



Basic Analytical Training

October 15, 2026

BNSIC

Borny Analytical Services International Consulting

Introductions

Name

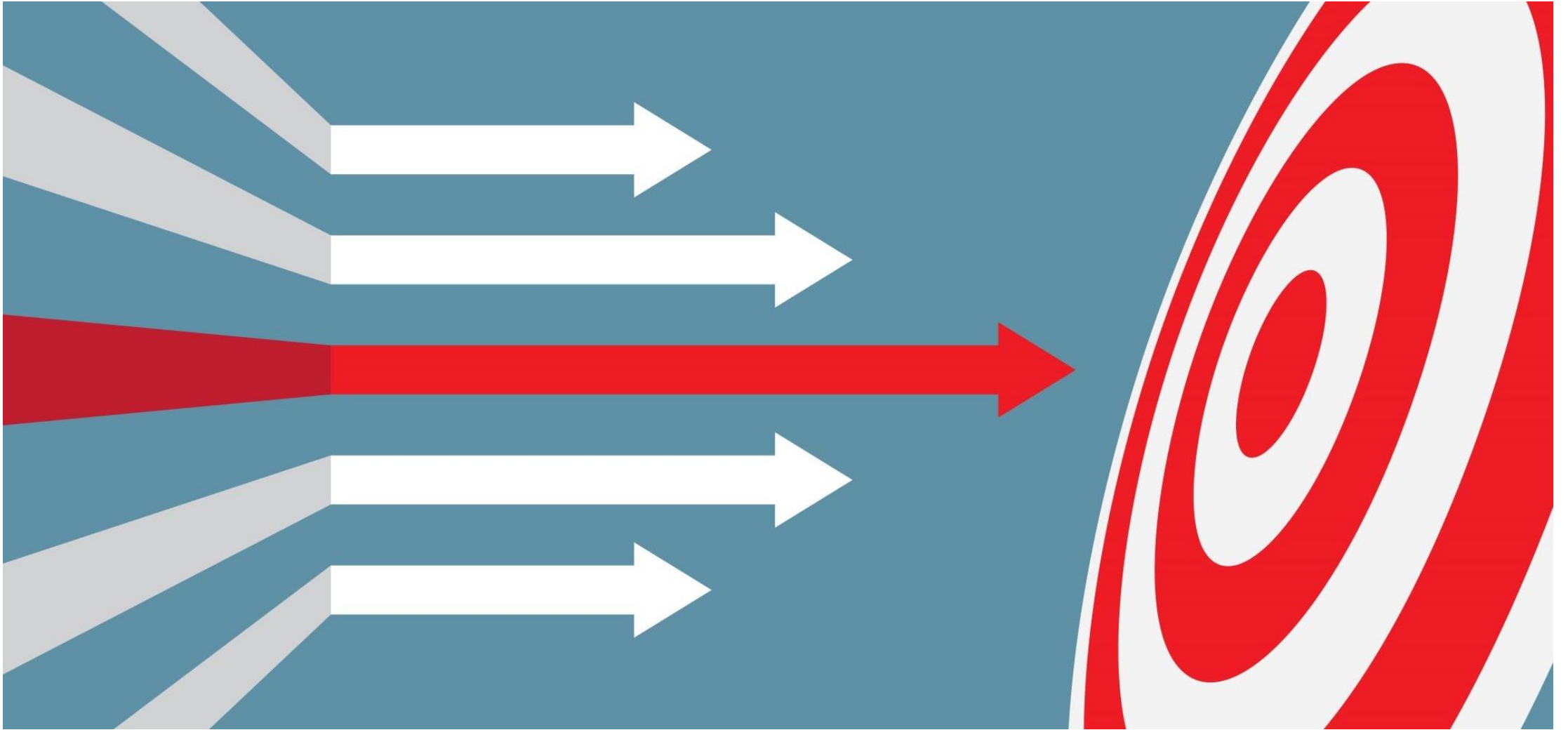
Company

Background

Analytical Experience

Expectation for Workshop

Analytical Goals



ANALYTICAL GOALS

- To determine the physical, chemical, and mechanical properties of:
 - Feeds & Catalysts
 - Products & By-Products
 - Process Streams & Waste Streams
 - Other Process Materials

To Support:

- Unit Operations
- Process Control
- Troubleshooting
- Specification Requirements
- Environmental Requirements
- Determination of Contaminants

Good Analytical Measurements & Operating Data Are Essential To:

- Make critical decisions
- Achieve process goals
- Maintain product quality

ANALYTICAL GOALS

Safety Issues Need to be Understood & Addressed

- How to Prevent Accidents in the Laboratory
- Hazards from Common Industrial Chemicals
- Sampling Considerations

Flammable Compressed Gases

Toxic Gases

LP Gases

Hydrocarbon Liquids

Aqueous Liquids

Acid Samples

Steam and High-Pressure Condensate



Analytical General Overview



GOOD ANALYSES REQUIRE GOOD SAMPLES!

Avoid

- Avoid altering composition prior to analysis

Need

- Need representative material samples

Preserve

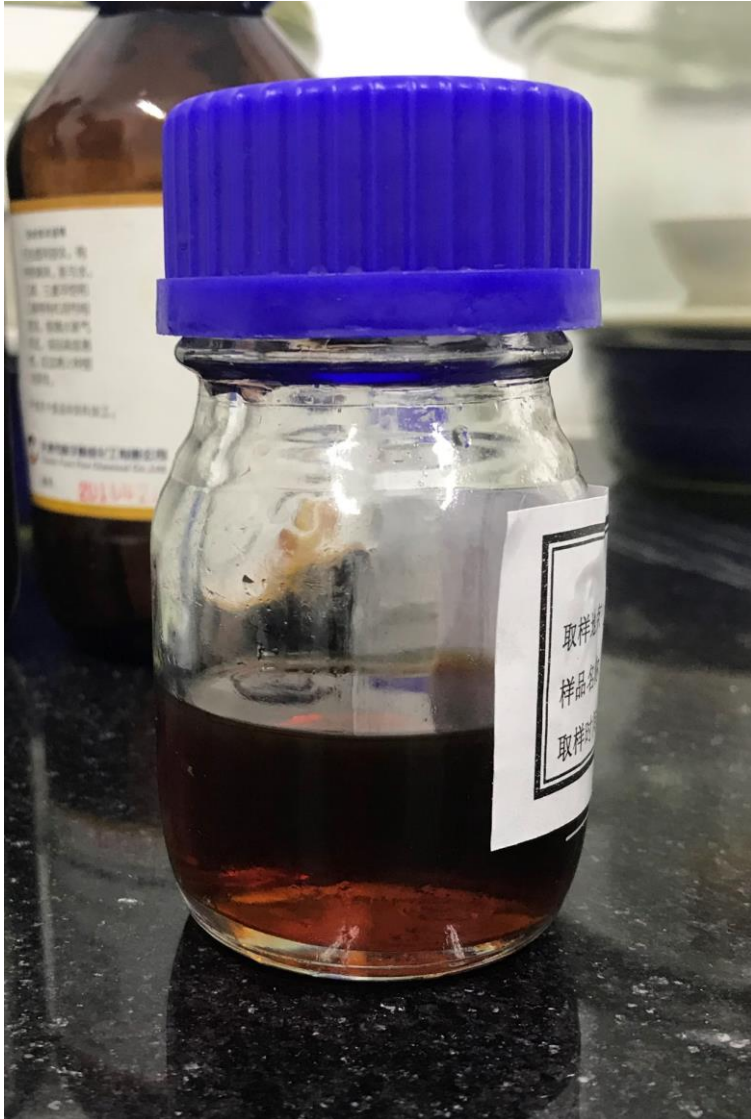
- Preserve composition during storage

GOOD ANALYSES REQUIRE GOOD SAMPLES!

Sampling and sample handling need to be carefully considered:

- Material state (solid, gas, liquid)
- Volatile loss
- Phase separation
- Precipitation
- Temperature, pressure effects

ADDITIONAL SAMPLING REQUIREMENTS



Get enough material

- Talk with the laboratory
- Present and future testing
- Future process reference

Use a proper container

- Very clean, inert, stable material
- Minimum headspace
- Dedicated



Sampling in a water bottle?

ADDITIONAL SAMPLING REQUIREMENTS

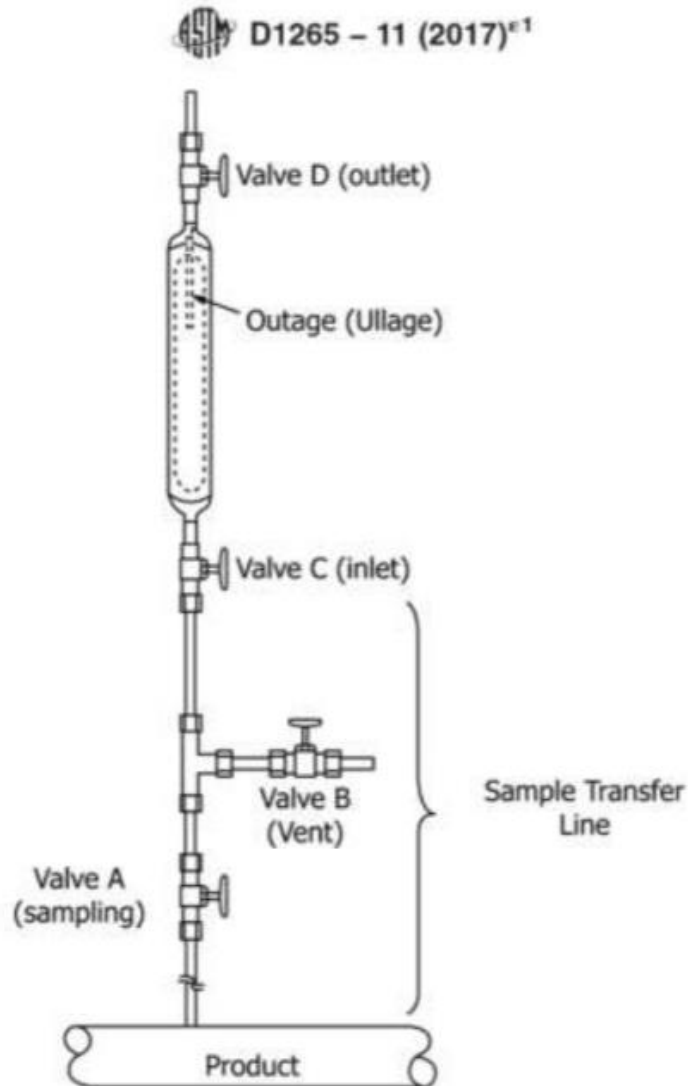


FIG. 1 Typical Sample Container and Sampling Connections

Get enough material

- Talk with the laboratory
- Present and future testing
- Future process reference

Use a proper container

- Very clean, inert, stable material
- Minimum headspace
- Dedicated

ADDITIONAL SAMPLING REQUIREMENTS

Document Source

- Description - Date - Time - Location

Storage

- Time - Temperature - Inert Atmosphere
- Save samples until results accepted or problems resolved

Analytical Methodology

A chalkboard filled with various mathematical equations, including:

- $$F = G \frac{m_1 m_2}{d^2}$$
- $$F - E + V = 2$$
- $$i\hbar \frac{\partial}{\partial t} \psi = \hat{H} \psi$$
- $$\phi(x) = \frac{1}{\sqrt{2\pi\sigma}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}$$
- $$E = mc^2$$
- $$ds \geq 0$$
- $$\frac{\partial^2 u}{\partial t^2} = c^2 \frac{\partial^2 u}{\partial x^2}$$
- $$\frac{df}{dt} = \lim_{h \rightarrow 0} \frac{f(t+h) - f(t)}{h}$$

GAS CHROMATOGRAPHY

Characterization of complex mixtures

- Gas streams
- Petroleum liquids
- Many others

Applications cover analysis of

- Refinery gas streams
- Combustion product gases
- Inorganic gases
- Liquid streams

GAS CHROMATOGRAPHY - Broad Concentration Ranges

Major
(to 100%)

Minor
(1000 ppm to
1%)

Trace
(ppm or less)

BASIC GC PRINCIPLES

Separation Results from Vapor / Adsorbed Phase Partitioning

- First Out: Most Volatile & Least Adsorbed (lower MW, less polar)
- Last Out: Least Volatile & Most Adsorbed (higher MW, more polar)



Inlet (split/splitless)

Syringe (manual or Autosampler)

Gas Sampling Valve (GSV)

Liquid Sampling Valve (LSV)

Column

1 to 150 meters

0.1 mm to 3 mm

Capillary or Packed

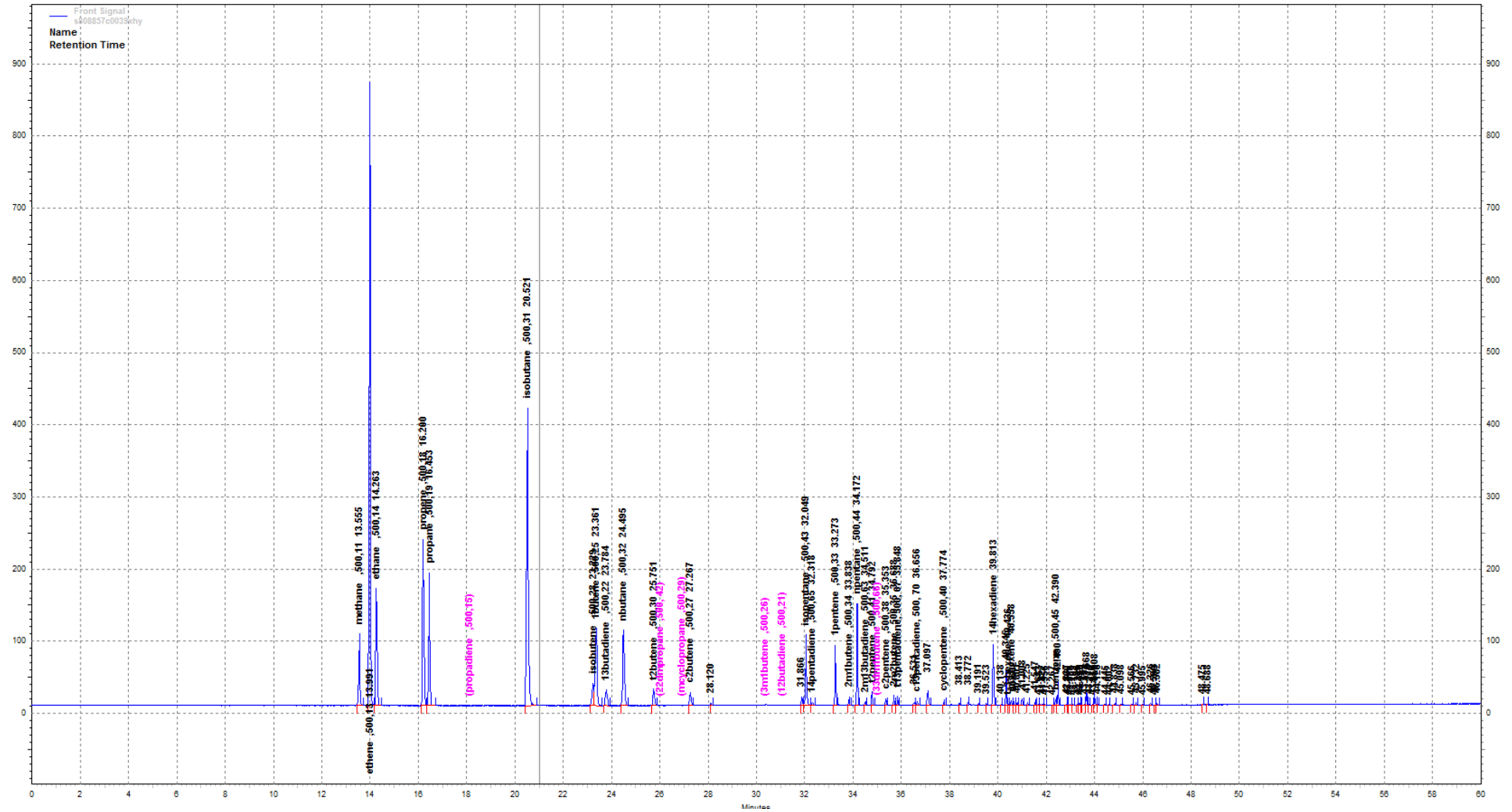
Phase (non-polar, polar, PLOT)

Outlet

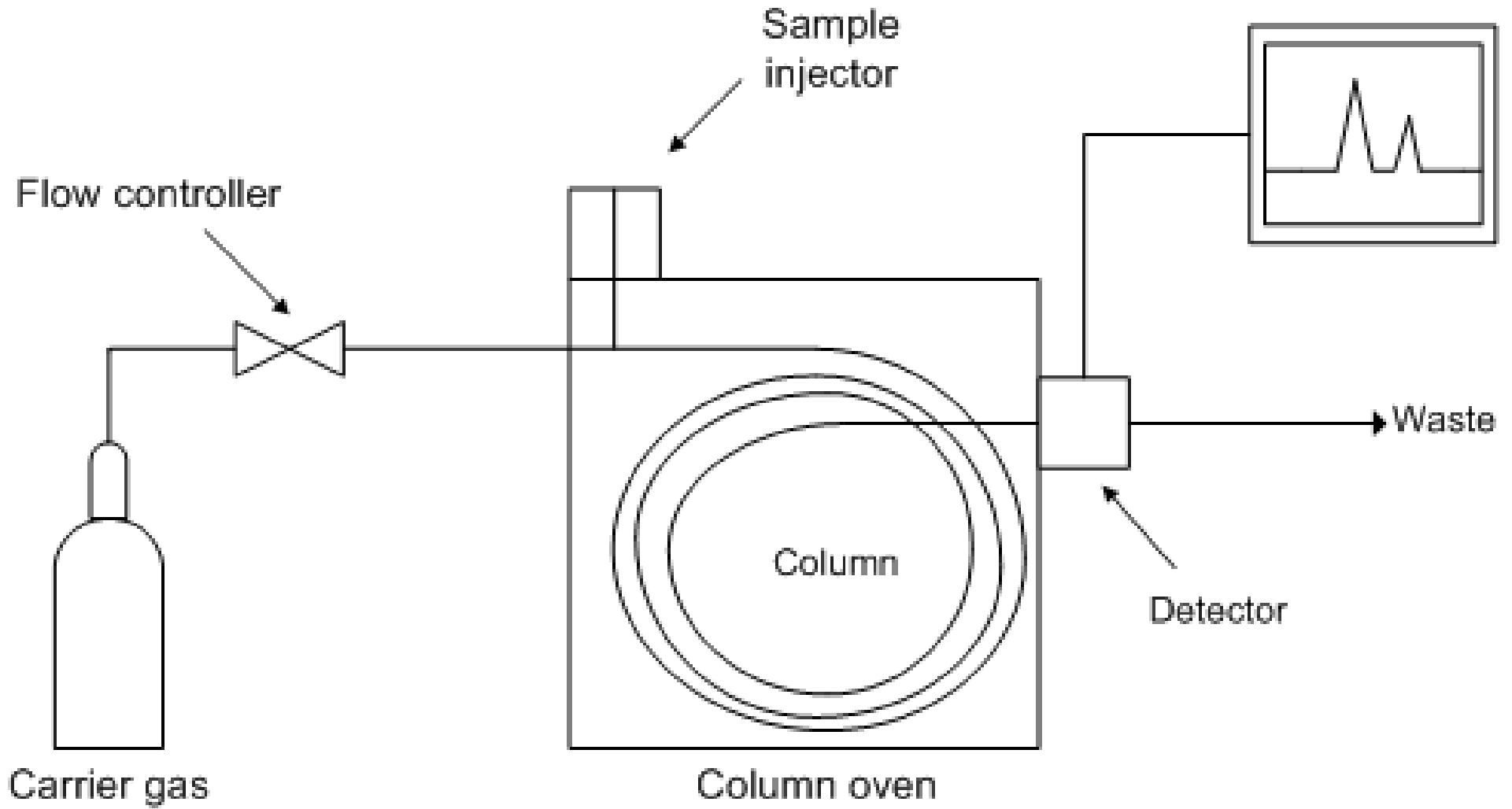
Detector

(FID, TCD, SCD,...)

Full Chromatogram



BASIC GC SYSTEM



GC TECHNOLOGY: THREE PRINCIPAL EVENTS

Injection

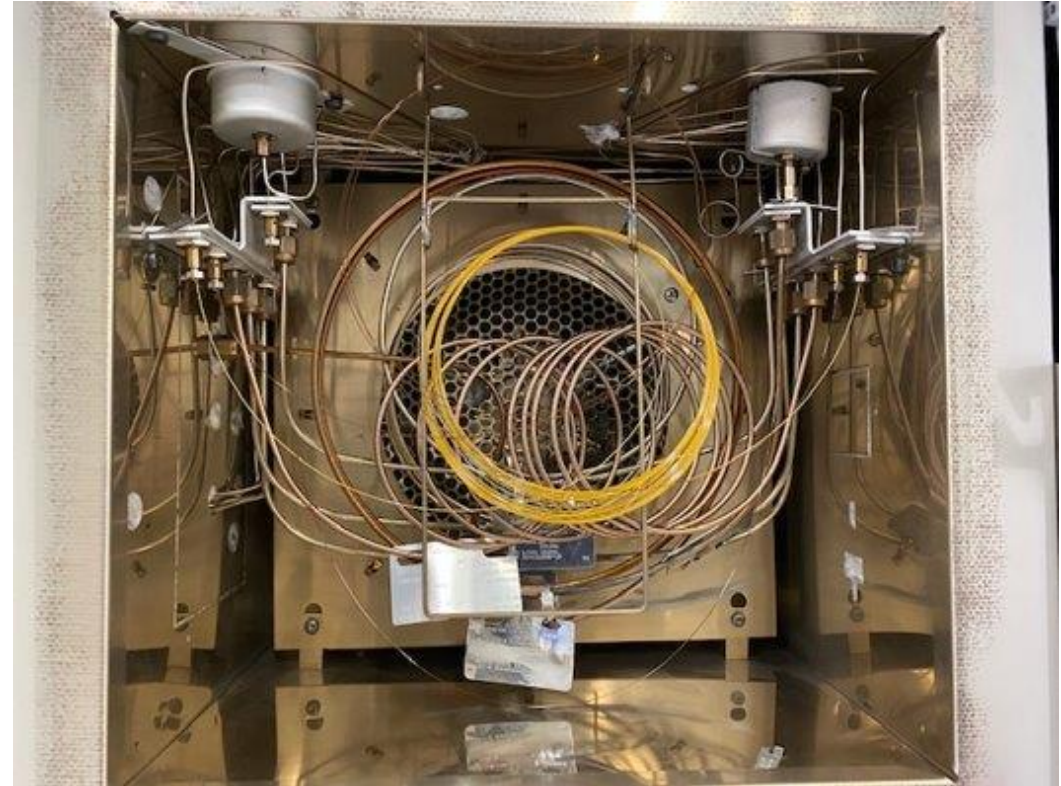
- Representative Sample
- Sample Size



GC TECHNOLOGY: THREE PRINCIPAL EVENTS

Separation

- Resolution
- Analysis Time
- Relative Retention Indices



GC TECHNOLOGY: THREE PRINCIPAL EVENTS



Detection

- Is anything eluting?
What is it?
- How much is present?
- What is its composition?

GC TECHNOLOGY: INJECTION

TYPES of SAMPLES

- Gas sample
- Compressed Gas sample (LPG)
- Liquid Sample



GC TECHNOLOGY: INJECTION

Syringes (one shot; short hold time)

- Standard, low pressure liquids
- Special, high-pressure liquids (LPG)

Mylar Bags (many shots; intermediate hold time)

- Non-reactive, low pressure gases
- cc to Liters

Metal Cylinders (high and low pressure BUT one phase only)

- Non-condensable gases
- Liquefied gases (LPG)

Injector Valves (on- and off- line)

- Gases (cc)
- Liquids (μL)

Headspace (liquid or solid)

- Volatile components
- Purge and Trap

GC TECHNOLOGY: INJECTION

Minimum needed

- carrier gas inlet
- a septum
- septum purge
- injector insert
- heater block
- column connection

Split/Splitless

- split line or vent - another set of gas lines out of the injector
- Designed so the carrier gas flow onto the column is constant
- Controls the amount of gas out the split vent to control the amount of sample to the column
 - Split vent is closed – Splitless injection
 - Split vent is open – Split injection, only a small portion of the sample to the column

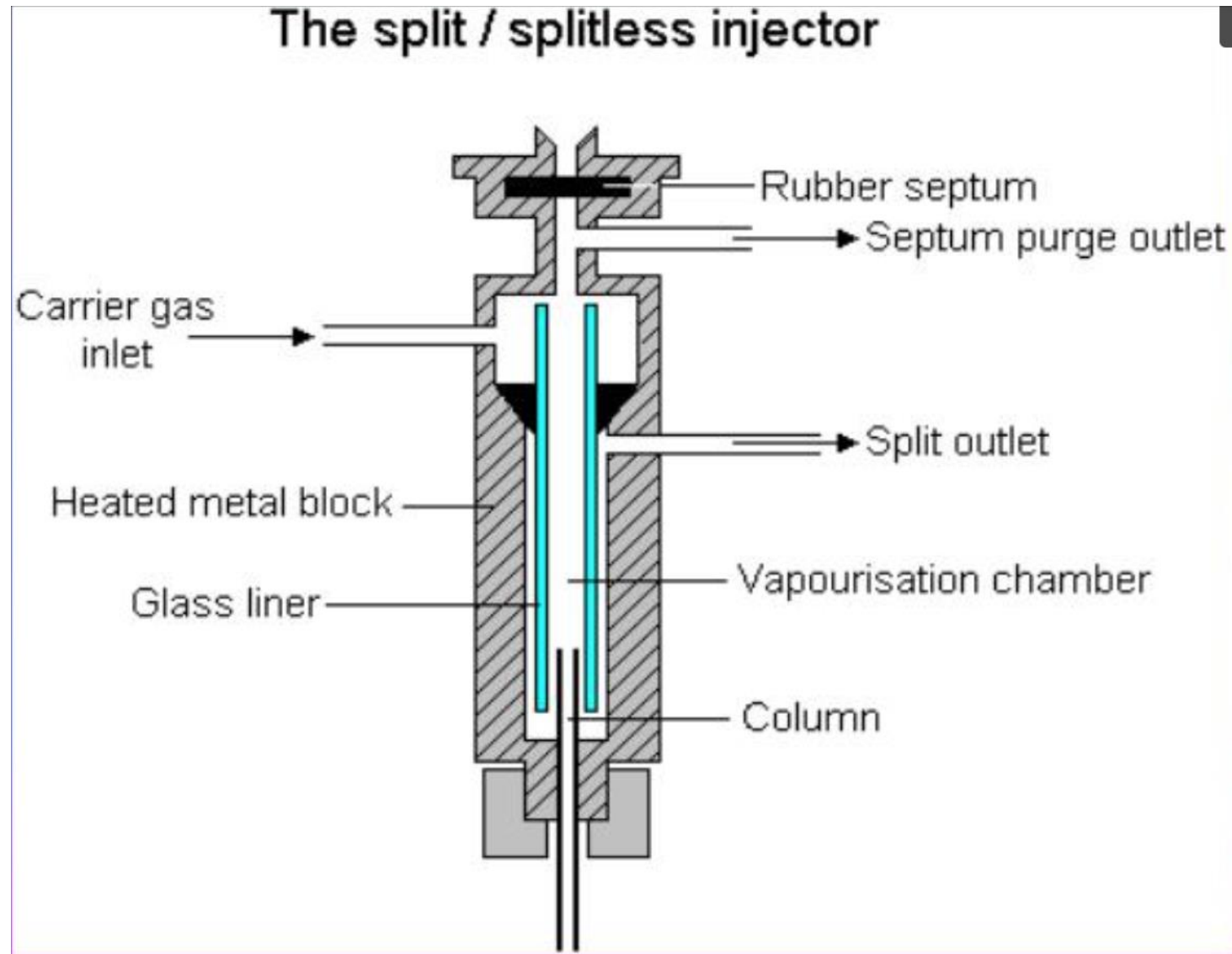
Cool on Column

- Liquid sample is drawn into the on-column syringe.
- Opening of the duck-bill septum—and stopping of carrier gas flow—is initiated by pressing down on the needle guide which splits open the duck-bill septum's "lips".
- Syringe's capillary needle is inserted down through the needle guide, through the opened duck-bill septum, completely through the cool injector into the GC column.
- Liquid sample is injected directly into a cool column ("on" the column)
- Capillary needle is withdrawn; the duck-bill septum closes when the needle guide is released; and carrier gas flow is reestablished.
- Oven's temperature program begins, and the sample vaporized to begin chromatography

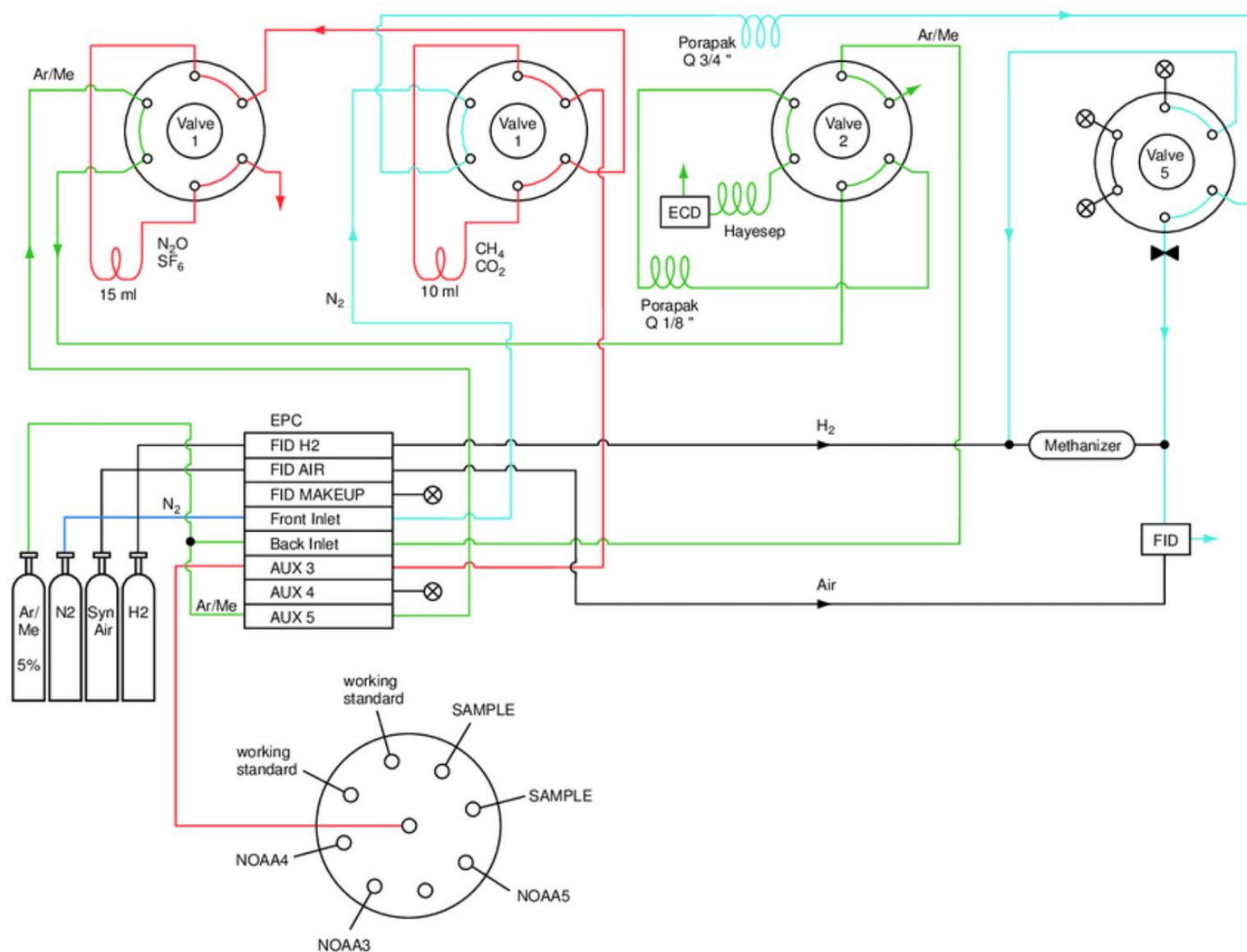
Direct on Column

- Gases (cc)
- Liquids (μL)

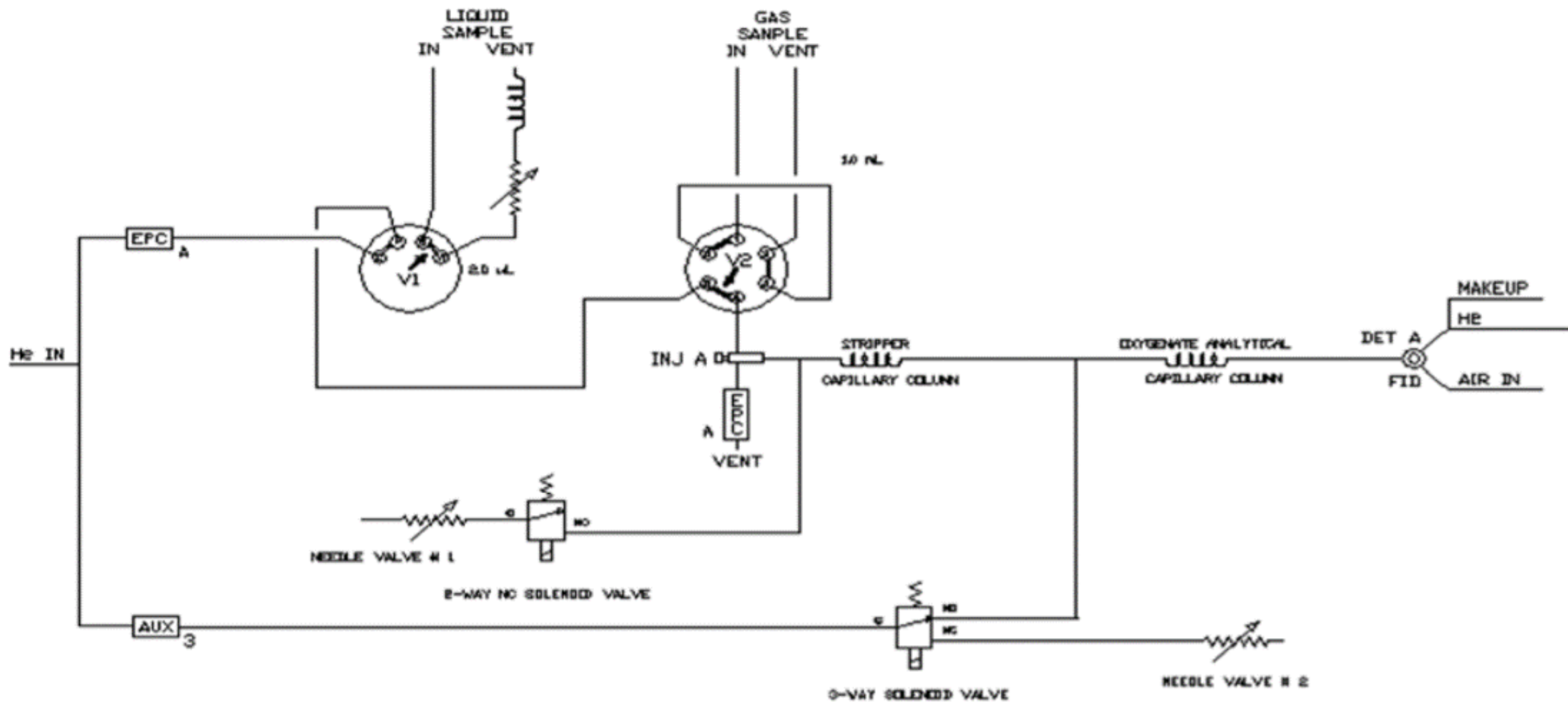
Split/Splitless



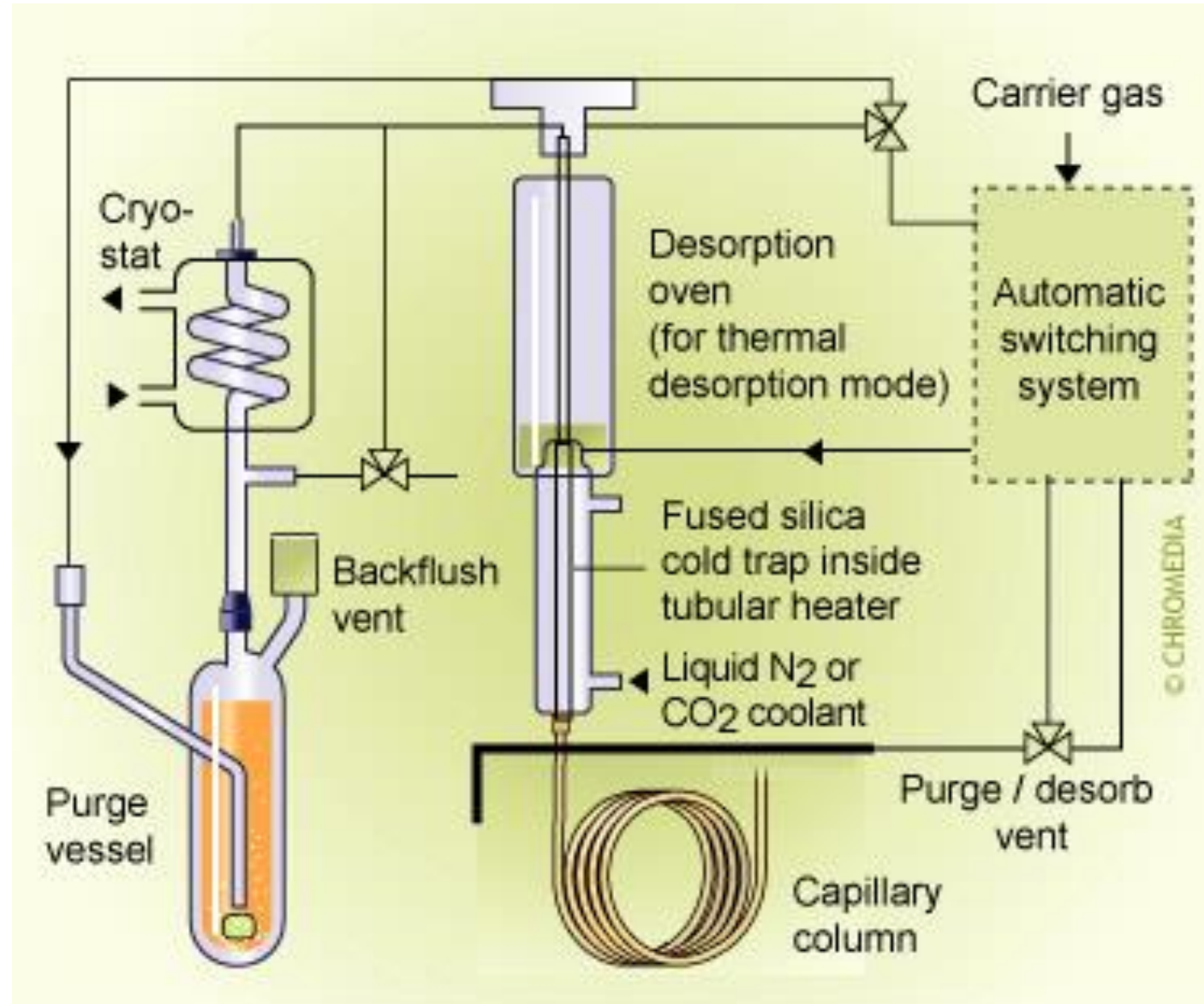
GC Valving Configuration



Schematic of a Low Level Oxygenates Multidimensional Column Configuration (Dean's Switching Method Split Inlet)

