

# Energy & Chemical Sciences

Restek Solutions for the Petrochemical/Refinery Market

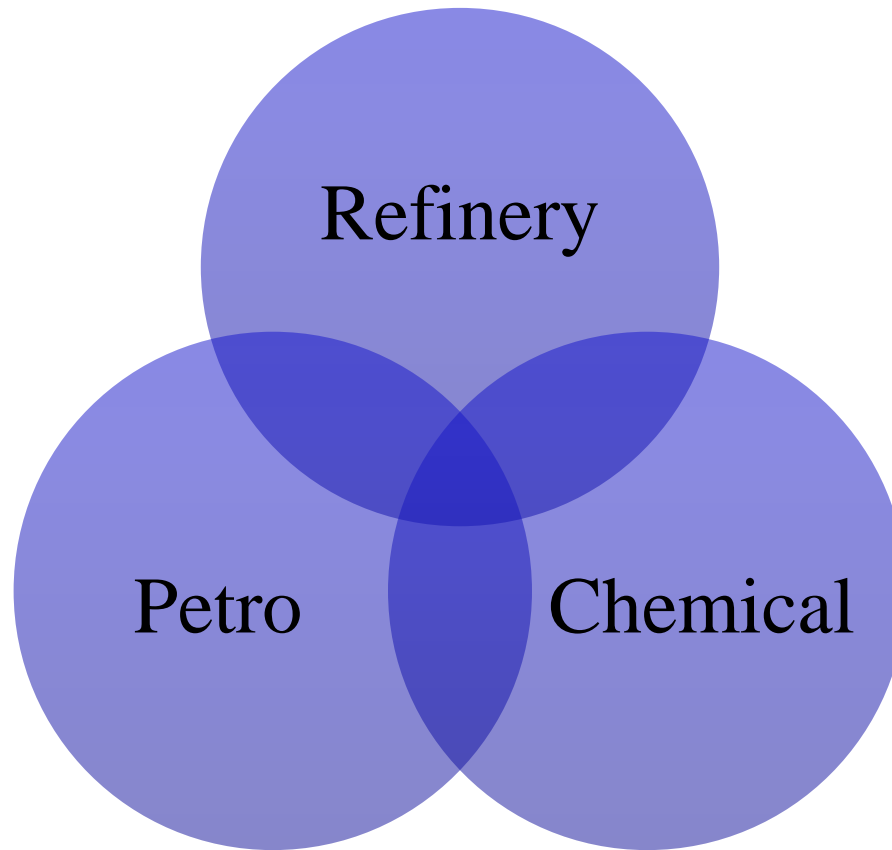


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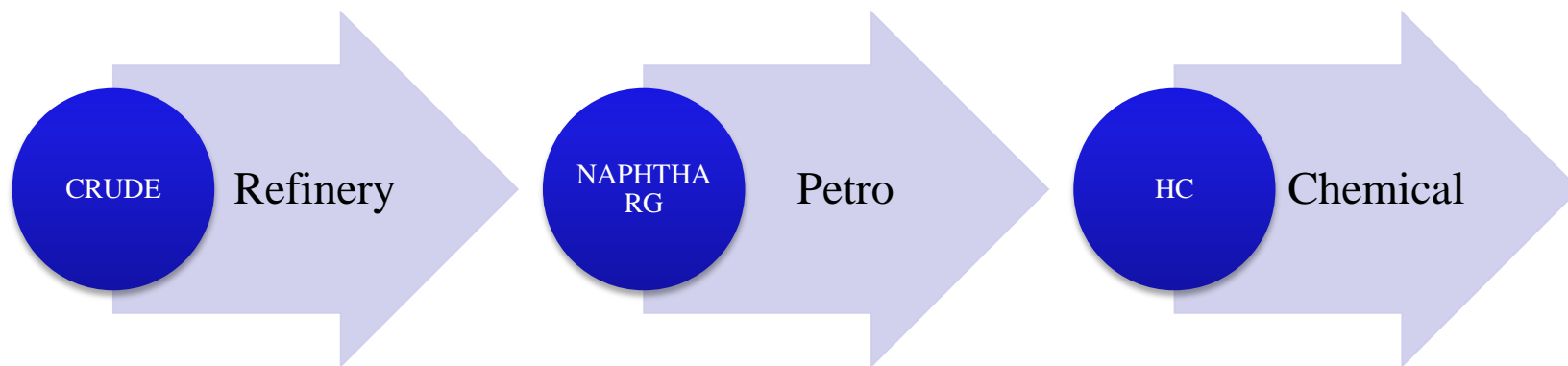
Pure Chromatography

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# Application overlap



# Feedstock process





# Focus Market

## Typical Customers

- Refining/Fuel Production
- Biofuels
- Chemical Gas Production
- Petrochemicals Production
- Contract Labs



# Common Pain Points

- Lifetime of certain columns, due to very dirty samples
- Number of analyses per hour; chemists are monitoring processes, time is crucial.
- Follow ASTM methods; chemists cannot deviate from the methods or the results will become invalid



# Petrochemical Focus Markets

**Simulated Distillation**

**Detailed Hydrocarbon Analysis**



**Refinery Gas Analysis**

**Benzene and Toluene in Gasoline**

**Gas Analysis: Impurities, LPG, and Permanent Gases**



# What is Simulated Distillation?

Chromatographic procedure designed to simulate the physical process of distilling crude oils and petroleum products

Establish a correlation between retention time and boiling point

Results are used to control refining operations

Results are also an indicator of the range of products that can be produced from a starting material and their potential yield



# What is Simulated Distillation?

## ASTM Methods:

**D2887** – Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography

**D7213** – Standard Test Method for Boiling Range Distribution of Petroleum Distillates in the Boiling Range from 100°C to 615°C by Gas Chromatography

**D6352** – Standard Test Method for Boiling Range Distribution of Petroleum Distillates in the Boiling Range from 174°C to 700°C by Gas Chromatography

