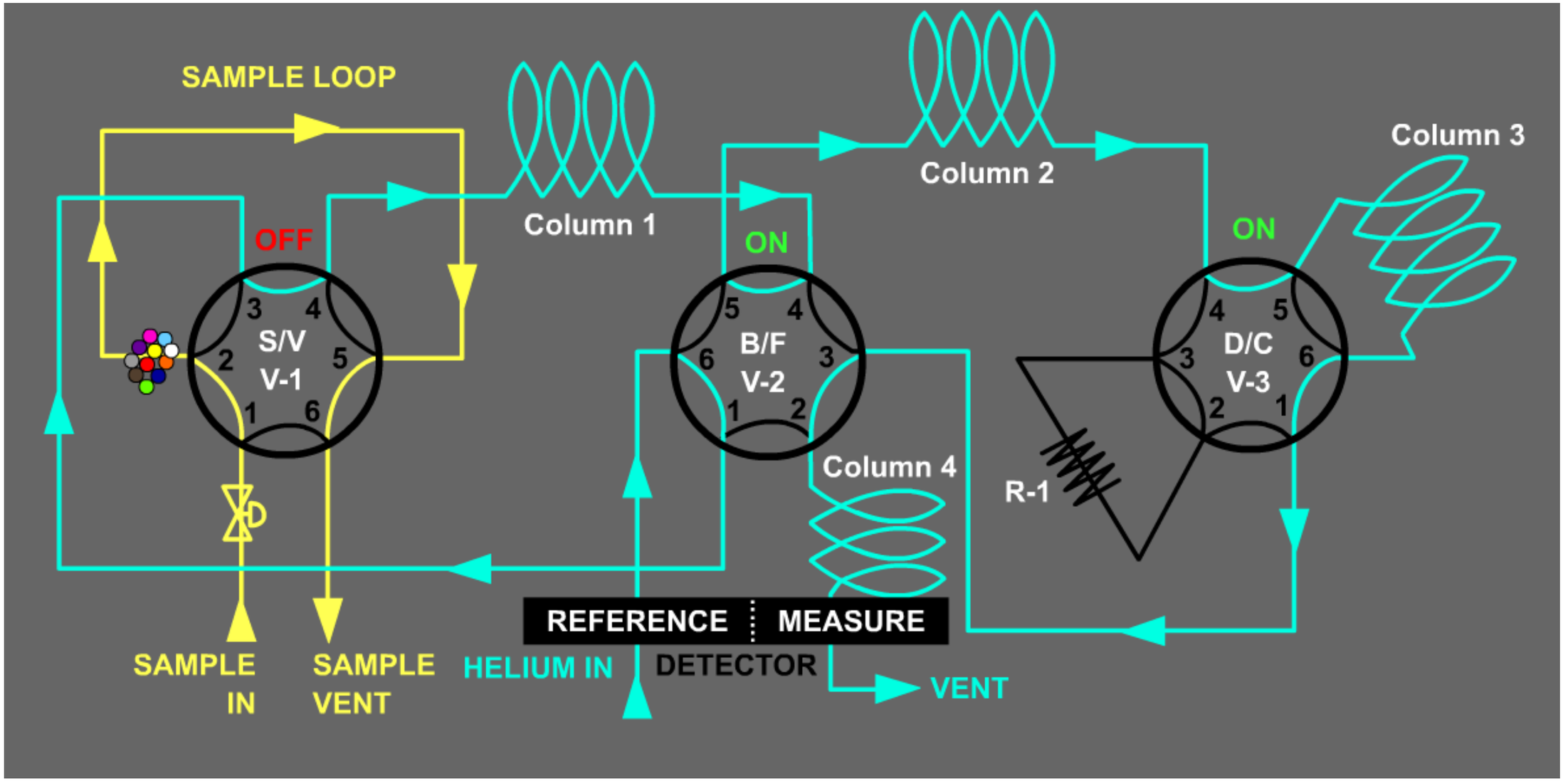
Column Separation



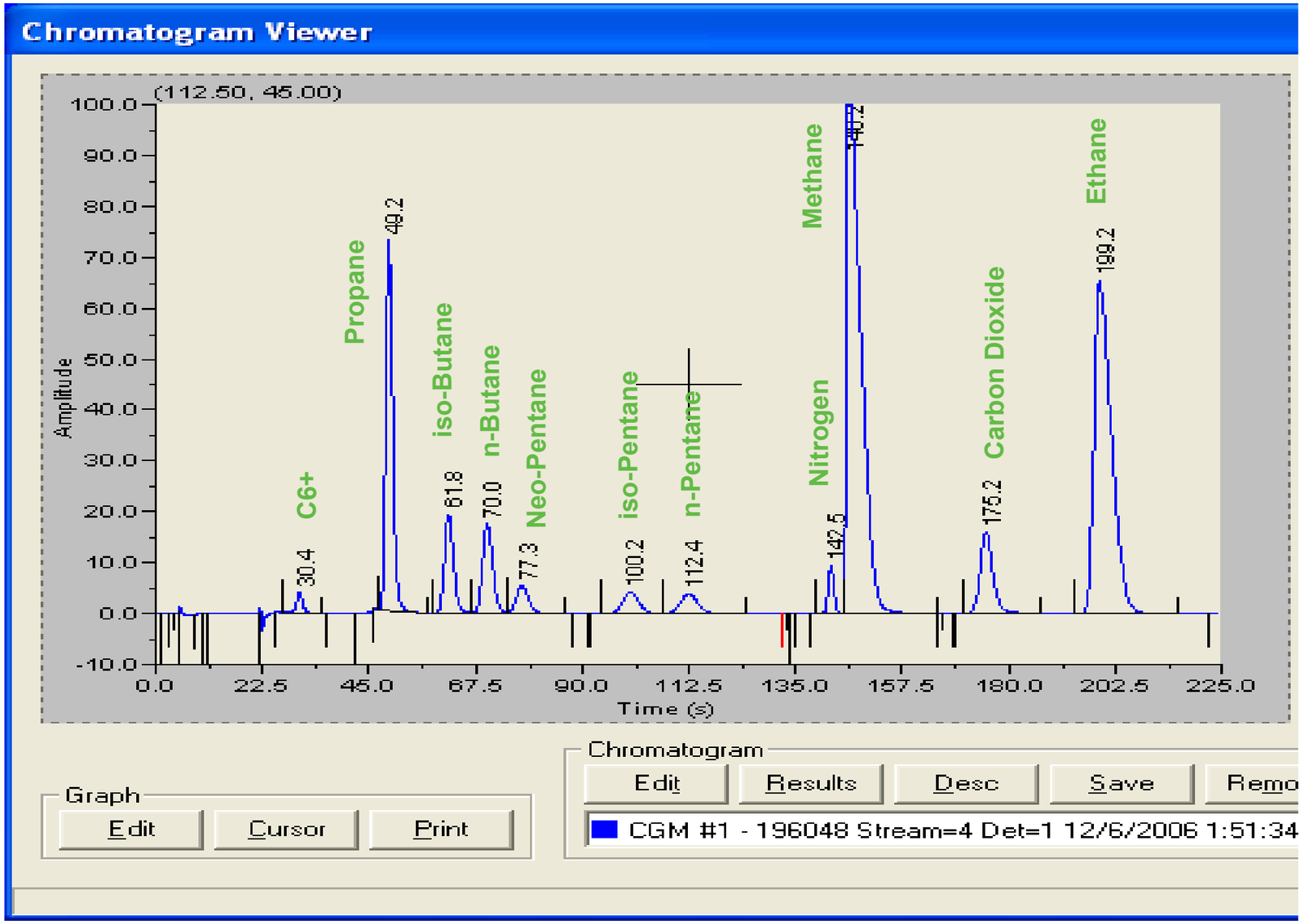
Carrier Gas

- The sample is pushed through the columns (or carried) through to the detector by the *Carrier Gas*
- Helium is a very common Carrier Gas because:
  - It is inert
  - It is not usually a component of interest