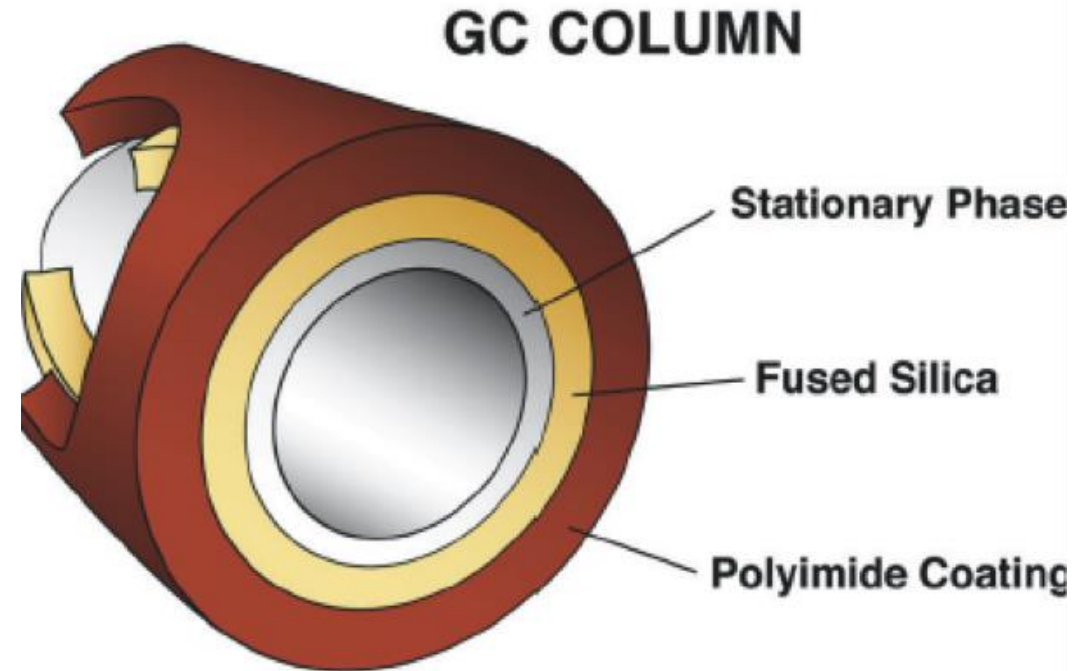


Headspace (Purge & Trap) Configuration



Separation

- Boiling Point
- Carbowax
- PLOT
- Packed
- Dean Switch (multicolumn)



GC TECHNOLOGY: COLUMNS

Separation

- Kováts Retention Index
- Boiling Point
- Polar
- PLOT

GC TECHNOLOGY: COLUMNS

- The Kováts retention index (or Kováts index) of a compound is its retention time normalized to the retention times of adjacently eluting n-alkanes.
- It depends on the fact that $\log t \propto n$, where t is the retention time and n is the number of carbon atoms in the alkane.
- For an isothermal chromatogram, the following equation is used to calculate the Kováts index:

$$I = 100 \times \left[n + \frac{\log t_x - \log t_n}{\log t_{n+1} - \log t_n} \right]$$

- n is the number of carbon atoms in the n-alkane, and t is the retention time.
- Run a chromatogram of a standard alkane mixture in the range of interest
- Do a co-injection of your sample with the standard alkanes.
- Assume that the retention times were:
 - sample = 3.12 min; n-nonane = 2.71 min; n-decane = 3.89 min.
- The Kováts index for your sample is

$$I = 100 \times \left[n + \frac{\log t_x - \log t_n}{\log t_{n+1} - \log t_n} \right] = 100 \times \left[9 + \frac{\log 3.12 - \log 2.71}{\log 3.89 - \log 2.71} \right] = 939$$

Types of Columns

100% Dimethyl polysiloxane
(5%-Phenyl)-methylpolysiloxane
(35%-Phenyl)-methylpolysiloxane
(50%-Phenyl)-methylpolysiloxane
(50%-Cyanopropylphenyl)-methylpolysiloxane
Polyethylene glycol
(70%-Cyanopropylphenyl)-methylpolysiloxane
(90%-Cyanopropylphenyl)-methylpolysiloxane

Low polarity → High polarity

Types of Columns

Type of Solid Phase	Polarity	Separation Characteristics	Application	Operational Temperature Range (Approx.)
Methyl silicone DB-1, SPB-1, RTX-1	Non-polar	Boiling point order	Petroleum, solvents, high boiling point compounds	-60 to 360 °C
Phenylmethyl DB-5, RTX-5	Slightly polar Moderately polar	Phenyl groups retain aromatic compounds.	Perfumes, environmental compounds, aromatic compounds	-60 to 340 °C
Cyanopropyl phenol	Moderately polar Strongly polar	Effective at separating oxygen-containing compounds, isomers, etc.	Agricultural chemicals, PCBs, oxygen-containing compounds *Better to avoid use with FTDs (NPDs)	-20 to 280 °C
Trifluoropropyl	Moderately polar Strongly polar	Specifically retains compounds that contain halogens.	Halogen-containing compounds, polar compounds, solvents	-20 to 340 °C
Polyethylene glycol DB-Wax	Strongly polar	Strong retention of polar compounds	Polar compounds, solvents, perfumes, fatty acid methyl esters	40 to 250 °C
Porous Layer Open Tubular GS-Alumina KCl		Separation by degree of saturation	Light hydrocarbons and fixed gases	To 200 °C

GC TECHNOLOGY: DETECTION



Detection

- FID
- TCD
- SCD
- FPD/PFPD
- MS
- NCD
- TSD
- VUV
- ECD
- HID

Sensitivity

Selectivity & Speciation

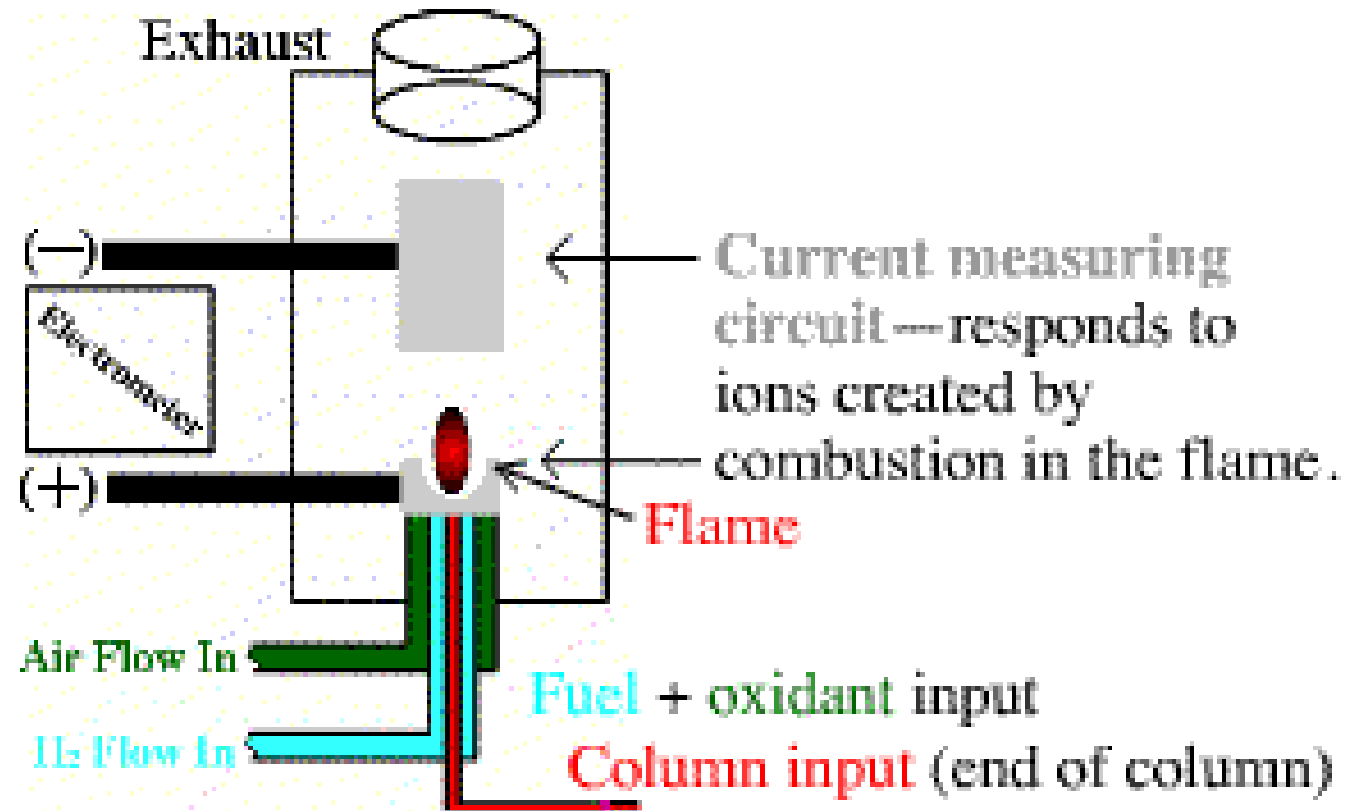
Linearity & Dynamic Range

Complexity & Reliability

GC TECHNOLOGY: FID

- Flame Ionization Detector
- Carbon specific detector
- Response is $\frac{C}{MW}$
- Theoretical response factors possible

Flame Ionization Detector (FID)



FID Response factor calculations

$\frac{C}{MW}$ = calculated = normalized to C7

$$\text{CH}_4 = \frac{C}{MW} = \frac{12}{16} = 0.75 = 1.12$$

$$\text{C}_4\text{H}_8 = \frac{C}{MW} = \frac{48}{56} = 0.86 = 0.98$$

$$\text{C}_4\text{H}_6 = \frac{C}{MW} = \frac{48}{54} = 0.89 = 0.94$$

$$\text{C}_7\text{H}_{16} = \frac{C}{MW} = \frac{84}{100} = 0.84 = 1.00$$

$$\text{CH}_3\text{OH} = \frac{C}{MW} = \frac{12}{32} = 0.38 = 2.21$$

Response Factors for Gas Chromatographic Analyses

by **W. A. Dietz**, Esso Research and Engineering Company
Analytical Research Division, Linden, New Jersey

Abstract

While there are many types of detectors employed in gas chromatographs, most units employ either flame ionization or thermal conductivity detectors. To obtain quantitative results from the GC trace, it is necessary to use correction factors; the amount of the correction is a function of the response of a given compound to the detecting device.

Flame Ionization Detectors

Relative sensitivity values for the flame ionization detector are listed in Table I. Each area is divided by the relative sensitivity to get true area. Normalizing the results gives weight percent of each component.

For hydrocarbons, with two ex-

ceptions, the values are all approximately 1.0. The two exceptions are benzene 1.12, and toluene 1.07.

For other compounds, the relative sensitivity values vary appreciably. Alcohols, for example, vary from 0.23 to 0.85; acids, from 0.01 to 0.65, etc. The use of the correct relative sensitivity is, therefore, most important when dealing with nonhydrocarbons.

Thermal Conductivity Detectors

Rosie and Grob (2) and others determined relative response values for many of the hydrocarbons and some oxygenated compounds to thermal conductivity detectors. They found the same thermal response for thermistors and hot wire

filaments. Further, the response values were independent of temperature, carrier gas, flow rate, and concentration. These response values have a precision of about $\pm 3\%$. A tabulation of thermal response values are shown in Table II. These values are used as follows:

Area under the curve divided by the relative response value of that compound gives a true response value. Normalizing the true response values gives the mole percent of any component. If the sample analyzed is a gas, the normalized true response values are equal to the gas volume %.

Area under the curve multiplied by the Weight Factor gives the true weight area. When these values are normalized, the results are weight percent of each compound. ■

FID Response factor calculations

Table II. Effective Carbon Numbers from Published Response Data (12) Calculated Relative to Heptane

Compound	Factor (reference)	ECN	Factor (calculated)	ECN (theory)
Acetylene	1.07	1.95	1.10	2
Ethylene	1.02	2.00	1.02	2
Hexene	0.99	5.82	1.02	6
Methanol	0.23	0.52	0.222	0.5
Ethanol	0.46	1.48	0.466	1.5
n-Propanol	0.60	2.52	0.595	2.5
i-Propanol	0.53	2.24	0.595(0.54)	2.5(2.25)
n-Butanol	0.66	3.42	0.676	3.5
Amyl alcohol	0.71	4.37	0.731	4.5
Butanal	0.62	3.12	0.596	3
Heptanal	0.77	6.14	0.752	6
Octanal	0.78	6.99	0.782	7
Capric aldehyde	0.80	8.73	0.824	9
Acetic acid	0.24	1.01	0.238	1
Propionic acid	0.40	2.07	0.386	2
Butyric acid	0.48	2.95	0.487	3
Hexanoic acid	0.63	5.11	0.616	5
Heptanoic acid	0.61	5.55	0.660	6
Octanoic acid	0.65	6.55	0.695	7
Methyl acetate	0.20	1.04	0.386	2.0*
Ethyl acetate	0.38	2.33	0.487	3.0*
i-Propyl acetate	0.49	3.52	0.561	4.0*
n-Butyl acetate	0.55	4.46	0.616	5.0*
Acetone	0.49	2.00	0.49	2
Methyl ethyl ketone	0.61	3.07	0.596	3
Methyl i-butyl ketone	0.71	4.97	0.716	5
Ethyl butyl ketone	0.71	5.66	0.752	6
Di-i-butyl ketone	0.72	7.15	0.805	8
Ethyl amyl ketone	0.80	7.16	0.782	7
Cyclohexanone	0.72	4.94	0.729	5

Journal of Chromatographic Science, Vol. 23, August, 1985

Calculation of Flame Ionization Detector Relative Response Factors Using the Effective Carbon Number Concept

James T. Scanlon and Donald E. Willis*

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Abstract

Equations are given for relating flame ionization detector relative response factors to the effective carbon number (ECN) of neat and derivatized components. The ECN approach can be used for calculating relative response factors in cases where pure materials are not available for detector calibration. Examples of this approach are given for the analysis of polycyclic aromatic hydrocarbons and oxygenated organics in neat form, alcohols and acids as the trimethylsilylated derivatives, and carbohydrates as the trimethylsilyl-oxime derivatives.

of this paper to show how the ECN has been used for column evaluation, as a check on experimentally determined response factors for neat and derivatized compounds, and for the calculation of response factors for compounds which cannot be obtained in pure form.

Experimental

All of the data were obtained using Model 3700 gas chromatographs (Varian) and a Model 3353-E lab automation system (Hewlett-Packard). Two columns were used. The first was a

This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.



Designation: D5441 – 98 (Reapproved 2017)

Standard Test Method for Analysis of Methyl Tert-Butyl Ether (MTBE) by Gas Chromatography¹

This standard is issued under the fixed designation D5441; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of the purity of methyl tert-butyl ether (MTBE) by gas chromatography. It also provides a procedure to measure impurities in MTBE such as C₄ to C₁₂ olefins, methyl, isopropyl and tert-butyl alcohols, methyl sec-butyl and methyl tert-amyl ethers, acetone, and methyl ethyl ketone. Impurities are determined to a minimum concentration of 0.02 mass %.

1.2 This test method is not applicable to the determination of MTBE in gasoline.

1.3 Water cannot be determined by this test method and must be measured by a procedure such as Test Method D1364 and the result used to normalize the chromatographic values.

1.4 A majority of the impurities in MTBE is resolved by the test method, however, some co-elution is encountered.

1.5 This test method is inappropriate for impurities that boil

mentations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

2. Referenced Documents

2.1 ASTM Standards:²

D1364 Test Method for Water in Volatile Solvents (Karl Fischer Reagent Titration Method)

D3700 Practice for Obtaining LPG Samples Using a Floating Piston Cylinder

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards

D4626 Practice for Calculation of Gas Chromatographic Response Factors

E355 Practice for Gas Chromatography Terms and Relationships

E594 Practice for Testing Flame Ionization Detectors Used

TABLE 2 Typical Retention Times on Three Columns, Relative Mass Response Factors^A and Densities^{B,C} for Common MTBE Product Components

No. Component	Retention Time m, min			Typical Response Factor	Density at approximately 20 °C g/mL
	50	100	150		
1 Methanol ^D	3.72	7.84	12.89	3.20	0.7914
2 Isobutylene ^E	3.85	8.00	13.39	1.18	0.5942
3 Butane	3.92	8.08	13.59	1.17	0.5788
4 Trans-2-butene	3.99	8.16	13.77	1.13	0.6042
5 Cis-2-butene	4.10	8.29	14.11	1.10	0.6213
6 3-methyl-1-butene	4.41	8.67	14.95	1.05	0.6272
7 Acetone	4.61	8.91	15.29	1.85	0.7899
8 Isopentane	4.66	8.93	15.51	1.04	0.6201
9 2-propanol	4.77	9.06	15.69	1.88	0.7855
10 1-pentene	4.82	9.15	15.95	1.05	0.6405
11 2-methyl-1-butene	4.95	9.31	16.15	1.00	0.6504
12 Pentane	5.00	9.37	16.37	1.05	0.6262
13 Trans-2-pentene	5.12	9.49	16.61	1.05	0.6482
14 Tert-butanol	5.20	9.57	16.70	1.30	0.7887
15 Cis-2-pentene	5.26	9.67	16.94	1.05	0.6556
16 2-methyl-2-butene	5.37	9.78	17.13	1.00	0.6623
17 Cyclopentene	6.17	10.72	18.84	1.00	0.7457
18 Methyl tert-butyl ether	6.51	11.11	19.15	1.53	0.7405
19 2,3-dimethyl-1-butene	6.55	11.17	19.25	1.00	0.6803
20 4-methyl-cis-2-pentene	6.57	11.21	19.36	1.00	0.669
21 2-methylpentane	6.63	11.28	19.39	1.00	0.6532
22 Methyl ethyl ketone	6.86	11.48	19.65	1.51	0.8054
23 3-methylpentane	7.09	11.80	20.17	1.00	0.6645
24 Sec-butyl methyl ether	7.22	11.93	20.23	1.53	0.7415
25 Ethyl tert-butyl ether	8.54	13.36	21.85	1.50	0.7519
26 Tert-amyl methyl ether	11.93	16.27	25.19	1.41	0.7703
27 3,5-dimethyl-1-hexene	14.85	18.23	27.39	0.90	0.708
28 2,4,4-trimethyl-1-pentene	15.03	18.40	27.65	0.90	0.715
29 2,4,4-trimethyl-2-pentene	16.17	19.27	28.47	0.90	0.7218
30 3,4,4-trimethyl-trans-2-pentene	17.86	20.86	30.19	0.90	0.739
31 2,3,4-trimethyl-2-pentene	19.02	22.00	31.28	0.90	0.7434
32 4,4-dimethyl-2-neopentyl-1-pentene	26.26	30.67	41.33	0.90	0.759
33 2,2,4,6,6-pentamethyl-3-heptene	26.46	30.92	41.64	0.90	0.759

^A Response factors are relative to heptane = 1.00.

^B See Driesbach.¹²

^C See Weast.¹¹

^D Methanol coelutes with isobutane on the 50 m and 100 m columns but is separated on the 150 m column. Subambient temperature conditions will separate these compounds.

^E Isobutylene and 1-butene co-elute on all three columns at the typical temperature conditions. These components are known to separate using subambient temperature.

TABLE 3 Theoretical FID Relative Response Factors

Carbon No.	Saturated Paraffins	Unsaturated Paraffins	Saturated Naphthenes	Unsaturated Naphthenes	Aromatics
1	1.1207	-	-	-	-
2	1.0503	-	-	-	-
3	1.0268	0.9799	-	-	-
4	1.0151	0.9799	-	-	-
5	1.0080	0.9799	0.9799	0.9517	-
6	1.0034	0.9799	0.9799	0.9564	0.9095
7	1.0000	0.9799	0.9799	0.9598	0.9195
8	0.9975	0.9799	0.9799	0.9623	0.9271
9	0.9955	0.9799	0.9799	0.9642	0.9329
10	0.9940	0.9799	0.9799	0.9658	0.9376
11	0.9927	0.9799	0.9799	0.9671	0.9415
12	0.9916	0.9799	0.9799	0.9681	0.9447
13	0.9907	0.9799	0.9799	0.9690	0.9474
14	0.9899	0.9799	0.9799	0.9698	0.9497
15	0.9893	0.9799	0.9799	0.9705	0.9517

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D6730 – 01 (2016)

Oxygenates Relative Response Factors

	Lab 1	Lab 2	Lab 3	Lab 4	Ave.	Std. Dev.	%SD	Auto/Oil RRF
Methanol	3.0760	3.0477	2.9779	2.9230	3.0062	0.0691	2.30	3.0965
Ethanol	2.1888	2.0797	2.1755	2.0640	2.1270	0.0642	3.02	2.0953
t-Butanol	1.2975	1.3189	1.3312	1.2989	1.3116	0.0163	1.24	1.3368
MTBE	1.5279	1.5590	1.4860	1.5024	1.5188	0.0318	2.09	1.5016
ETBE	1.3848	1.3720	1.3804	1.3720	1.3773	0.0064	0.46	1.4032
TAME	1.3383	1.2993	1.3598	1.3340	1.3329	0.0250	1.88	1.3775

ASTM D6733

TABLE A1.1 Method 1–Peak Numbers, Retention Time, Response Factor, Hydrocarbon Type and Carbon Number for Each Component

No	Compounds	Retention time	Response factor	Hydrocarbon type	Carbon No.
1	Hexane	6.47	1.112	CH ₂	6
2	Heptane	8.62	1.045	CH ₂	7
3	Octane	10.76	1.045	CH ₂	8
4	Nonane	12.91	1.112	MAP	9
5	Decane	15.05	1.045	CH ₂	10
6	1,4-Dimethyl	16.80	1.045	CH ₂	10
7	C12 n-alkane	18.95	1.045	CH ₂	12
8	1-Methyl 1-octene	19.45	1.045	CH	10
9	1-Methyl 1-octene	20.70	1.045	CH	10
10	1-Methyl 1-octene	22.00	1.045	CH	10
11	1-octene	22.05	1.045	CH	10
12	1-octene	23.35	1.045	CH	10
13	1-octene	24.65	1.045	CH	10
14	1-octene	25.95	1.045	CH	10
15	1-octene	27.25	1.045	CH	10
16	1-octene	28.55	1.045	CH	10
17	1-octene	29.85	1.045	CH	10
18	1-octene	31.15	1.045	CH	10
19	1-octene	32.45	1.045	CH	10
20	1-octene	33.75	1.045	CH	10
21	1-octene	35.05	1.045	CH	10
22	1-octene	36.35	1.045	CH	10
23	1-octene	37.65	1.045	CH	10
24	1-octene	38.95	1.045	CH	10
25	1-octene	40.25	1.045	CH	10
26	1-octene	41.55	1.045	CH	10
27	1-octene	42.85	1.045	CH	10
28	1-octene	44.15	1.045	CH	10
29	1-octene	45.45	1.045	CH	10
30	1-octene	46.75	1.045	CH	10
31	1-octene	48.05	1.045	CH	10
32	1-octene	49.35	1.045	CH	10
33	1-octene	50.65	1.045	CH	10
34	1-octene	51.95	1.045	CH	10
35	1-octene	53.25	1.045	CH	10
36	1-octene	54.55	1.045	CH	10
37	1-octene	55.85	1.045	CH	10
38	1-octene	57.15	1.045	CH	10
39	1-octene	58.45	1.045	CH	10
40	1-octene	59.75	1.045	CH	10
41	1-octene	61.05	1.045	CH	10
42	1-octene	62.35	1.045	CH	10
43	1-octene	63.65	1.045	CH	10
44	1-octene	64.95	1.045	CH	10
45	1-octene	66.25	1.045	CH	10
46	1-octene	67.55	1.045	CH	10
47	1-octene	68.85	1.045	CH	10
48	1-octene	70.15	1.045	CH	10
49	1-octene	71.45	1.045	CH	10
50	1-octene	72.75	1.045	CH	10
51	2,2,3-Trimethylbutane	15.05	1.045	CH ₃	7
52	2,2,3-Trimethylbutane	16.35	1.045	CH ₃	7
53	2,2,3-Trimethylbutane	17.65	1.045	CH ₃	7
54	2,2,3-Trimethylbutane	18.95	1.045	CH ₃	7
55	2,2,3-Trimethylbutane	20.25	1.045	CH ₃	7
56	2,2,3-Trimethylbutane	21.55	1.045	CH ₃	7
57	2,2,3-Trimethylbutane	22.85	1.045	CH ₃	7
58	2,2,3-Trimethylbutane	24.15	1.045	CH ₃	7
59	2,2,3-Trimethylbutane	25.45	1.045	CH ₃	7
60	2,2,3-Trimethylbutane	26.75	1.045	CH ₃	7
61	2,2,3-Trimethylbutane	28.05	1.045	CH ₃	7
62	2,2,3-Trimethylbutane	29.35	1.045	CH ₃	7
63	2,2,3-Trimethylbutane	30.65	1.045	CH ₃	7
64	2,2,3-Trimethylbutane	31.95	1.045	CH ₃	7
65	2,2,3-Trimethylbutane	33.25	1.045	CH ₃	7
66	2,2,3-Trimethylbutane	34.55	1.045	CH ₃	7
67	2,2,3-Trimethylbutane	35.85	1.045	CH ₃	7
68	2,2,3-Trimethylbutane	37.15	1.045	CH ₃	7
69	2,2,3-Trimethylbutane	38.45	1.045	CH ₃	7
70	2,2,3-Trimethylbutane	39.75	1.045	CH ₃	7

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TABLE A.1 Continued					
Id.	Component	Iteration, min	Response Factor	Hydrolysis Type	Cation No.
71	C ₁₂ -amide	17.08	1.075	NA	7
72	diethylglycine	17.61	1.075	NA	7
73	diethylglycine	17.72	1.088	AF	7
74	2,3,4-triaminopropane	17.75	1.075	NA	7
75	diethylglycine	18.15	1.096	AF	7
76	C ₁₂ -amide	18.16	1.075	NA	7
77	C ₁₂ -amide	18.18	1.075	NA	7
78	C ₁₂ -amide	18.26	1.099	NA	7
79	C ₁₂ -amide	18.27	1.075	NA	7
81	C ₁₂ -amide	18.98	1.075	NA	7
82	C ₁₂ -amide	19.00	1.075	NA	7
83	C ₁₂ -amide	20.47	1.075	NA	7
84	C ₁₂ -amide	20.48	1.075	NA	7
85	C ₁₂ -amide	21.13	1.075	NA	7
86	C ₁₂ -amide	21.13	1.075	NA	7
87	1,4-diaminopropane	21.81	1.075	NA	7
88	2,3,4-triaminopropane	21.81	1.075	NA	7
89	2,3,4-triaminopropane	22.02	1.075	NA	8
90	2,3,4-triaminopropane	22.02	1.096	AF	8
91	C ₁₂ -amide	22.48	1.075	NA	7
92	1,4-diaminopropane	22.50	1.075	NA	7
93	2,3,4-triaminopropane	22.52	1.075	NA	7
94	2,3,4-triaminopropane	22.53	1.096	AF	8
95	2,3,4-triaminopropane	22.57	1.096	AF	8
96	2,3,4-triaminopropane	23.24	1.075	NA	7
97	diethylglycine	24.44	1.096	AF	7
98	C ₁₂ -amide	24.94	1.075	NA	7
99	C ₁₂ -amide	25.25	1.075	NA	7
100	2,3,4-triaminopropane	25.17	1.096	AF	8
101	C ₁₂ -amide	25.18	1.075	NA	7
102	diethylglycine	25.17	1.098	NA	7
103	C ₁₂ -amide	25.18	1.075	NA	7
104	C ₁₂ -amide	25.19	1.075	NA	7
105	2,3,4-triaminopropane	25.19	1.075	NA	7
106	2,3,4-triaminopropane	25.20	1.096	AF	8
107	C ₁₂ -amide	25.24	1.075	NA	7
108	1,4-diaminopropane	25.22	1.096	AF	8
109	C ₁₂ -amide	25.23	1.096	AF	8
110	1,4-diaminopropane	25.23	1.096	AF	8
111	C ₁₂ -amide	25.87	1.075	NA	7
112	diethylglycine	26.81	1.075	NA	7
113	diethylglycine	26.81	1.075	NA	7
114	diethylglycine	26.81	1.075	NA	7
115	diethylglycine	26.81	1.075	NA	7
116	1,4-diaminopropane	26.81	1.075	NA	7
117	2,3,4-triaminopropane	26.84	1.075	NA	7
118	2,3,4-triaminopropane	26.85	1.075	NA	7
119	1,4-diaminopropane	26.85	1.075	NA	8
120	1,4-diaminopropane	26.85	1.075	NA	8
121	1,4-diaminopropane	26.85	1.075	NA	8
122	1,4-diaminopropane	26.85	1.075	NA	8
123	1,4-diaminopropane	26.85	1.075	NA	8
124	1,4-diaminopropane	26.85	1.075	NA	8
125	1,4-diaminopropane	26.85	1.075	NA	8
126	1,4-diaminopropane	26.85	1.075	NA	8
127	1,4-diaminopropane	26.85	1.075	NA	8
128	1,4-diaminopropane	26.85	1.075	NA	8
129	1,4-diaminopropane	26.85	1.075	NA	8
130	1,4-diaminopropane	26.85	1.075	NA	8
131	1,4-diaminopropane	26.85	1.075	NA	8
132	1,4-diaminopropane	26.85	1.075	NA	8

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TABLE A.1 Continued					
ID	Category	Value	Relative Error	Hydrograph Type	Catchment Area
122	1.6.1.1.1.1	31.63	1.05	NA	8
123	C ₁ -depth	1.3	1.05	NA	8
124	C ₂ -depth	1.38	1.05	NA	7
125	0.6.1.1.1.1	31.63	1.05	NA	8
126	0.6.1.1.1.1	31.63	1.05	NA	8
127	C ₁ -depth	1.38	1.05	NA	8
128	C ₂ -depth	1.38	1.05	NA	8
129	C ₁ -depth	1.38	1.05	NA	8
130	C ₂ -depth	1.38	1.05	NA	8
131	2.2.1.1.1.1	31.63	1.05	NA	8
132	C ₁ -depth	1.38	1.05	NA	8
133	C ₂ -depth	1.38	1.05	NA	8
134	2.2.1.1.1.1	31.63	1.05	NA	8
135	2.2.1.1.1.1	31.63	1.05	NA	8
136	2.2.1.1.1.1	31.63	1.05	NA	8
137	2.2.1.1.1.1	31.63	1.05	NA	8
138	0.6.1.1.1.1	31.63	1.05	NA	8
139	0.6.1.1.1.1	31.63	1.05	NA	8
140	0.6.1.1.1.1	31.63	1.05	NA	8
141	0.6.1.1.1.1	31.63	1.05	NA	8
142	0.6.1.1.1.1	31.63	1.05	NA	8
143	0.6.1.1.1.1	31.63	1.05	NA	8
144	0.6.1.1.1.1	31.63	1.05	NA	8
145	0.6.1.1.1.1	31.63	1.05	NA	8
146	C ₁ -depth	1.38	1.05	NA	8
147	C ₂ -depth	1.38	1.05	NA	8
148	0.6.1.1.1.1	31.63	1.05	NA	8
149	C ₁ -depth	1.38	1.05	NA	8
150	C ₂ -depth	1.38	1.05	NA	8
151	C ₁ -depth	1.38	1.05	NA	8
152	C ₂ -depth	1.38	1.05	NA	8
153	0.6.1.1.1.1	31.63	1.05	NA	8
154	0.6.1.1.1.1	31.63	1.05	NA	8
155	0.6.1.1.1.1	31.63	1.05	NA	8
156	0.6.1.1.1.1	31.63	1.05	NA	8
157	0.6.1.1.1.1	31.63	1.05	NA	8
158	0.6.1.1.1.1	31.63	1.05	NA	8
159	0.6.1.1.1.1	31.63	1.05	NA	8
160	0.6.1.1.1.1	31.63	1.05	NA	8
161	0.6.1.1.1.1	31.63	1.05	NA	8
162	0.6.1.1.1.1	31.63	1.05	NA	8
163	0.6.1.1.1.1	31.63	1.05	NA	8
164	0.6.1.1.1.1	31.63	1.05	NA	8
165	0.6.1.1.1.1	31.63	1.05	NA	8
166	0.6.1.1.1.1	31.63	1.05	NA	8
167	0.6.1.1.1.1	31.63	1.05	NA	8
168	0.6.1.1.1.1	31.63	1.05	NA	8
169	0.6.1.1.1.1	31.63	1.05	NA	8
170	0.6.1.1.1.1	31.63	1.05	NA	8
171	0.6.1.1.1.1	31.63	1.05	NA	8
172	0.6.1.1.1.1	31.63	1.05	NA	8
173	C ₁ -depth	1.38	1.05	NA	8
174	C ₂ -depth	1.38	1.05	NA	8
175	C ₁ -depth	1.38	1.05	NA	8
176	C ₂ -depth	1.38	1.05	NA	8
177	C ₁ -depth	1.38	1.05	NA	10
178	C ₂ -depth	1.38	1.05	NA	10
179	C ₁ -depth	1.38	1.05	NA	10
180	C ₂ -depth	1.38	1.05	NA	10
181	C ₁ -depth	1.38	1.05	NA	10
182	C ₂ -depth	1.38	1.05	NA	10
183	C ₁ -depth	1.38	1.05	NA	10
184	C ₂ -depth	1.38	1.05	NA	10
185	0.6.1.1.1.1	31.63	1.05	NA	8
186	0.6.1.1.1.1	31.63	1.05	NA	8
187	0.6.1.1.1.1	31.63	1.05	NA	8
188	0.6.1.1.1.1	31.63	1.05	NA	8
189	0.6.1.1.1.1	31.63	1.05	NA	8
190	0.6.1.1.1.1	31.63	1.05	NA	8
191	C ₁ -depth	1.38	1.05	NA	8
192	C ₂ -depth	1.38	1.05	NA	8