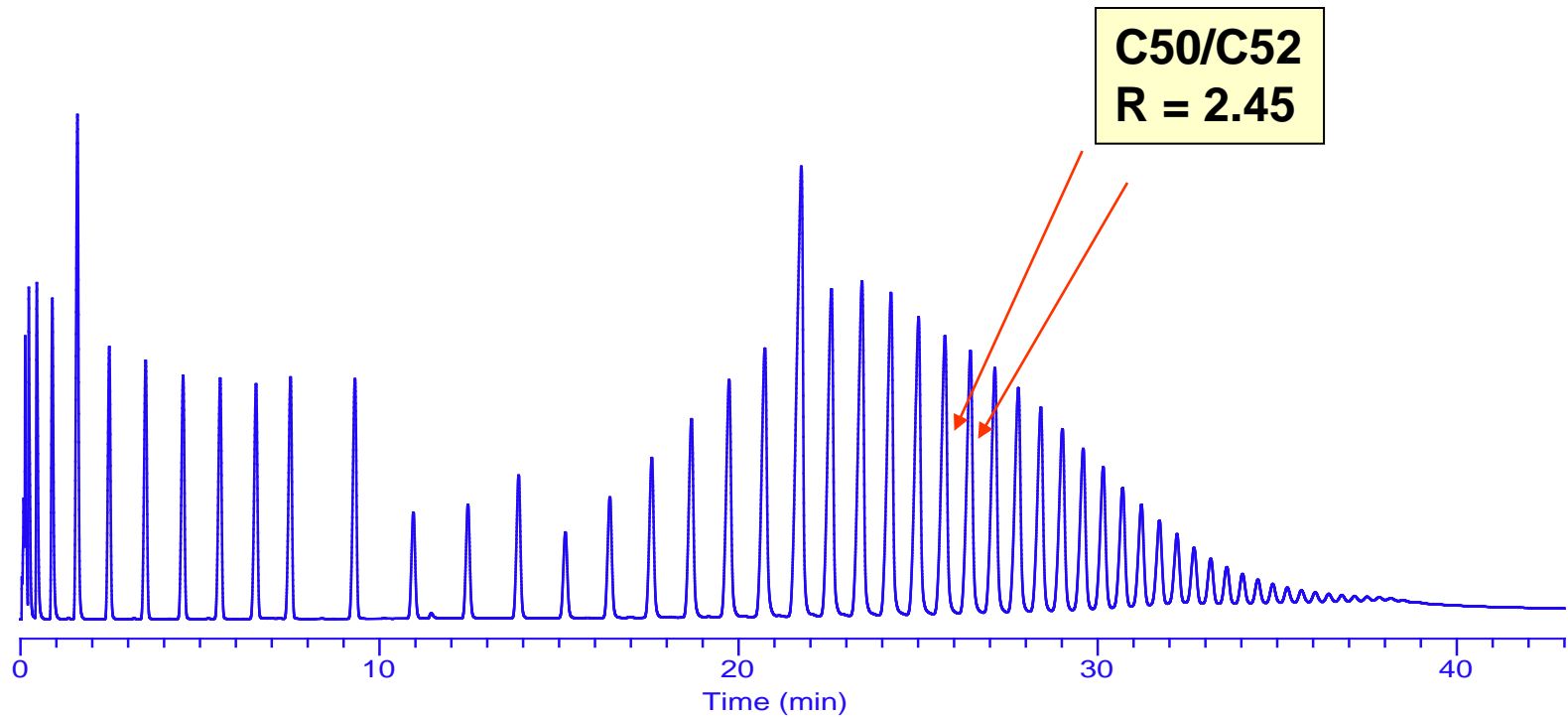
**D7169** – Standard Test Method for Boiling Point Distribution of Samples with Residues Such as Crude Oils and Atmospheric and Vacuum Residues by High Temperature Gas Chromatography

**D7500** – Standard Test Method for Boiling Range Distribution of Petroleum Distillates in the Boiling Range from 100°C to 735°C by Gas Chromatography





# Simulated Distillation



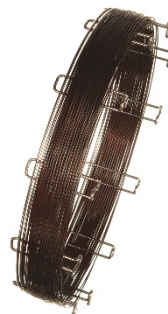
# Workflow for Simulated Distillation D7169

Sample Matrix Crude Oil



## RESTEK WORKFLOW SOLUTION

Reference Materials	Sample Preparation	Sample Collection	Chromatography	Complimentary	Cross-Sell
Polywax 1000 (cat# 36227)	N/A	N/A	MXT-1HT 5m x 0.53mm x 0.10um (cat #70112)	Liners Septa	Syringes Leak Detector



# Simulated Distillation

ASTM D7169

Standard Test Method for Boiling Point Distribution of Samples with Residues Such as Crude Oils and Atmospheric and Vacuum Residues by High Temperature Gas Chromatography