  - It has a very large difference in Thermal Conductivity to the components typically measured in the Natural gas Industry
- Ultra High Purity Helium must always be used
  - Helium is produced by extracting it from Natural Gas, so any contaminants will be hydrocarbons

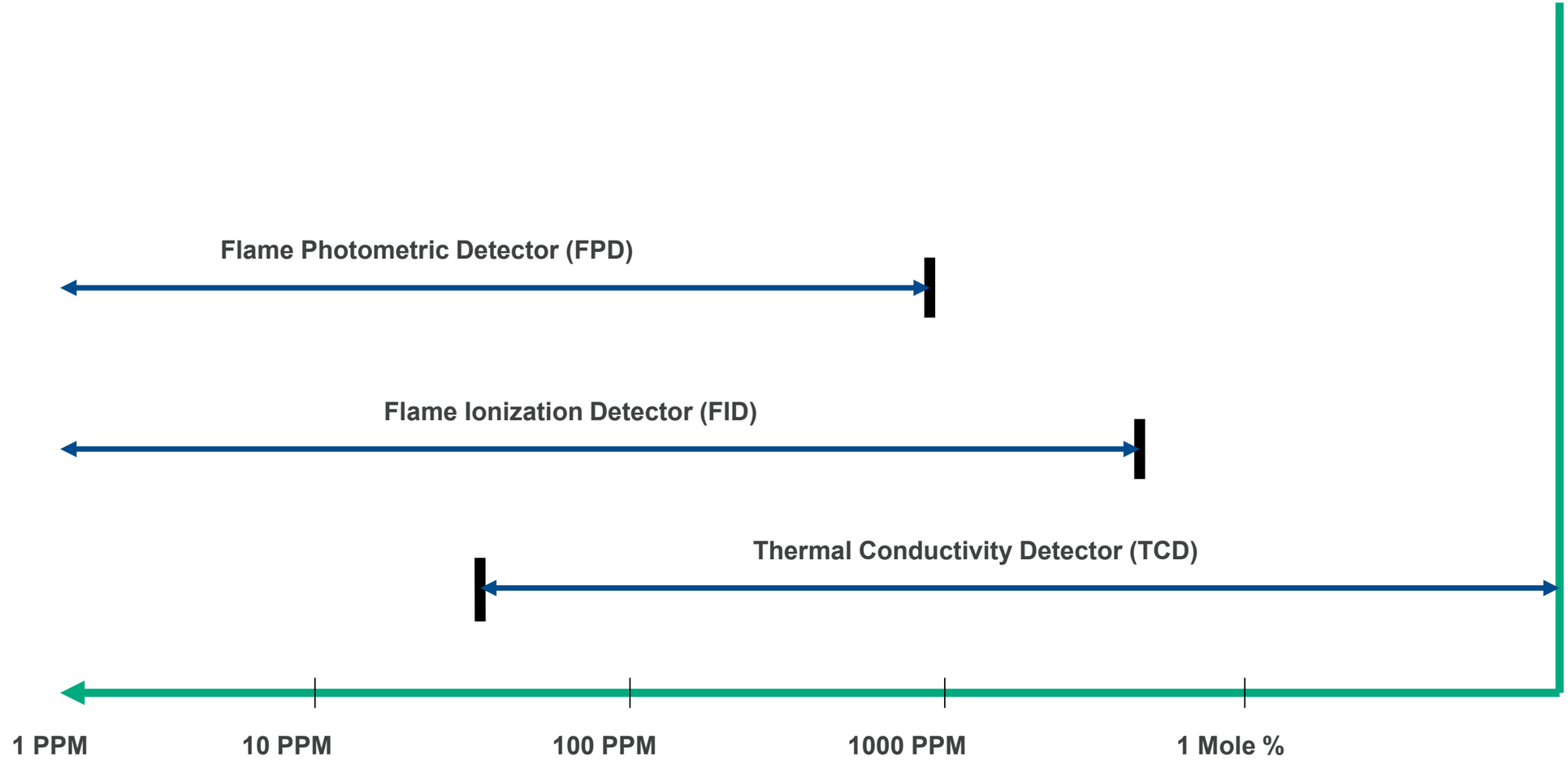
Fundamentals of Chromatography Typical C6+ Analysis