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No	Compounds	TABLE A1.1 Continued		Hazardous type	Cation No.
		Relative mass	Relative toxicity		
192	C ₁₀ hydro	11.51	1.075	CH	9
193	C ₁₀ hydro	11.51	1.075	CH	9
194	C ₁₀ hydro	11.51	1.075	CH	9
195	C ₁₀ hydro	11.51	1.075	CH	9
196	C ₁₀ hydro	11.51	1.075	CH	9
197	C ₁₀ hydro	11.51	1.075	CH	9
198	C ₁₀ hydro	11.51	1.075	CH	9
199	C ₁₀ hydro	11.51	1.075	CH	9
200	C ₁₀ hydro	11.51	1.075	CH	9
201	C ₁₀ hydro	11.51	1.075	CH	9
202	C ₁₀ hydro	11.51	1.075	CH	9
203	C ₁₀ hydro	11.51	1.075	CH	9
204	C ₁₀ hydro	11.51	1.075	CH	9
205	C ₁₀ hydro	11.51	1.075	CH	9
206	C ₁₀ hydro	11.51	1.075	CH	9
207	C ₁₀ hydro	11.51	1.075	CH	9
208	C ₁₀ hydro	11.51	1.075	CH	9
209	C ₁₀ hydro	11.51	1.075	CH	9
210	C ₁₀ hydro	11.51	1.075	CH	9
211	C ₁₀ hydro	11.51	1.075	CH	9
212	C ₁₀ hydro	11.51	1.075	CH	9
213	C ₁₀ hydro	11.51	1.075	CH	9
214	C ₁₀ hydro	11.51	1.075	CH	9
215	C ₁₀ hydro	11.51	1.075	CH	9
216	C ₁₀ hydro	11.51	1.075	CH	9
217	C ₁₀ hydro	11.51	1.075	CH	9
218	C ₁₀ hydro	11.51	1.075	CH	9
219	C ₁₀ hydro	11.51	1.075	CH	9
220	C ₁₀ hydro	11.51	1.075	CH	9
221	C ₁₀ hydro	11.51	1.075	CH	9
222	C ₁₀ hydro	11.51	1.075	CH	9
223	C ₁₀ hydro	11.51	1.075	CH	9
224	C ₁₀ hydro	11.51	1.075	CH	9
225	C ₁₀ hydro	11.51	1.075	CH	9
226	C ₁₀ hydro	11.51	1.075	CH	9
227	C ₁₀ hydro	11.51	1.075	CH	9
228	C ₁₀ hydro	11.51	1.075	CH	9
229	C ₁₀ hydro	11.51	1.075	CH	9
230	C ₁₀ hydro	11.51	1.075	CH	9
231	C ₁₀ hydro	11.51	1.075	CH	9
232	C ₁₀ hydro	11.51	1.075	CH	9
233	C ₁₀ hydro	11.51	1.075	CH	9
234	C ₁₀ hydro	11.51	1.075	CH	9
235	C ₁₀ hydro	11.51	1.075	CH	9
236	C ₁₀ hydro	11.51	1.075	CH	9
237	C ₁₀ hydro	11.51	1.075	CH	9
238	C ₁₀ hydro	11.51	1.075	CH	9
239	C ₁₀ hydro	11.51	1.075	CH	9
240	C ₁₀ hydro	11.51	1.075	CH	9
241	C ₁₀ hydro	11.51	1.075	CH	9
242	C ₁₀ hydro	11.51	1.075	CH	9
243	C ₁₀ hydro	11.51	1.075	CH	9
244	C ₁₀ hydro	11.51	1.075	CH	9
245	C ₁₀ hydro	11.51	1.075	CH	9
246	C ₁₀ hydro	11.51	1.075	CH	9
247	C ₁₀ hydro	11.51	1.075	CH	9
248	C ₁₀ hydro	11.51	1.075	CH	9
249	C ₁₀ hydro	11.51	1.075	CH	9
250	C ₁₀ hydro	11.51	1.075	CH	9
251	C ₁₀ hydro	11.51	1.075	CH	9
252	C ₁₀ hydro	11.51	1.075	CH	9
253	C ₁₀ hydro	11.51	1.075	CH	9
254	C ₁₀ hydro	11.51	1.075	CH	9
255	C ₁₀ hydro	11.51	1.075	CH	9
256	C ₁₀ hydro	11.51	1.075	CH	9
257	C ₁₀ hydro	11.51	1.075	CH	9
258	C ₁₀ hydro	11.51	1.075	CH	9
259	C ₁₀ hydro	11.51	1.075	CH	9
260	C ₁₀ hydro	11.51	1.075	CH	9
261	C ₁₀ hydro	11.51	1.075	CH	9

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TABLE A.1 Continued					
Nb	Chemical	Ionization Energy (eV)	Regulator factor	Hydrogen Type	Cation No.
267	1,3-Dioxolene	74.69	1.000	A0	10
268	C ₆ H ₆	89.36	1.000	A0	10
269	1,4-Dioxane	75.75	1.000	A0	10
284	1,4-Dioxane	75.75	1.000	A0	10
285	1,4-Dioxane	75.75	1.000	A0	10
286	1,4-Dioxane	75.75	1.000	A0	10
287	1,4-Dioxane	75.75	1.000	A0	10
288-310, 312	1,2-Dioxane	80.98-82.64	1.000	A0	10
289	1,2-Dioxane	81.31	1.000	A0	10
273	C ₆ H ₆	79.75	0.075	NA	10
274	C ₆ H ₆	79.75	0.075	NA	10
275	C ₆ H ₆	79.75	0.075	NA	10
276	C ₆ H ₆	79.75	0.075	NA	10
277	N ₂	16.01	1.000	NA	11
278	N ₂	16.01	1.000	NA	11
279	Hydrocyanic acid	13.12	1.000	A0	10
280	Hydrocyanic acid	13.12	1.000	A0	10
281-300	Hydrocyanic acid	80.98-81.13	1.075	NA	11
281	5-Methylthiophene	81.33	1.000	A0	10
282	C ₆ H ₆	82.71	1.000	A0	10
283	C ₆ H ₆	82.71	1.000	A0	10
284	C ₆ H ₆	82.71	1.000	A0	10
285	C ₆ H ₆	82.71	1.000	A0	10
286	C ₆ H ₆	82.71	1.000	A0	10
287	C ₆ H ₆	82.71	1.000	A0	10
288	C ₆ H ₆	82.71	1.000	A0	10
289	C ₆ H ₆	82.71	1.000	A0	10
290	C ₆ H ₆	82.71	1.000	A0	10
291	C ₆ H ₆	82.71	1.000	A0	10
292	C ₆ H ₆	82.71	1.000	A0	10
293	C ₆ H ₆	82.71	1.000	A0	10
294	C ₆ H ₆	82.71	1.000	A0	10
295-302	C ₆ H ₆	80.98-81.13	1.000	A0	10
303	C ₆ H ₆	82.71	1.000	A0	10
304	C ₆ H ₆	82.71	1.000	A0	10
305	C ₆ H ₆	82.71	1.000	A0	10
306	C ₆ H ₆	82.71	1.000	A0	10
307	C ₆ H ₆	82.71	1.000	A0	10
308	C ₆ H ₆	82.71	1.000	A0	10
309	C ₆ H ₆	82.71	1.000	A0	10
310	C ₆ H ₆	82.71	1.000	A0	10
311	C ₆ H ₆	82.71	1.000	A0	10
312	C ₆ H ₆	82.71	1.000	A0	10
313-320	C ₆ H ₆	80.98-81.13	1.000	A0	10
321	N ₂	16.01	1.000	NA	11
322	C ₆ H ₆	82.71	1.000	A0	10
323	C ₆ H ₆	82.71	1.000	A0	10
324-340	C ₆ H ₆	80.98-81.13	1.000	A0	10
341-347	C ₆ H ₆	81.33-82.71	1.000	A0	11+
348	2-Methylthiophene	81.14	1.000	A0	10
349-352	2-Methylthiophene	81.14-81.29	1.000	A0	11
353	C ₆ H ₆	82.71	1.000	A0	10
354	C ₆ H ₆	82.71	1.000	A0	10
355	C ₆ H ₆	82.71	1.000	A0	10
356	C ₆ H ₆	82.71	1.000	A0	10
357	C ₆ H ₆	82.71	1.000	A0	10
358	C ₆ H ₆	82.71	1.000	A0	10
359	C ₆ H ₆	82.71	1.000	A0	10
360	C ₆ H ₆	82.71	1.000	A0	10
361	C ₆ H ₆	82.71	1.000	A0	10
362	C ₆ H ₆	82.71	1.000	A0	10
363	C ₆ H ₆	82.71	1.000	A0	10
364	C ₆ H ₆	82.71	1.000	A0	10

Only use these tags: `math`, `chem`, `math display="block"`

TABLE A1.2 Method 2—Peak Number, Retention Time, Response Factor, Hydrocarbon Type and Carbon Number for Each Component

No	Compounds	Retention time	Response Factor	Hydrophobicity	Category
1	Acetone	1.84	1.112	0.1	0
2	Methanol	1.84	1.112	0.1	0
3	Methanol	1.84	1.112	0.1	0
4	Methanol	1.84	1.112	0.1	0
5	n-Butanol	5.25	1.015	0.7	0
6	n-Butanol	5.25	1.015	0.7	0
7	n-Butanol	5.25	1.015	0.7	0
8	n-Butanol	5.25	1.015	0.7	0
9	n-Butanol	5.25	1.015	0.7	0
10	n-Butanol	5.25	1.015	0.7	0
11	n-Butanol	5.25	1.015	0.7	0
12	n-Butanol	5.25	1.015	0.7	0
13	n-Butanol	5.25	1.015	0.7	0
14	n-Butanol	5.25	1.015	0.7	0
15	n-Butanol	5.25	1.015	0.7	0
16	n-Butanol	5.25	1.015	0.7	0
17	n-Butanol	5.25	1.015	0.7	0
18	n-Butanol	5.25	1.015	0.7	0
19	n-Butanol	5.25	1.015	0.7	0
20	n-Butanol	5.25	1.015	0.7	0
21	n-Butanol	5.25	1.015	0.7	0
22	n-Butanol	5.25	1.015	0.7	0
23	n-Butanol	5.25	1.015	0.7	0
24	n-Butanol	5.25	1.015	0.7	0
25	n-Butanol	5.25	1.015	0.7	0
26	n-Butanol	5.25	1.015	0.7	0
27	n-Butanol	5.25	1.015	0.7	0
28	n-Butanol	5.25	1.015	0.7	0
29	n-Butanol	5.25	1.015	0.7	0
30	n-Butanol	5.25	1.015	0.7	0
31	n-Butanol	5.25	1.015	0.7	0
32	n-Butanol	5.25	1.015	0.7	0
33	n-Butanol	5.25	1.015	0.7	0
34	n-Butanol	5.25	1.015	0.7	0
35	n-Butanol	5.25	1.015	0.7	0
36	n-Butanol	5.25	1.015	0.7	0
37	n-Butanol	5.25	1.015	0.7	0
38	n-Butanol	5.25	1.015	0.7	0
39	n-Butanol	5.25	1.015	0.7	0
40	n-Butanol	5.25	1.015	0.7	0
41	n-Butanol	5.25	1.015	0.7	0
42	n-Butanol	5.25	1.015	0.7	0
43	n-Butanol	5.25	1.015	0.7	0
44	n-Butanol	5.25	1.015	0.7	0
45	n-Butanol	5.25	1.015	0.7	0
46	n-Butanol	5.25	1.015	0.7	0
47	n-Butanol	5.25	1.015	0.7	0
48	n-Butanol	5.25	1.015	0.7	0
49	n-Butanol	5.25	1.015	0.7	0
50	n-Butanol	5.25	1.015	0.7	0
51	n-Butanol	5.25	1.015	0.7	0
52	n-Butanol	5.25	1.015	0.7	0
53	n-Butanol	5.25	1.015	0.7	0
54	n-Butanol	5.25	1.015	0.7	0
55	n-Butanol	5.25	1.015	0.7	0
56	n-Butanol	5.25	1.015	0.7	0
57	n-Butanol	5.25	1.015	0.7	0
58	n-Butanol	5.25	1.015	0.7	0
59	n-Butanol	5.25	1.015	0.7	0
60	n-Butanol	5.25	1.015	0.7	0
61	n-Butanol	5.25	1.015	0.7	0
62	n-Butanol	5.25	1.015	0.7	0
63	n-Butanol	5.25	1.015	0.7	0
64	n-Butanol	5.25	1.015	0.7	0
65	n-Butanol	5.25	1.015	0.7	0
66	n-Butanol	5.25	1.015	0.7	0
67	n-Butanol	5.25	1.015	0.7	0
68	n-Butanol	5.25	1.015	0.7	0
69	n-Butanol	5.25	1.015	0.7	0
70	n-Butanol	5.25	1.015	0.7	0
71	n-Butanol	5.25	1.015	0.7	0
72	n-Butanol	5.25	1.015	0.7	0
73	n-Butanol	5.25	1.015	0.7	0
74	n-Butanol	5.25	1.015	0.7	0
75	n-Butanol	5.25	1.015	0.7	0
76	n-Butanol	5.25	1.015	0.7	0
77	n-Butanol	5.25	1.015	0.7	0
78	n-Butanol	5.25	1.015	0.7	0
79	n-Butanol	5.25	1.015	0.7	0
80	n-Butanol	5.25	1.015	0.7	0
81	n-Butanol	5.25	1.015	0.7	0
82	n-Butanol	5.25	1.015	0.7	0
83	n-Butanol	5.25	1.015	0.7	0
84	n-Butanol	5.25	1.015	0.7	0
85	n-Butanol	5.25	1.015	0.7	0
86	n-Butanol	5.25	1.015	0.7	0
87	n-Butanol	5.25	1.015	0.7	0
88	n-Butanol	5.25	1.015	0.7	0
89	n-Butanol	5.25	1.015	0.7	0
90	n-Butanol	5.25	1.015	0.7	0
91	n-Butanol	5.25	1.015	0.7	0
92	n-Butanol	5.25	1.015	0.7	0
93	n-Butanol	5.25	1.015	0.7	0
94	n-Butanol	5.25	1.015	0.7	0
95	n-Butanol	5.25	1.015	0.7	0
96	n-Butanol	5.25	1.015	0.7	0
97	n-Butanol	5.25	1.015	0.7	0
98	n-Butanol	5.25	1.015	0.7	0
99	n-Butanol	5.25	1.015	0.7	0
100	n-Butanol	5.25	1.015	0.7	0

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No.	Component	RA [h:m:s]	Dec [°:′:″]	Hydrogen Type	Class No.
68	1.48E+04	56:25	1:09	SP	8
69	C ₁ -center	56:25	1:09	CL	8
70	C ₂ -center	56:30	1:07	NA	7
71	C ₃ -center	57:40	1:07	NA	7
72	C ₄ -center	58:00	1:09	SP	7
73	C ₅ -center	58:10	1:07	NA	7
74	2.2.1.1E+04	58:10	1:07	NA	8
75	C ₁ -center	58:18	1:07	CL	8
76	C ₂ -center	58:21	1:07	CL	8
77	C ₃ -center	58:21	1:07	CL	8
78	C ₄ -center	58:21	1:07	CL	8
79	C ₅ -center	58:21	1:07	CL	8
80	C ₆ -center	58:21	1:07	CL	8
81	C ₇ -center	58:21	1:07	CL	8
82	C ₈ -center	58:21	1:07	CL	8
83	C ₉ -center	58:21	1:07	CL	8
84	C ₁₀ -center	58:21	1:07	CL	8
85	C ₁₁ -center	58:21	1:07	CL	8
86	C ₁₂ -center	58:21	1:07	CL	8
87	C ₁₃ -center	58:21	1:07	CL	8
88	C ₁₄ -center	58:21	1:07	CL	8
89	C ₁₅ -center	58:21	1:07	CL	8
90	1.48E+04	58:21	1:07	CL	8
91	C ₁₆ -center	58:21	1:07	CL	8
92	C ₁₇ -center	58:21	1:07	CL	8
93	C ₁₈ -center	58:21	1:07	CL	8
94	2.2.1.1E+04	58:21	1:07	CL	8
95	C ₁ -center	58:21	1:07	CL	8
96	C ₂ -center	58:21	1:07	CL	8
97	C ₃ -center	58:21	1:07	CL	8
98	C ₄ -center	58:21	1:07	CL	8
99	C ₅ -center	58:21	1:07	CL	8
100	2.2.1.1E+04	58:21	1:07	CL	8
101	C ₁ -center	58:21	1:07	CL	8
102	C ₂ -center	58:21	1:07	CL	8
103	C ₃ -center	58:21	1:07	CL	8
104	C ₄ -center	58:21	1:07	CL	8
105	C ₅ -center	58:21	1:07	CL	8
106	C ₆ -center	58:21	1:07	CL	8
107	C ₇ -center	58:21	1:07	CL	8
108	C ₈ -center	58:21	1:07	CL	8
109	C ₉ -center	58:21	1:07	CL	8
110	C ₁₀ -center	58:21	1:07	CL	8
111	C ₁₁ -center	58:21	1:07	CL	8
112	C ₁₂ -center	58:21	1:07	CL	8
113	C ₁₃ -center	58:21	1:07	CL	8
114	2.2E+04	58:21	1:07	CL	8
115	2.2E+04	58:21	1:07	CL	8
116	2.2E+04	58:21	1:07	CL	8
117	2.2E+04	58:21	1:07	CL	8
118	2.2E+04	58:21	1:07	CL	8
119	2.2E+04	58:21	1:07	CL	8
120	2.2E+04	58:21	1:07	CL	8
121	2.2E+04	58:21	1:07	CL	8
122	2.2E+04	58:21	1:07	CL	8
123	2.2E+04	58:21	1:07	CL	8
124	2.2E+04	58:21	1:07	CL	8
125	2.2E+04	58:21	1:07	CL	8
126	2.2E+04	58:21	1:07	CL	8
127	2.2E+04	58:21	1:07	CL	8

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TABLE A1.3. Continued

Nb	Compounds	Enthalpies, kJ/s	Resonance Ratio	Hydrogenation Type	Carbon No.
128	C ₂ -alkyne	15.45	1.075	NA	2
129	1-Methyl-C ₂	15.63	1.075	NA	2
130	2-Methyl-C ₂	15.62	1.075	NA	2
131	Hydrogen-2-C ₂	15.65	1.075	NA	2
132	C ₂ -alkene	15.64	1.075	CS	2
133	1-Methyl-1-C ₂	15.66	1.075	NA	2
134	Hydrogen-1-C ₂	15.66	1.075	CS	2
135	2-Methyl-2-C ₂	15.67	1.075	NA	2
136	C ₂ -alkyne	16.00	1.075	CS	2
137	C ₂ -alkene	16.00	1.075	CS	2
138	C ₂ -alkyne	16.00	1.075	CS	2
139	C ₂ -alkene	16.00	1.075	CS	2
140	C ₂ -alkyne	16.00	1.075	CS	2
141	C ₂ -alkene	16.00	1.075	CS	2
142	2,3-Di-methyl-C ₂	16.00	1.075	CS	2
143	C ₂ -alkyne	16.00	1.075	CS	2
144	2,3-Di-methyl-C ₂	16.00	1.075	CS	2
145	C ₂ -alkyne	16.00	1.075	CS	2
146	C ₂ -alkyne	16.00	1.075	CS	2
147	2,3-Di-methyl-C ₂	16.00	1.075	CS	2
148	C ₂ -alkyne	16.00	1.075	CS	2
149	1,2-Di-methyl-C ₂	16.00	1.075	CS	2
150	C ₂ -alkyne	16.00	1.075	CS	2
151	C ₂ -alkyne	16.00	1.075	CS	2
152	C ₂ -alkyne	16.00	1.075	CS	2
153	C ₂ -alkyne	16.00	1.075	CS	2
154	C ₂ -alkyne	16.00	1.075	CS	2
155	C ₂ -alkyne	16.00	1.075	CS	2
156	C ₂ -alkyne	16.00	1.075	CS	2
157	C ₂ -alkyne	16.00	1.075	CS	2
158	C ₂ -alkyne	16.00	1.075	CS	2
159	C ₂ -alkyne	16.00	1.075	CS	2
160	C ₂ -alkyne	16.00	1.075	CS	2
161	C ₂ -alkyne	16.00	1.075	CS	2
162	C ₂ -alkyne	16.00	1.075	CS	2
163	C ₂ -alkyne	16.00	1.075	CS	2
164	C ₂ -alkyne	16.00	1.075	CS	2
165	C ₂ -alkyne	16.00	1.075	CS	2
166	C ₂ -alkyne	16.00	1.075	CS	2
167	C ₂ -alkyne	16.00	1.075	CS	2
168	C ₂ -alkyne	16.00	1.075	CS	2
169	C ₂ -alkyne	16.00	1.075	CS	2
170	C ₂ -alkyne	16.00	1.075	CS	2
171	C ₂ -alkyne	16.00	1.075	CS	2
172	C ₂ -alkyne	16.00	1.075	CS	2
173	C ₂ -alkyne	16.00	1.075	CS	2
174	C ₂ -alkyne	16.00	1.075	CS	2
175	C ₂ -alkyne	16.00	1.075	CS	2
176	C ₂ -alkyne	16.00	1.075	CS	2
177	C ₂ -alkyne	16.00	1.075	CS	2
178	C ₂ -alkyne	16.00	1.075	CS	2
179	C ₂ -alkyne	16.00	1.075	CS	2
180	C ₂ -alkyne	16.00	1.075	CS	2
181	C ₂ -alkyne	16.00	1.075	CS	2
182	C ₂ -alkyne	16.00	1.075	CS	2
183	C ₂ -alkyne	16.00	1.075	CS	2
184	C ₂ -alkyne	16.00	1.075	CS	2
185	C ₂ -alkyne	16.00	1.075	CS	2
186	C ₂ -alkyne	16.00	1.075	CS	2
187	C ₂ -alkyne	16.00	1.075	CS	2
188	C ₂ -alkyne	16.00	1.075	CS	2
189	C ₂ -alkyne	16.00	1.075	CS	2

1000

Table S2.1 Continued					
No.	Compounds	Elemental (%)	Calculated (%)	Hydrolyzable Type	Carbon No.
195	C ₁₂ -hydroperoxide	78.14	1.006	AI ^a	10
196	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
197	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
198	C ₁₂ -hydroperoxide	78.14	1.006	AI ^a	10
199	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
200	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
201	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
202	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
203	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
204	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
205	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
206	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
207	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
208	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
209	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
210	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
211	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
212	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
213	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
214	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
215	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
216	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
217	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
218	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
219	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
220	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
221	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
222	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
223	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
224	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
225	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
226	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
227	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
228	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
229	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
230	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
231	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
232	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
233	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
234	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
235	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
236	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
237	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
238	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
239	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
240	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
241	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
242	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
243	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
244	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
245	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
246	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
247	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9
248	C ₁₂ -hydroperoxide	78.15	1.006	AI ^a	9

1000

No	Compounds	Historical, nL	Respective factor	hydrocarbon type	Carbon No.
249 to 254	C ₁₀ -aromatic	101.25	1.033	Al	11
255	Naphthalene	101.25	1.033	Al	10
256	C ₁₀ -hydroaromatic	101.25	1.033	Al	12
257 to 263	C ₁₁ -aromatic	104.16	1.035	Al	11
264	N-diolene	107.81	1.066	MP	12
265 to 276	C ₁₂ -aromatic	107.81	1.033	Al	11+
277	2-Methylphenanthrene	114.09	1.033	Al	11
278	1-Methylphenanthrene	115.54	1.033	Al	11
277 and +	hydrocarbon C ₁₂	+115.54	1.035		

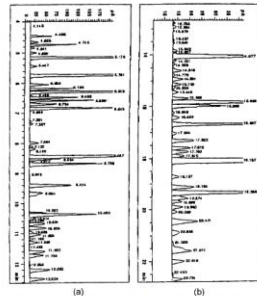
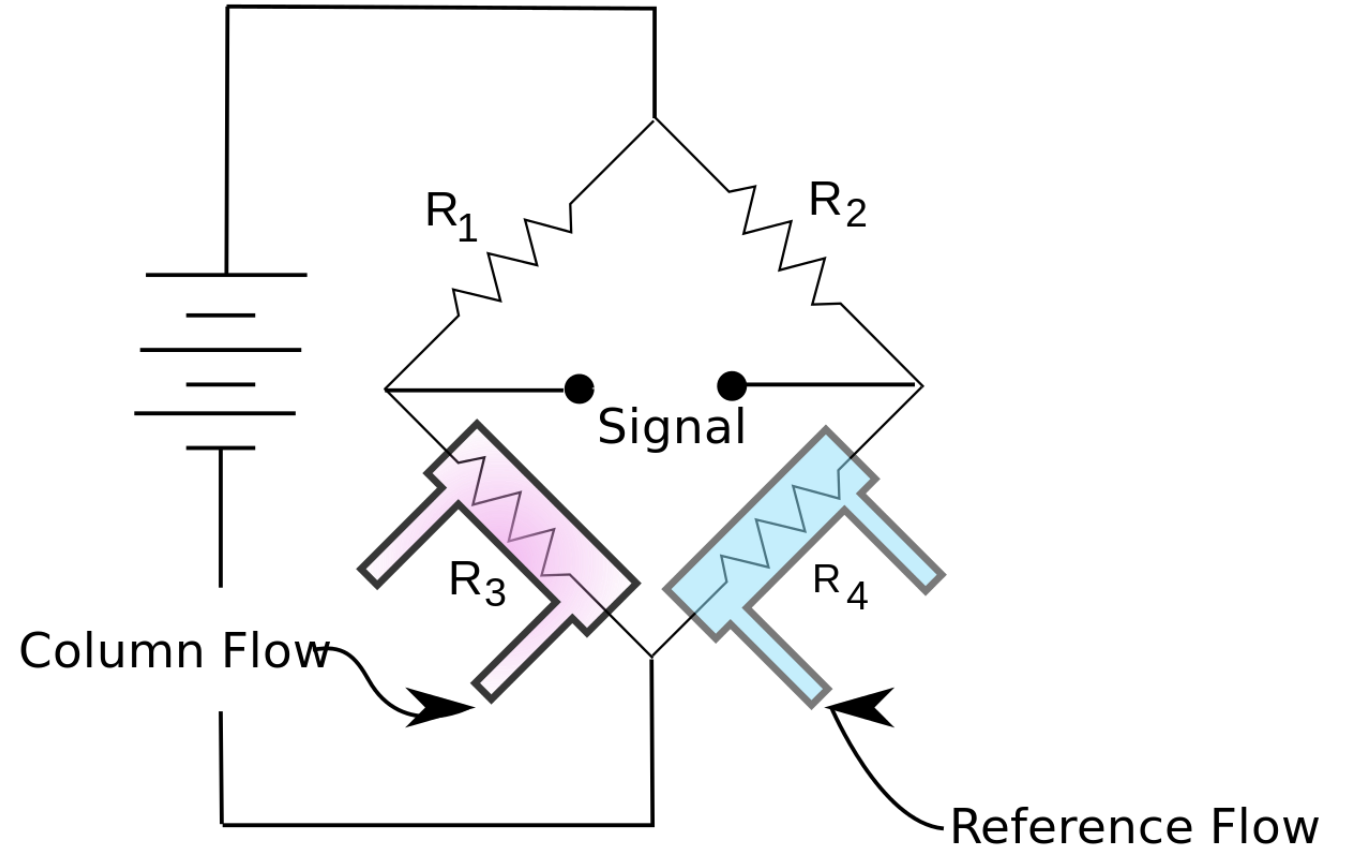


FIG. A1.1 Method 1-Reference Chromatogram with Retention Times and Peak Number

GC TECHNOLOGY: TCD

- Thermal Conductivity Detector
- Universal Detector
- Response is based on reference filament
- External standard needed



TCD Response factor

Table II. Response Factors for Thermal Conductivity Detectors.

B.P. °C	Compound	MW	Thermal Response	Weight Factor
<i>Normal Paraffins (2,3)</i>				
— 161	Methane	16	35.7	0.45
— 89	Ethane	30	51.2	0.59
— 42	Propane	44	64.5	0.68
— 0.5	Butane	58	85	0.68
+ 36	Pentane	72	105	0.69
68	Hexane	86	123	0.70
98	Heptane	100	143	0.70
126	Octane	114	160	0.71
151	Nonane	128	177	0.72
174	Decane	142	199	0.71
196	Undecane	156	198	0.79
254	Tetradecane	198	234	0.85
	C ₂₀ -C ₃₆	—	—	0.72
<i>Branched Paraffins (2,3)</i>				
— 12	Isobutane	58	82	0.710
+ 28	Isopentane	72	102	0.707
10	Neopentane	72	99	0.727
50	2,2-Dimethylbutane	86	116	0.741
58	2,3-Dimethylbutane	86	116	0.741
60	2-Methylpentane	86	120	0.714
63	3-Methylpentane	86	119	0.725
79	2,2-Dimethylketone	100	133	0.752
81	2,4-Dimethylpentane	100	129	0.775
90	2,3-Dimethylpentane	100	135	0.741

Response Factors for Gas Chromatographic Analyses

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Abstract

While there are many types of detectors employed in gas chromatographs, most units employ either flame ionization or thermal conductivity detectors. To obtain quantitative results from the GC trace, it is necessary to use correction factors; the amount of the correction is a function of the response of a given compound to the detecting device.

ceptions, the values are all approximately 1.0. The two exceptions are benzene 1.12, and toluene 1.07.

For other compounds, the relative sensitivity values vary appreciably. Alcohols, for example, vary from 0.23 to 0.85; acids, from 0.01 to 0.65, etc. The use of the correct relative sensitivity is, therefore, most important when dealing with nonhydrocarbons.

Flame Ionization Detectors

Relative sensitivity values for the flame ionization detector are listed in Table I. Each area is divided by the relative sensitivity to get true area. Normalizing the results gives weight percent of each component.

For hydrocarbons, with two ex-

Thermal Conductivity Detectors

Rosie and Grob (2) and others determined relative response values for many of the hydrocarbons and some oxygenated compounds to thermal conductivity detectors. They found the same thermal response for thermistors and hot wire

filaments. Further, the response values were independent of temperature, carrier gas, flow rate, and concentration. These response values have a precision of about $\pm 3\%$. A tabulation of thermal response values are shown in Table II. These values are used as follows:

Area under the curve divided by the relative response value of that compound gives a true response value. Normalizing the true response values gives the mole percent of any component. If the sample analyzed is a gas, the normalized true response values are equal to the gas volume %.

Area under the curve multiplied by the Weight Factor gives the true weight area. When these values are normalized, the results are weight percent of each compound. ■

TCD Response factor

Table II. (continued)

B.P. °C	Compound	MW	Thermal Response	Weight Factor
<i>Cycloparaffins</i>				
49	Cyclopentane	70	97	0.720
72	Methylcyclopentane	84	115	0.730
88	1,1-Dimethylcyclopentane	98	124	0.787
103	Ethylcyclopentane	98	126	0.775
100	cis-1,2-Dimethylcyclopentane	98	125	0.780
91	cis + trans-1,3-Dimethylcyclopentane	98	125	0.780
116	1,2,4-Trimethylcyclopentane (CTC)	112	136	0.825
109	1,2,4-Trimethylcyclopentane (CCT)	112	143	0.783
81	Cyclohexane	84	114	0.735
101	Methylcyclohexane	98	120	0.820
120	1,1-Dimethylcyclohexane	112	141	0.794
119-124	1,4-Dimethylcyclohexane	112	146	0.769
132	Ethylcyclohexane	112	145	0.775
155	n-Propylcyclohexane	126	158	0.800
139	1,1,3-Trimethylcyclohexane	126	139	0.907
<i>Inorganic Compounds</i>				
	Argon	40	42	0.95
	Nitrogen	28	42	0.67
	Oxygen	32	40	0.80
	Carbon dioxide	44	48	0.915
	Carbon monoxide	28	42	0.67
	Carbon tetrachloride	154	108	1.43
	Iron carbonyl (Fe(CO) ₅)	195	150	1.30
	Hydrogen sulfide	34	38	0.89
	Water	18	33	0.55
<i>Hetero Compounds</i>				
131	Pyrrole	67	86	0.780
132	Hexylamine	101	104	0.970
11	Ethyleneoxide	44	58	0.758
35	Propyleneoxide	58	80	0.730
— 62	Hydrogen sulfide	34	38	0.890
7	Methyl mercaptan	48	59	0.810
35	Ethyl mercaptan	62	87	0.720
68	1-Propanethiol	76	101	0.750
66	Tetrahydrofuran	72	83	0.870
119	Thiophane (cyclic sulfide)	88	103	0.855
165	Ethyl silicate	208	208	0.995
21	Acetaldehyde	44	65	0.680

Response Factors for Gas Chromatographic Analyses

by W. A. Dietz, Esso Research and Engineering Company
Analytical Research Division, Linden, New Jersey

Abstract

While there are many types of detectors employed in gas chromatographs, most units employ either flame ionization or thermal conductivity detectors. To obtain quantitative results from the GC trace, it is necessary to use correction factors; the amount of the correction is a function of the response of a given compound to the detecting device.

Flame Ionization Detectors

Relative sensitivity values for the flame ionization detector are listed in Table I. Each area is divided by the relative sensitivity to get true area. Normalizing the results gives weight percent of each component.

For hydrocarbons, with two ex-

ceptions, the values are all approximately 1.0. The two exceptions are benzene 1.12, and toluene 1.07.

For other compounds, the relative sensitivity values vary appreciably. Alcohols, for example, vary from 0.23 to 0.85; acids, from 0.01 to 0.65, etc. The use of the correct relative sensitivity is, therefore, most important when dealing with nonhydrocarbons.

Thermal Conductivity Detectors

Rosie and Grob (2) and others determined relative response values for many of the hydrocarbons and some oxygenated compounds to thermal conductivity detectors. They found the same thermal response for thermistors and hot wire

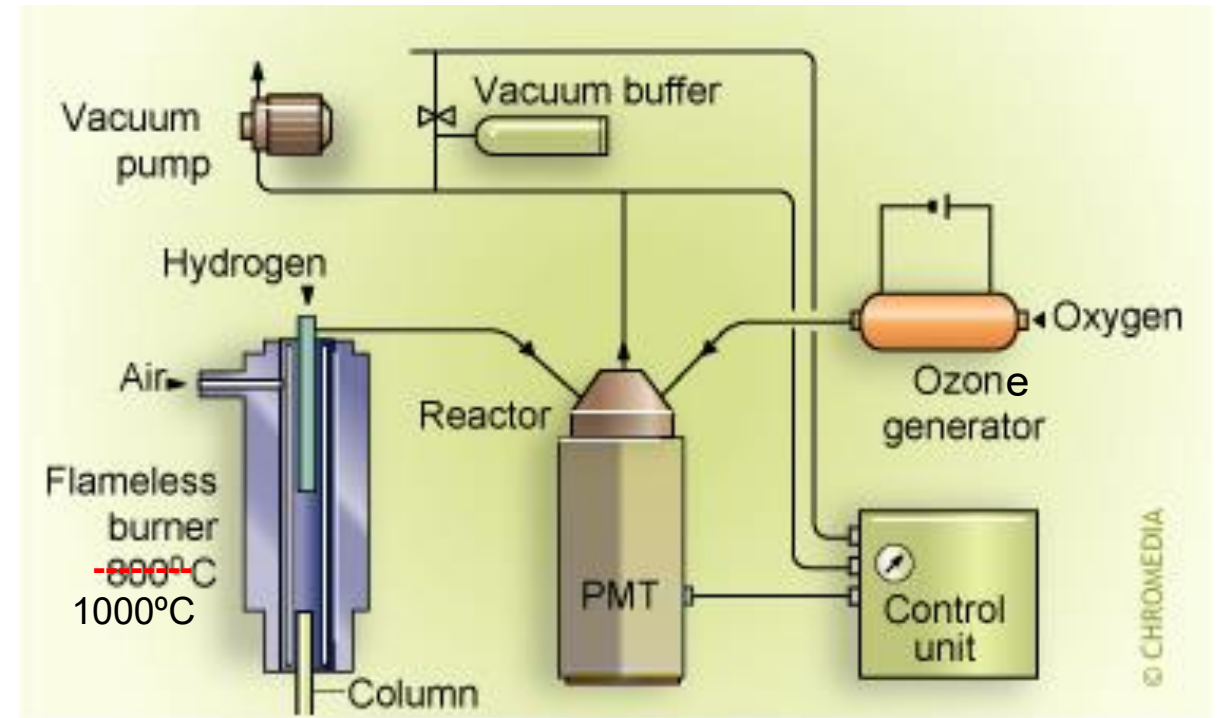
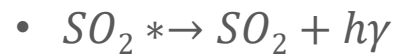
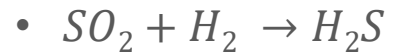
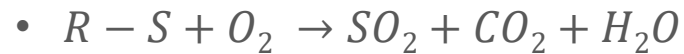
filaments. Further, the response values were independent of temperature, carrier gas, flow rate, and concentration. These response values have a precision of about $\pm 3\%$. A tabulation of thermal response values are shown in Table II. These values are used as follows:

Area under the curve divided by the relative response value of that compound gives a true response value. Normalizing the true response values gives the mole percent of any component. If the sample analyzed is a gas, the normalized true response values are equal to the gas volume %.