**SimDist C5 – C100**

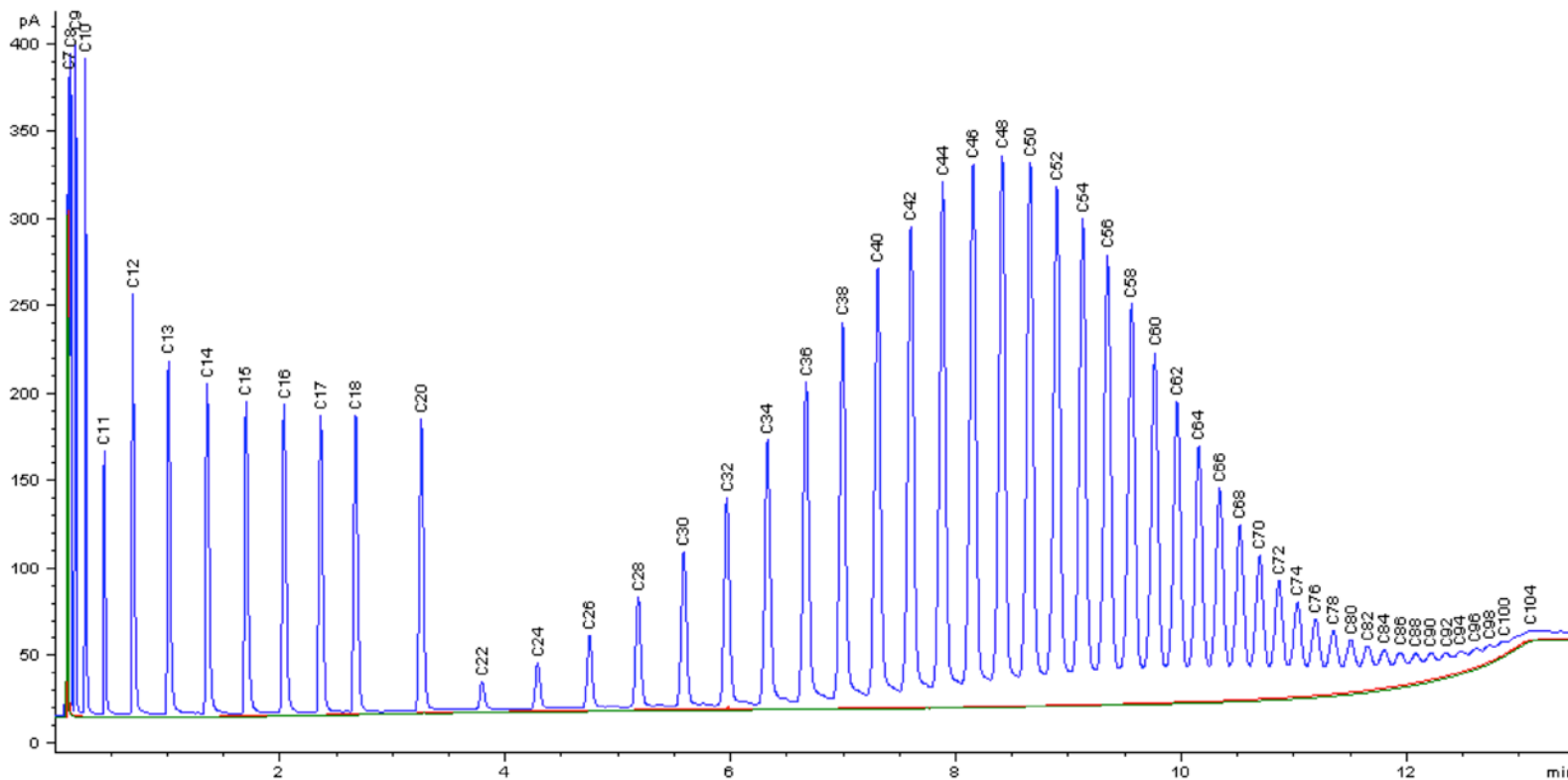
Column: 5m x 0.53mm x 0.1um MXT-1HT



# High Temperature SimDist ASTM D7169

Column: 5m, 0.53mm ID, 0.1 $\mu$ m Mxt-1HT-SimDist

Oven temp.: 40°C to 430°C @ 30°C/min. (hold 1 min.)



# SimDist Methods for Specific Refinery Products

Crude oil and heavy distillates – D6352, D7500, D7169, D7213

Light Naphtha – D2887, D7213

Gasoline – D2887

(Bio)Diesel – D2887

Jet Fuel – D2887





# Simulated Distillation

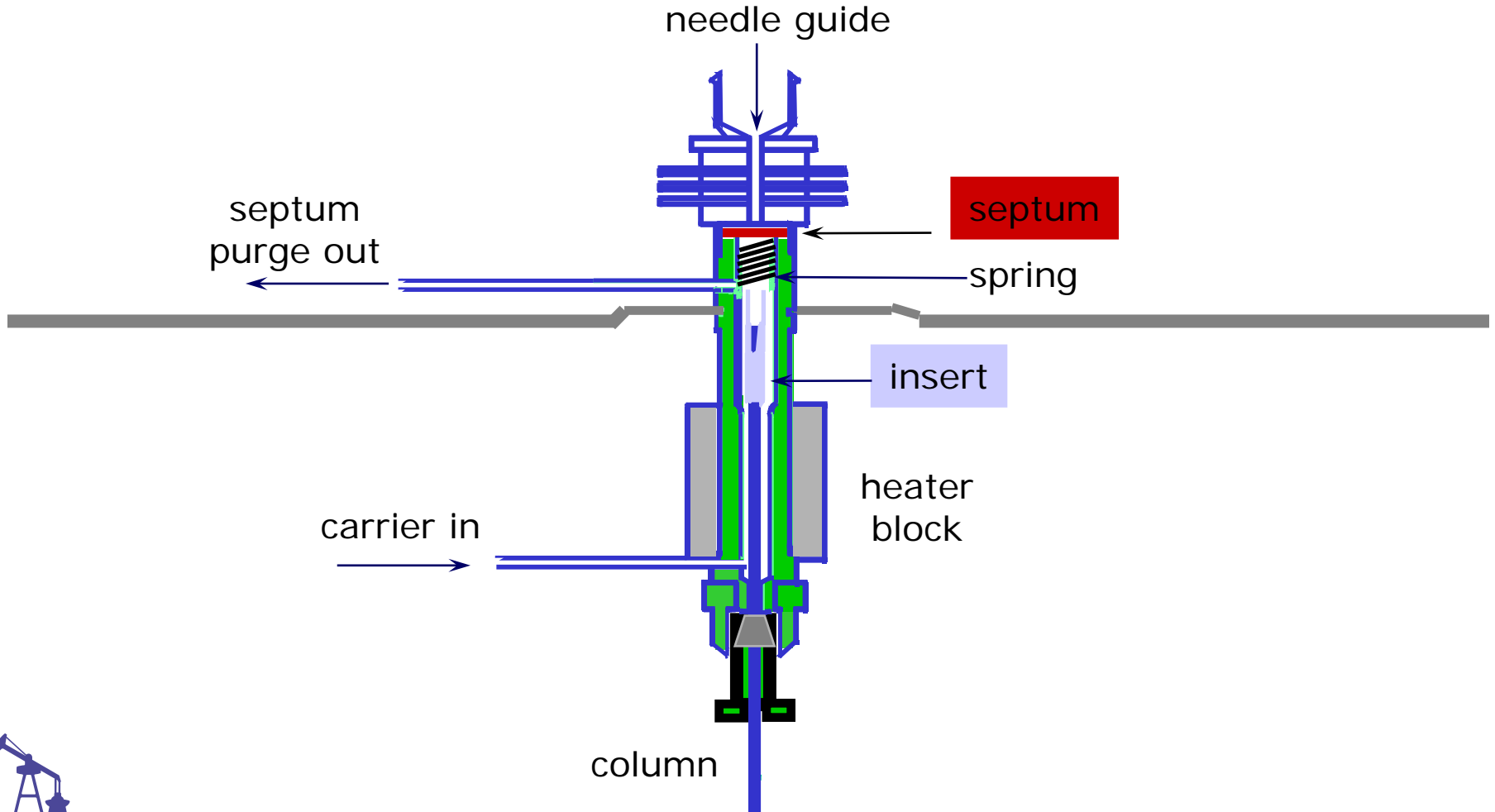
## Injection Techniques

**Cool on-column injection** - All components of the sample are injected onto the column to avoid discrimination.

**High-Temp PTV injection** - All components of the sample are injected FAST onto the column for even distribution and small band width.