Natural Gas Chromatogram



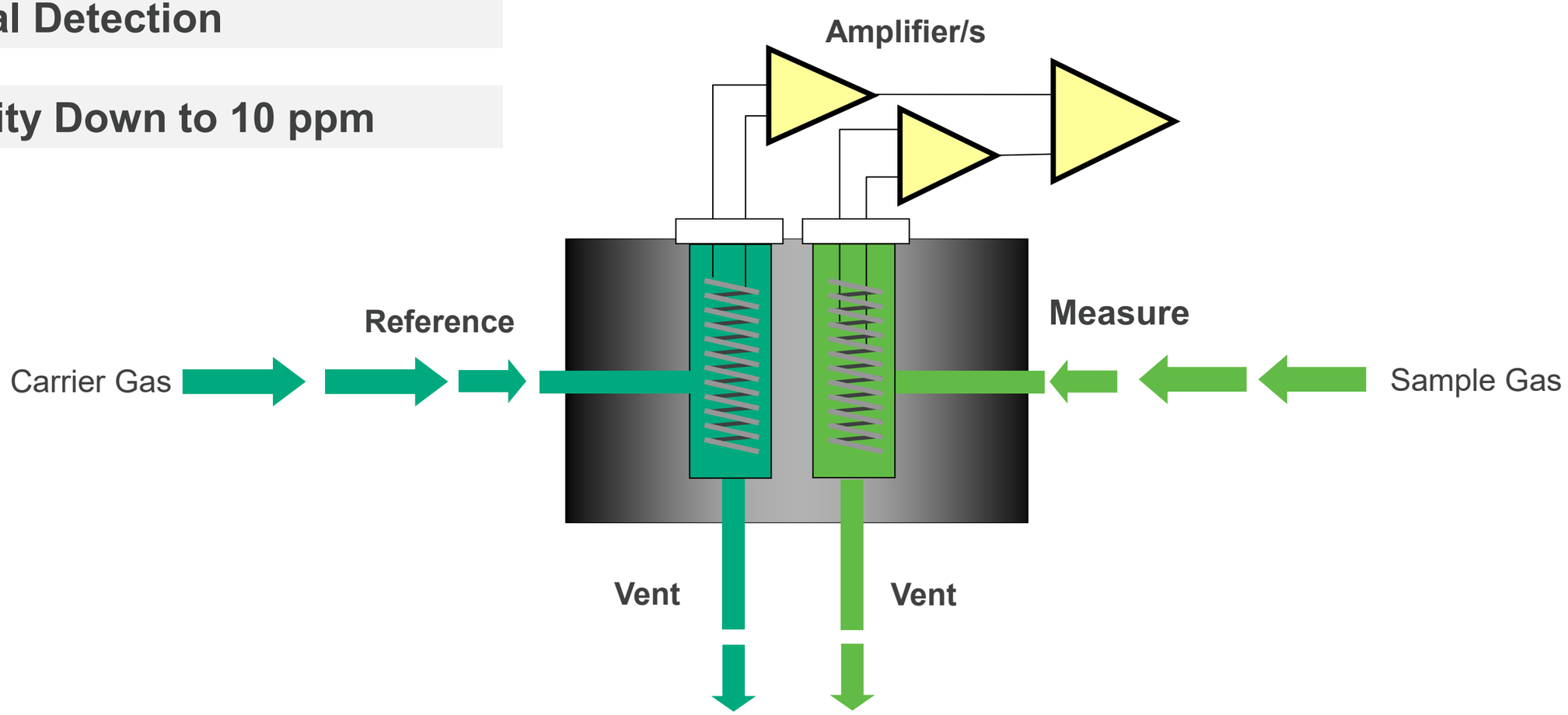
Types Of Detectors Available



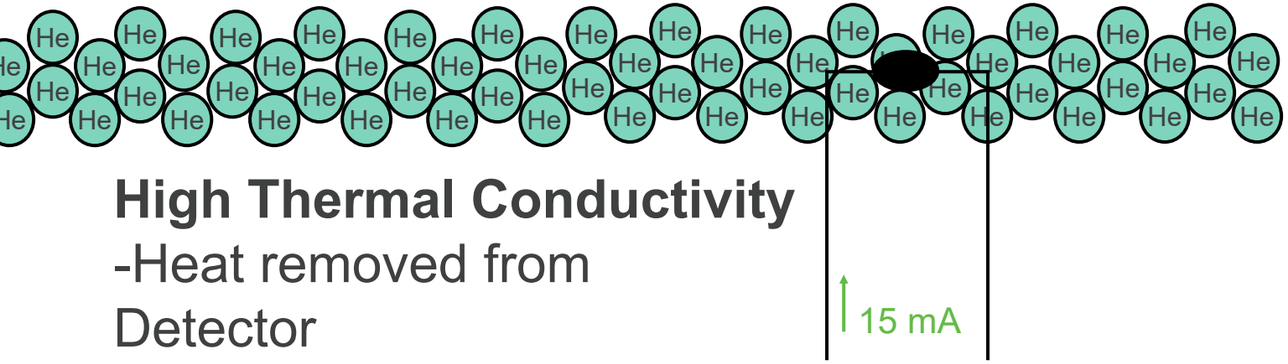
Thermal Conductivity Detector

Universal Detection

Sensitivity Down to 10 ppm



Thermal Conductivity Detector

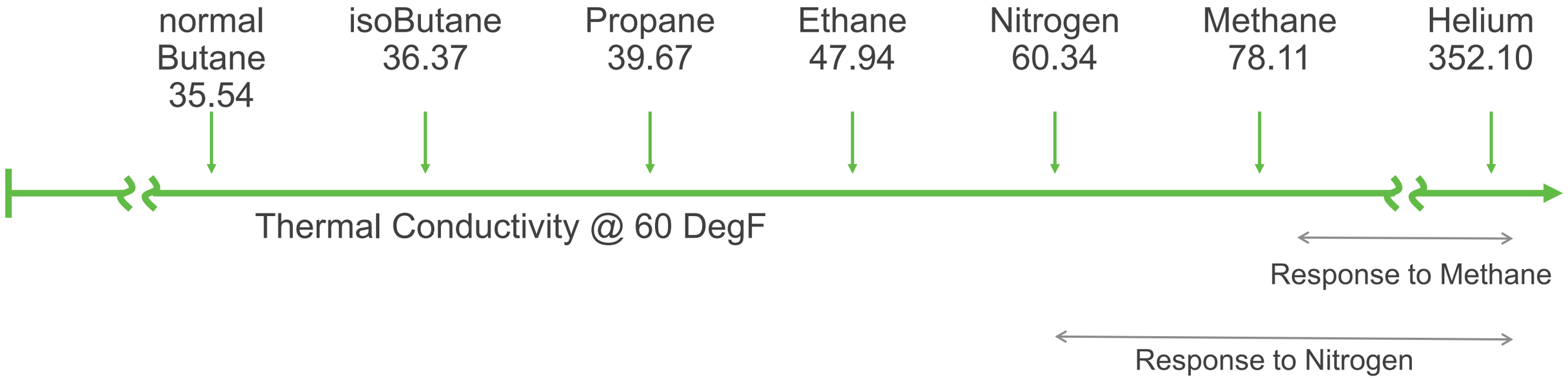


High Thermal Conductivity
-Heat removed from Detector
-Temperature of detector reduced
-Resistance of detector INCREASES

Lower Thermal Conductivity
-Less Heat removed from Detector
-Temperature of detector increases
-Resistance of Detector DECREASES