Area under the curve multiplied by the Weight Factor gives the true weight area. When these values are normalized, the results are weight percent of each compound. ■

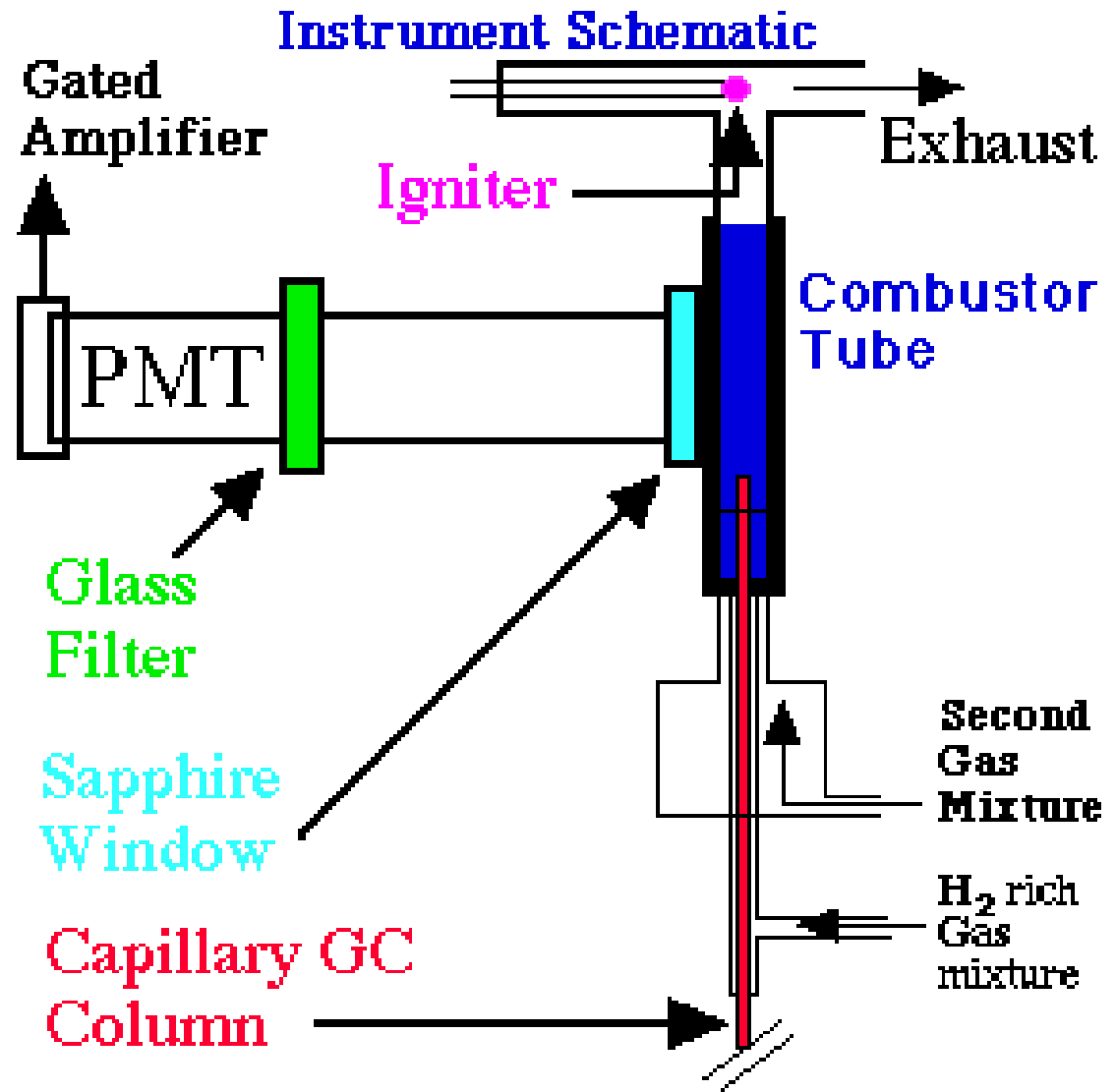
GC TECHNOLOGY: SCD

- Sulfur Chemiluminescence Detector
- Sulfur specific detector
- Response is equimolar for all sulfur
- External Standard calibration needed, but only one sulfur-containing compound necessary

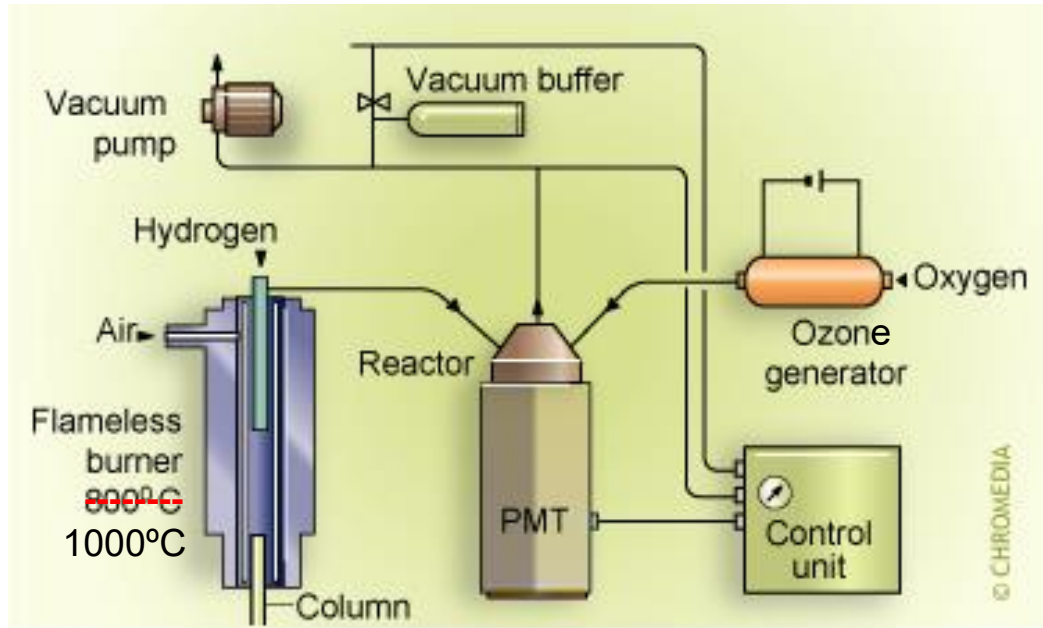


GC TECHNOLOGY: FPD/PFPD

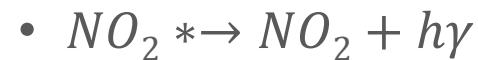
- Pulsed Flame Photometric Detector
- Multielement specific detector, up to 28
S, P, N, As, Se, Sn, Ge, Ga, Sb, Te, Br, Cu, In, Mn, Fe, Ru, Rh, Cr, Ni, Eu, V, W, B, Si, Al, Pb, Bi and C
- Response is proportionally related to the square root of the mass
- External Standard Needed



GC TECHNOLOGY: NCD

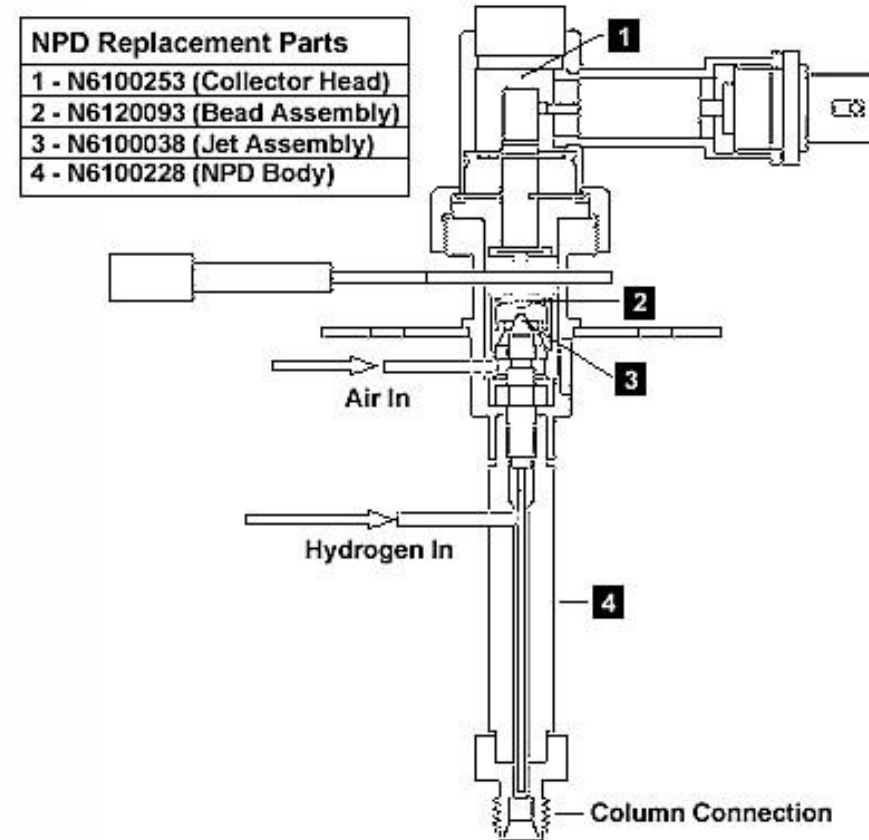


- Nitrogen Chemiluminescence Detector
- Nitrogen specific detector
- Response is equimolar for all nitrogen
- External standard needed but only one nitrogen-containing compound necessary



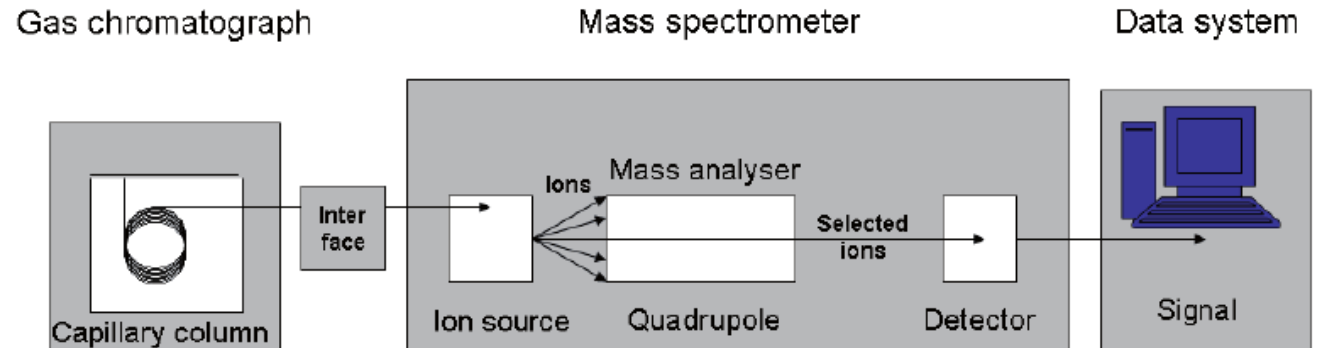
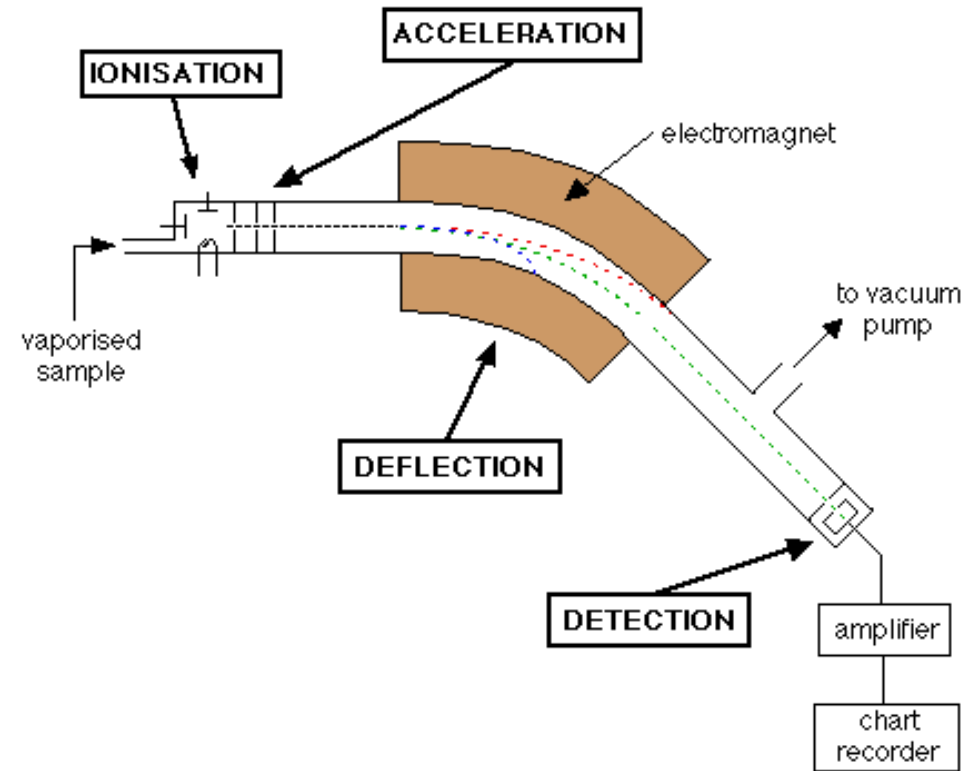
GC TECHNOLOGY: TSD/NPD

- Thermionic Specific Detector
- Nitrogen and Phosphorous specific detector
- Response is based on ionization



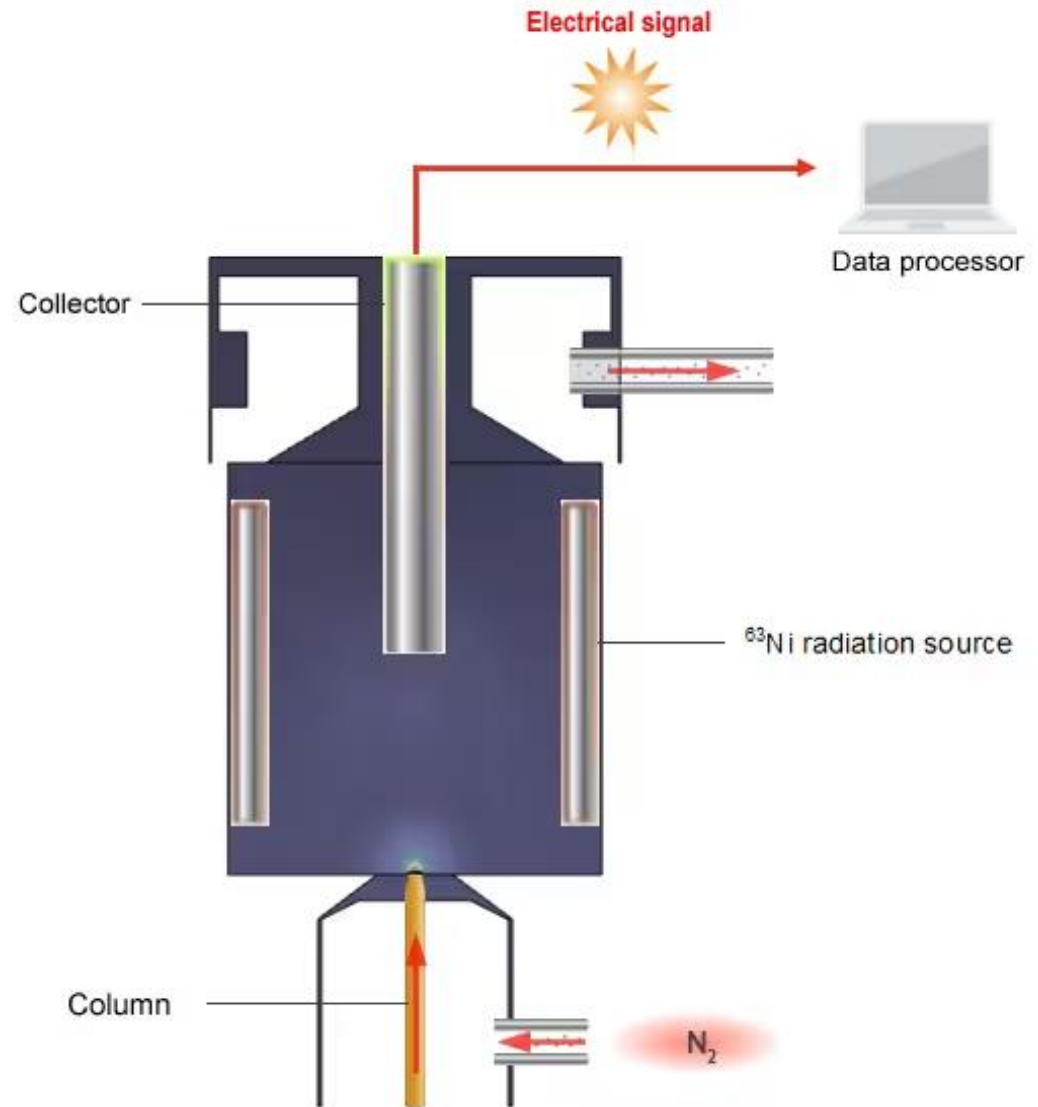
GC TECHNOLOGY: MS

- Mass Spectrometer Detector
- Mass selective detector
- Response is based on ionization
- **Stage 1: Ionization**
- **Stage 2: Acceleration:**
- **Stage 3: Deflection:**
- **Stage 4: Detection**



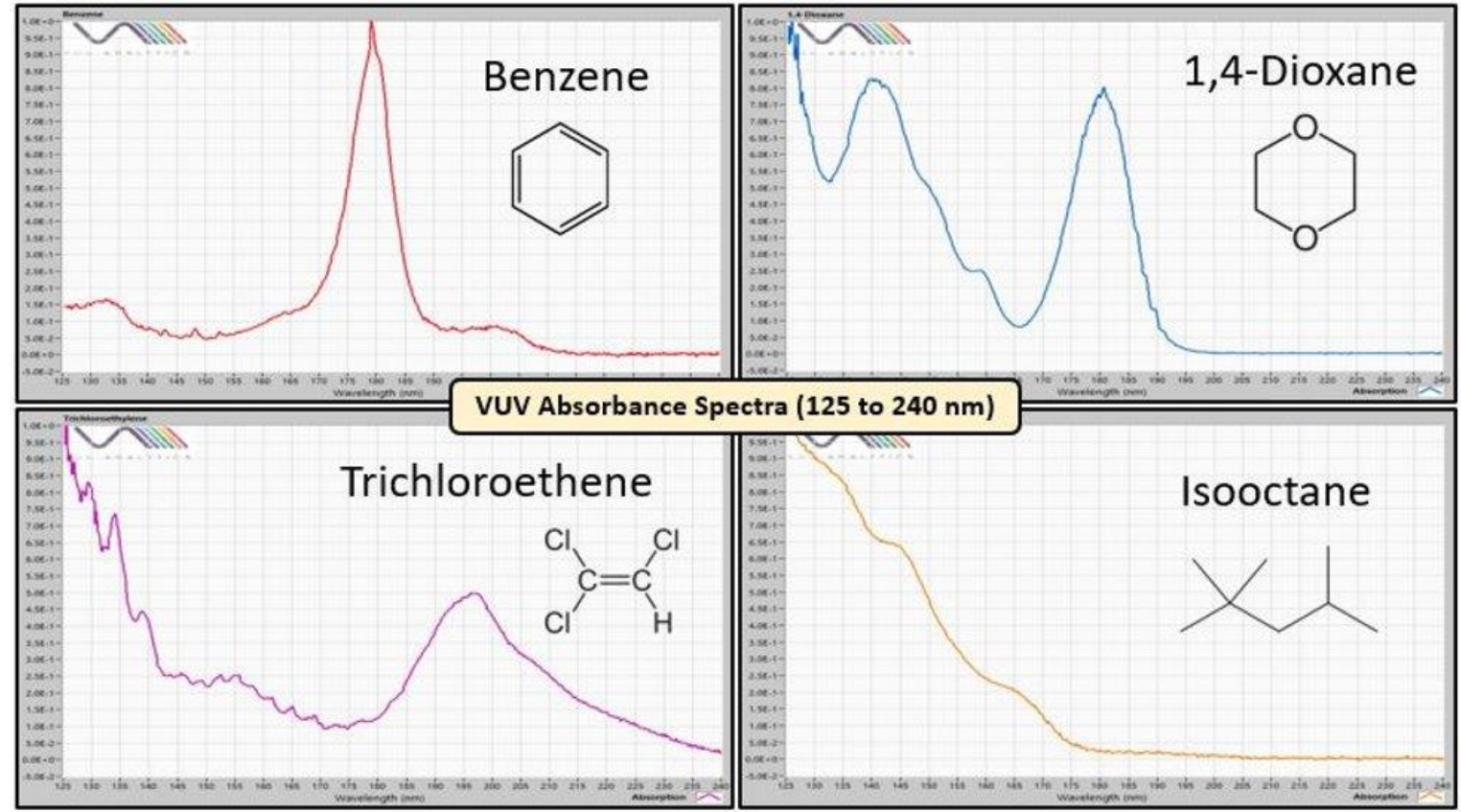
GC TECHNOLOGY: ECD

- Electron Capture Detector
- Detect organic halogen compounds
- Has a radioactive source
- Compound of interest absorbs electron and reduce the number of electrons the collectors sees



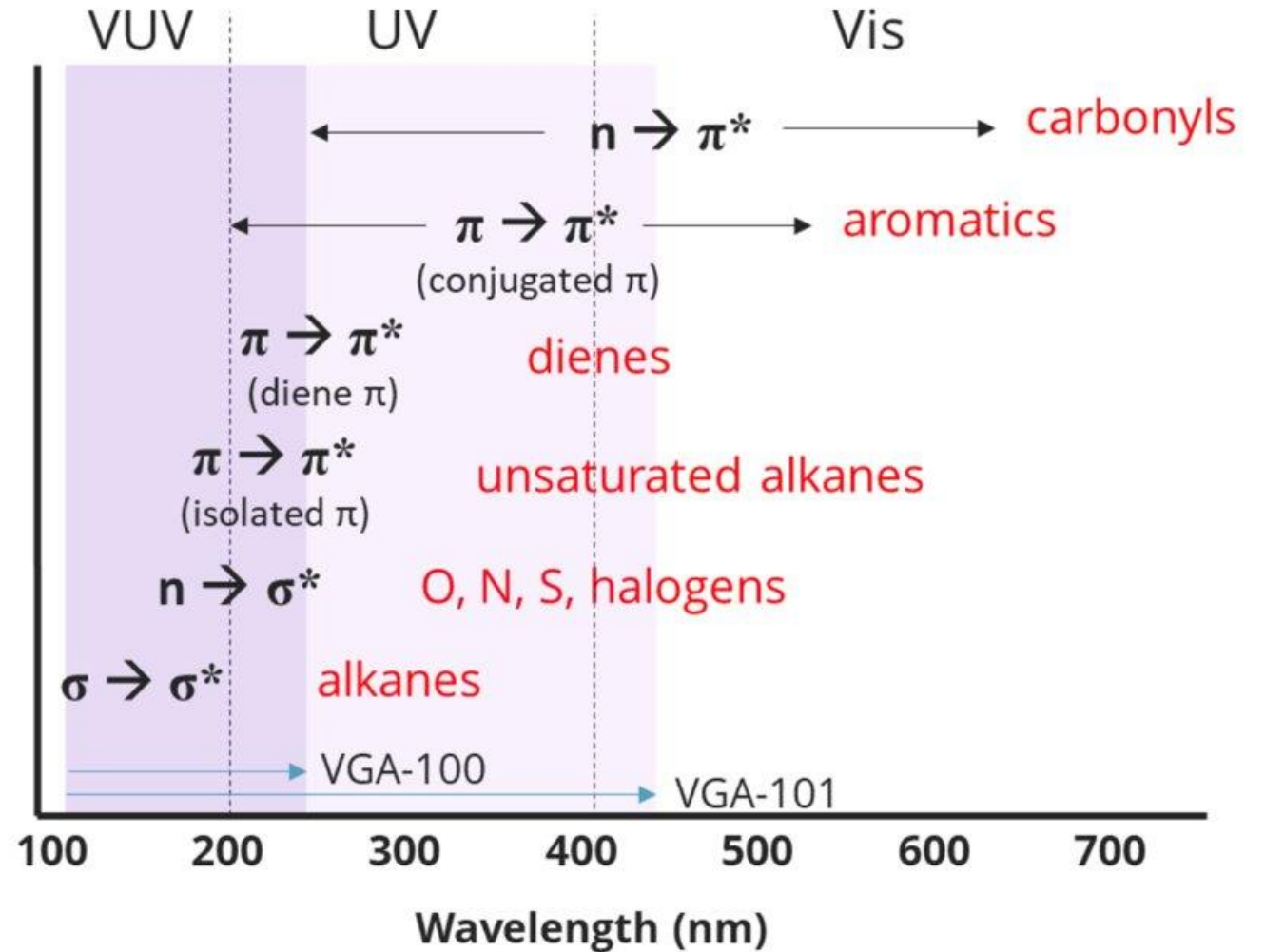
GC TECHNOLOGY: VUV

- Vacuum Ultraviolet Detector
- Nearly Universal Detector



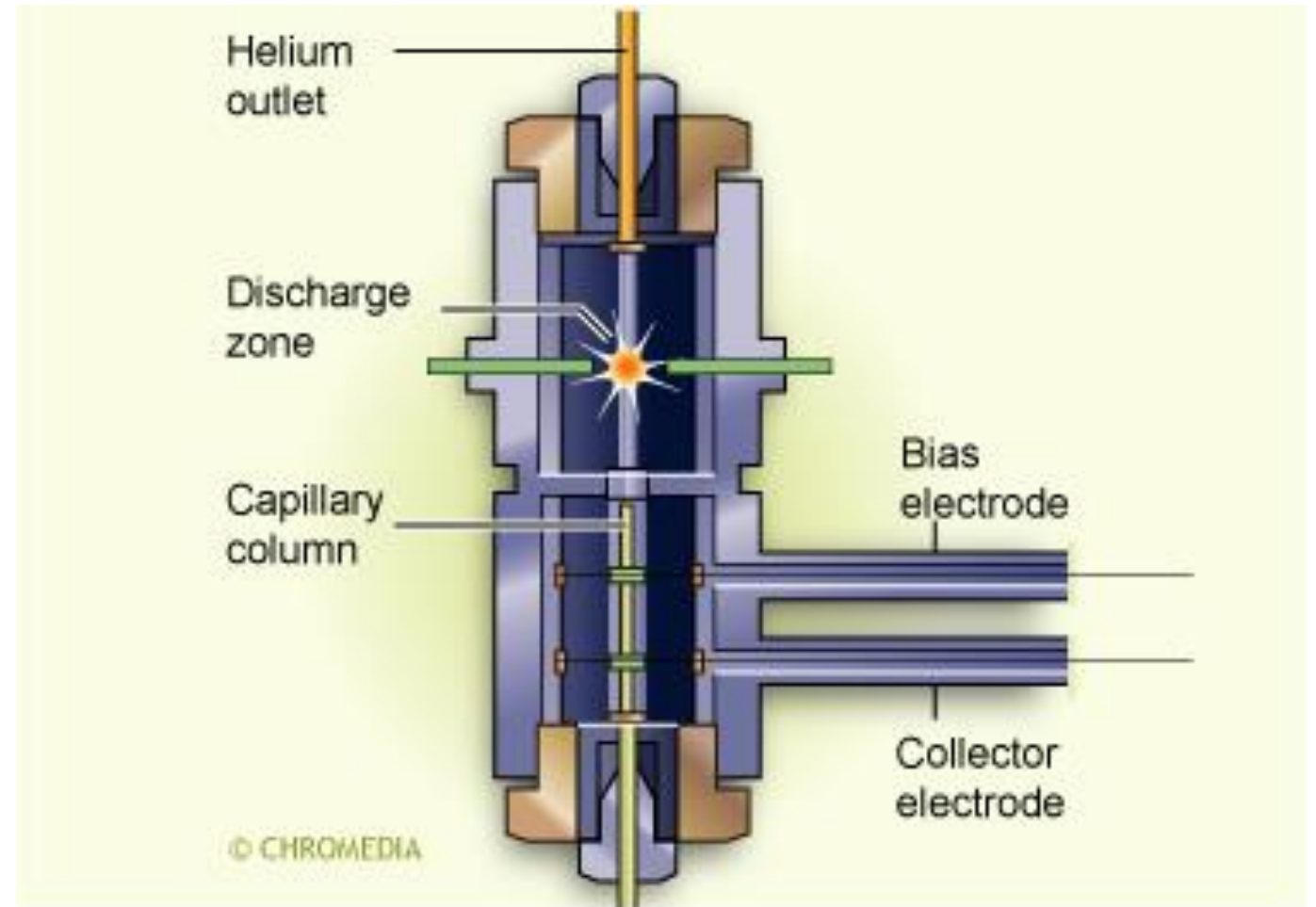
GC TECHNOLOGY: VUV

- Vacuum Ultraviolet Detector
- Nearly Universal Detector



GC TECHNOLOGY: HID

- Helium Ionization Detector
 BID
 PDHID
 PDD
- Ultra trace analysis
- Has a beta-emitter radioactive source
- Excited helium atoms produce a secondary ionization of the compound of interest.



GC TECHNOLOGY: OTHER DETECTORS

BID
Barrier Discharge Ionization
Detector

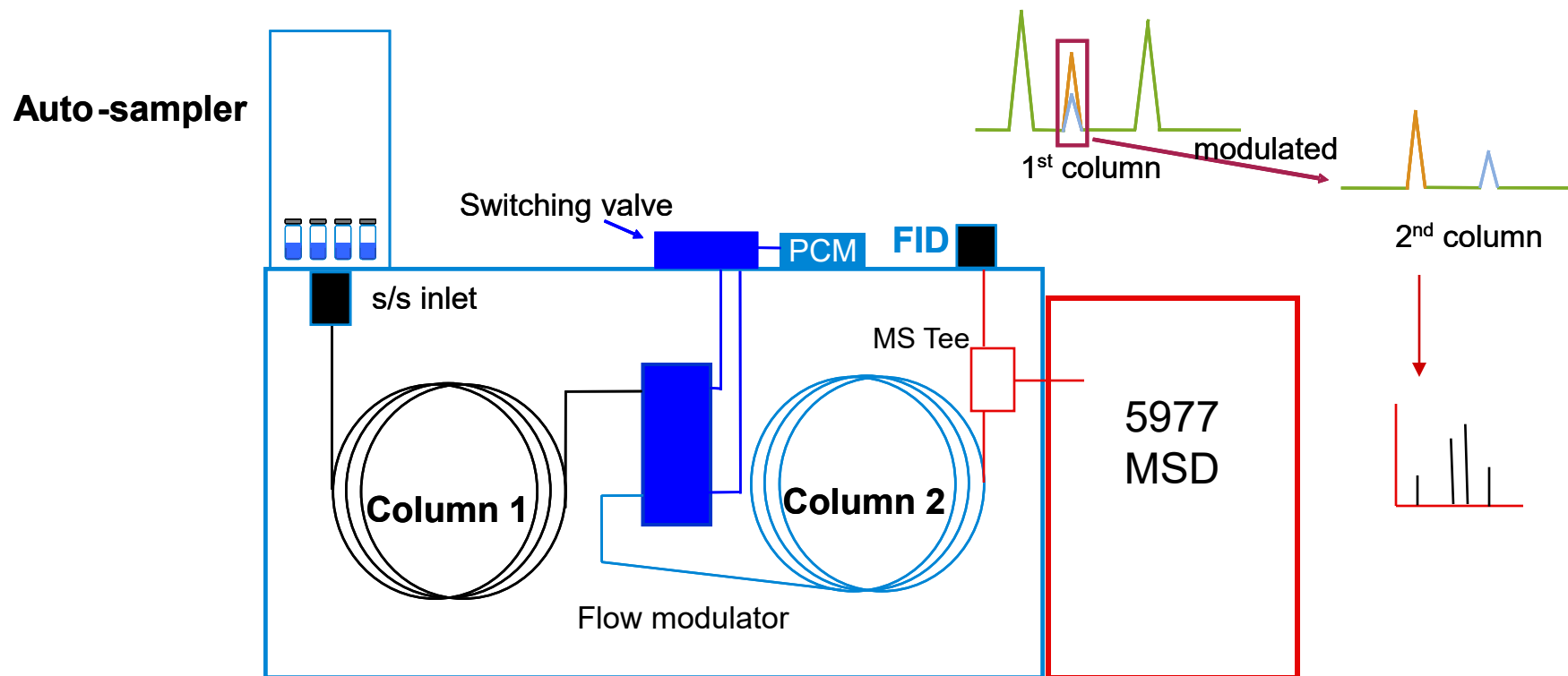
HID
Helium Discharge Ionization
Detector

PDD
Pulsed Discharge Detector

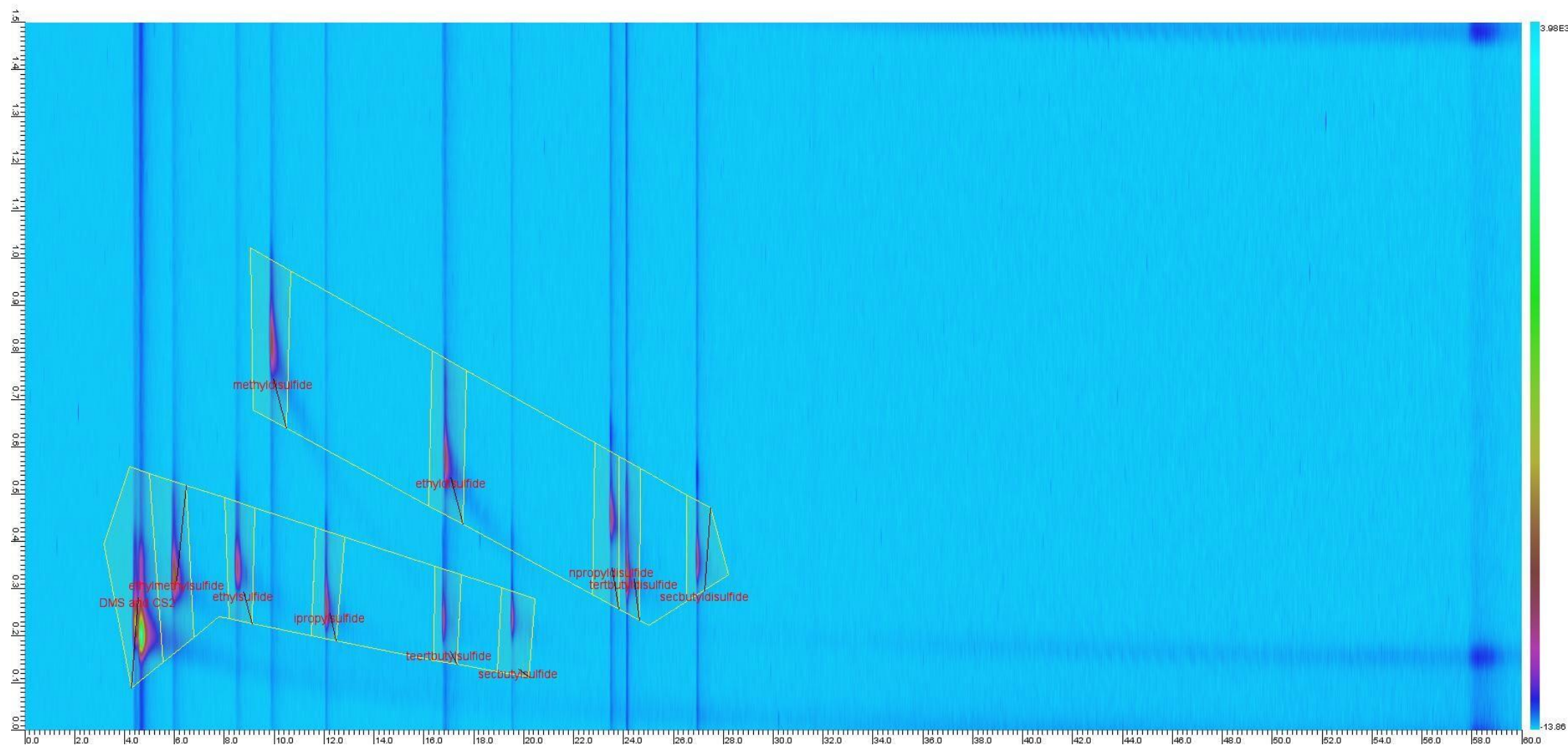
GC TECHNOLOGY

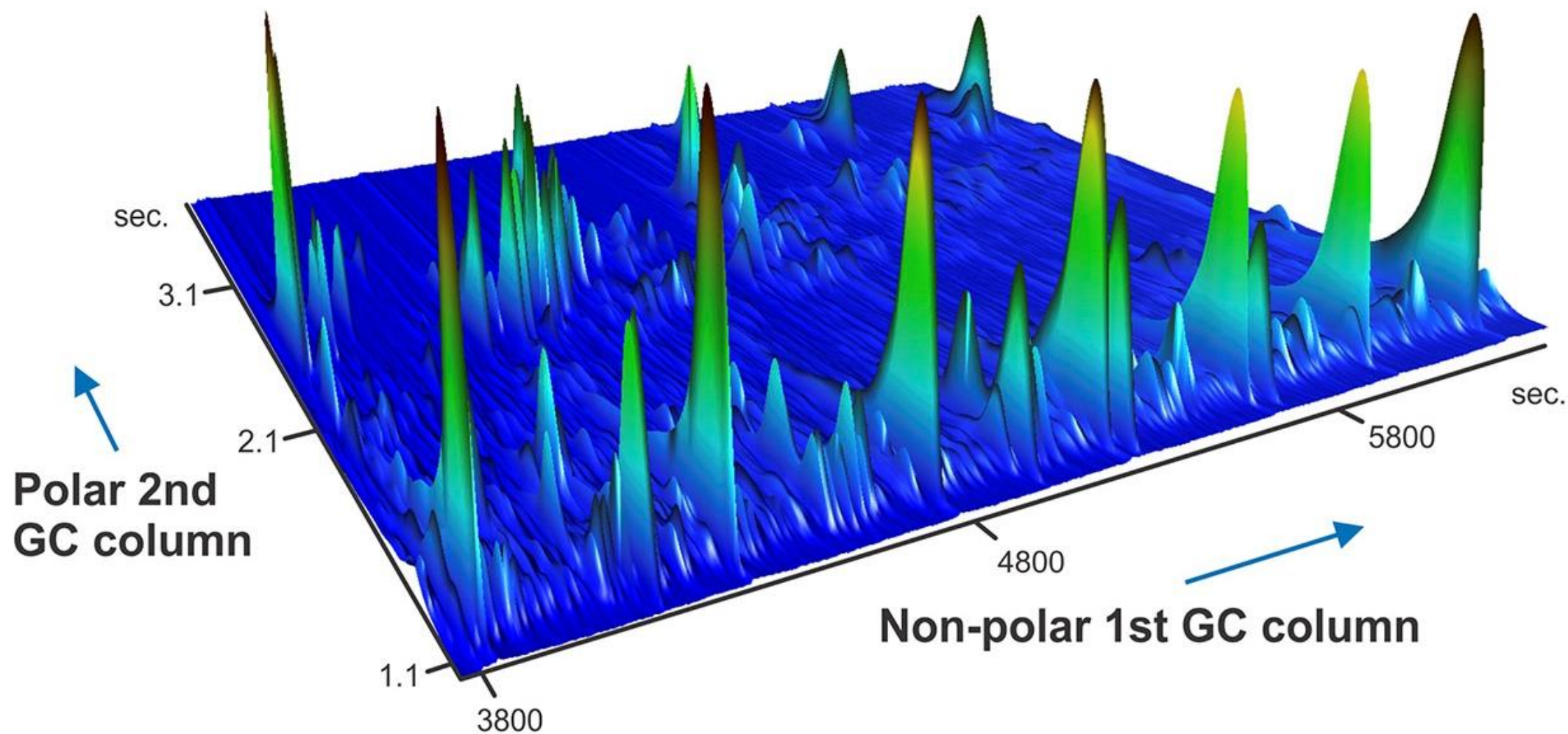
GC x GC

Basic system layout for GCxGC FID/MSD



GC x GC - SCD





The power of GC×GC-TOFMS for your samples!