# On-Column Injection



# Programmable Temperature Vaporizer (PTV)

The sample is injected into a cool liner

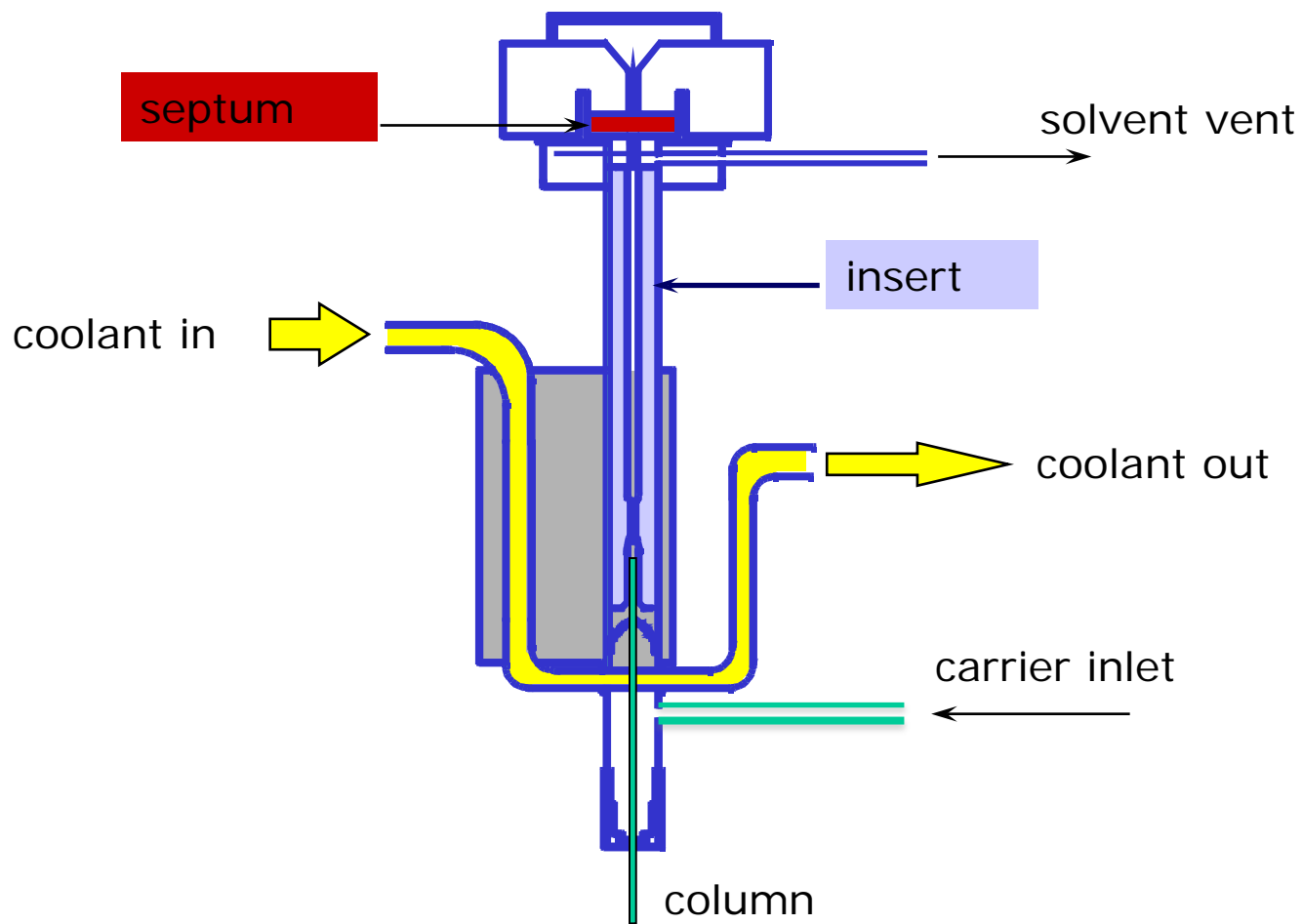
The liner is rapidly heated to vaporize the sample

Solvent vent valve times and temperatures can be programmed to achieve the equivalent of split, splitless or large volume transfer of sample vapors to the column

Combines the benefits of split, splitless, on-column and large volume injection



# Programmable Temperature Vaporizer (PTV)



# What is Refinery Gas Analysis?

Produced during distillation or treatment processes like thermal cracking

Non-condensable fraction

Important feedstock for petrochemical processes





# Workflow for Refinery Gas Analysis

Sample Matrix Refinery Gas



## RESTEK WORKFLOW SOLUTION

Reference Materials	Sample Preparation	Sample Collection	Chromatography	Complimentary	Cross-Sell
Refinery Gas Standard #5 (cat #34443)	N/A	Sample cylinders	Packed or PLOT Columns (Alumina, MoleSieve 5A)	Methanizer	Leak Detector



# Refinery Gas Analysis

Refinery Gas: mix of **light hydrocarbons** (C1-C5) and **permanent gases** (H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, Ar, CO, CO<sub>2</sub>)

ASTM D1946/UOP 539

Packed columns, valve switching or (simplified)  
Alumina/Na<sub>2</sub>SO<sub>4</sub> and Molesieve 5A (both 0.53 mm ID)



# Refinery Gas Analysis

Multiple valve / multiple column / multiple detector configuration

FID used to quantify C1 through C6 hydrocarbons

TCD-1 used to quantify Hydrogen

TCD-2 used to quantify CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub> and CO



# Refinery Gas Analysis

Low concentrations CO and CO<sub>2</sub> will not be detected by a TCD

A special device is required for the detection of low ppm CO and CO<sub>2</sub>, the Methanizer

At 380°C, CO and CO<sub>2</sub> are converted to Methane using a Nickel oxide catalyst and Hydrogen