Detector mV output

Response Factors from the Thermal Conductivity Detector are Predictable

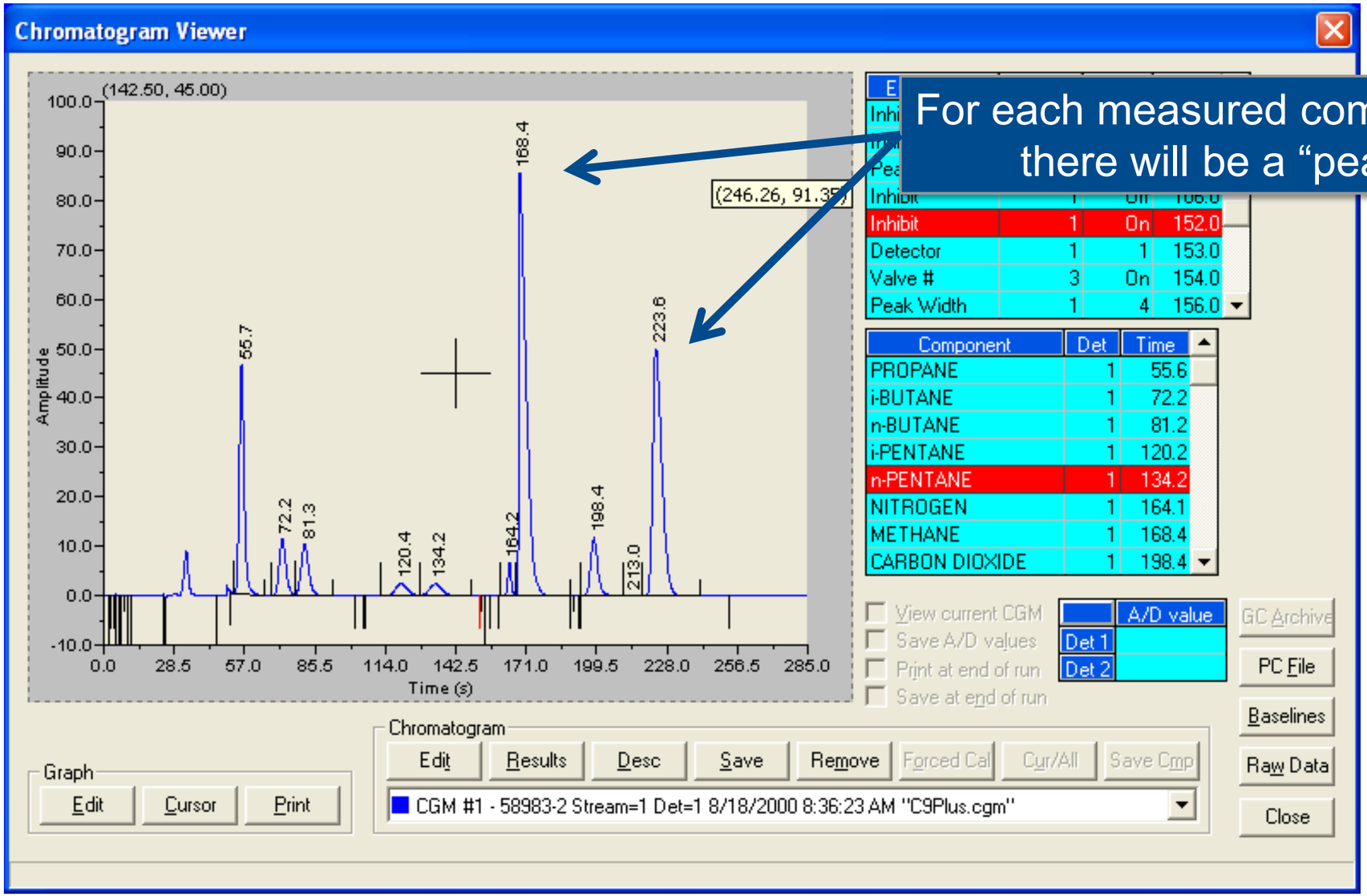


The response of the detector is due to the difference in thermal conductivity between helium and the component

Nitrogen has a larger difference to helium than methane, so the response to nitrogen will be larger than for methane