CHEMISTRY
IS LIKE COOKING



JUST DON'T LICK THE SPOON

GC TECHNOLOGY: CALCULATIONS

Normalization

- Using theoretical response factor or calculated response factors, the total is equal to 100%

External Standard

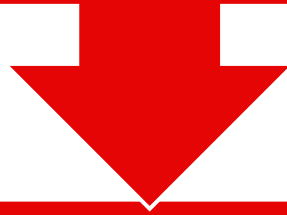
- Peak area is compared to a known standard and used to calculate a response factor

Internal Standard

- A known amount of non-interfering compound is added to the sample and is used to calculate the amount of the components

GC TECHNOLOGY: INTERNAL STANDARD (ISTD)

Since the ratio of concentration between an ISTD and an analyte remains constant, even when instrument drift or sample is lost during treatment, the ratio of concentrations (analyte concentration / ISTD concentration) remain the constant.



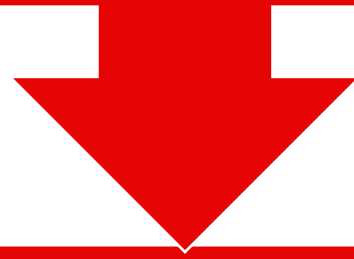
To use the ISTD method:

Solutions of known concentration of the analyte are prepared	To each of those standards a known and similar amount of the internal standard solution	Similar amount of the internal standard is added to the samples too	Instrumental signal of the analyte and the internal standard are recorded	Ratio of analyte signal/internal standard signal are plotted against the concentration of the analyte in the standard solutions	Ratio of analyte signal in the sample / internal standard is calculated	A linear equation ($y=mx + b$) is obtained Concentration of the analyte is calculated by solving for x when y is the ratio of analyte signal/internal standard signal in the unknown sample	Either one standard or several standards, to create a calibration curve, may be used.
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GC TECHNOLOGY: EXTERNAL STANDARD (ESTD)

An ESTD quantitation uses a known data from a calibration standard and unknown data from the sample are combined to generate a quantitative report.

It is called external standard because the standard material is external to the unknown material.



ESTD Response Factor Calculation:

$$RF = (A_x) / (C_x)$$

A_x = Area of the compound

C_x = Concentration of the compound

SCD – External Standard

\\lms01\EZChromData\Projects\GC 51\Result\r899303c0033wac.rsl\r899303c0033wac.dat					
Back Signal Results					
Name	Retention Time	Area	ESTD concentration	CALC Resp Factor	
1propanethiol ,200,10	9.995	8177678	58.7	7.17808E-06	
nbutanethiol ,200,20	17.233	10399294	62.4	6.00041E-06	
2mthiophene ,200,22	20.559	8652322	52.1	6.0215E-06	
edisulfide ,200,37	27.492	18458636	55	2.97964E-06	
benzothiophene ,200,39	37.565	8705206	61.4	7.05325E-06	
light sulfur ,200,4		0	0		
heavy sulfur ,200,2		0	0		
Totals					
		54393136	289.6		
\\lms01\EZChromData\Projects\GC 51\Result\r899571c0033aoq.rsl\r899571c0033aoq.dat					
Back Signal Results					
Name	Retention Time	Area	ESTD concentration	n-butanethiol CALC	1propanethiol CALC
ethanethiol ,200,7	4.541	2954381			21.2
thiophene ,200,19	14.393	16890253	101.4	101.3	121.2
2mthiophene ,200,22	20.558	455228	2.7	2.7	3.3
3mthiophene ,200,23	20.943	234646	1.4	1.4	1.7
light sulfur ,200,4		0	0		
heavy sulfur ,200,2		0	0		
Totals					
		20534508	123.3		

SCD – External Standard

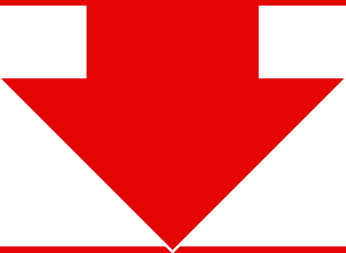
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Back Signal Results					
Name	Retention Time	Area	ESTD concentration	CALC Resp Factor	
1propanethiol ,200,10	9.995	8177678	58.7	7.17808E-06	
nbutanethiol ,200,20	17.233	10399294	62.4	6.00041E-06	
2mthiophene ,200,22	20.559	8652322	52.1	6.0215E-06	
edisulfide ,200,37	27.492	18458636	55	2.97964E-06	
benzothiophene ,200,39	37.565	8705206	61.4	7.05325E-06	
light sulfur ,200,4		0	0		
heavy sulfur ,200,2		0	0		
Totals					
		54393136	289.6		
\\lms01\EZChromData\Projects\GC 51\Result\r899571c0033aoq.rsl\r899571c0033aoq.dat					
Back Signal Results					
Name	Retention Time	Area	ESTD concentration	n-butanethiol CALC	1-propanethiol CALC
ethanethiol ,200,7	4.541	2954381	17.7	17.7	21.2
thiophene ,200,19	14.393	16890253	101.4	101.3	121.2
2mthiophene ,200,22	20.558	455228	2.7	2.7	3.3
3mthiophene ,200,23	20.943	234646	1.4	1.4	1.7
light sulfur ,200,4		0	0		
heavy sulfur ,200,2		0	0		
Totals					
		20534508	123.3		

SCD – External Standard

\\lms01\EZChromData\Projects\GC 51\Result\r899303c0033wac.rsl\r899303c0033wac.dat					
Back Signal Results					
Name	Retention Time	Area	ESTD concentration	CALC Resp Factor	
1propanethiol ,200,10	9.995	8177678	58.7	7.17808E-06	
nbutanethiol ,200,20	17.233	10399294	62.4	6.00041E-06	
2mthiophene ,200,22	20.559	8652322	52.1	6.0215E-06	
edisulfide ,200,37	27.492	18458636	55	2.97964E-06	
benzothiophene ,200,39	37.565	8705206	61.4	7.05325E-06	
light sulfur ,200,4		0	0		
heavy sulfur ,200,2		0	0		
Totals					
		54393136	289.6		
\\lms01\EZChromData\Projects\GC 51\Result\r899571c0033aoq.rsl\r899571c0033aoq.dat					
Back Signal Results					
Name	Retention Time	Area	ESTD concentration	n-butanethiol CALC	1-propanethiol CALC
ethanethiol ,200,7	4.541	2954381	17.7	17.7	21.2
thiophene ,200,19	14.393	16890253	101.4	101.3	121.2
2mthiophene ,200,22	20.558	455228	2.7	2.7	3.3
3mthiophene ,200,23	20.943	234646	1.4	1.4	1.7
light sulfur ,200,4		0	0		
heavy sulfur ,200,2		0	0		
Totals					
		20534508	123.3		

GC TECHNOLOGY: NORMALIZATION

Different components have different response factors to compensates for different detector response for different components. These factors may be calculated by preparing a synthetic mixture or by calculating a theoretical response factor.



Normalization Calculation:

$$\% X = \frac{Ax \cdot fx}{\Sigma Af} \times 100$$

$$\frac{Ax \text{ is Area} \cdot fx \text{ is response factor}}{\Sigma Af \text{ is Sum of all RF modified areas}} \times 100$$

FID - Normalization

\\lms01\EZChromData\Projects\GC 46\Result\r898280c0039udk.rsl\r898280c0039udk.dat					
Back Signal Results					
Name	Retention Time	Area	RRF	NORM Area	NORM concentration
ethene ,100,28	13.233	197236	0.966		
		24383	1		
propane ,100,34	15.875	4542	1.01		
isobutane ,100,48	20.313	146189	1		
1butene ,100,40	23.303	10481868	0.966		
		8852	1		
nbutane ,100,49	24.515	122391584	1		
		16738	1		
t2butene ,100,45	25.868	155159516	0.966		
		226016	1		
22dmpropane ,100, 69	26.562	21733	0.994		
c2butene ,100,42	27.484	69035406	0.966		
isopentane ,100,71	32.432	4068	0.994		
2m2butene ,100,62	36.172	13229	0.966		
3m1pentene ,100,63	38.591	5458209	0.965		
		41	1		
23dm-butane ,100,106	39.045	6435	0.994		
2m-pentane ,100,107	39.279	35130	0.994		
3m-pentane ,100,93	40.034	99455	0.994		
1-hexene ,100,84	40.317	1830098	0.966		
n-hexane ,100,109	40.823	16327607	0.966		
		6327414	1		
t-3-hexene ,100,102	40.937	8337254	0.966		
c-3-hexene ,100,95	41.005	1219428	0.966		
t-2-hexene ,100,101	41.065	17768128	0.966		
				405415994	100.0000

FID - Normalization

\\lms01\EZChromData\Projects\GC 46\Result\r898280c0039udk.rsl\r898280c0039udk.dat					
Back Signal Results					
Name	Retention Time	Area	RRF	NORM Area	NORM concentration
ethene ,100,28	13.233	197236	0.966	190529.976	
		24383	1	24383	
propane ,100,34	15.875	4542	1.01	4587.42	
isobutane ,100,48	20.313	146189	1	146189	
1butene ,100,40	23.303	10481868	0.966	10125484.49	
		8852	1	8852	
nbutane ,100,49	24.515	122391584	1	122391584	
		16738	1	16738	
t2butene ,100,45	25.868	155159516	0.966	149884092.5	
		226016	1	226016	
22dmpropane ,100, 69	26.562	21733	0.994	21602.602	
c2butene ,100,42	27.484	69035406	0.966	66688202.2	
isopentane ,100,71	32.432	4068	0.994	4043.592	
2m2butene ,100,62	36.172	13229	0.966	12779.214	
3m1pentene ,100,63	38.591	5458209	0.965	5267171.685	
		41	1	41	
23dm-butane ,100,106	39.045	6435	0.994	6396.39	
2m-pentane ,100,107	39.279	35130	0.994	34919.22	
3m-pentane ,100,93	40.034	99455	0.994	98858.27	
1-hexene ,100,84	40.317	1830098	0.966	1767874.668	
n-hexane ,100,109	40.823	16327607	0.966	15772468.36	
		6327414	1	6327414	
t-3-hexene ,100,102	40.937	8337254	0.966	8053787.364	
c-3-hexene ,100,95	41.005	1219428	0.966	1177967.448	
t-2-hexene ,100,101	41.065	17768128	0.966	17164011.65	
				405415994	100.0000

FID - Normalization

\\lms01\EZChromData\Projects\GC 46\Result\r898280c0039udk.rsl\r898280c0039udk.dat					
Back Signal Results					
Name	Retention Time	Area	RRF	NORM Area	NORM concentration
ethene ,100,28	13.233	197236	0.966	190529.976	0.0470
		24383	1	24383	0.0060
propane ,100,34	15.875	4542	1.01	4587.42	0.0011
isobutane ,100,48	20.313	146189	1	146189	0.0361
1butene ,100,40	23.303	10481868	0.966	10125484.49	2.4976
		8852	1	8852	0.0022
nbutane ,100,49	24.515	122391584	1	122391584	30.1891
		16738	1	16738	0.0041
t2butene ,100,45	25.868	155159516	0.966	149884092.5	36.9704
		226016	1	226016	0.0557
22dmpropane ,100, 69	26.562	21733	0.994	21602.602	0.0053
c2butene ,100,42	27.484	69035406	0.966	66688202.2	16.4493
isopentane ,100,71	32.432	4068	0.994	4043.592	0.0010
2m2butene ,100,62	36.172	13229	0.966	12779.214	0.0032
3m1pentene ,100,63	38.591	5458209	0.965	5267171.685	1.2992
		41	1	41	0.0000
23dm-butane ,100,106	39.045	6435	0.994	6396.39	0.0016
2m-pentane ,100,107	39.279	35130	0.994	34919.22	0.0086
3m-pentane ,100,93	40.034	99455	0.994	98858.27	0.0244
1-hexene ,100,84	40.317	1830098	0.966	1767874.668	0.4361
n-hexane ,100,109	40.823	16327607	0.966	15772468.36	3.8904
		6327414	1	6327414	1.5607
t-3-hexene ,100,102	40.937	8337254	0.966	8053787.364	1.9865
c-3-hexene ,100,95	41.005	1219428	0.966	1177967.448	0.2906
t-2-hexene ,100,101	41.065	17768128	0.966	17164011.65	4.2337
				405415994	100.0000

BASIC GC EVENT FLOW

Sample Introduction

Liquid/Gas Valve

Syringe

Manual/Automatic

Component Detection

Flame “FID”

Thermal “TCD”

Sulfur “SCD”, “FPD”

Many Others

Separation Process

Capillary Column

Packed Column

Multi-Valve/Column

Data Handling

References

Calibration

Quantification

LIQUID CHROMATOGRAPHY

Characterization of complex mixtures

- ability to separate, identify, and quantitate the compounds that are present in any sample that can be dissolved in a liquid

Applications cover analysis of Liquid streams

- Pharmaceuticals
- Food
- Nutraceuticals
- Cosmetics
- Environmental matrices
- Forensic samples
- Industrial chemicals.

Types of HPLC

Normal phase:

Column packing is polar (e.g. silica) and the mobile phase is non-polar. It is used for water-sensitive compounds, geometric isomers, cis-trans isomers, and chiral compounds.

Reverse phase:

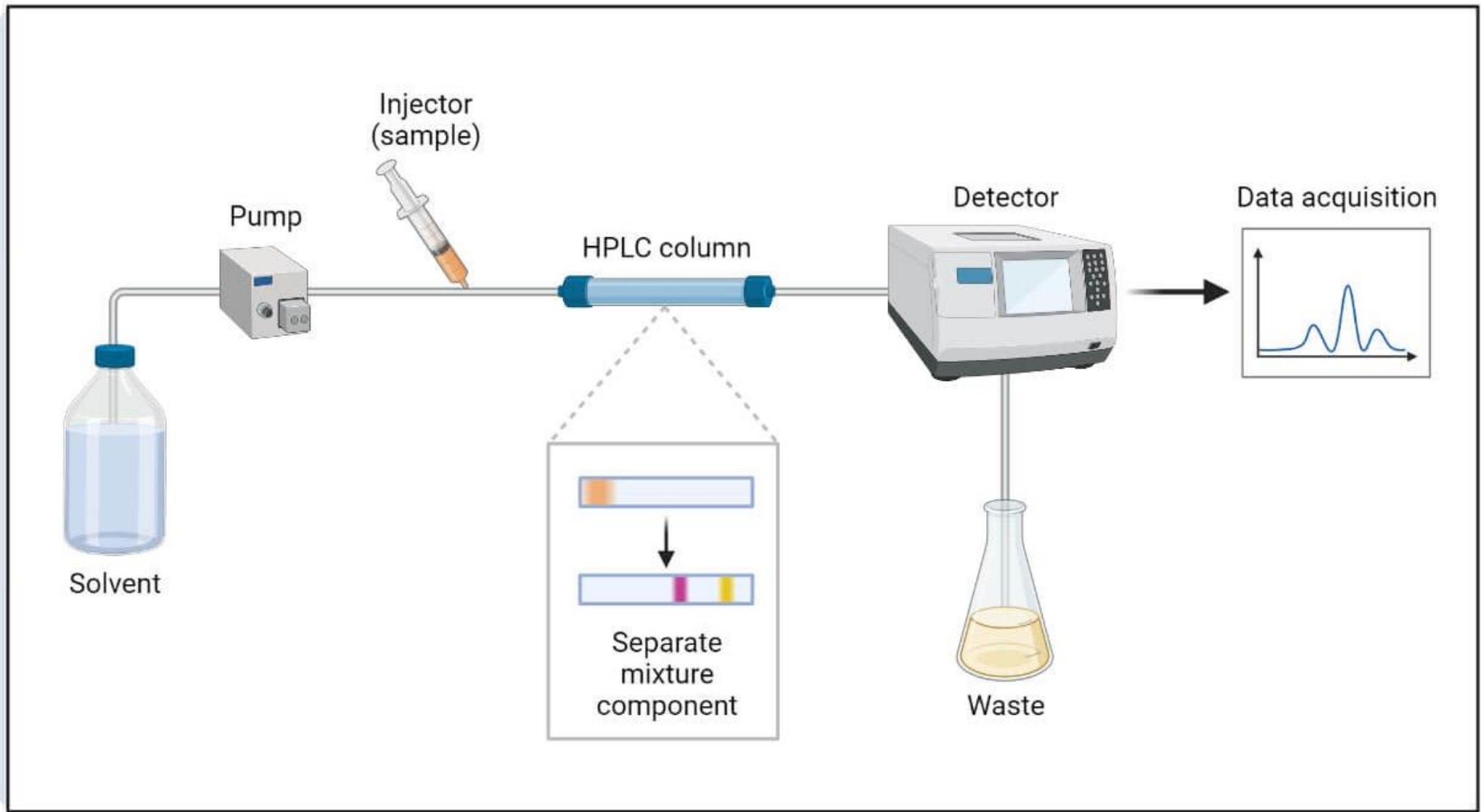
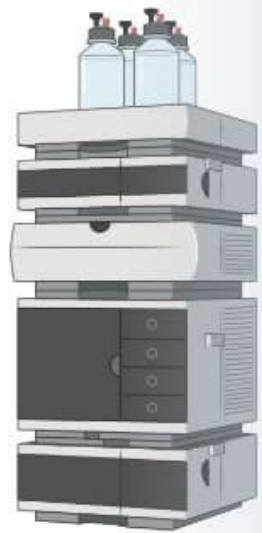
The column packing is non-polar (e.g. C18), the mobile phase is water + miscible solvent (e.g. methanol). It can be used for polar, non-polar, ionizable, and ionic samples.

Ion exchange:

Column packing contains ionic groups, and the mobile phase is buffer. It is used to separate anions and cations.

Size exclusion:

Molecules diffuse into pores of a porous medium and are separated according to their relative size to the pore size. Large molecules elute first and smaller molecules elute later.



The Pump



The development of HPLC led to the development of the pump system.



The pump is positioned in the most upper stream of the liquid chromatography system and generates a flow of eluent from the solvent reservoir into the system.

High-pressure generation is a “standard” requirement of pumps besides which, it should also be able to provide a consistent pressure at any condition and a controllable and reproducible flow rate.



Most pumps used in current LC systems generate the flow by back-and-forth motion of a motor-driven piston (reciprocating pumps). Because of this piston motion, it produces “pulses”.

The Injector

An injector is placed next to the pump.

The simplest method is to use a syringe, and the sample is introduced to the flow of eluent.

The most widely used injection method is based on sampling loops.

The use of the autosampler (auto-injector) system is also widely used that allows repeated injections in a set scheduled-timing.

The Column

The separation is performed inside the column.

The recent columns are often prepared in a stainless-steel housing, instead of glass columns.

The packing material generally used is silica or polymer gels compared to calcium carbonate.

The eluent used for LC varies from acidic to basic solvents.

Most column housing is made of stainless steel since stainless is tolerant towards a large variety of solvents.

The Detector

Separation of analytes is performed inside the column, whereas a detector is used to observe the obtained separation.

The composition of the eluent is consistent when no analyte is present. While the presence of analyte changes the composition of the eluent. What the detector does is to measure these differences.

This difference is monitored as a form of an electronic signal. There are different types of detectors available.

The Degasser

The eluent used for LC analysis may contain gases such as oxygen that are non-visible to our eyes.

When gas is present in the eluent, this is detected as noise and causes an unstable baseline.

Degasser uses special polymer membrane tubing to remove gases.

The numerous very small pores on the surface of the polymer tube allow the air to go through while preventing any liquid to go through the pore.

The Column Heater

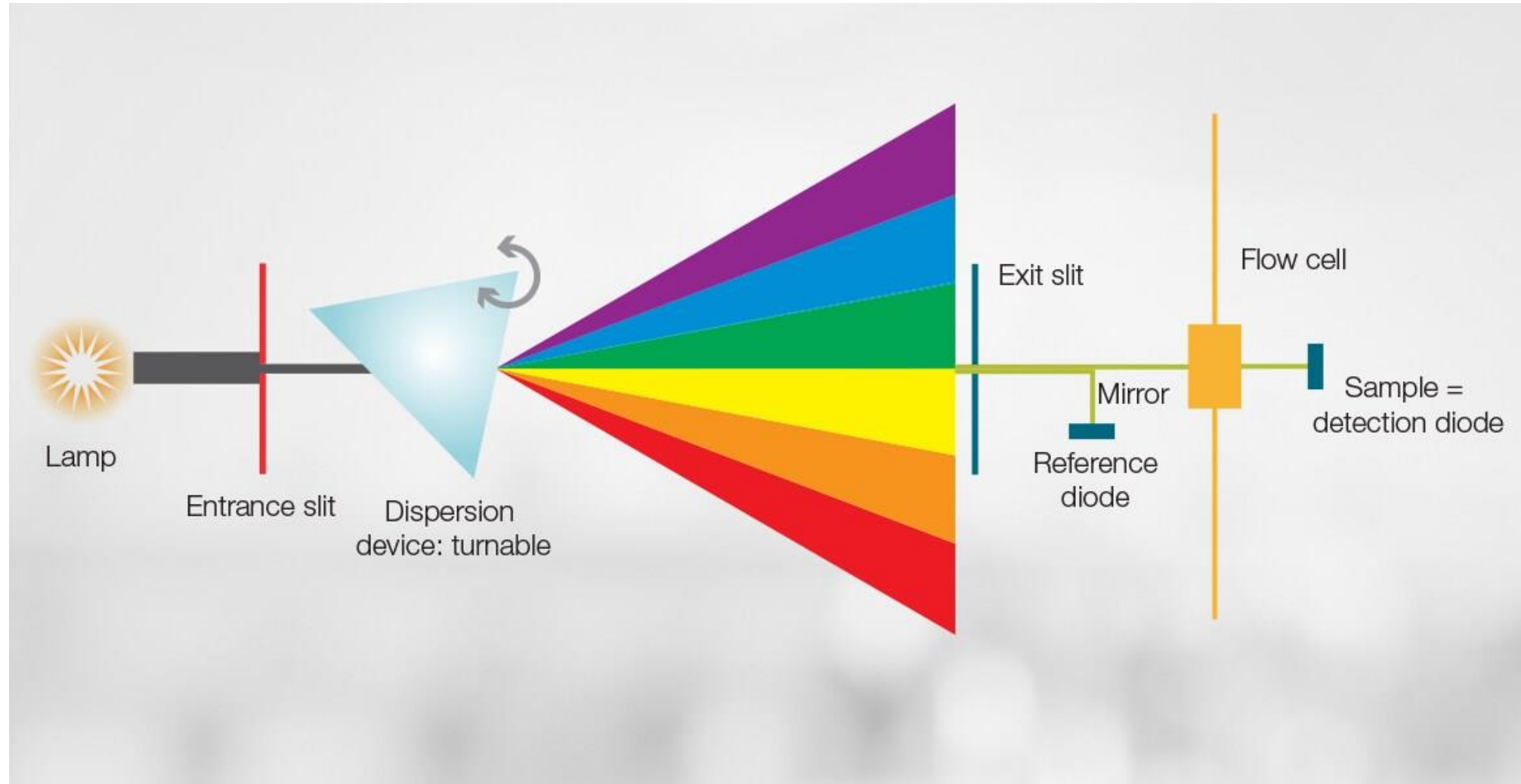
The LC separation is often largely influenced by the column temperature.

In order to obtain repeatable results, it is important to keep consistent temperature conditions.

Also for some analysis, such as sugar and organic acid, better resolutions can be obtained at elevated temperatures (50 to 80°C).

Thus columns are generally kept inside the column oven (column heater).

HPLC Detectors – UV-Vis – Variable wavelength



HPLC Detectors – UV-Vis – Variable wavelength



A variable wavelength detector uses a rotating grating to disperse polychromatic light into the spectrum. The light of a single wavelength is then selected and passed through the exit slit.



After the light passes through the exit slit, a beam splitter or semipermeable mirror divides the beam into two parts:

one part of the light goes to a reference diode to measure the intensity without absorption.

The second part passes through the flow cell, where the sample partially absorbs the light. The intensity of the remaining light is measured by the detection photodiode and translated into a quantitative signal.

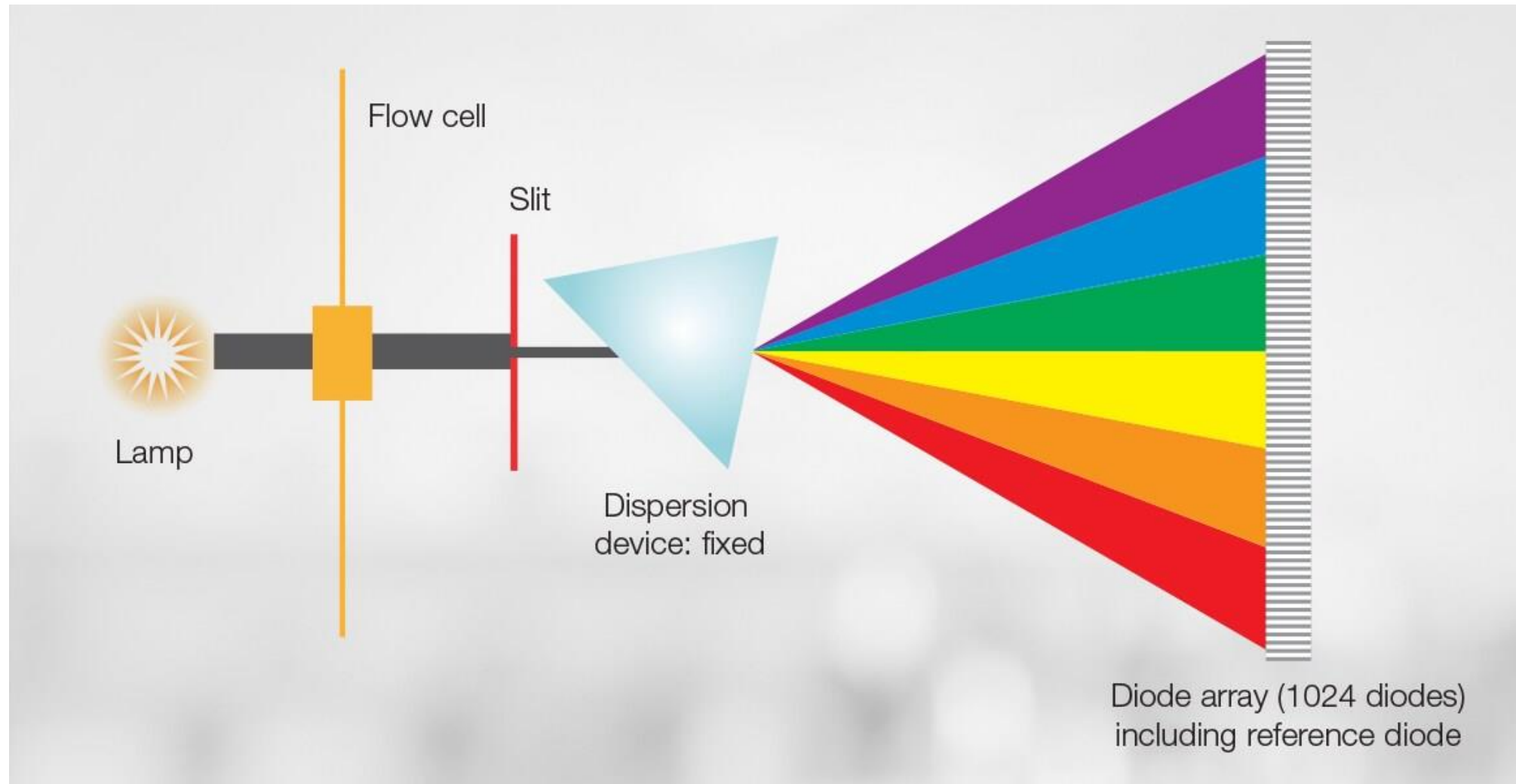


By selecting a wavelength before exposing the sample, light from one wavelength is used to measure the absorption. This detection method offers high sensitivity due to the simultaneous measurement of an actual reference and reduces the total light exposure of the sample during detection.



The enhanced sensitivity of a VWD versus a DAD is essential for light-sensitive compounds.

HPLC Detectors – UV-Vis – Diode Array



HPLC Detectors – UV-Vis – Diode Array



How diode array and multiple wavelength detectors work

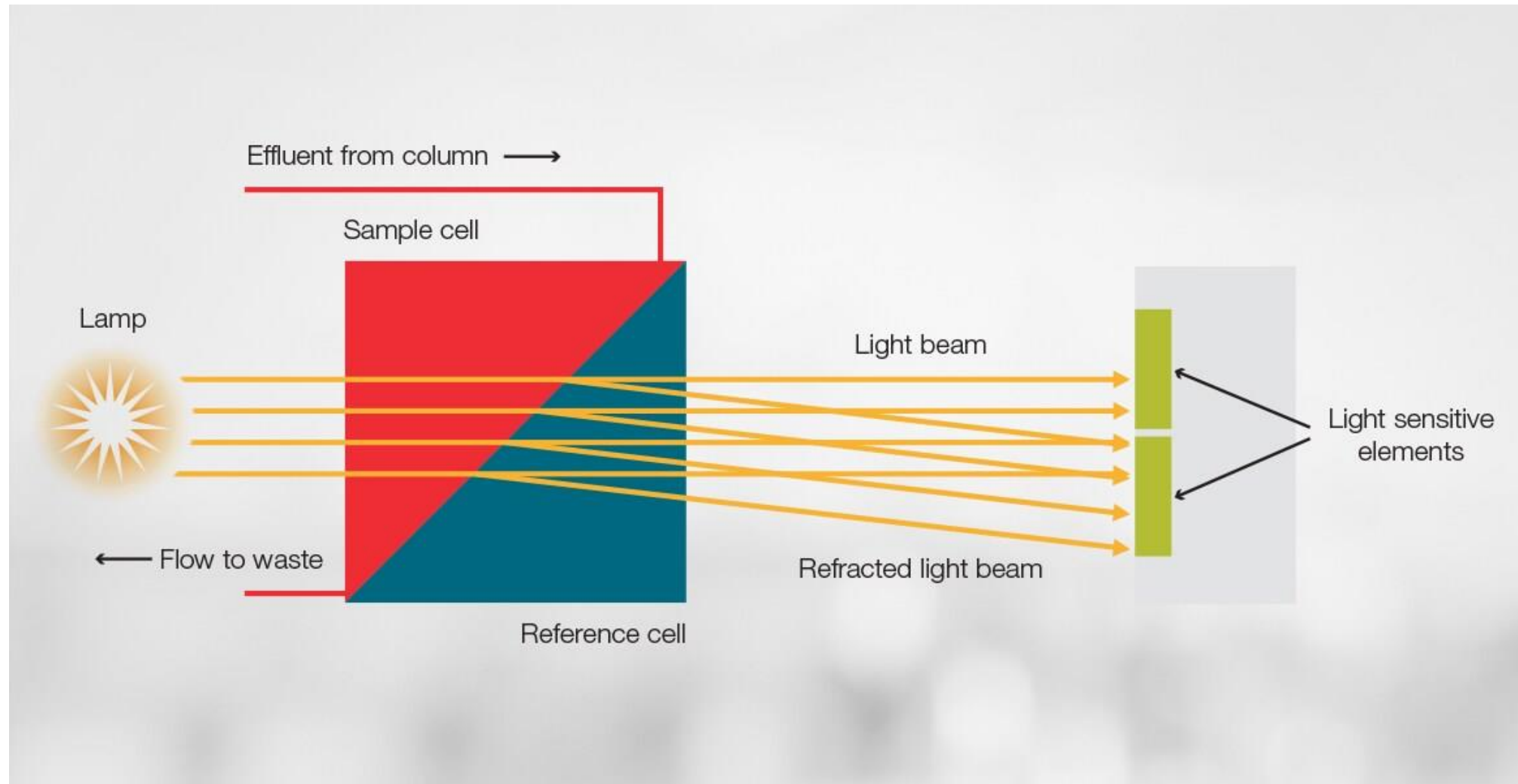


Diode array and multiple wavelength detectors both use a grating to disperse the light onto a photodiode array after the light has passed through the flow cell. As a result, the absorption of all wavelengths is simultaneous, giving the analyte a full absorption spectrum.



This detection method is preferred when analyzing complex mixtures or samples of unknown composition, for example, during method development or peak purity analysis.

HPLC Detectors – Refractive Index



HPLC Detectors – Refractive Index



A refractive index is a dimensionless number describing how fast light propagates through a medium compared to the vacuum. Snell's law defines the refraction of light as it crosses the border between media with different refractive indices.



The most common refractive index detector is the deflection type. In this type of detector, the flow cell has a sample cell flow path and a reference cell flow path to compare against the mobile phase.