Methane is detected by an FID

Individual retention times as for CO and CO<sub>2</sub> remain **unchanged**



# Refinery Gas Analysis - Methanizer



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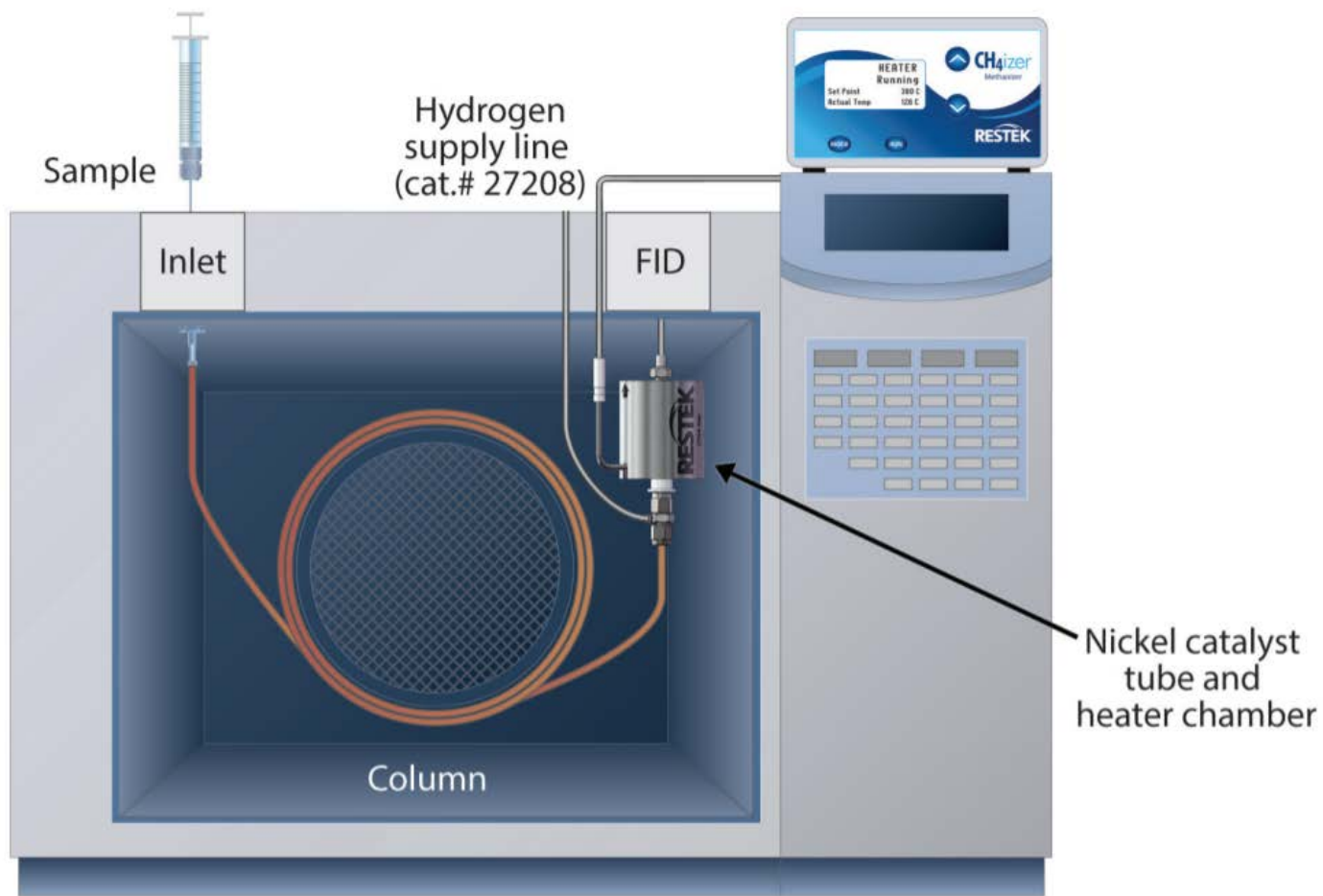
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# Refinery Gas Analysis - Methanizer



# What is Detailed Hydrocarbon Analysis?

Detailed Hydrocarbon Analysis (DHA) is done for process monitoring of the individual streams before gasoline blending

DHA is important for Octane Number prediction of the finished product



# Detailed Hydrocarbon Analysis

## Gasoline Composition – not a single Distillation Product

It is a blend of the following:

**Isomerate** - high Octane petroleum

**Reformate** - high Octane, high Aromatics petroleum

**Hydrocracked gasoline** - medium to low Octane petroleum

**Alkylate** - high Octane paraffin

**FCC gasoline** - medium Octane petroleum

**Coker Naphtha** - heavy fraction; complex hydrocarbon mix



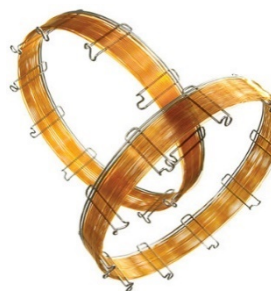
# Workflow for Detailed Hydrocarbon Analysis

Sample Matrix Refinery Feedstocks



## RESTEK WORKFLOW SOLUTION

Reference Materials	Sample Preparation	Sample Collection	Chromatography	Complimentary	Cross-Sell
DHA PONA Standard (cat #30731)	N/A	N/A	Rtx-DHA 100m x 0.25mm x 0.5um (cat# 10148)	Liners Septa	Leak Detector



# Detailed Hydrocarbon Analysis

## ASTM D6730

Standard Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100-meter Capillary (with pre-column) High Resolution Gas Chromatography

Requires extremely high resolution capillary column

Rtx-DHA column 100m x 0.25mm x 0.5um

Goal is to obtain complete resolution for as many individual hydrocarbons as possible (350+)