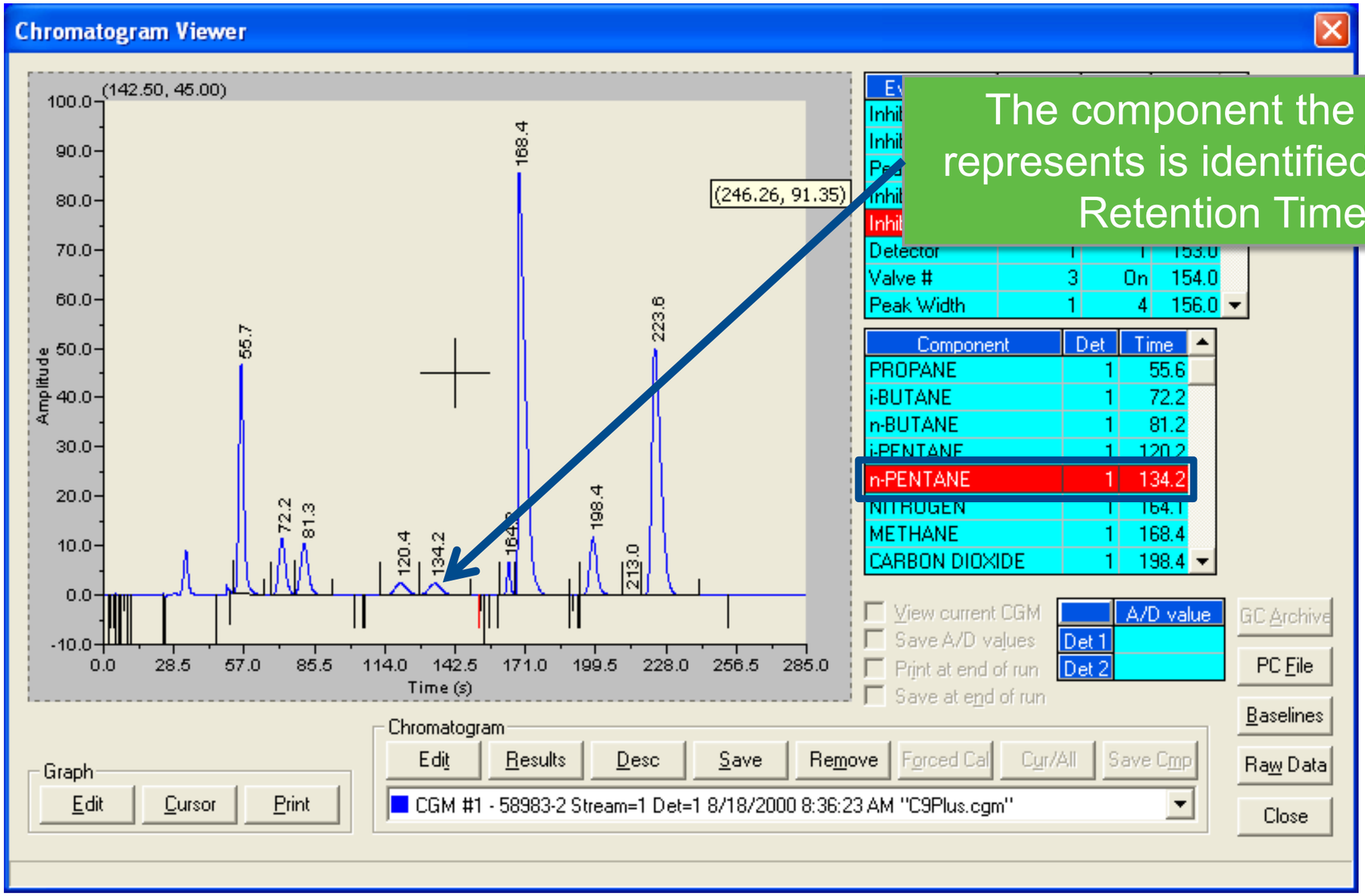
Chromatograms

Chromatogram



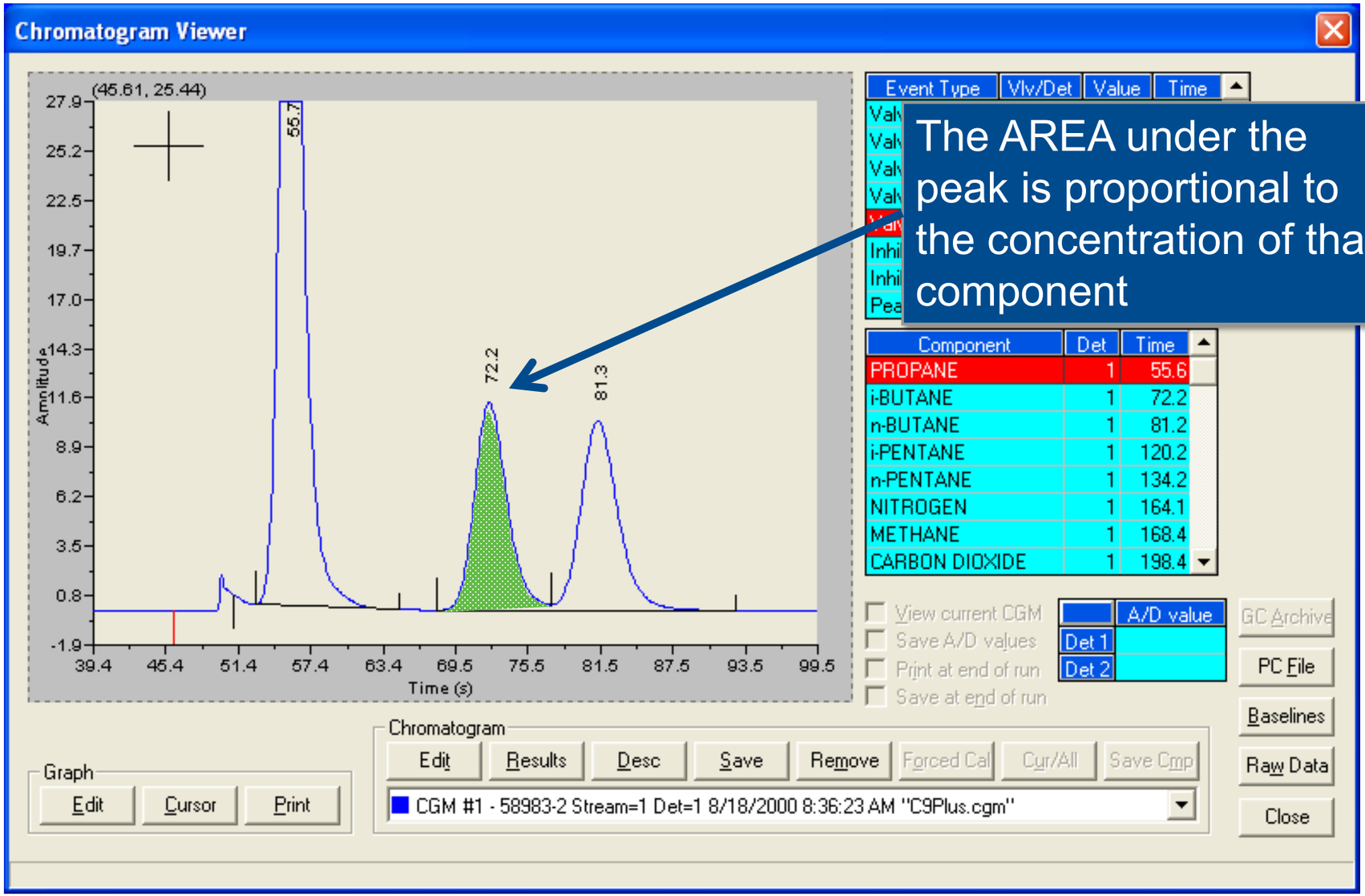
For each measured component, there will be a “peak”