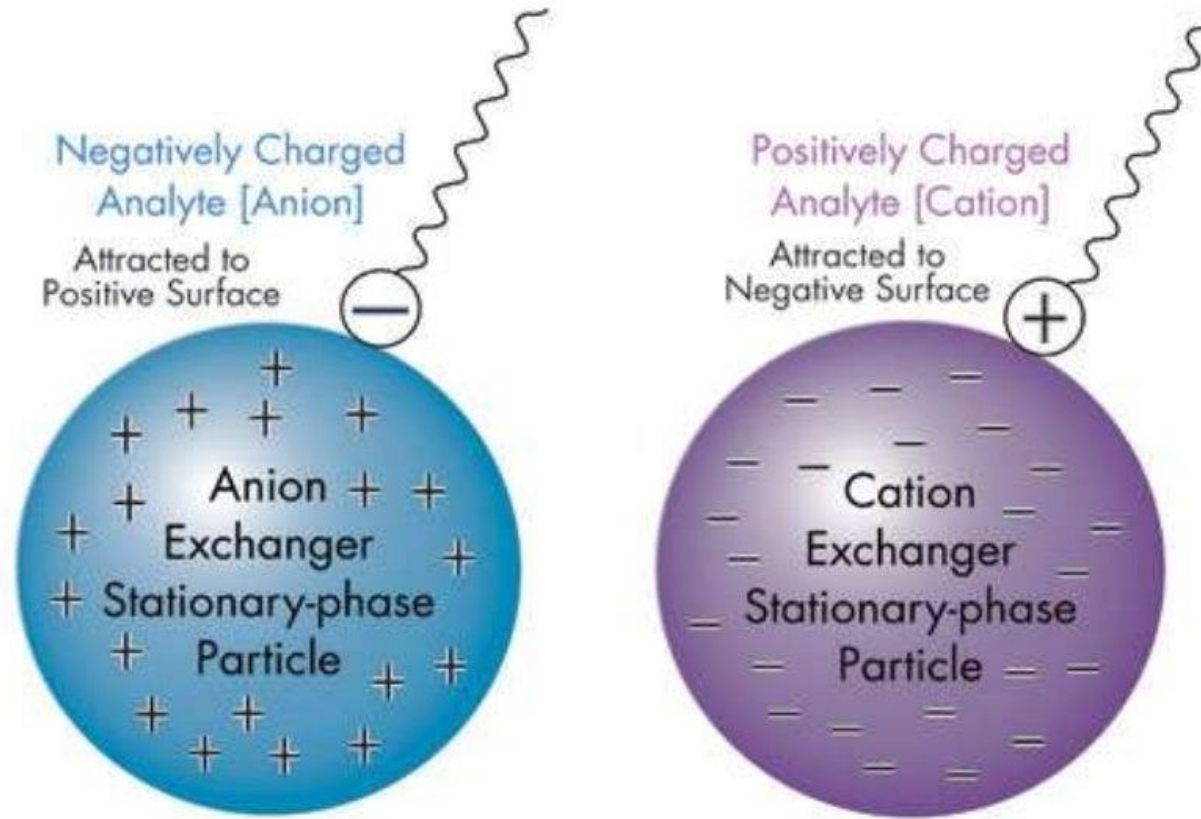


When an analyte passes through the sample flow cell, the refractive index, and direction of the light inside the flow cell change in proportion to the concentration of the analyte. A subsequent shift in the direction of light intensity is applied to determine the concentration when the system is calibrated for a particular analyte/mobile phase combination.

HPLC Detectors - Summary

Detection method	Analyte requirements	Detection limit	Destructive detector?
UV-Vis (UVD)	Absorbs UV-Vis light between 190 – 800 nm	Nanograms	No
Fluorescence (FLD)	Has a fluorophore or labelled with a fluorescent tag	Femtograms	No
Refractive Index (RID)	No analyte restrictions	Micrograms	No
Evaporative Light Scattering (ELSD)	Non- and semi-volatile analytes	Nanograms	Yes
Electrochemical (ECD)	Undergoes a redox reaction in the presence of an electric potential	Femtograms	Yes
Charged Aerosol (CAD)	Non- and semi-volatile analytes	Picograms	Yes
Mass Spectrometry (MS)	Volatile and semi-volatile ionizable analytes	Picograms	Yes

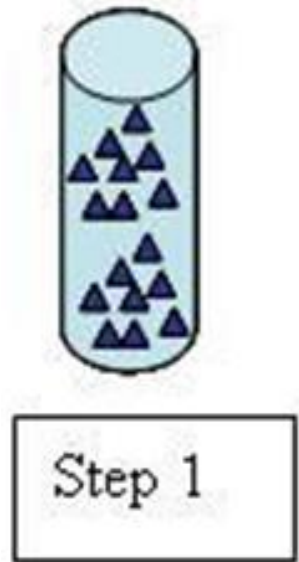
ION CHROMATOGRAPHY



Principle of Ion Chromatography

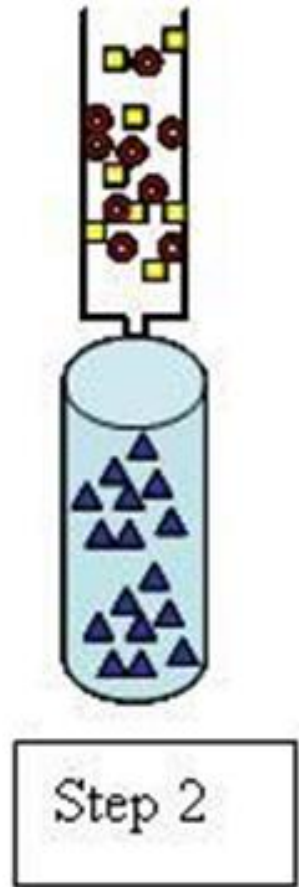
- The interactions of an ion with the resin (the stationary phase) and the eluent (the mobile phase) are the basis of ion chromatography.
- The ion chromatographer uses the differences in charge and size of the ions to cause the ions to travel through the columns at various rates, allowing for separation.
- As the ions leave the column, their electrical conductivity is measured by a special detector. The chromatogram generated by this detector is a function of conductivity vs time.

Ion Chromatography



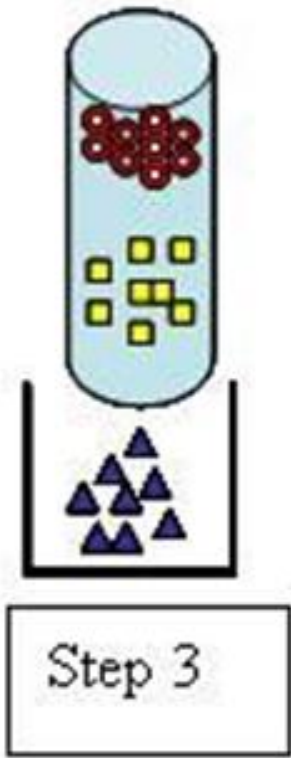
To displace any other anions bound to the resin, run the eluent anion through the column. During this loading phase, the eluent anion is used to completely saturate the resin surface. Remember, if you want consistent chromatographic outcomes, you need to make sure all the column's ionic sites are filled with eluent ions before you run the analysis.

Ion Chromatography



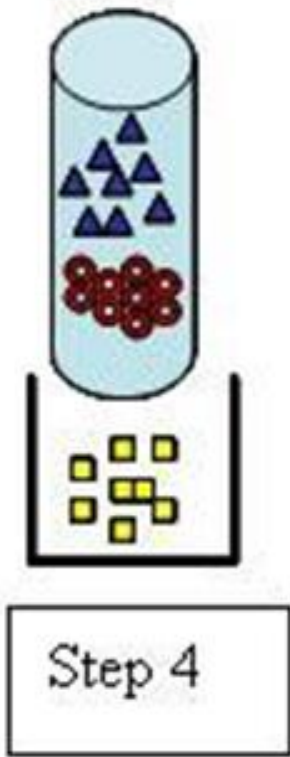
Small amounts of A- and B- containing samples (often less than 100 L) are injected into the column. This sample could contain a wide variety of ions; however, just two are used here for clarity.

Ion Chromatography



Ion exchange allows A^- and B^- to flow through the column after the sample has been injected by continuously adding eluent anion to the mobile phase.

Ion Chromatography



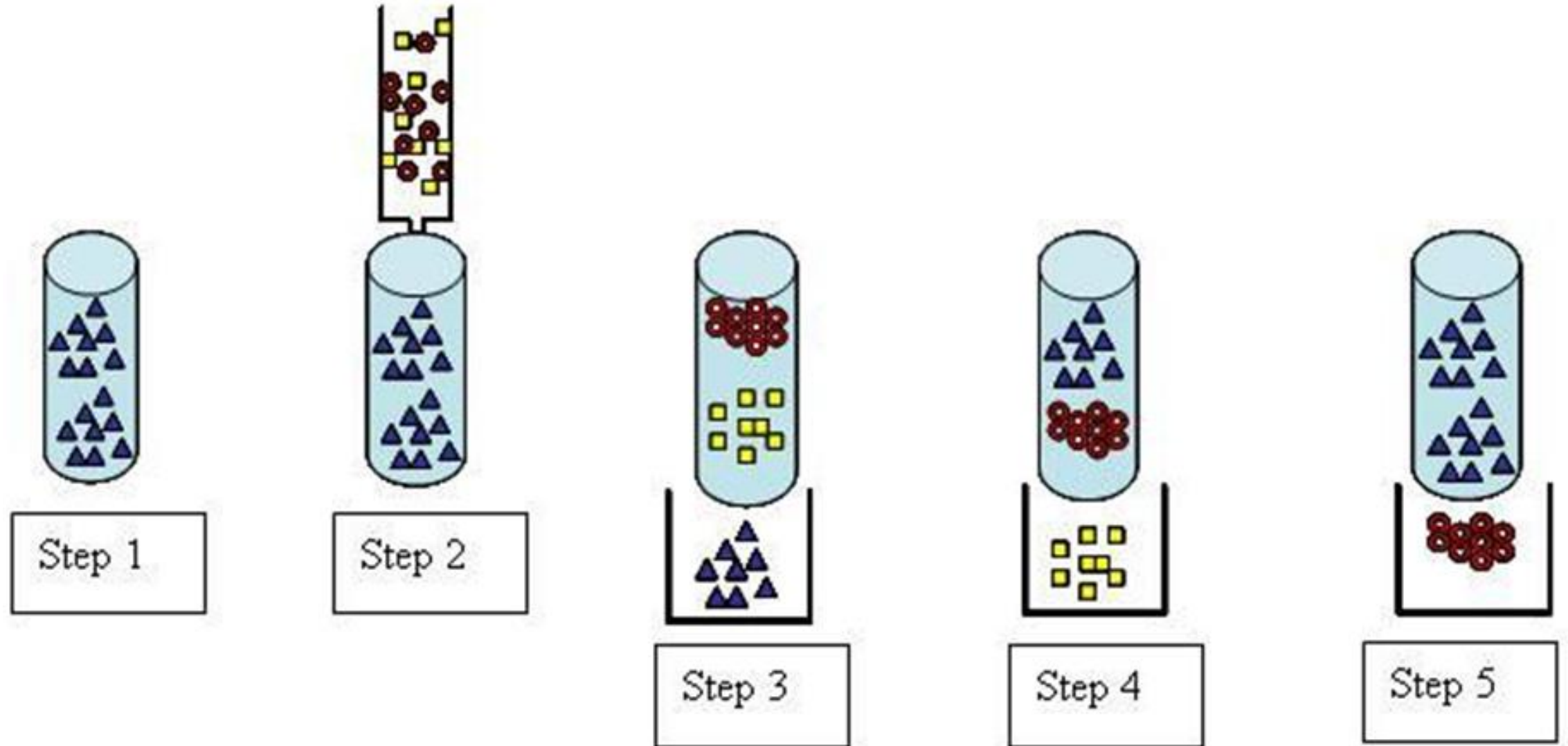
A^- migrates in a band across the column as the eluent is applied and finally elutes out of the column.

Ion Chromatography



B^- is finally eluted from the column as a result of the eluent.

Ion Chromatography



Ion Chromatography

1. To displace any other anions bound to the resin, run the eluent anion through the column. During this loading phase, the eluent anion is used to completely saturate the resin surface. Remember, if you want consistent chromatographic outcomes, you need to make sure all the column's ionic sites are filled with eluent ions before you run the analysis.
2. Small amounts of A⁻ and B⁻ containing samples (often less than 100 L) are injected into the column. This sample could contain a wide variety of ions; however, just two are used here for clarity.
3. Ion exchange allows A⁻ and B⁻ to flow through the column after the sample has been injected by continuously adding eluent anion to the mobile phase.
4. A⁻ migrates in a band across the column as the eluent is applied and finally elutes out of the column.
5. B⁻ is finally eluted from the column as a result of the eluent.

Combustion Ion Chromatography

- Pyrolysis takes place in the combustion system at temperatures above 900 °C.
- Sulfur-containing compounds are oxidized to sulfur dioxide (SO₂) and halogen-containing substances are transformed into hydrogen halides (X⁻) or elemental halogens (X₂).
- These gaseous combustion products are fed into an oxidizing absorption solution and are subsequently detected as sulfate and halogenide by way of the ion chromatography that follows.

Combustion Ion Chromatography Flow

1. Introduce sample

Liquid, solid or semisolid samples are introduced into the horizontal furnace using an automatic sample changer. For gaseous samples, an injector is used.

2. Perform pyrolysis

Samples are decomposed in the presence of humidified oxygen at high temperature (800–1100 °C).

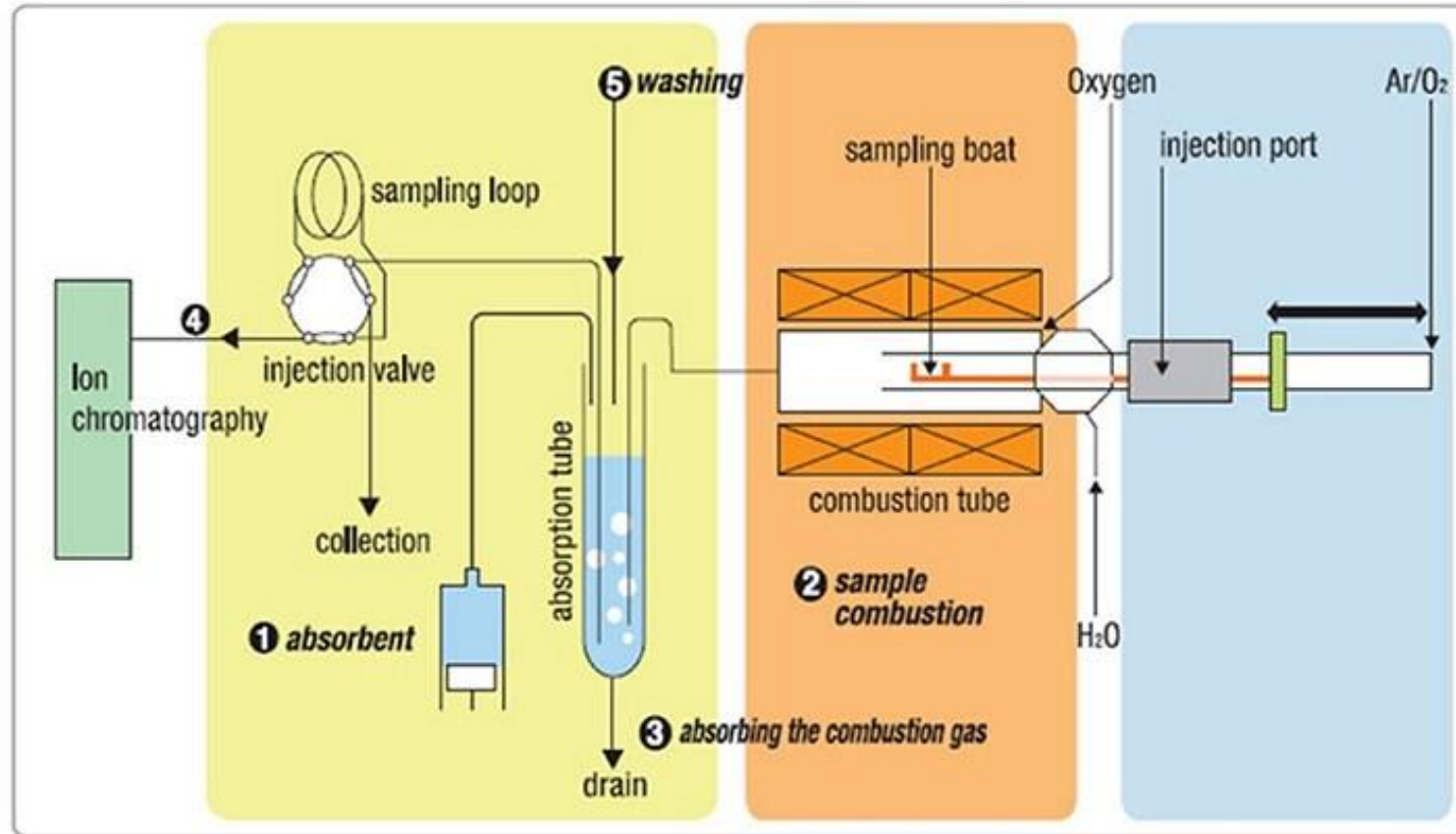
3. Trap volatiles

Volatile products are trapped in an aqueous absorbing solution, which may contain phosphate as an internal standard for calibration.

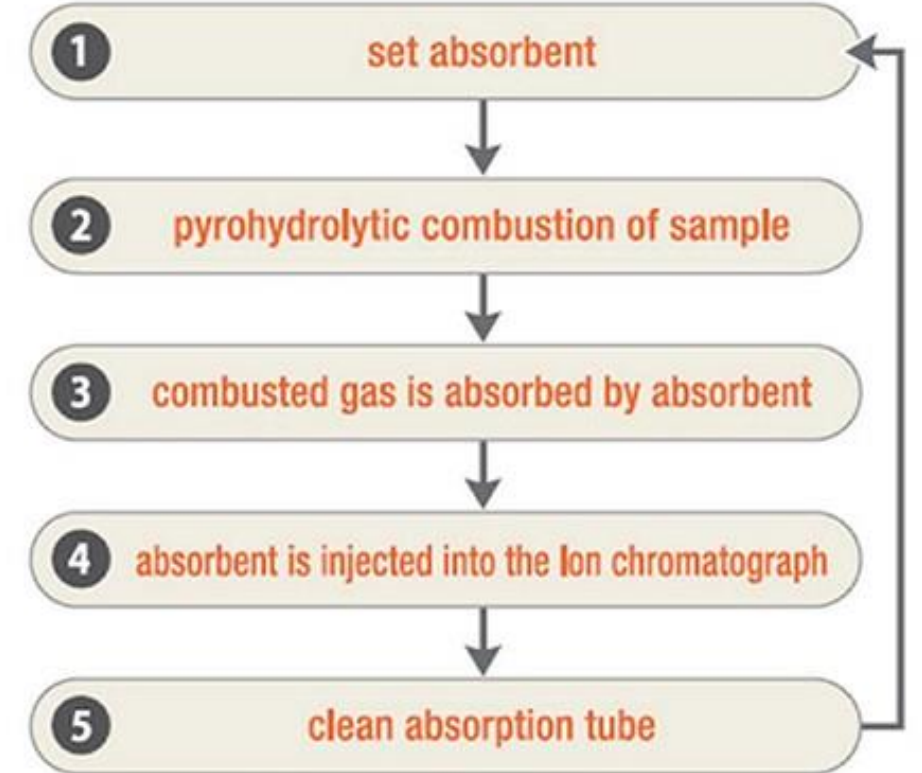
4. Perform ion analysis

Samples in the absorption solution are transferred to the IC system to determine the concentrations of individual halides and sulfur species (e.g., sulfite, sulfate, and thiosulfate). Total sulfate can be determined by further oxidizing the sulfur species using hydrogen peroxide.

Combustion Ion Chromatography Flow



Process Flowchart



TITRATION



Characterization of single component in mixtures

Water
Petroleum liquids
Many others



Applications cover analysis of

Liquid streams
Water analysis
Environment samples
Final Product

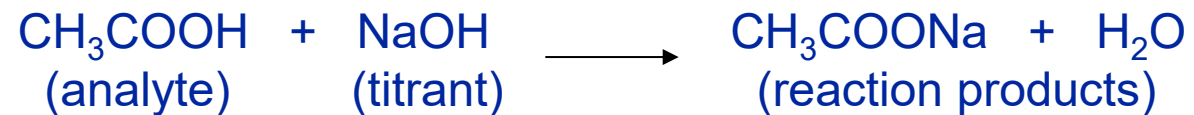


Overview – What is A Titration?

What is a titration?

- *A technique where a solution of known concentration is used to determine the concentration of an unknown solution.*
- *Typically, the titrant (the known solution) is added from a burette to a known quantity of the analyte (the unknown solution) until the reaction is complete.*
- *Knowing the volume of titrant used allows the determination of the unknown concentration.*
- *Often, an indicator is used to signal the end of the reaction, the endpoint.*
- *An automatic titrator uses potentiometric changes to determine the endpoint.*

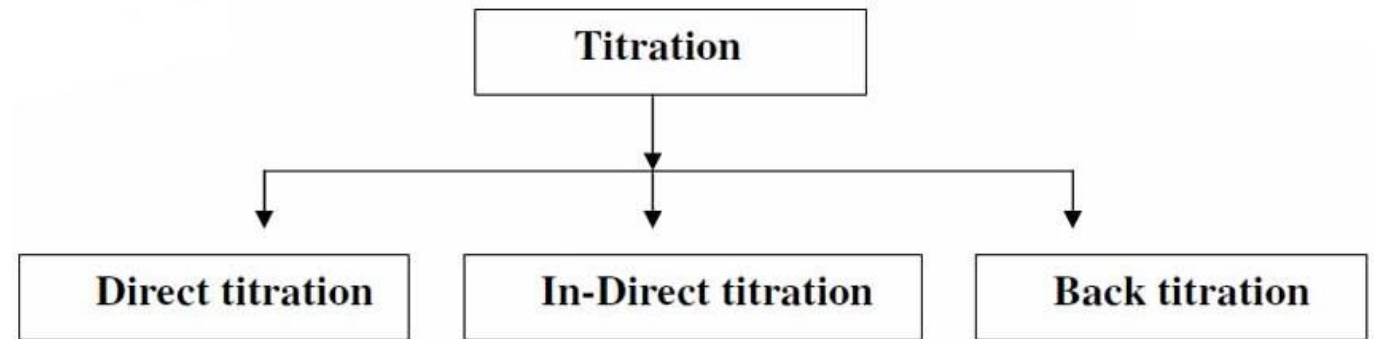
Example: *Determination of acetic acid (CH₃COOH) by titration with sodium hydroxide (NaOH)*



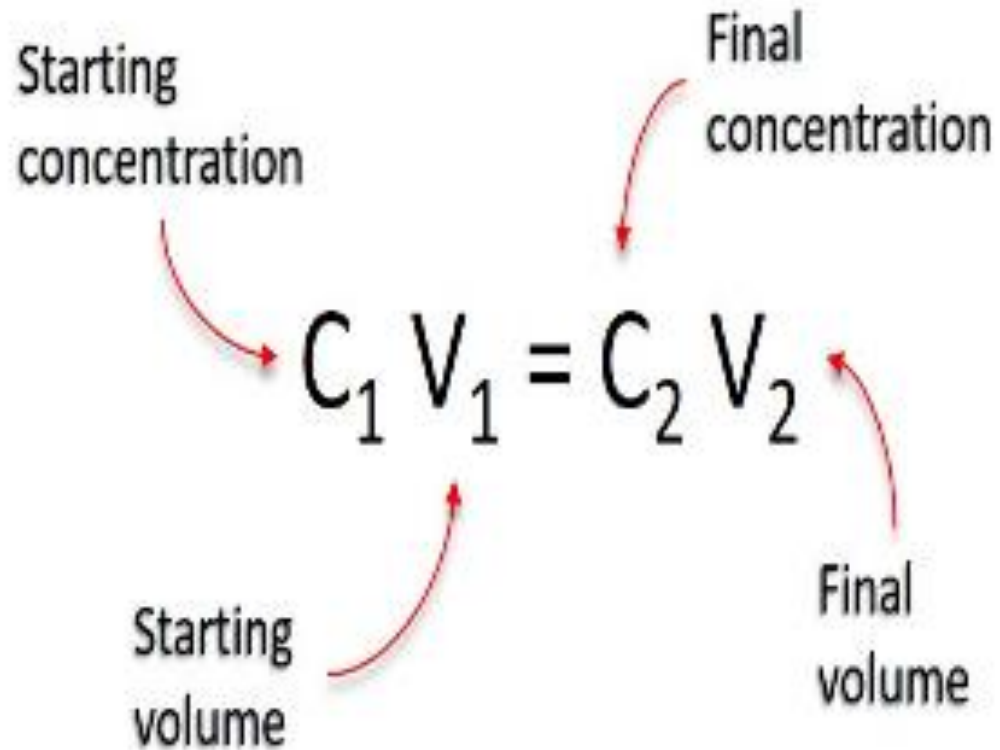
Overview – Methods of Titration

- **Methods of Titration:**

- There are of three types of titration based on the method used in the process of titration.



Overview – Titration Types



- **Direct Titration:**
 - A conventional titration where a known amount of titrant is added from a burette to a sample taken in a flask.
 - One substance is analyzed for its quantity by another substance of known volume and concentration.
- **Indirect Titration:**
 - Theoretically, it is converting a substance into acid and analyzing it with a base. (vice-versa).
 - This is a method for non readily reactive substances.
 - If a substance is weakly acidic it might not permit a precise analysis by direct titration.
 - So first that substance is chemically altered to be more reactive in acidic or basic form and then analyzed by adding a titrant.
- **Back Titration:**
 - This method is suitable for weakly reactive or non-reactive substances.
 - The sample is allowed to react with excess and known quantity of a titrant before starting the titration.
 - The remaining excess base or acid is estimated by a known quantity of acid or base back titrated to an endpoint.

Overview -Titration Types

Volumetric Titration:

- With volumetric titration, the titrant is added to the sample by a burette from an external source. The volume of titrant added to the sample is measured during the titration.

Coulometric Titration:

- In coulometric titration, the titrant is generated electrochemically in the sample within in the titration cell. This means that a precursor of the titrant that reacts with the analyte is already present in the sample before the analysis starts.

Overview – Titration Types

- **Advantages of Titration:**

- There are several reasons why titration is used in laboratories worldwide:
 - Titration is an established analytical technique.
 - It is fast.
 - It is a very accurate and precise technique.
 - A high degree of automation can be implemented.
 - Titration offers a good price/performance ratio compared to more sophisticated techniques.
 - It can be used by low-skilled and low-trained operators.
 - No need for highly specialized chemical knowledge.

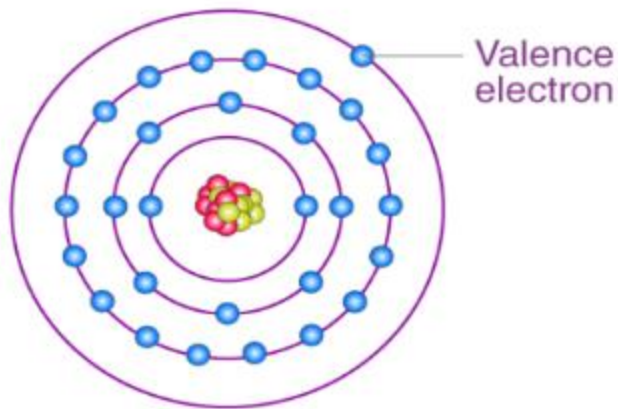
Terminology and Definitions

- **Buffer Solution:**
 - A solution that resists changes in pH even when a strong acid or base is added or when it is diluted with water.
- **Analyte:**
 - The chemical substance within our test sample to be determined with the analysis.
 - *Example: Mercaptan sulfur*
- **Matrix:**
 - Everything in the sample besides the analyte(s). Side reactions can occur due to other components.
 - *Matrix Examples: Water, hydrocarbons, acids, etc.*
- **Titrant:**
 - Solution of known concentration which is added to the sample (titration) and reacts with the analyte. The analyte content is calculated from the consumption of the titrant.
 - *Titrant Examples: KOH, BrBrO₃, AgNO₃, etc.*

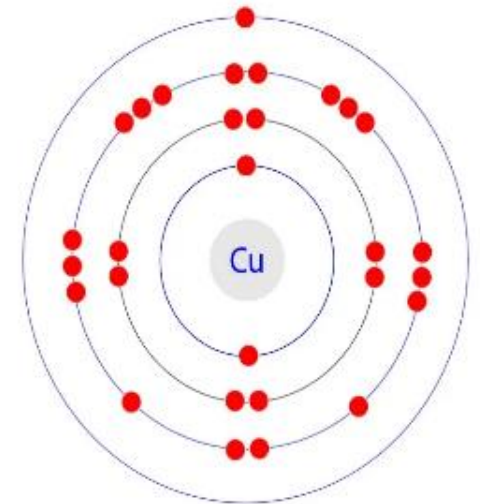


Terminology and Definitions

- **Valence Electrons:**
 - Valence electrons are electrons located in the outermost electron shell of an atom.
 - These electrons, being the furthest from the nucleus and thus the least tightly held by the atom, are the electrons that participate in bonds and reactions.
 - The number of valence electrons that an element has determines its reactivity, electronegativity, and the number of bonds it can form.



Name	Copper
Atomic Number	29
Symbol	Cu
Valency	1,2
Valence Electrons	1



■ Valence Electrons Continued:

Periodic table with Valence Electrons

The periodic table is organized into groups (columns) and periods (rows). The valence electrons are indicated by the number of electrons in the outermost shell, which is the same as the group number for main group elements.

Atomic No. → 1
Name → Hydrogen
Symbol → H
Valence Electron → 1

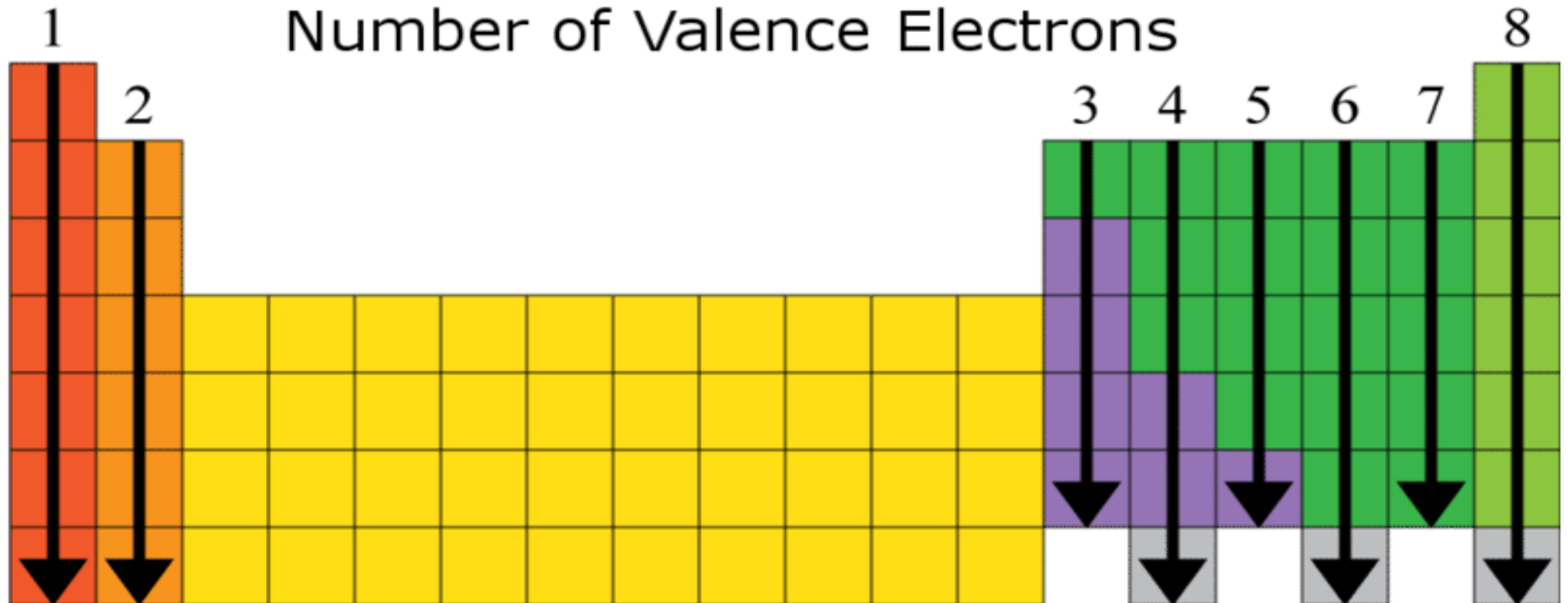
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H Hydrogen 1																	2 He Helium 2
3 Li Lithium 1	4 Be Beryllium 2											5 B Boron 3	6 C Carbon 4	7 N Nitrogen 5	8 O Oxygen 6	9 F Fluorine 7	10 Ne Neon 8
11 Na Sodium 1	12 Mg Magnesium 2											13 Al Aluminum 3	14 Si Silicon 4	15 P Phosphorus 5	16 S Sulphur 6	17 Cl Chlorine 7	18 Ar Argon 8
19 K Potassium 1	20 Ca Calcium 2	21 Sc Scandium 3	22 Ti Titanium 4	23 V Vanadium 5	24 Cr Chromium 6	25 Mn Manganese 7	26 Fe Iron 8	27 Co Cobalt 9	28 Ni Nickel 10	29 Cu Copper 11	30 Zn Zinc 12	31 Ga Gallium 3	32 Ge Germanium 4	33 As Arsenic 5	34 Se Selenium 6	35 Br Bromine 7	36 Kr Krypton 8
37 Rb Rubidium 1	38 Sr Strontium 2	39 Y Yttrium 3	40 Zr Zirconium 4	41 Nb Niobium 5	42 Mo Molybdenum 6	43 Tc Technetium 7	44 Ru Ruthenium 8	45 Rh Rhodium 9	46 Pd Palladium 10	47 Ag Silver 11	48 Cd Cadmium 12	49 In Indium 3	50 Sn Tin 4	51 Sb Antimony 5	52 Te Tellurium 6	53 I Iodine 7	54 Xe Xenon 8
55 Cs Caesium 1	56 Ba Barium 2	57 La Lanthanum 3	58 Ce Cerium 4	59 Pr Praseodymium 5	60 Nd Neodymium 6	61 Pm Promethium 7	62 Sm Samarium 8	63 Eu Europium 9	64 Gd Gadolinium 10	65 Tb Terbium 11	66 Dy Dysprosium 12	67 Ho Holmium 13	68 Er Erbium 14	69 Tm Thulium 15	70 Yb Ytterbium 16	71 Lu Lutetium 3	
87 Fr Francium 1	88 Ra Radium 2	89 Ac Actinium 3	90 Th Thorium 4	91 Pa Protactinium 5	92 U Uranium 6	93 Np Neptunium 7	94 Pu Plutonium 8	95 Am Americium 9	96 Cm Curium 10	97 Bk Berkelium 11	98 Cf Californium 12	99 Es Einsteinium 13	100 Fm Fermium 14	101 Md Mendelevium 15	102 No Nobelium 16	103 Lr Lawrencium 3	

Lanthanides

Actinides

Terminology and Definitions

- Valence Electrons Continued:



Terminology and Definitions

Molarity:

- The number of moles of solute per liter of solution.
- The units of molarity are *M* or mol/L. A 1 *M* solution is said to be “one molar.”

Normality:

- The number of grams equivalent to solute that is present in a one-liter solution.
- Common units of normality include N, eq/L, or meq/L.