Needs a tuning column for adjusting selectivity of Aromatics

# Detailed Hydrocarbon Analysis

Capillary column requirements according to ASTM

Theoretical plates (N) 450,000 to 550,000 for n-C5 at 35°C

Retention Factor (k) 0.45 – 0.50 for pentane at 35°C

Resolution (R) 3.25 – 5.25 for t-butanol and 2-methylbutene-2 at 35°C

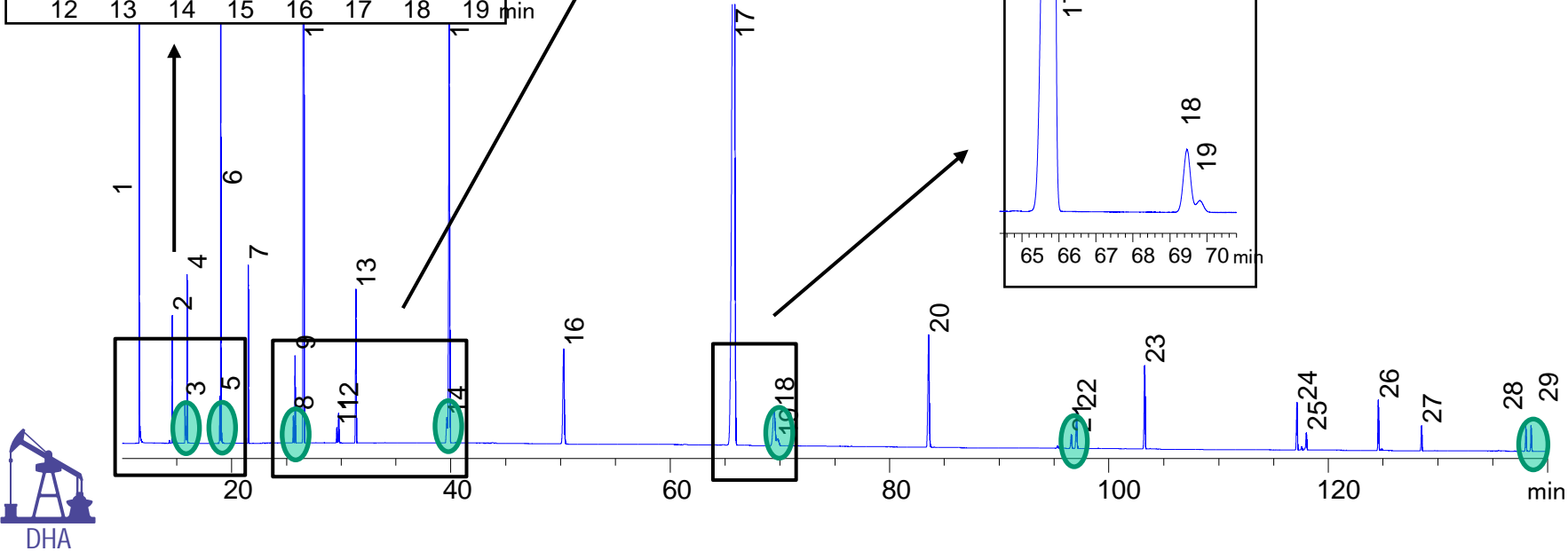
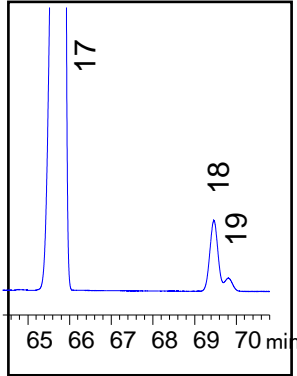
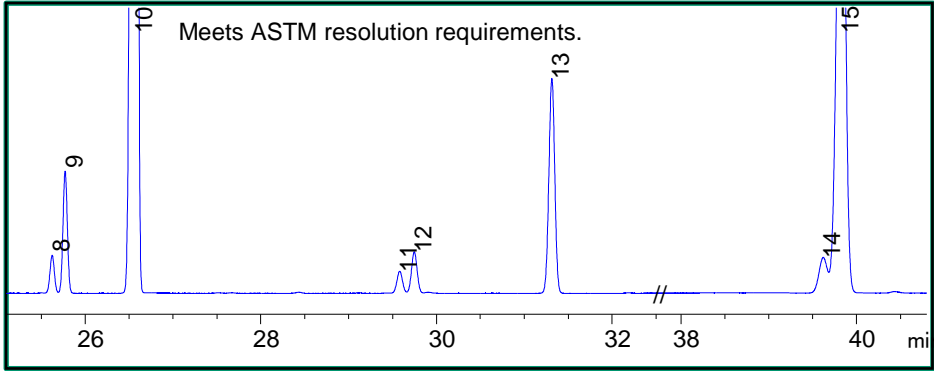
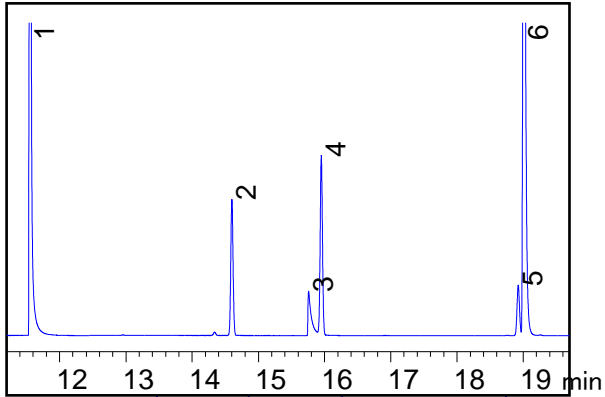
Peak Symmetry >1.0 and <5.0

**Restek Rtx-DHA is 10% better than above requirements**



# Detailed Hydrocarbon Analysis

Excellent peak shape for oxygenated compounds at 5° C!



# PiONA vs DHA

## PiONA

- Split/splitless inlet
- Auxiliary oven
- 6 column switching valves
- 6 packed columns
- 25 meter capillary column in GC oven
- FID
- software

## DHA

- Split/splitless inlet
- 100 meter capillary column in GC oven
- FID
- software



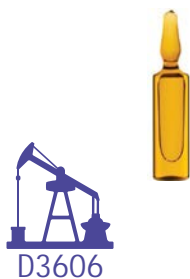
# Workflow for Benzene and Toluene in Gasoline