Chromatogram

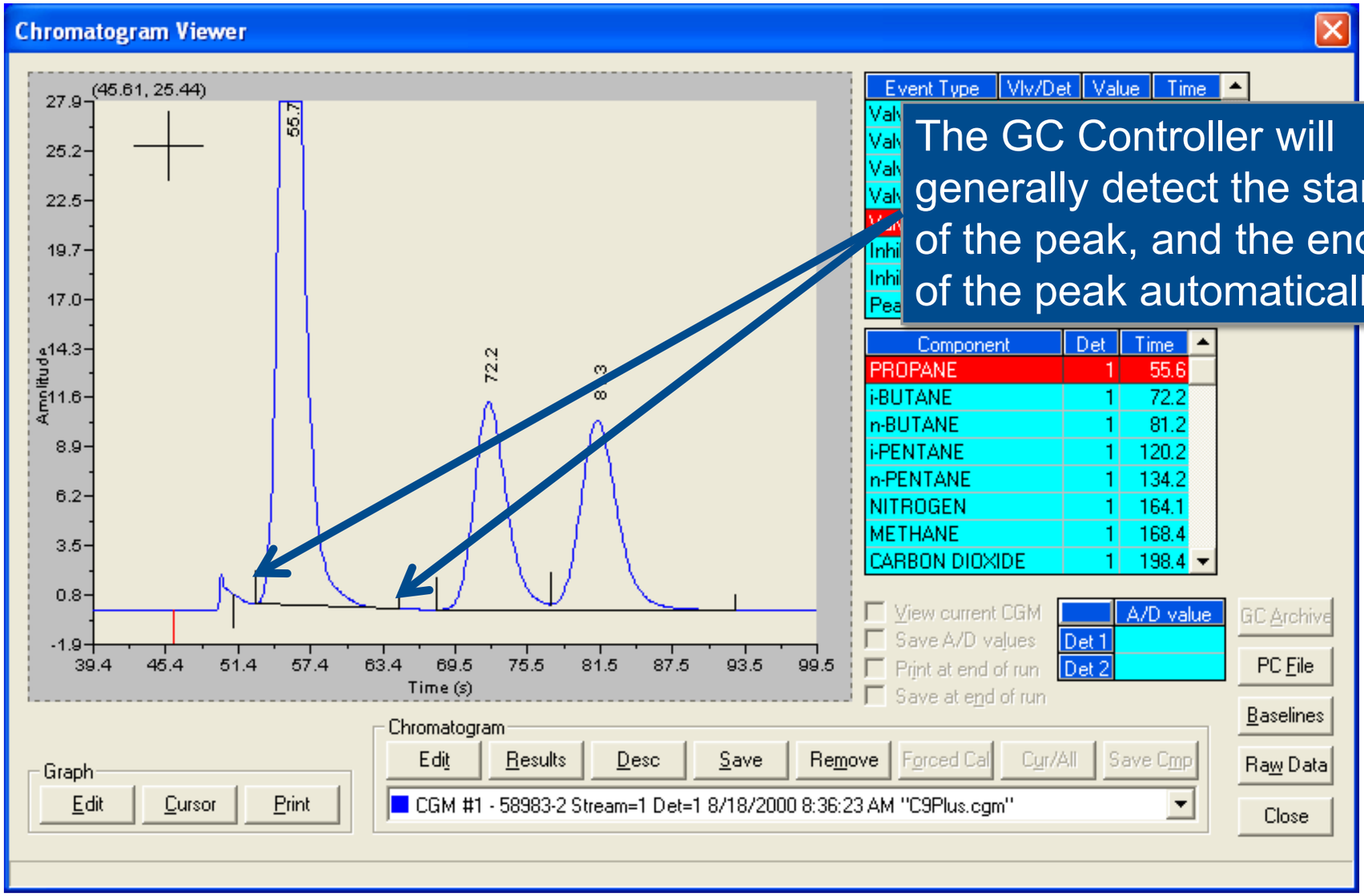


The component the peak represents is identified by the Retention Time

Chromatograms

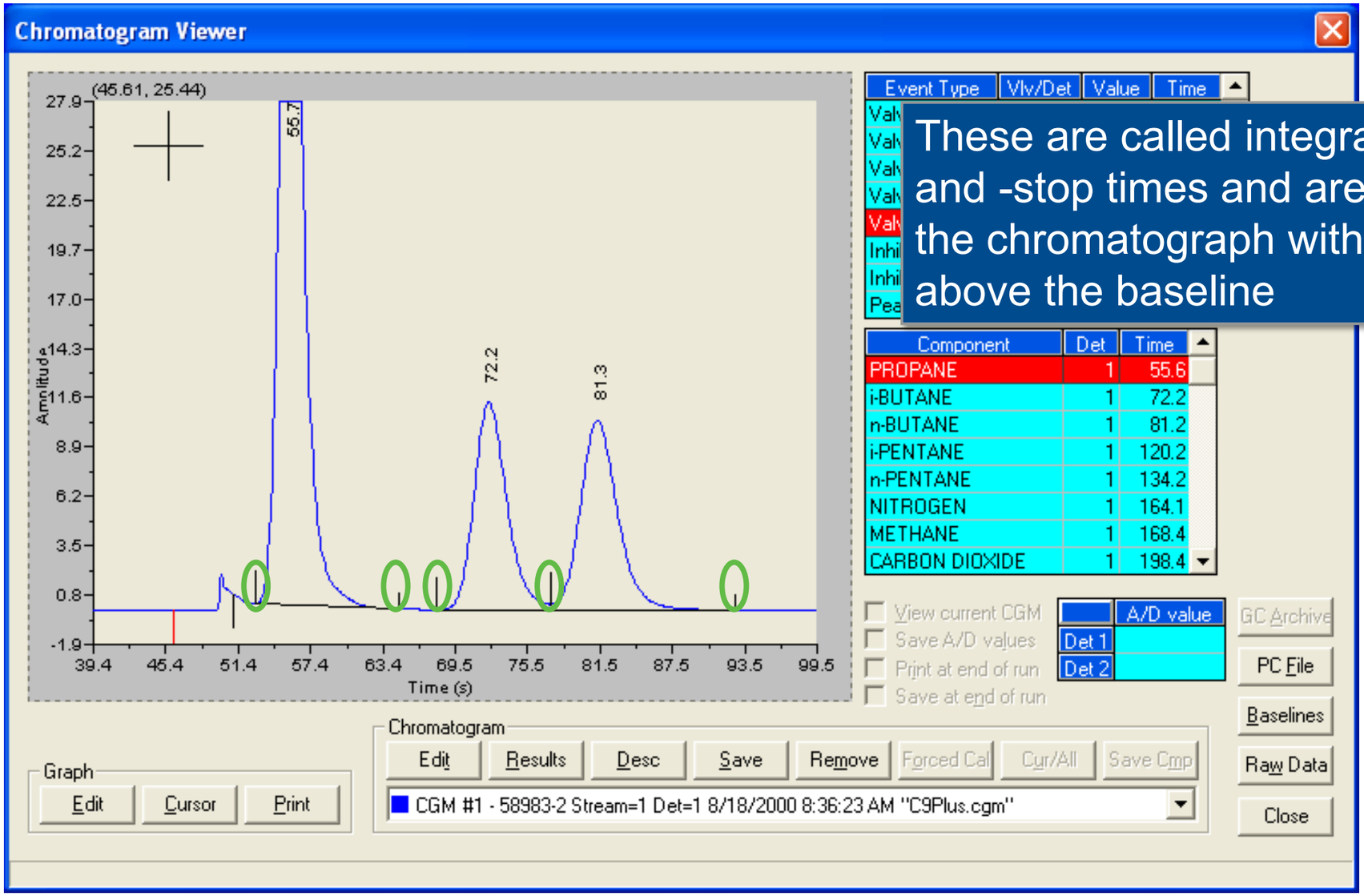