Molarity to Normality Conversions:

- When doing normality and molarity conversions, remember when the valence is one, the normality and molarity are the same. Thus, for NaOH, it is the same.
- Normality = Valence x Molarity
- Molarity = Normality/Valence

Terminology and Definitions

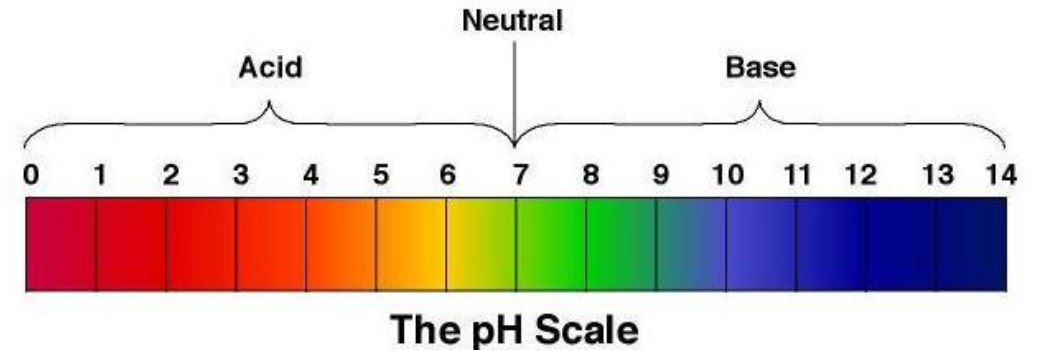
- **Molarity/Normality Conversions Examples:**
 - **NaOH Example:**
 - To go from 0.1 molarity to normality:
 - valence = 1
 - Molarity = 0.1
 - Therefore $(1 \text{ valence}) \times (0.1 \text{ molarity}) = 0.1 \text{ Normality}$.
 - To go from 0.1 normality to molarity:
 - valence = 1
 - Molarity = 0.1
 - Therefore $(0.1 \text{ normality}) / (1 \text{ valence}) = 0.1 \text{ Molarity}$

Terminology and Definitions

- **Molarity Normality Conversions Examples Continued:**
 - **H₂SO₄ Example:**
 - To go from 0.1 molarity to normality:
 - valence = 2
 - Molarity = 0.1
 - Therefore (2 valence) x (0.1 molarity) = 0.2 Normality.
 - To go from 0.1 normality to molarity:
 - valence = 2
 - Normality = 0.1
 - Therefore (0.1 normality) / (2 valence) = 0.05 Molarity

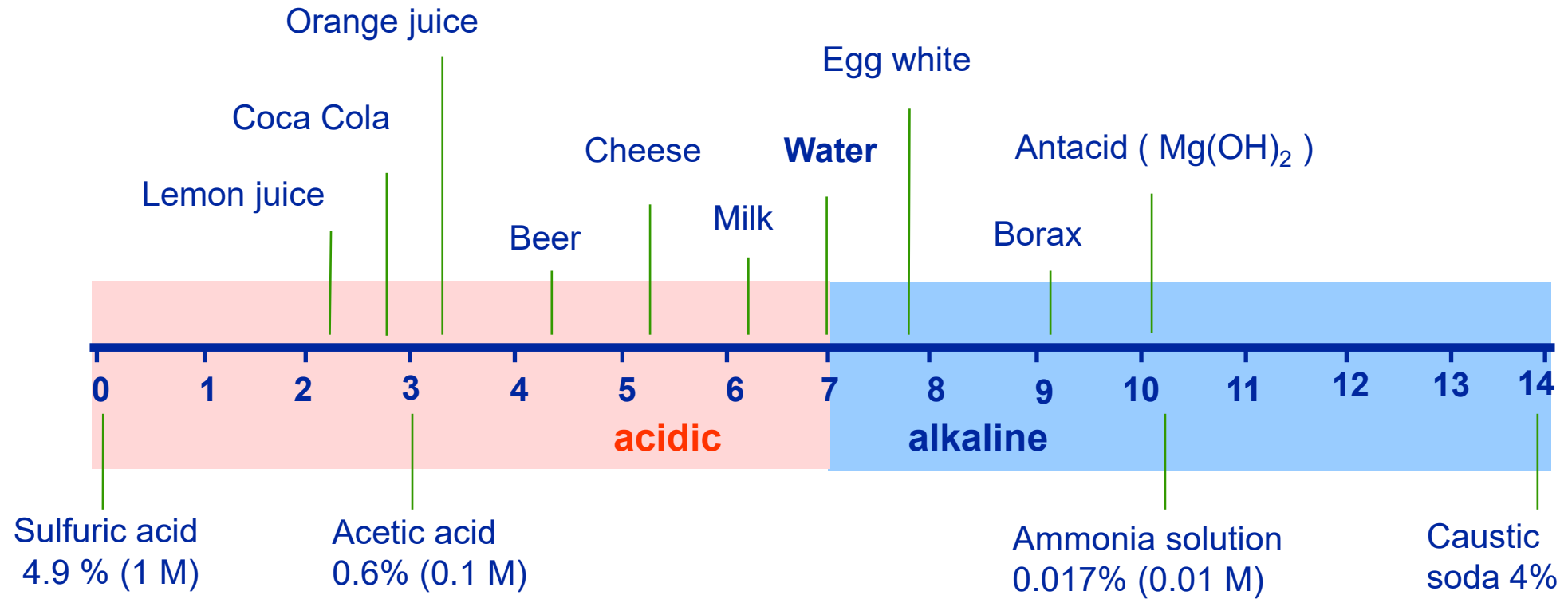
Terminology and Definitions

- **pH:** The negative logarithm of H^+ ion concentration. ($pH = -\log [H^+]$)
- **pH Scale:**
- **Hydronium Ion vs Hydroxide Ion**
 - **For acidic solution:** $[H_3O^+] > [OH^-]$
 - **For neutral solution:** $[H_3O^+] = [OH^-]$
 - **For basic solution:** $[H_3O^+] < [OH^-]$



Terminology and Definitions

■ pH of Typical Solutions:



Terminology and Definitions

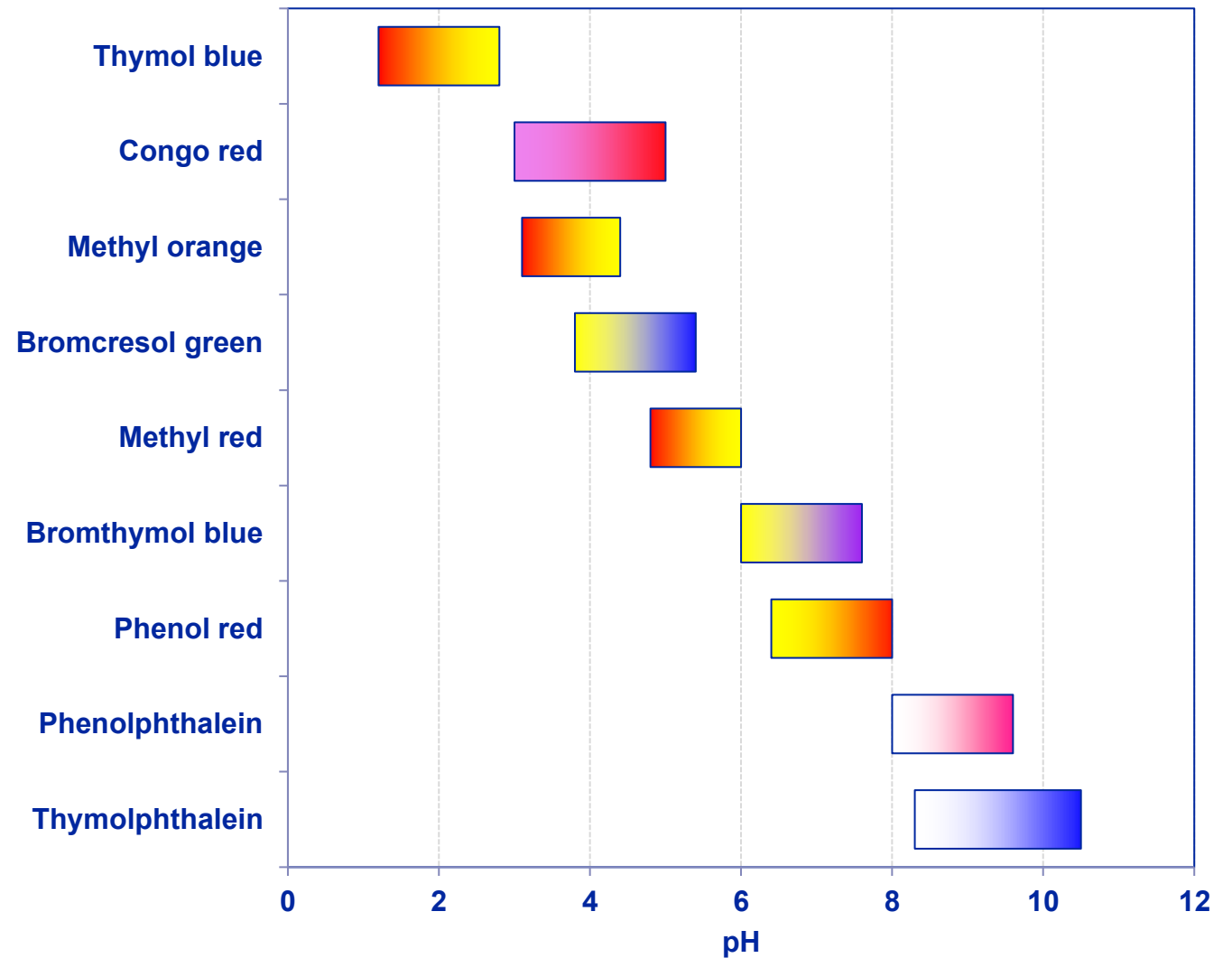


- Indications of Inflection Point:
 - The equivalence point of a titration should be easily visible or measurable.
 - The two basic indication principles are:
 - Indicator:
 - An indicator is a substance which changes its color at the equivalence point.
 - Small amounts of an indicator are added to the solution prior to the analysis.
 - Example:
 - Phenolphthalein is an indicator which is pink under basic conditions and colorless under acidic conditions.
 - At the equivalence point of an acetic acid titration by sodium hydroxide, the color will immediately change from colorless to pink.

Terminology and Definitions

- pH Indicators:

For a manual titrations, various pH indicators exist. The selection must be based on the pH range where the equivalence point occurs. The indicator must be chosen such that its color change occurs at the equivalence point. The following graph shows common pH indicators and their color change range:



Terminology and Definitions

- Indications of Inflection Point Continued:

Electrode: (potentiometric change)

An electrode is an instrument that measures a specific property of a solution electrochemically.

A suitable electrode must be chosen for each type of reaction.

The electrode must measure a property which is related to the titration reaction.

The whole titration procedure can be followed with an electrode by a titration curve

Example:

For the titration of acetic acid by sodium hydroxide a pH electrode is used. The pH electrode measures the H^+ concentration related to acetic acid that hasn't reacted. The equivalence point is reached when the pH value changes suddenly from acidic to basic.



Terminology and Definitions

- Indications of Inflection Point

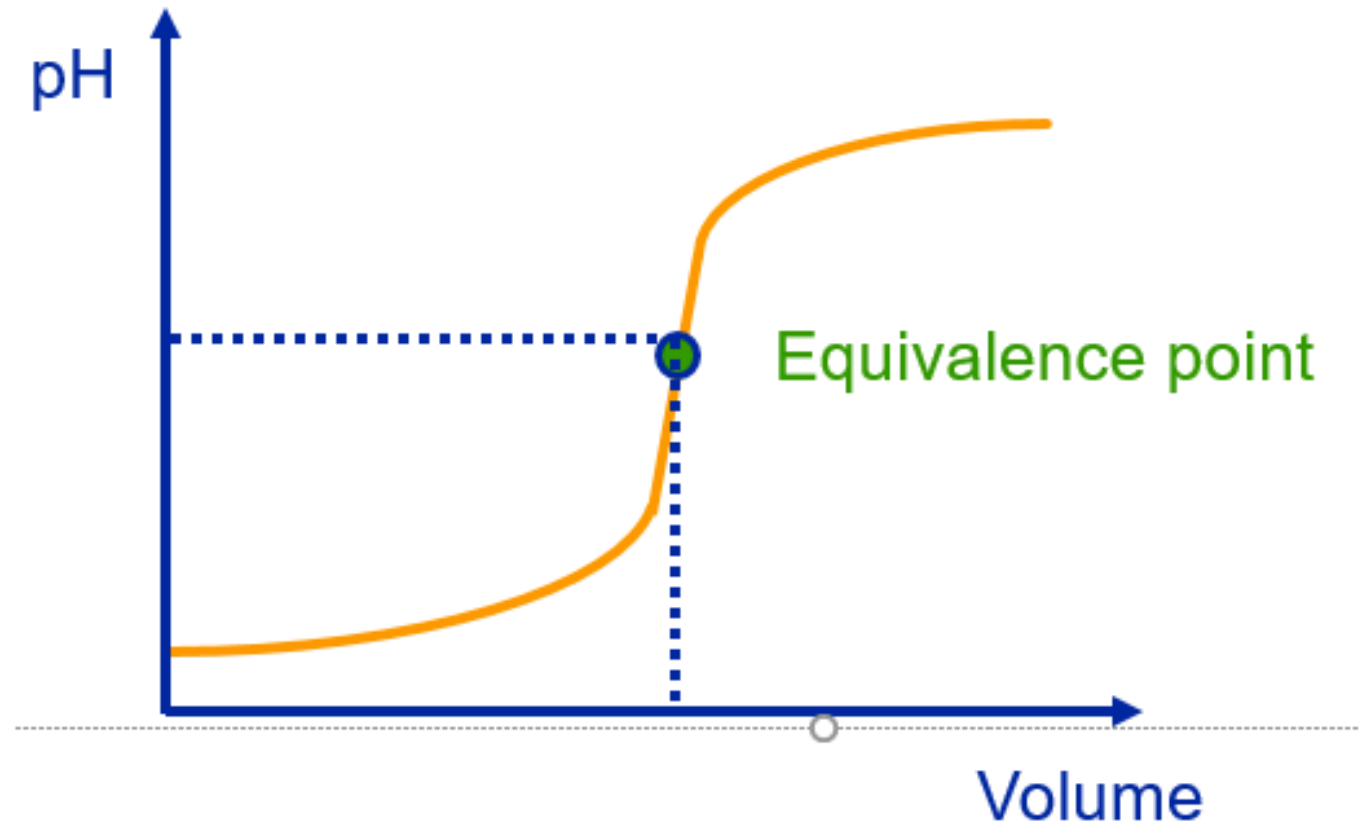
Continued:

If an electrode is used for a titration, the signal vs. titrant volume can be plotted.

Such a plot is called a titration curve.

The equivalence point can be determined directly from a titration curve and is the inflection point of the curve.

Example: Titration curve (pH vs. volume) of acetic acid titration with sodium hydroxide. The equivalence point is clearly visible.



Terminology and Definitions

Two different titration terminations are used:

- **Equivalence Point Titration (EQP)**
- **Endpoint Titration (EP)**

EQP:

- The EQP is reached as soon as all analyte has reacted with the titrant.
- In a titration curve, the EQP is the inflection point of the curve.
- The titration is carried out over the EQP and evaluated afterwards.

EP:

- The EP is reached as soon as the signal reaches a predefined value.
- The titration is usually stopped at the EP.

Terminology and Definitions

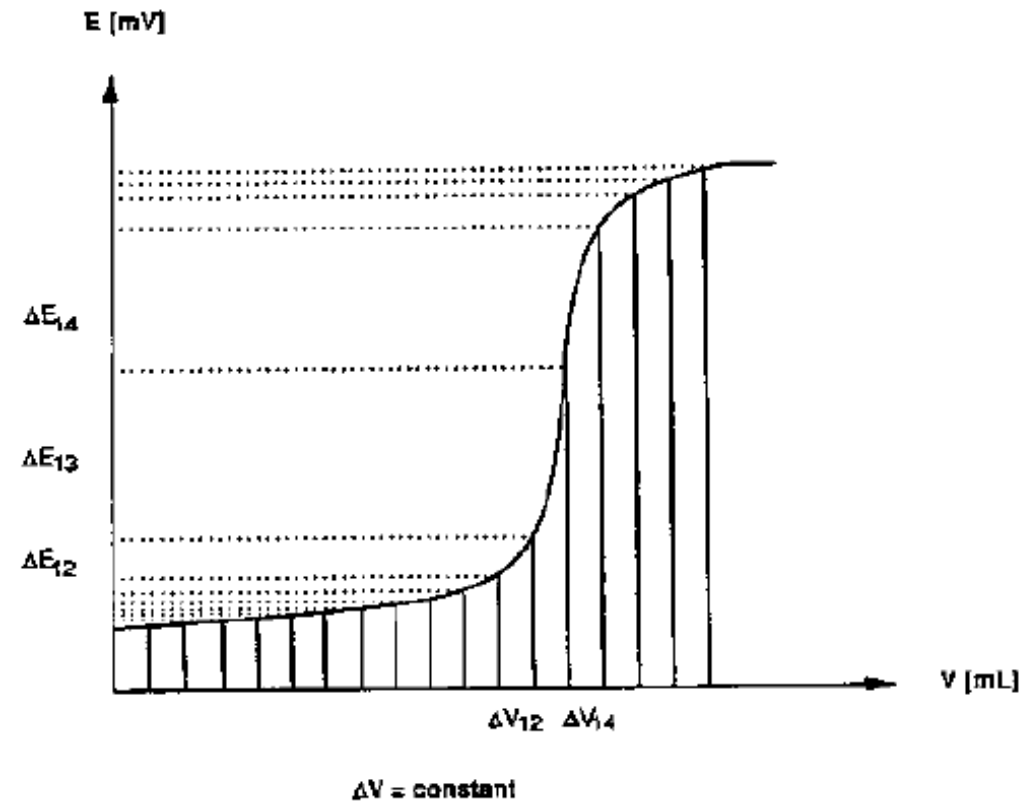
- **Equivalence Point (Inflection Point):**
 - The point when enough reagent is added to react completely with the analyte.
 - At the equivalence point, the number of moles of the titrant are equal to the number of moles of analyte.
 - It occurs before the endpoint.
 - It does not indicate the completion of a titration process.
 - Equivalence point means the completion of reaction between titrant and analyte.
 - A titration process can have multiple equivalence points.
 - Just before change in color.
 - For calculation of the result the equivalent number z has to be known.
 - The equivalent number of an analyte is determined by the stoichiometry. In general, the equivalent number is the number of moles "monovalent" titrant (e.g., NaOH, HCl, AgNO₃, Na₂S₂O₃) which are needed for the reaction with one mole of analyte.

Terminology and Definitions

- Equivalence Point (Inflection Point)

INFLECTION

INCREMENT: CONSTANT SIZE LARGE

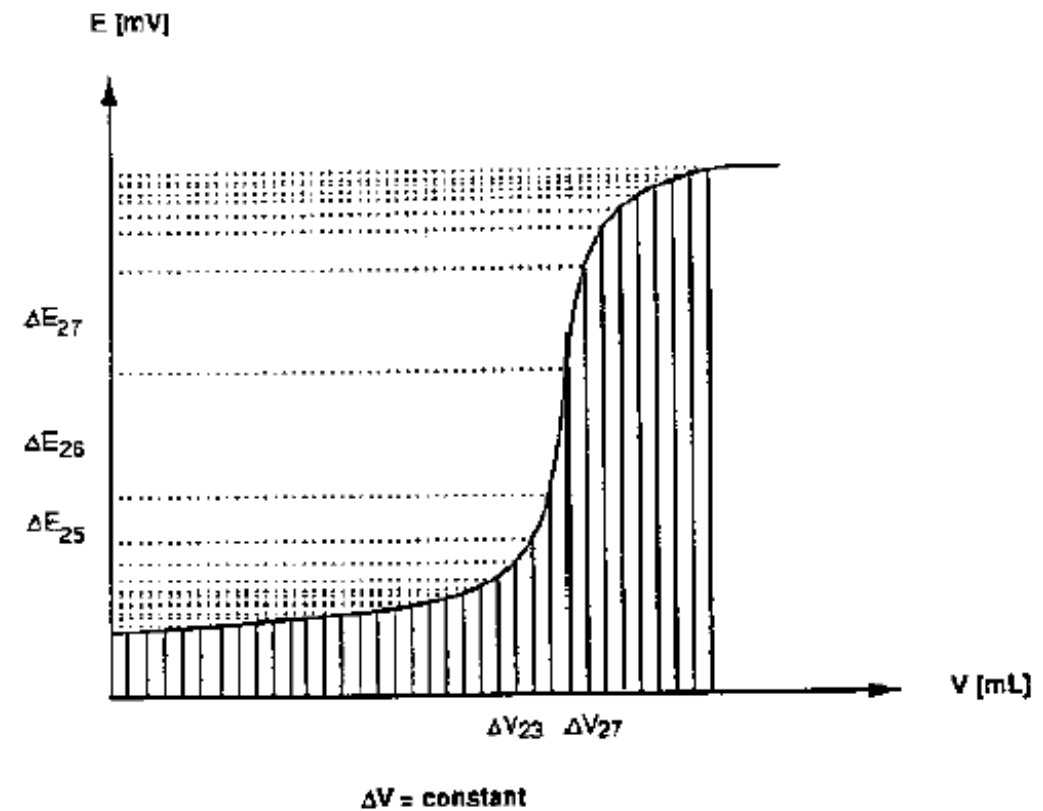


Terminology and Definitions

- Equivalence Point (Inflection Point)

INFLECTION

INCREMENT: CONSTANT SIZE SMALL

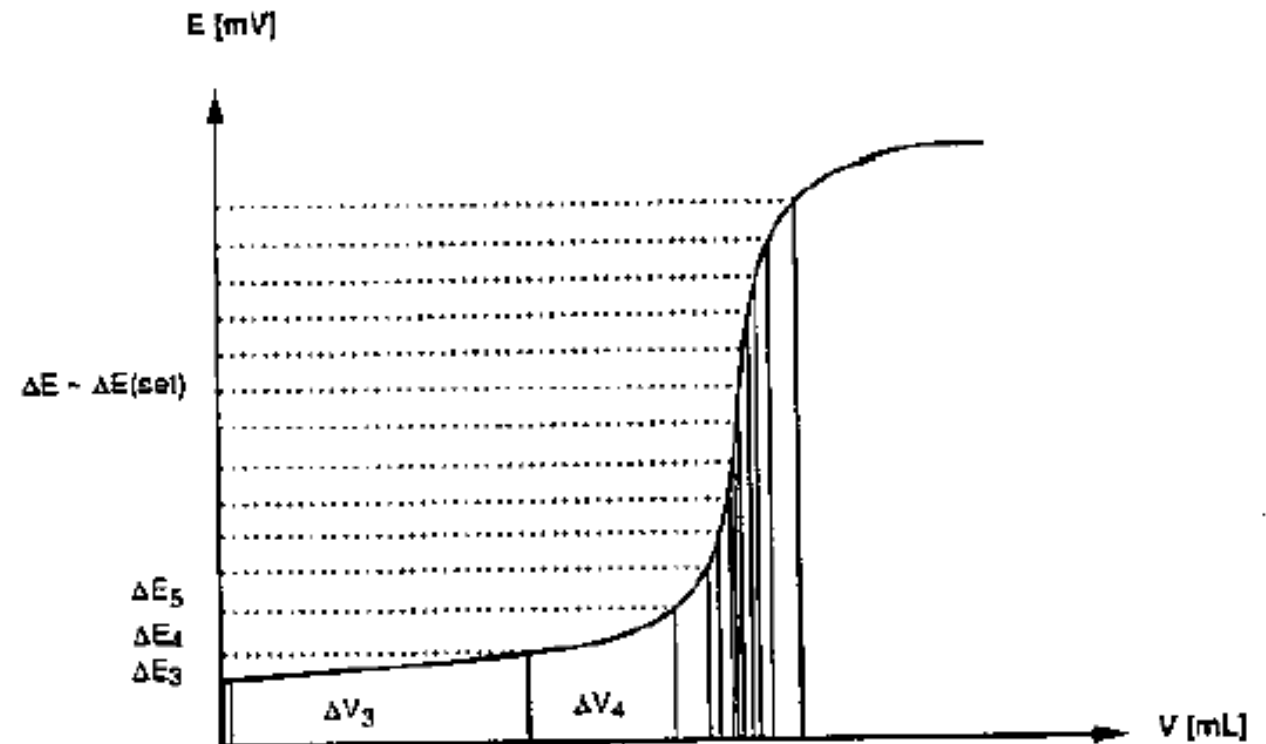


Terminology and Definitions

- Equivalence Point (Inflection Point)

INFLECTION

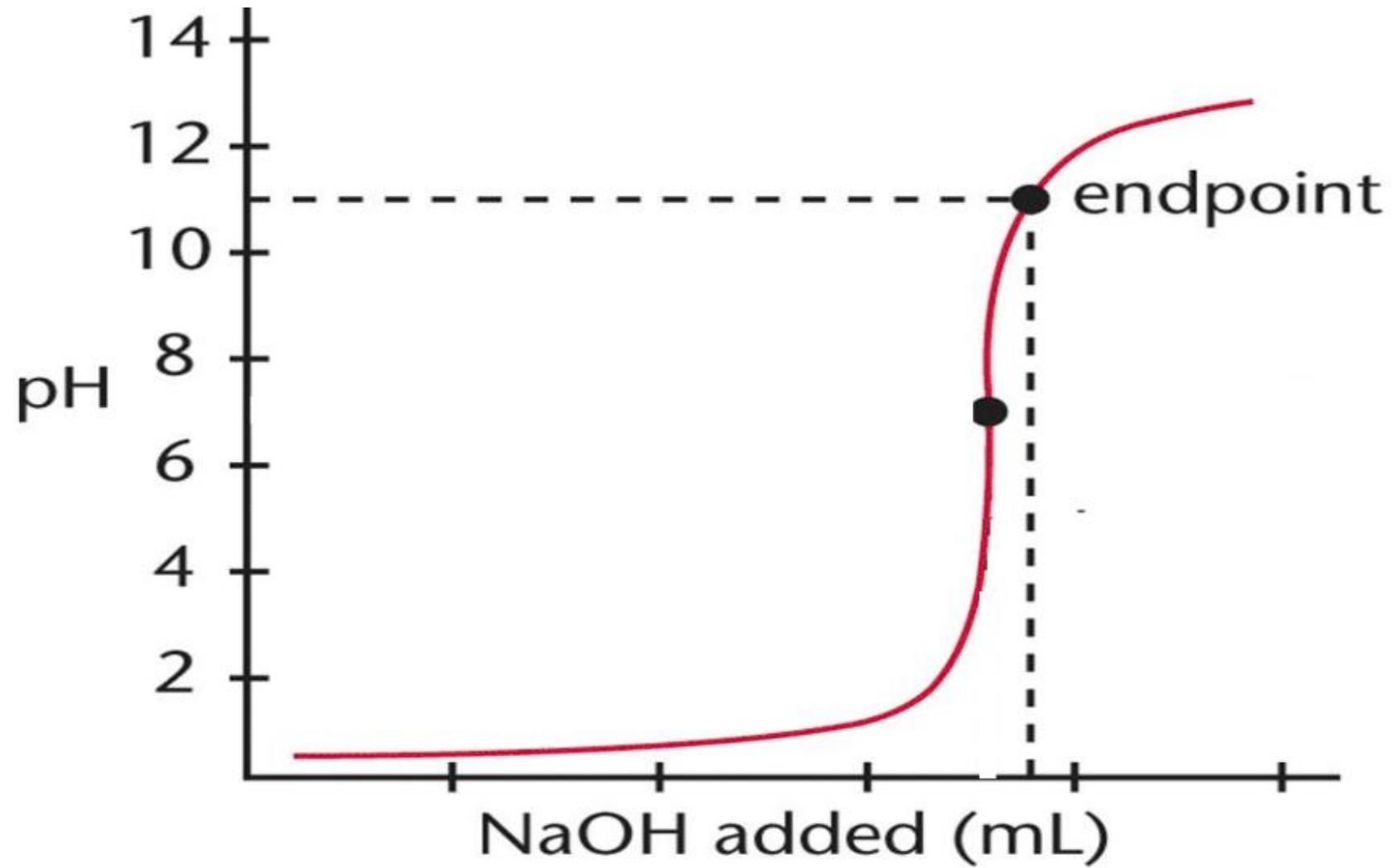
INCREMENT: DYNAMIC VARIABLE



Terminology and Definitions

- **End point:**
 - The point at which color change i.e. (medium change) occurs in the system due to pH change is called endpoint
 - At this point, the moles of titrant exceed the moles of the analyte. A sharp change in pH occurs resulting in color change.
 - It comes after equivalence point.
 - Titration is complete once the endpoint is reached.
 - Endpoint does not mean the completion of reaction between analyte and titrant.
 - It occurs once in a reaction.
 - Change in color.

Terminology and Definitions



Terminology and Definitions

Categories	Endpoint	Equivalence point
Definition	The point at which color change occurs due to a pH-change	A point when the chemical reaction in the titration mixture ends
Explanation	At this point, the moles of titrant exceed the moles of the analyte.	A point in a titration when the number of moles of titrant are equal to analyte
Occurrence	After equivalence point	Before the endpoint
Completion	Titration is complete once the endpoint reaches	It is not the completion of a titration reaction
Reaction completion	It does not mean the completion of reaction between analyte and titrant	It means the completion of reaction between titrant and analyte
Times of occurrence	Occurs only once in a reaction	Titration processes can have multiple equivalence points
Nutshell	Change in color	Just before change in color

Titration Reactions Need To Be:

Selective:

- The chemical reaction between the analyte and the titrant must be selective (only the analyte should react with the titrant).

Fast:

- The reaction should be fast in order to guarantee that the added titrant reacts immediately with the analyte.

Complete:

- The equilibrium of the reaction should lie strongly on the product side of the reaction to guarantee a complete reaction.

Unambiguous:

- The stoichiometry of the reaction must be known and unambiguous.

Accurate:

- The key point of a good titration is the accurate determination of the titrant volume used.
- For this reason, the following two requirements must be fulfilled:
 - A titrant addition in small quantities must be possible.
 - An accurate reading for the volume used is needed.

Types of Titration Reactions

- Acid-Base Titration Reaction

(Neutralization Reaction):

What is an Acid-Base Titration?

A quantitative analysis for determining the concentration of an acid or base by neutralizing it with a standard solution of base or acid having known concentration according to a stoichiometric proton-transfer reaction.

Acid-base reactions involve the transfer of hydrogen ions between reactants.

ACID/BASE REACTIONS



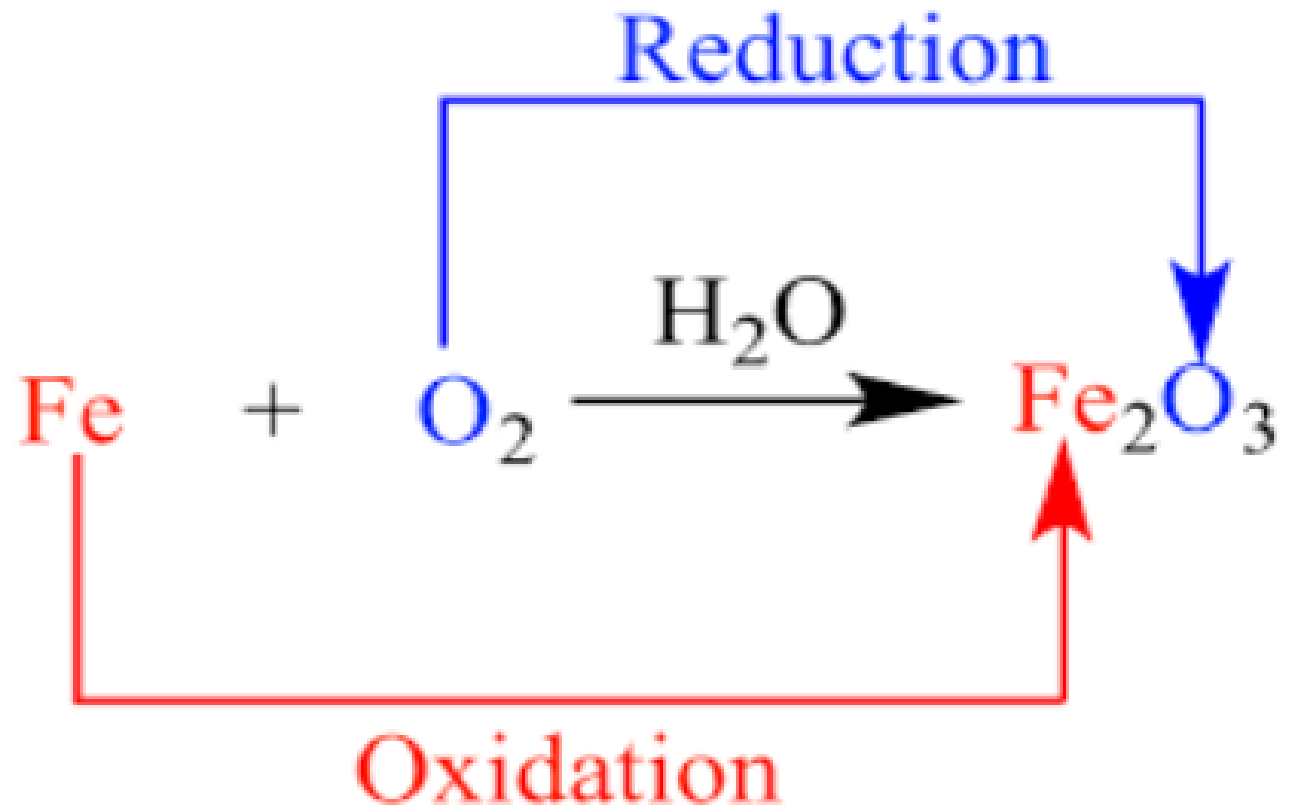
Types of Titration Reactions

- Oxidation-Reduction Reaction (Redox):
What is a Redox Reaction (Oxidation-Reduction)?

A Redox reaction is a chemical reaction that involves transfer of electrons between two species.

The oxidation number of a molecule, atom, or ion changes by gaining or losing an electron.

Redox reactions involve a change in oxidation number for one or more reactant elements.



Types of Titration Reactions

- Precipitation Reaction:

What is a Precipitation Reaction?

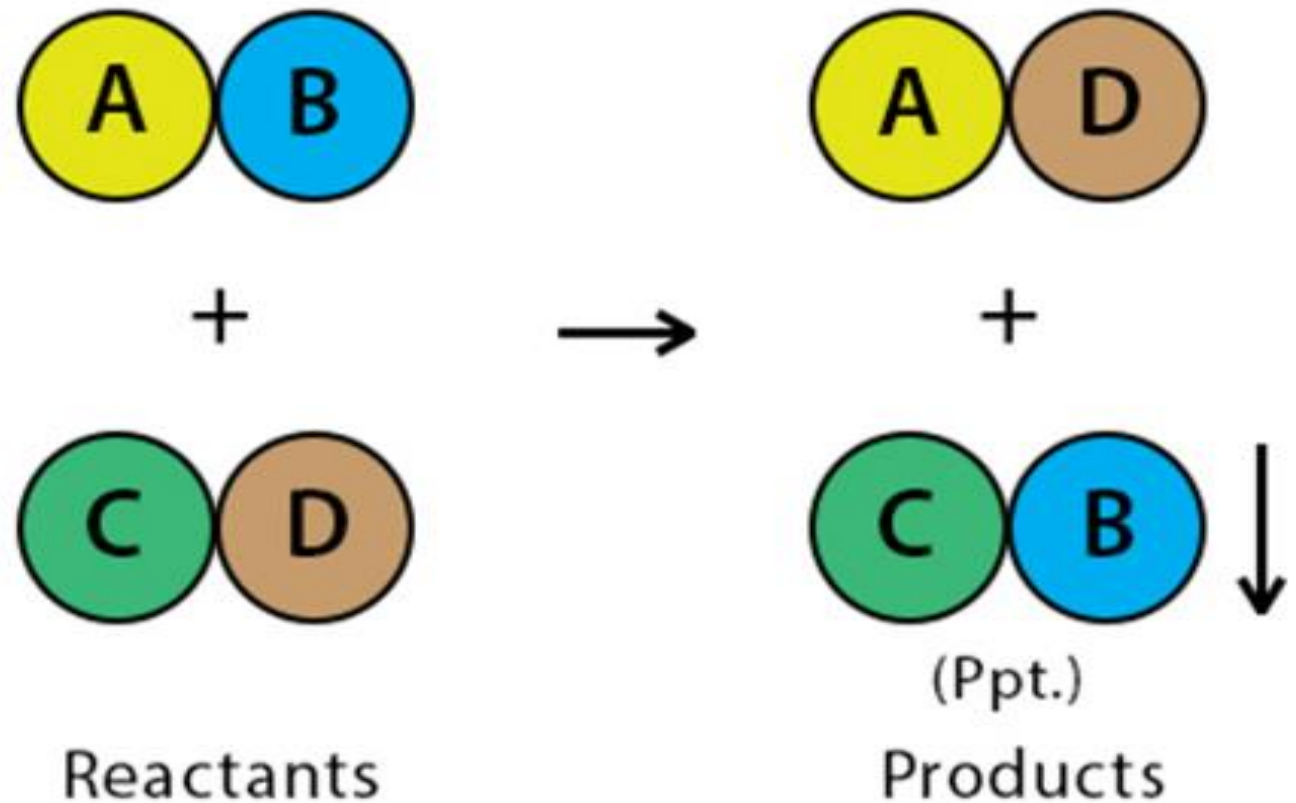
Reactions that involve the formation of one or more insoluble products.

Reactions that occur when cations and anions combine to form an insoluble ionic solid called a precipitate.

Many reactions of this type involve the exchange of ions between ionic compounds in aqueous solution and are sometimes referred to as double displacement, double replacement, or metathesis reactions.

Example: Removing H₂S for Mercaptan titration.