Sample Matrix Finished Gasoline

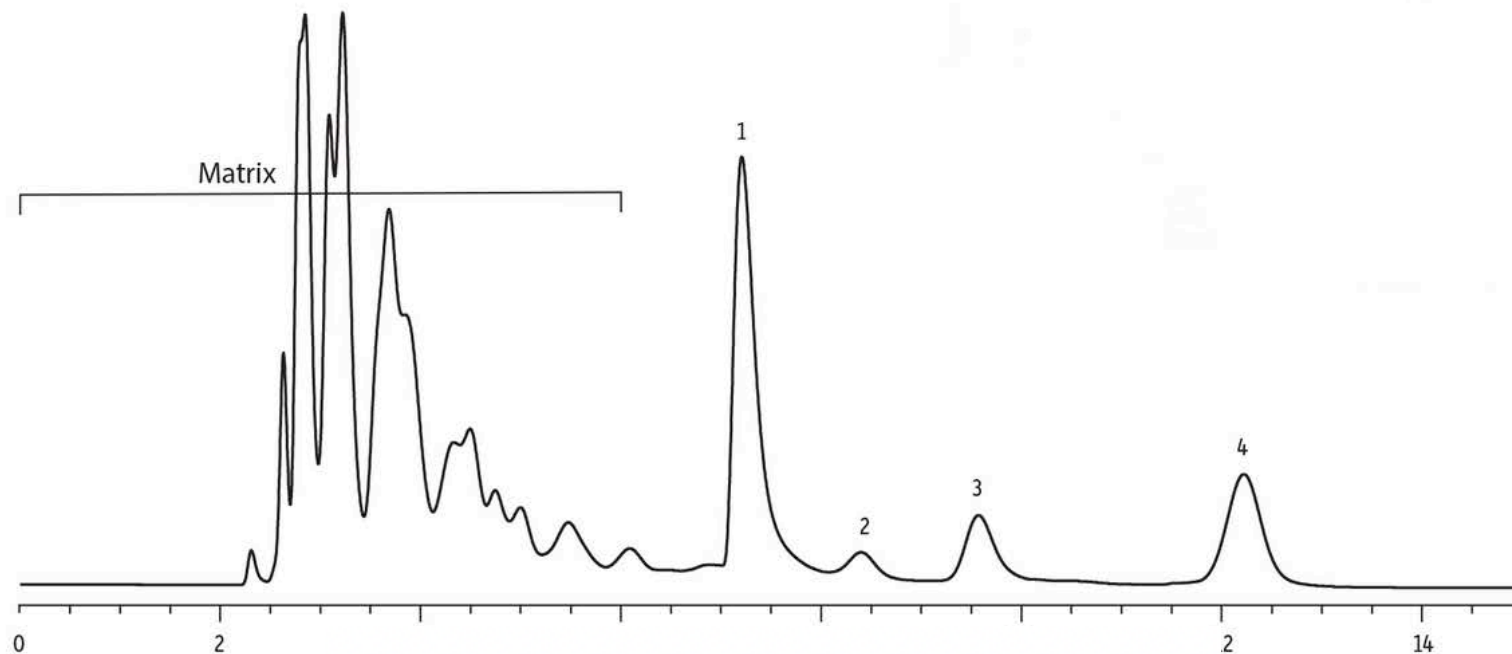


## RESTEK WORKFLOW SOLUTION

Reference Materials	Sample Preparation	Sample Collection	Chromatography	Complimentary	Cross-Sell
ASTM D3606 Calibration Kit (cat #30674)	N/A	N/A	D3606 Application Column Set (cat# 83606A-800)	Septa	Leak Detector



# Spark Ignition Fuel Containing Ethanol on D3606 Application Column Set by ASTM D3606-20

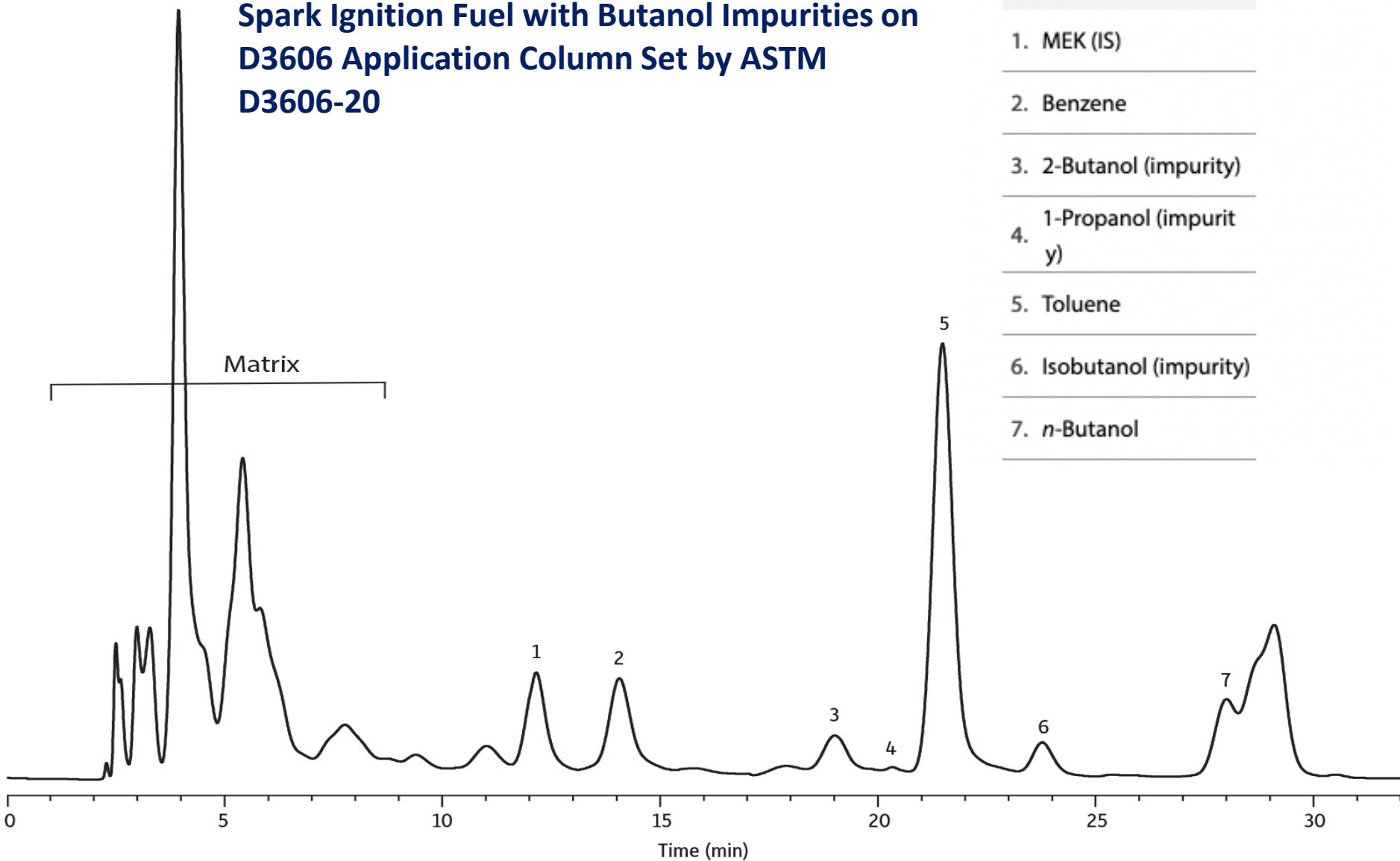


Peaks	$t_R$ (min)	Conc.
1. Ethanol	7.21	<10%
2. Benzene	8.40	<5%
3. 2-Butanol (IS)	9.57	4%
4. Toluene	12.22	<20%