Chromatograms



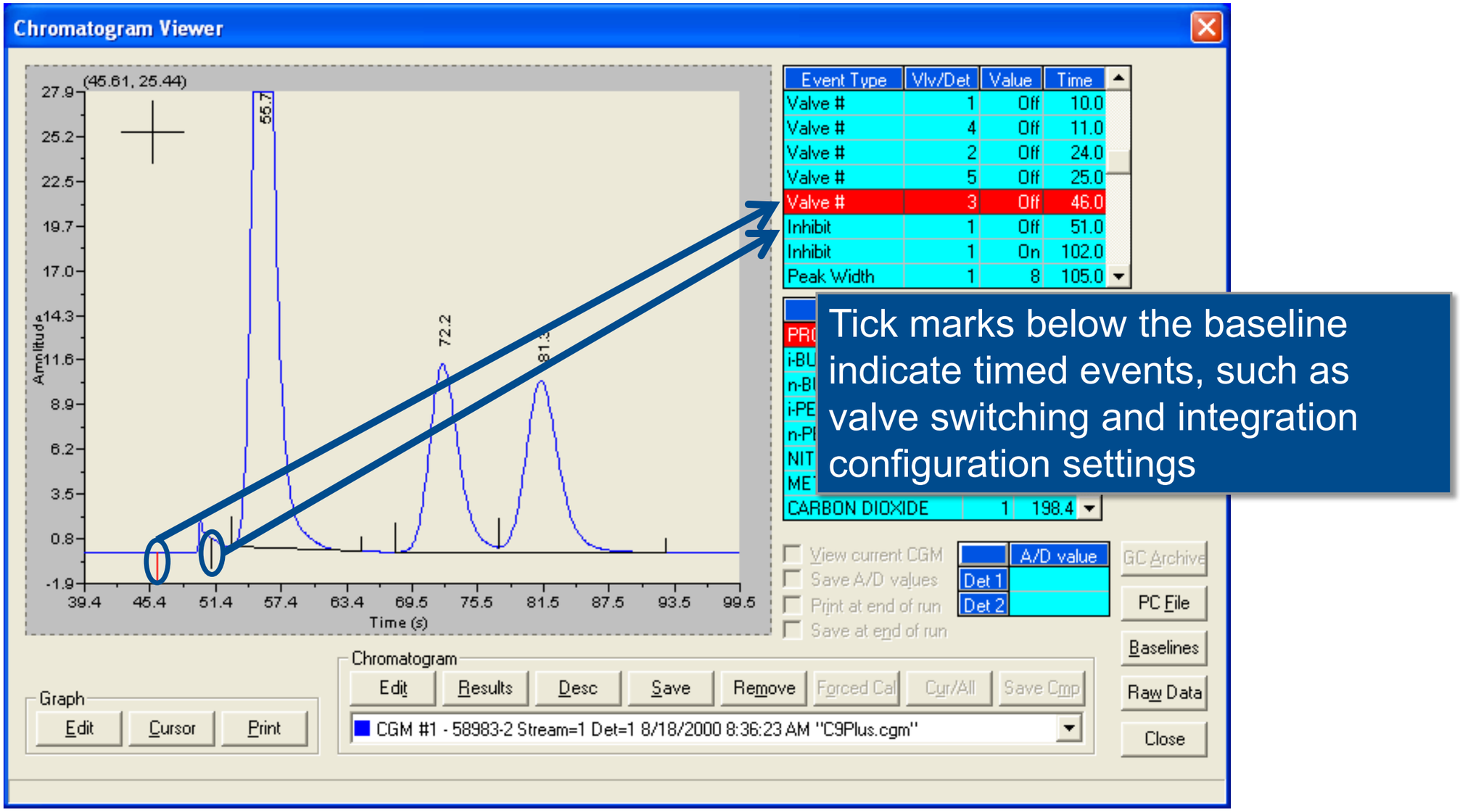
The GC Controller will generally detect the start of the peak, and the end of the peak automatically