# Spark Ignition Fuel with Butanol Impurities on D3606 Application Column Set by ASTM D3606-20

## Peaks

1. MEK (IS)
2. Benzene
3. 2-Butanol (impurity)
4. 1-Propanol (impurity)
5. Toluene
6. Isobutanol (impurity)
7. *n*-Butanol



# Workflow for Oxygenates in Gasoline

Sample Matrix Finished Gasoline



## RESTEK WORKFLOW SOLUTION

Reference Materials	Sample Preparation	Sample Collection	Chromatography	Complimentary	Cross-Sell
N/A	N/A	N/A	Micropacked 20% TCEP on 80/100 ChromoSorb PAW (cat# 19040)	Septa	Leak Detector



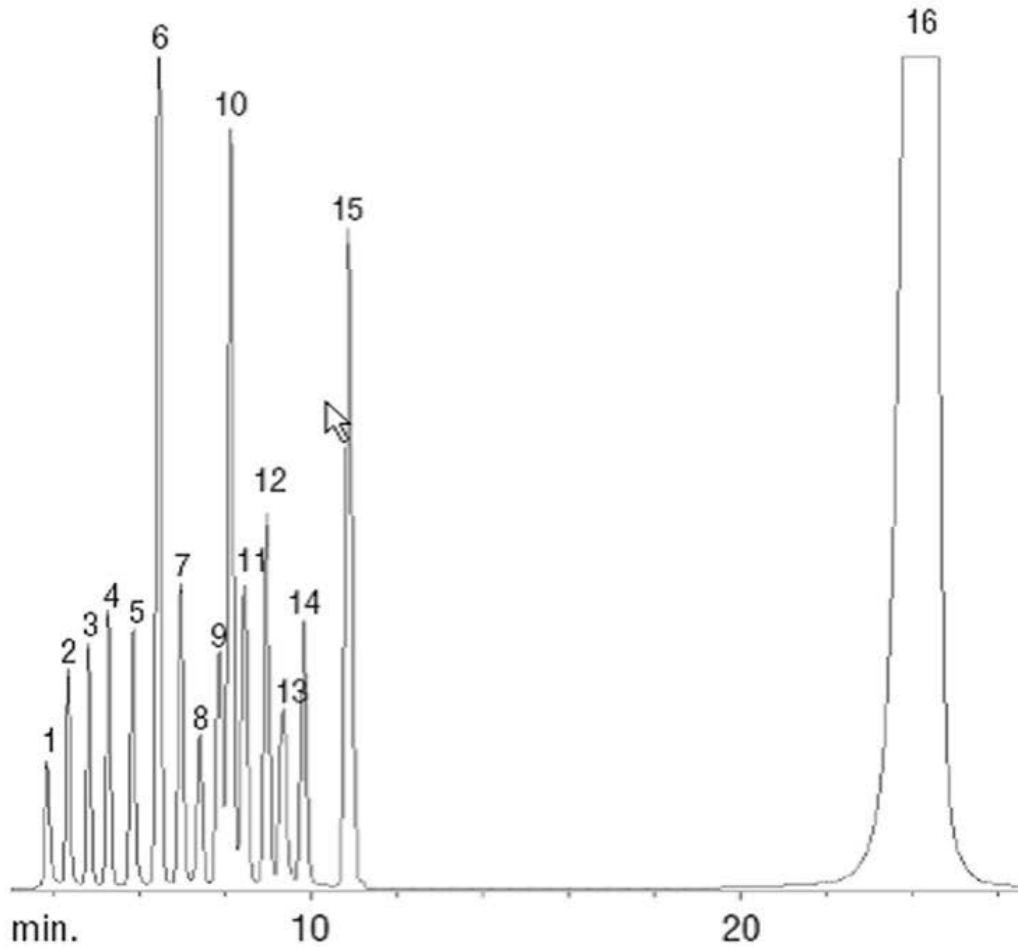
Oxygenates

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# Oxygenates ASTM D4815



1. methanol
2. ethanol
3. isopropanol
4. *tert*-butanol
5. *n*-propanol
6. methyl *tert*-butyl ether
7. *sec*-butanol
8. diisopropyl ether (DIPE)
9. isbutanol
10. ethyl-*tert*-butyl ether (ETBE)
11. *tert*-amyl ether
12. dimethoxyethane (DME)
13. *n*-butanol
14. benzene
15. *tert*-amyl methyl ether (TAME)
16. total heavy hydrocarbons



Oxygenates

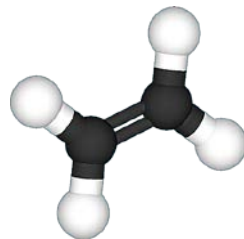
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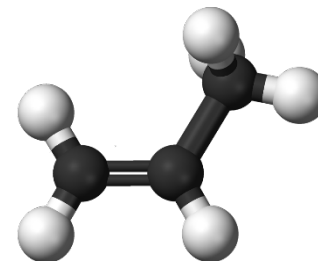
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# Gas Analysis: Impurities, LPG, and Permanent Gases

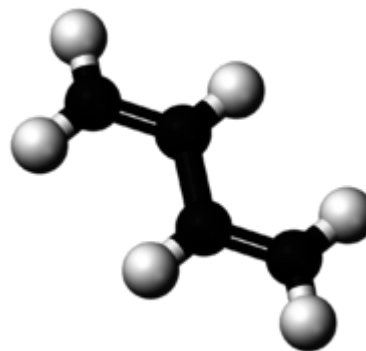
Impurities in Ethylene



Impurities in Propylene



Impurities in 1,3-Butadiene



Liquefied Petroleum Gas

Permanent Gas Analysis





# ASTM Petrochemical Method Chromatography Product Guide

Proven, Integrated Solutions and Veteran Expertise for Your Petrochemical & Chemical Analyses

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Thank You