Chromatograms

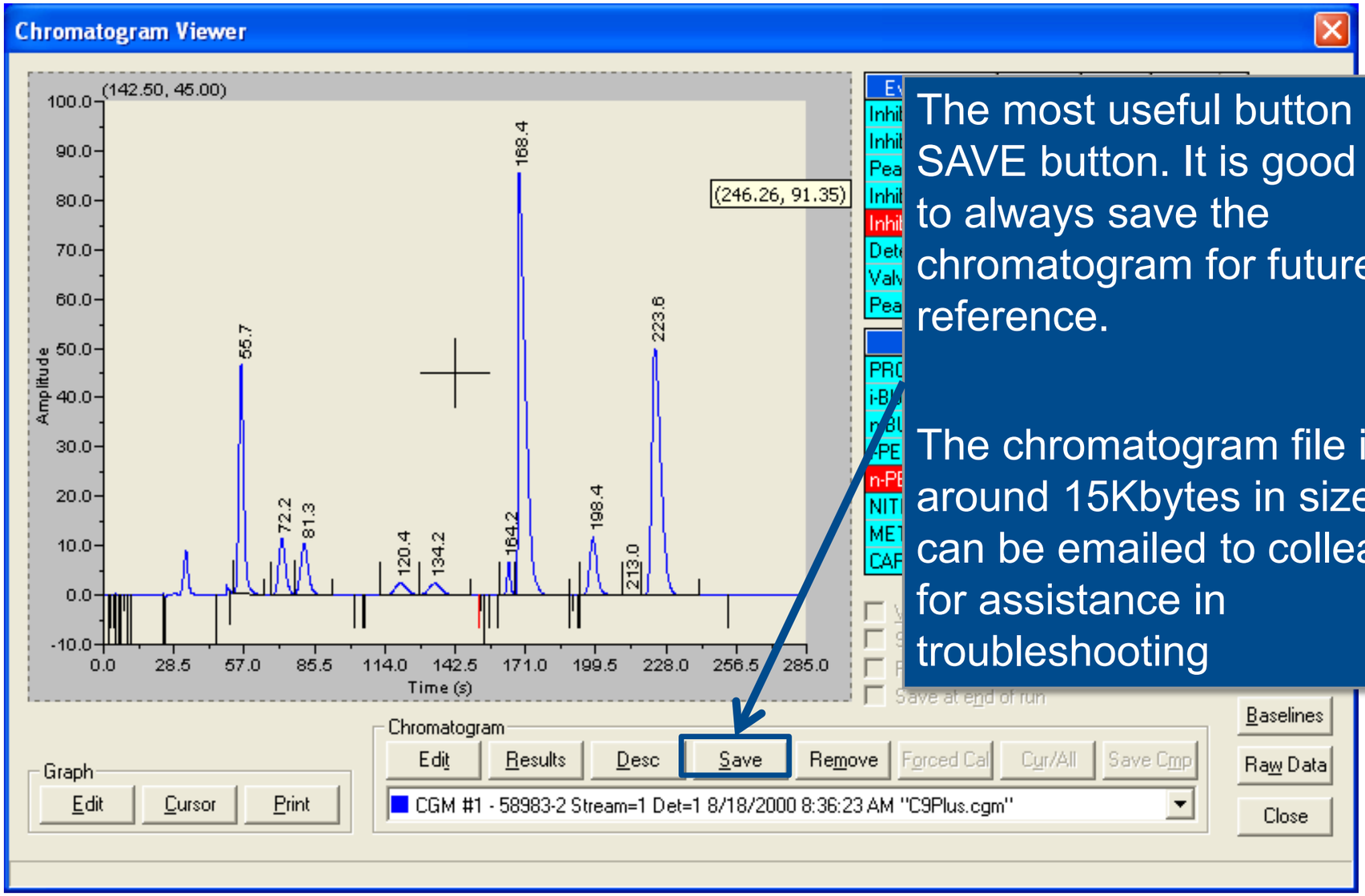


These are called integration-start and -stop times and are shown on the chromatograph with tick marks above the baseline

Chromatograms



Chromatograms



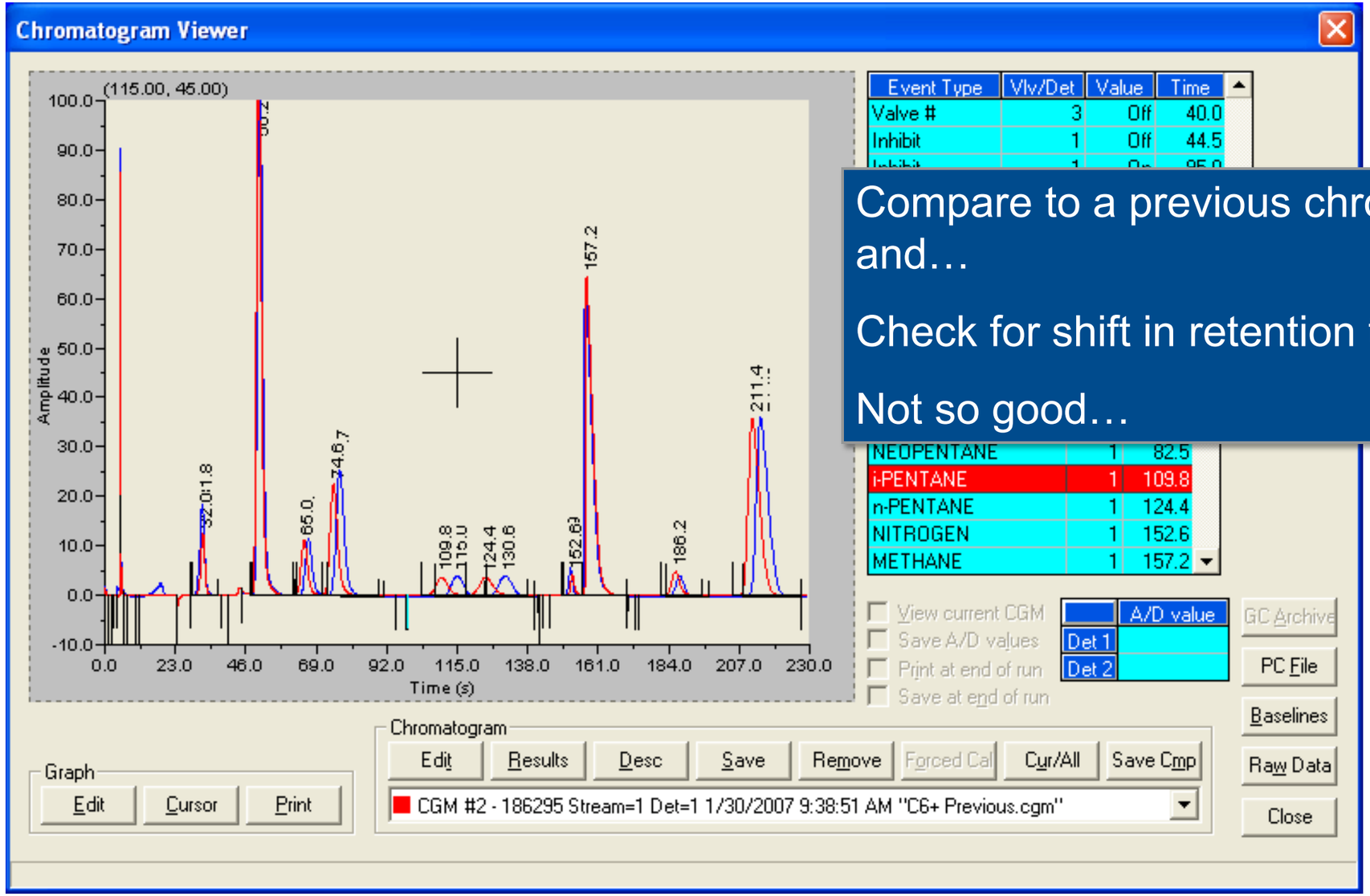
The most useful button is the SAVE button. It is good practice to always save the chromatogram for future reference.

The chromatogram file is only around 15Kbytes in size, and can be emailed to colleagues for assistance in troubleshooting

Rosemount Chromatograms

- Chromatograms should be inspected for:
  - Baseline Drift – Can be caused by poor Carrier Gas, incorrect valve timing causing C6 to enter columns or excessive moisture in the sample
  - Peak Detection – Inhibit On and Off times and/or Integration Settings (Peak Width and Slope Sensitivity) interfering with Integration Start and Stop detection

Chromatogram Viewer



Compare to a previous chromatogram and…

Check for shift in retention times.

Not so good…

Retention Time Shift

- Retention Times of the components will shift over time due to:
  - Changes in the atmospheric pressure
  - Changes in oven temperature (Fault condition)
  - Contamination of the Analysis valves
- The GC updates the Retention Time during calibration, and thus “track” the changes
- When the shift in retention times is excessive, it is an indication that the Analysis Valves are contaminated, and need to be overhauled