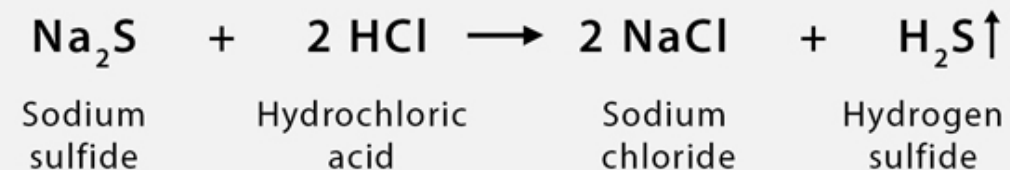
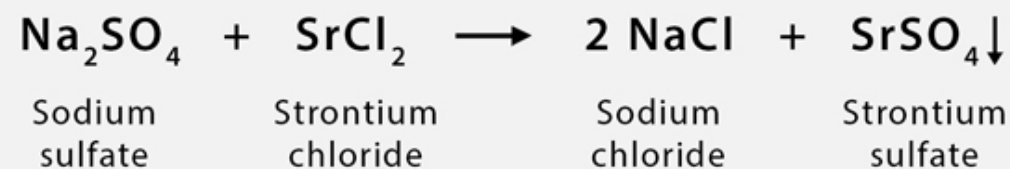
Precipitation Reaction



Types of Titration Reactions

- Examples of Precipitation Reactions:

Double-replacement Reaction Examples

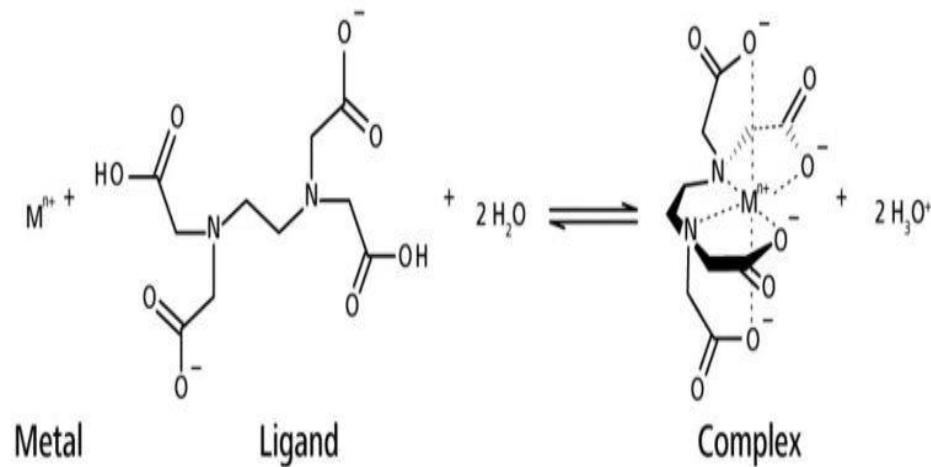


Types of Titration Reactions

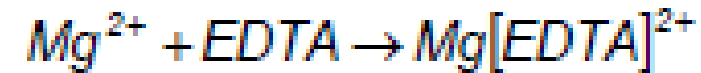
- Complexometric Reaction:

- What is a Complexometric reaction?

- When a simple ion is transformed into a complex ion and the equivalence point determined by using metal indicators or electrometrically.



Complexometric reactions:



Examples: Total hardness of water (Mg^{2+} and Ca^{2+})
 Calcium content in milk and cheese
 Cement analysis

Calculations

$$\bullet R = \frac{VEQ \cdot c \cdot t \cdot C}{m}$$

- For **Direct Titration Calculations:**
 - The analyte content in a direct titration is calculated from the titrant consumption at the equivalence or end point using the following formula:

R	= Result
VEQ	= Titrant consumption at the equivalence or end point (in mL)
c	= Titrant concentration (in mol/L)
t	= Titrant titer (no unit)
C	= Constant for unit conversion
m	= Sample size (in g or mL)
 - The constant C is dependent on the result unit wanted and on the unit of the sample size

Calculations

- Examples of Constants:

M = Molar mass of the analyte in g/mol

z = Equivalent number (no unit)

Sample size entry unit	g	mL	
Result unit	%		$C = \frac{M}{10 \cdot z}$
	mg/g	g/L	$C = \frac{M}{z}$
	ppm	mg/L	$C = \frac{M \cdot 1000}{z}$
	mmol/kg	mmol/L	$C = \frac{1000}{z}$
	mol/kg	mol/L	$C = \frac{1}{z}$

Calculations

- Example 1:
 - For the titration of the acetic acid ($M = 60.04 \text{ g/mol}$) in a 1 g sample of vinegar, 5 mL sodium hydroxide ($c = 0.1 \text{ mol/L}$, titer: 0.9900) were consumed until the equivalence point was reached.
 - To calculate the acetic acid content in % you have to use the following formula:

$$C = \frac{M}{10 \cdot z} = \frac{60.04 \text{ g/mol}}{10 \frac{\text{mg}}{\text{g} \cdot \%} \cdot 1} = 6.004 \frac{\text{g} \cdot \%}{\text{mmol}}$$

$$R = \frac{VEQ \cdot c \cdot t \cdot C}{m} = \frac{5 \text{ mL} \cdot 0.1 \frac{\text{mol}}{\text{L}} \cdot 0.9900 \cdot 6.004 \frac{\text{g} \cdot \%}{\text{mmol}}}{1 \text{ g}} = 2.97 \%$$

Calculations

- **Titer Determinations:**

- The **titer** is usually determined by a direct titration, but the calculation is a little different.
- The titer (t) is defined as the actual concentration (c_{act}) divided by the nominal concentration (c_{nom}) of a titrant:

$$t = \frac{c_{\text{act}}}{c_{\text{nom}}}$$

- The following formula can be used to calculate the titer of a titrant, if this titrant was used to titrate a titer standard by a direct titration:

t = Titrant titer (no unit)

m = Titer standard sample size (in g or mL)

VEQ = Titrant consumption at the equivalence or end point (in mL)

c = (Nominal) titrant concentration (in mol/L)

C = Constant for unit conversion

$$t = \frac{m}{VEQ \cdot c \cdot C}$$

Calculations

- **Titer Determinations Continued:**

- If the titer standard substance is a solid, use the following formula for the constant C:

$$C = \frac{M}{10 \cdot p \cdot z}$$

- For liquid titer standards the following constant is used:

$$C = \frac{1}{cst \cdot z}$$

M = Molar mass of the analyte (in g/mol)

p = Purity of the solid titer standard (in %)

z = Equivalent number of the titer standard (no unit)

cst = Concentration of the liquid titer standard (in mol/L)

•

Calculations

- Example 2:

- *Potassium hydrogen phthalate (KHP, $M = 204.23 \text{ g/mol}$) was used as a solid titer standard to determine the titer of sodium hydroxide ($c = 0.1 \text{ mol/L}$). 0.0931 g of KHP (purity: 99 %) was weighed into a titration beaker and diluted with deionized water.*
- *This solution was titrated with sodium hydroxide. The equivalence point was detected at a titrant consumption of 4.5238 mL . For this measurement the titer can be calculated as follows:*

$$C = \frac{M}{10 \cdot p \cdot z} = \frac{204.23 \frac{\text{g}}{\text{mol}}}{10 \frac{\text{mg}}{\text{g} \cdot \%} \cdot 99 \% \cdot 1} = 0.206 \frac{\text{g}}{\text{mmol}}$$

$$R = \frac{m}{VEQ \cdot c \cdot C} = \frac{0.0931 \text{ g}}{4.5238 \text{ mL} \cdot 0.1 \frac{\text{mol}}{\text{L}} \cdot 0.206 \frac{\text{g}}{\text{mmol}}} = 0.9990$$

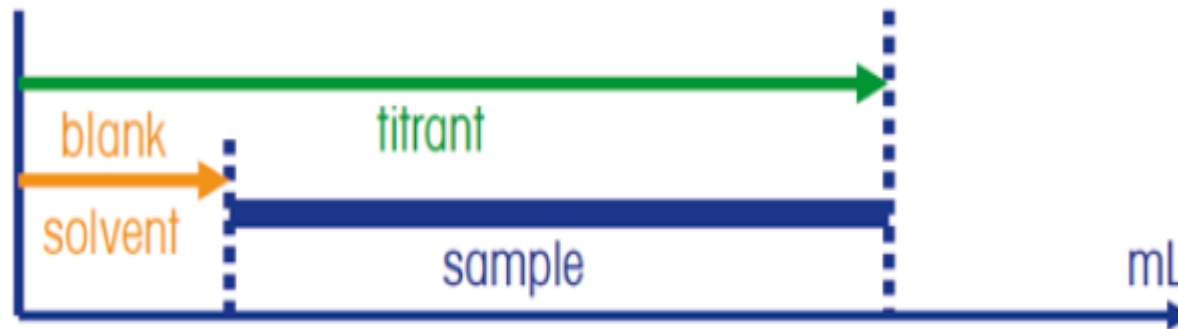
Calculations - Blanks

In some titrations it may happen that the solvent itself also reacts with the titrant. The amount of titrant used for the solvent is called the **blank value**.

The blank value must be **compensated** to get the correct result.

To determine the blank value a titration of the **solvent without any sample** has to be performed. The blank value is the volume of the titrant used until the equivalence or endpoint is reached.

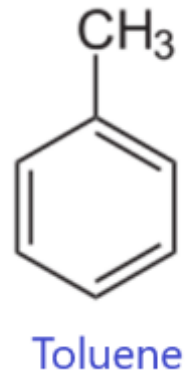
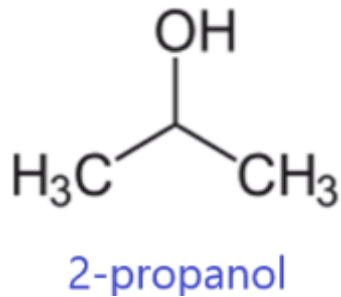
For a titration where a blank value is used, take care to always use the same solvent volume!



Calculations - Blanks

■ Example 3:

- *The acid number of motor oil is determined by a non-aqueous acid/base titration with potassium hydroxide (in 2-propanol) as titrant.*
- *The solvent mixture of toluene, 2-propanol and water is used.*
- *Before titrating the sample, the solvent mixture without any sample is titrated.*
- *The titrant consumption of this blank measurement is compensated in the calculation of the sample measurement.*



Calculations - Blanks

- The calculation of a blank value compensated titration is similar to the direct titration:

$$R = \frac{(VEQ - B) \cdot c \cdot t \cdot C}{m}$$

R = Result

VEQ = Used titrant volume until the equivalence or end point (in mL)

B = Blank value, titrant volume used for the titration of the solvent (in mL)

c = Titrant concentration (in mol/L)

t = Titrant titer (no unit)

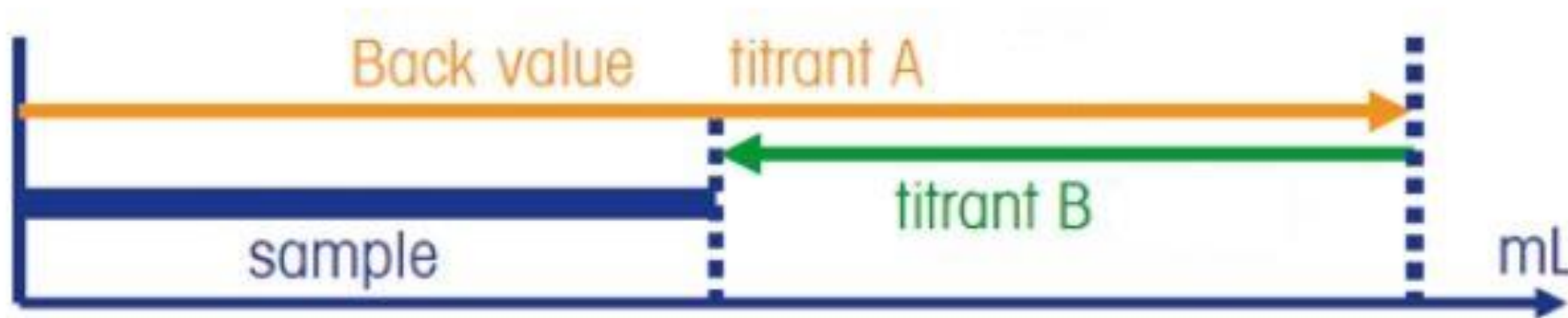
C = Constant for unit conversion

m = Sample size (in g or mL)

- The constant C is the same as for the direct titration

Calculations – Back Titrations

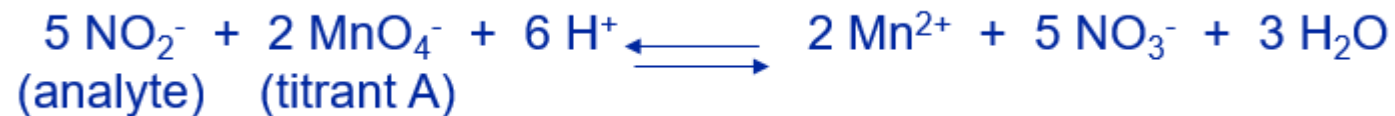
- In a **back titration** a known excess amount of reagent (titrant A with known concentration) is added to the sample. This titrant reacts with the analyte. Afterwards the amount of non-reacted titrant A will be titrated with a second titrant (titrant B).
- The added volume of titrant A must be known very precisely.
- For accurate measurements, a so called **back value** is determined by titrating the added volume of titrant A without any sample. The result is based on the used volume of titrant B without any sample.
- Such titrations are often used when the reaction between the analyte and the first titrant is slow.



Calculations – Back Titrations

■ Example 4:

- For the titration of nitrite in soya sauce a known volume of potassium permanganate (titrant A) is added to the sample.
- Potassium permanganate will react with the nitrite and the excess of the permanganate is titrated with ammonium ferrous sulfate(II) (titrant B).



Calculations – Back Titrations

- The analyte content in a back titration is calculated using the following formula:

$$R = \frac{(Bk - VEQ) \cdot c \cdot t \cdot C}{p \cdot m}$$

R = Result

Bk = Back value, volume of titrant B used for the titration of titrant A without sample (in mL)

VEQ = Volume of titrant B used to back titrate the excess of titrant A after sample addition (in mL)

c = Concentration of titrant B (in mol/L)

t = Titer of titrant B (no unit)

C = Constant for unit conversion (unit part, unit is depending on the result needed)

p = Stoichiometric proportion between titrant A and titrant B of the second reaction, stoichiometric factor of titrant B divided by factor of titrant A (no unit).

m = Sample size (in g or mL)

- The constant C is the same as for the direct titration

Calculations

- For calculation of the result the equivalent number, z must be known.
- The equivalent number of an analyte is determined by the stoichiometry. In general, the equivalent number is the number of moles "monovalent" titrant (e.g., NaOH, HCl, AgNO₃, Na₂S₂O₃) which are needed for the reaction with one mole of analyte.
- For acid/base titrations the equivalent number is the number of protons (H⁺) an acid releases by complete dissociation or the number of protons a base gains by reaction with an acid.
- For redox titrations the equivalent number is given by the number of electrons which are released or gained by a reductant or oxidant.

- ▶ Example 1: Sulfuric acid is a diprotic acid.



- ▶ Example 2: For the reduction of Cr⁶⁺ to Cr³⁺ three electrons are needed.



Calculations

- If a titrant is "polyvalent" the equivalent concentration (normality) must be used for calculation.
- The equivalent concentration of titrant A is calculated by the following formula, where z is the equivalent number of the titrant:

$$c(1/z A) = c(A) \cdot z$$

- Example 1: Sulfuric acid ($c(\text{H}_2\text{SO}_4) = 0.05 \text{ mol/L}$) as titrant:



$$c(1/2 \text{H}_2\text{SO}_4) = c(\text{H}_2\text{SO}_4) \cdot z = 0.05 \frac{\text{mol}}{\text{L}} \cdot 2 = 0.1 \frac{\text{mol}}{\text{L}}$$

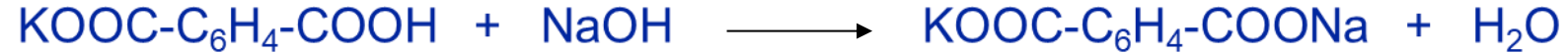
- Example 2: Potassium permanganate ($c(\text{KMnO}_4) = 0.02 \text{ mol/L}$) as titrant:



$$c(1/5 \text{KMnO}_4) = c(\text{KMnO}_4) \cdot z = 0.02 \frac{\text{mol}}{\text{L}} \cdot 5 = 0.1 \frac{\text{mol}}{\text{L}}$$

Calculations

- To calculate the content of the analyte, the titrant concentration must be known very accurately.
- To determine the exact titrant concentration, a titer determination is carried out prior to the sample analysis.
- For the titer determination, a substance of high purity (titrimetric standard) is titrated.
 - Example: The titer of sodium hydroxide is determined by titrating potassium hydrogen phthalate.



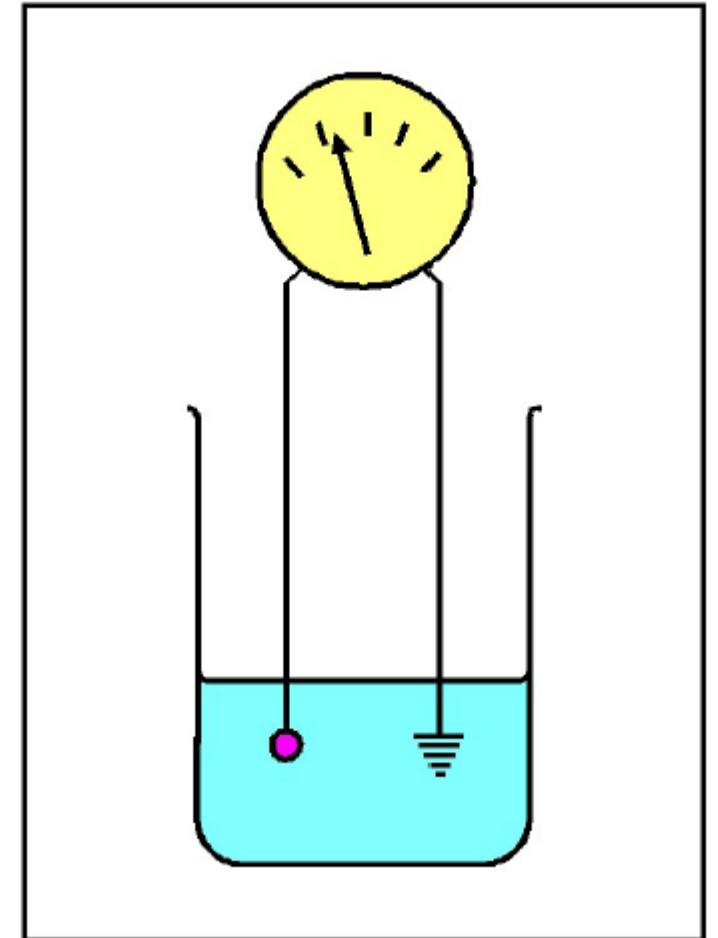
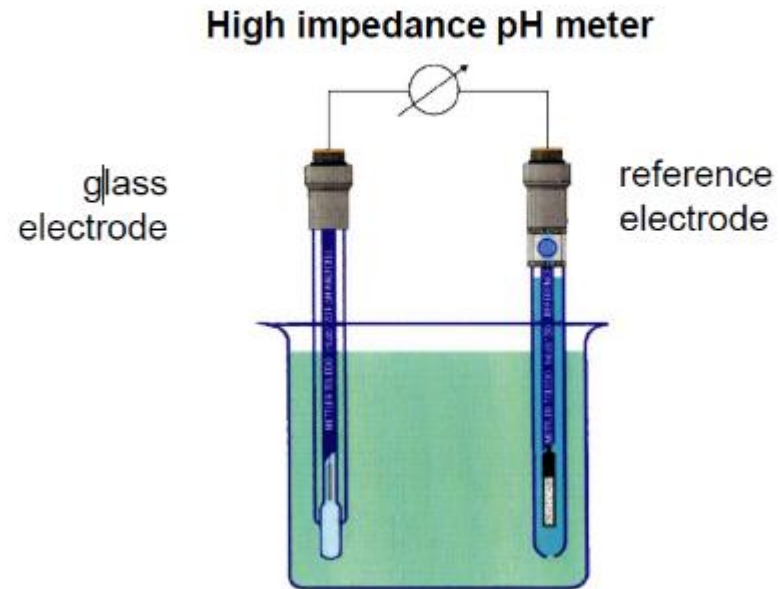
- The actual titrant concentration (c_{act}) is the nominal concentration (c_{nom}) times the titer (t)

$$c_{\text{act}} = c_{\text{nom}} \cdot t$$

Probes

- Probes (Electrodes):
 - Probes basically measure the current change between the analyte and the reference.

MEASUREMENT CIRCUIT



Probes – Reference vs Indicator

- What is the difference between Reference Electrodes and Indicator Electrodes?
 - Indicator electrode responds to changes in the activity of the analyte.
 - Reference electrode does not respond to changes, and its response is stable.



Probes – Reference vs Indicator

- Reference Electrode:
 - A reference electrode is an electrode which has a stable and well-known electrode potential.
 - Its high stability is achieved by employing the redox system, which must contain saturated concentrations in each of the participating solutions of the reaction.
 - For the measured potential to have meaning in this context, the reference electrode must be constructed so that its composition is fixed, and its response is stable over time, with observed changes in measured potential due solely to changes in analyte concentration.
 - Three types of reference electrodes:
 - Calomel: (Mercury/ Mercuric Chloride)
 - Silver/Silver Chloride
 - Safe and good temperature tolerance
 - Reversible reaction permits electro flow via ion carriers
 - Redox-Coupled Half Cell: (Platinum/Iodide Electrolyte Coupling)



Probes – Reference vs Indicator

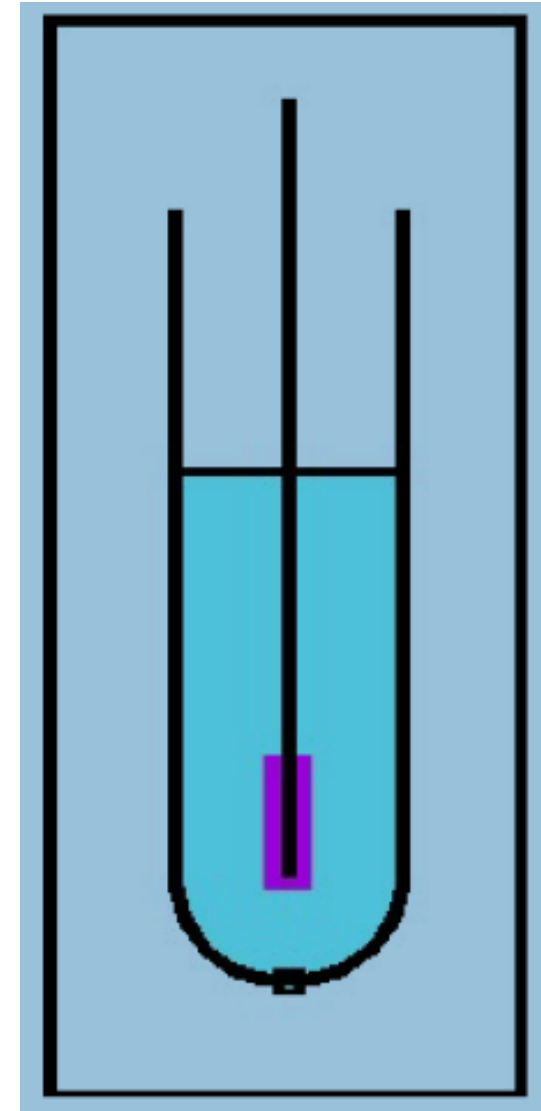
- Reference Electrode:

The silver reference wire **MUST** be coated with silver chloride.

Potassium chloride will dissolve the AgCl, thus it must be saturated in AgCl to prevent this.

Ionic travel is via a ceramic frit or “junction” and allow flow

Some have ceramic plug frit, annular porous ring or ground glass joint.



Probes – Reference vs Indicator

- Reference Electrode: Double Junction

Double Junction mean the electrolyte in the lower chamber may be difference from that in the upper chamber and perhaps less reactive to sample constituents.

Typical alternate electrolytes might be the following.

3 M KCl

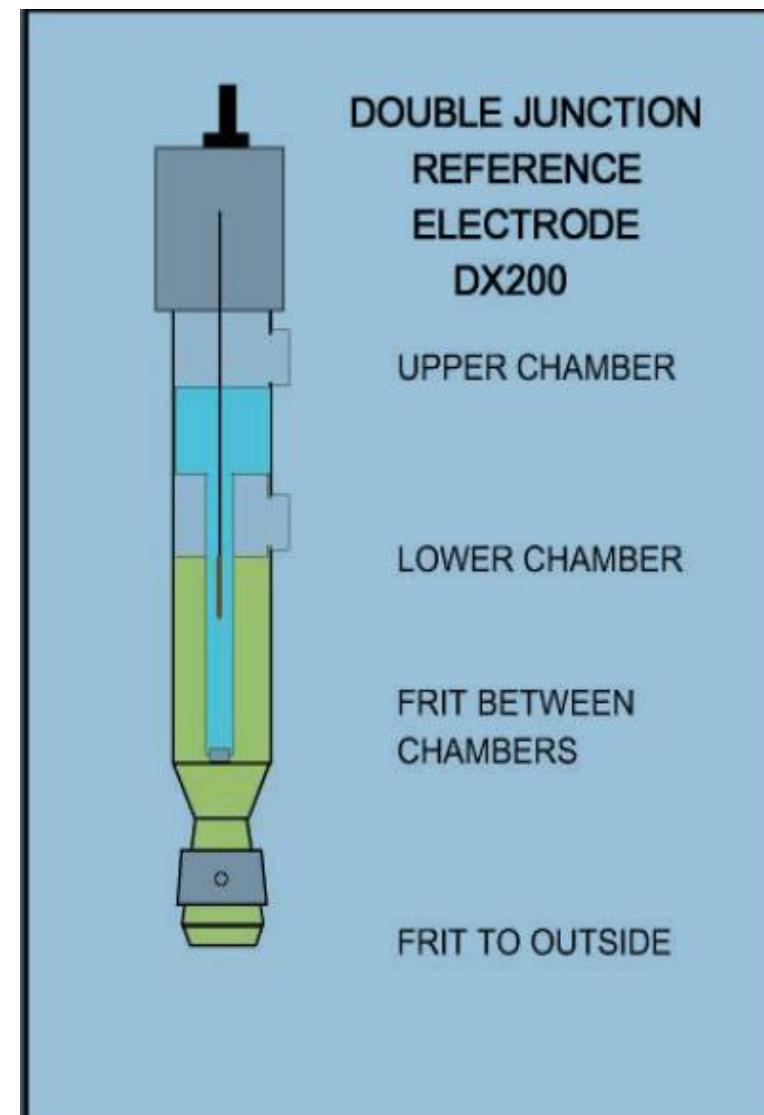
1 M NaCl

KNO_3

LiCl in EtOH

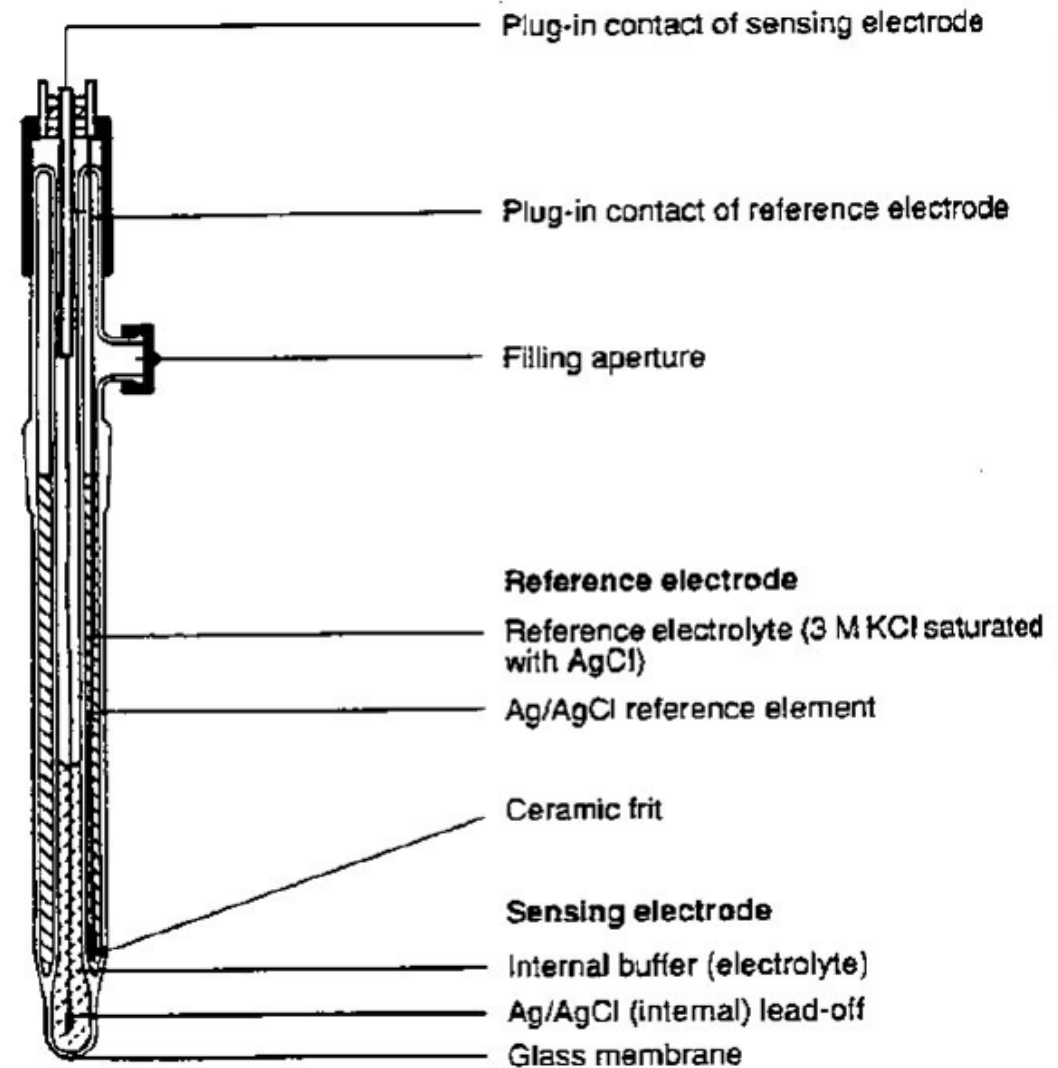
LiCl in glacial acetic acid

KClO_4 in glacial acetic acid



Probes

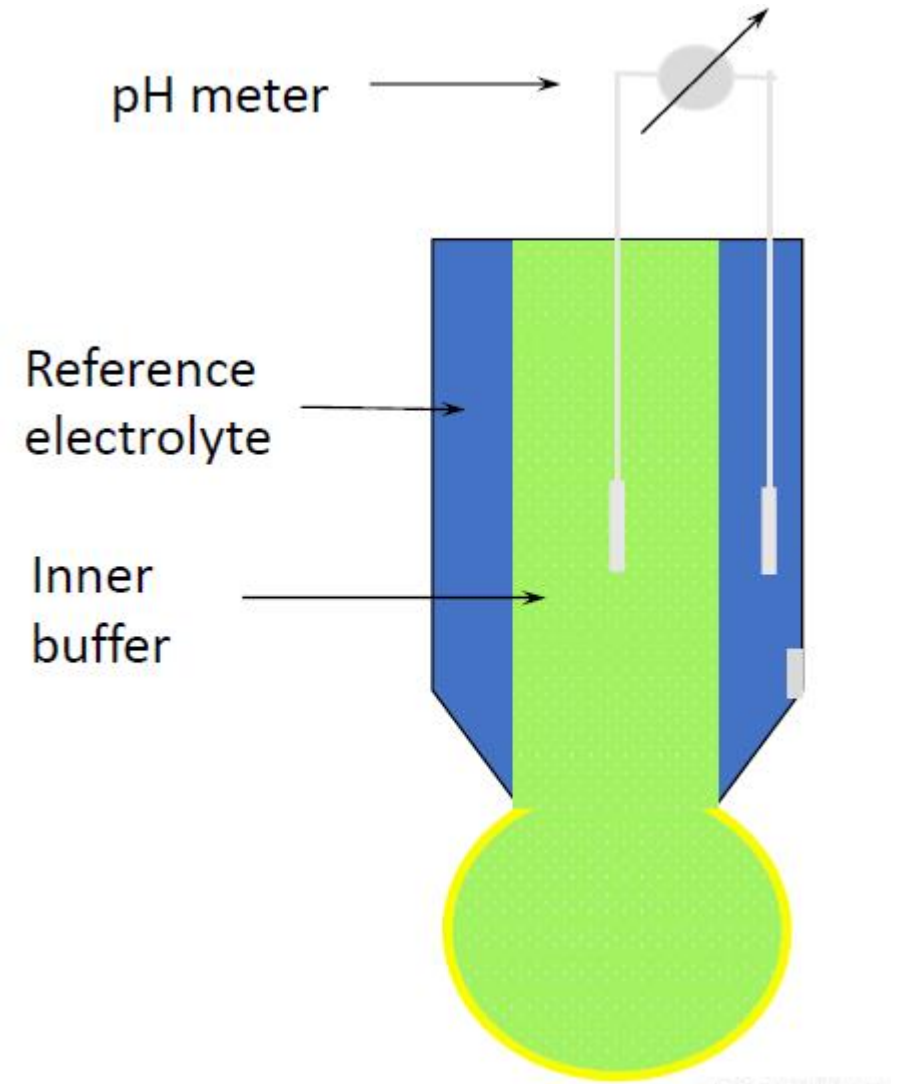
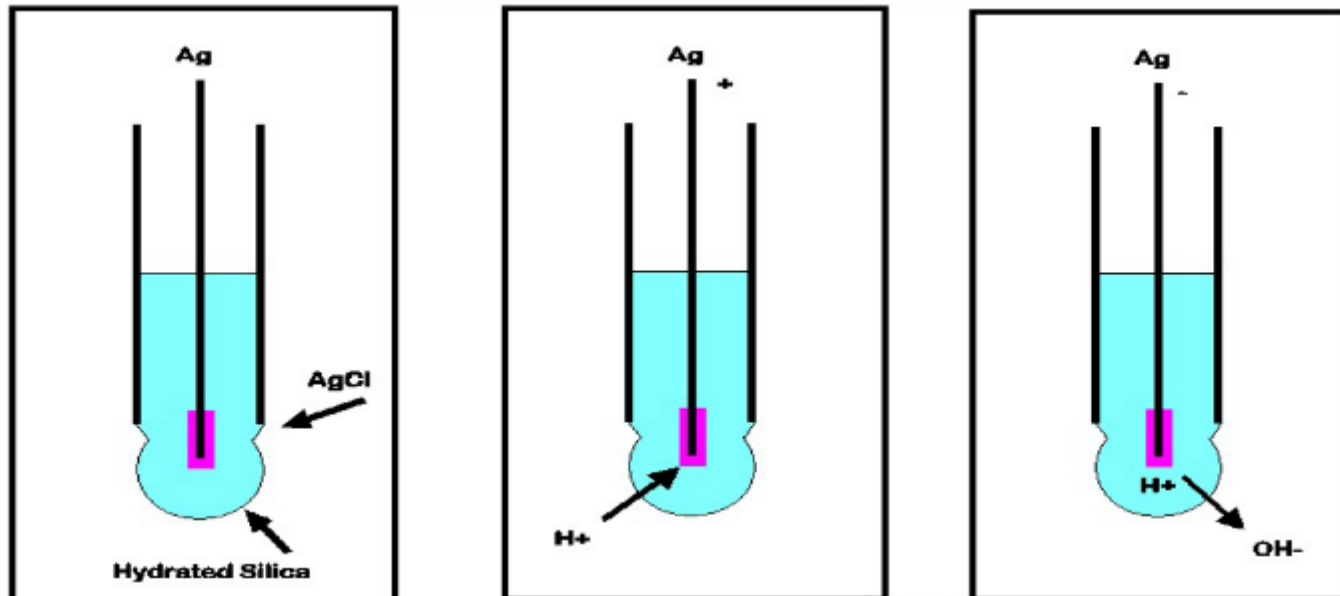
- Typical Combination pH Electrode



Probes

- pH Electrode:

- pH electrode is a chamber with a silver chloride coated silver wire in an enclosed by a thin membrane.
- The outer layer of glass is hydrated silicon oxide doped with metal ions.
- This layer transports positive charges through the glass.
- The concentration of the H^+ outside influences the charge inside and the potential changes.



OTHER ANALYSES



**Characterization of all
aspect of a sample**

Total Sulfur/Nitrogen
Analyzer
CHNS
Total Chloride
Density
Metal Content
Viscosity

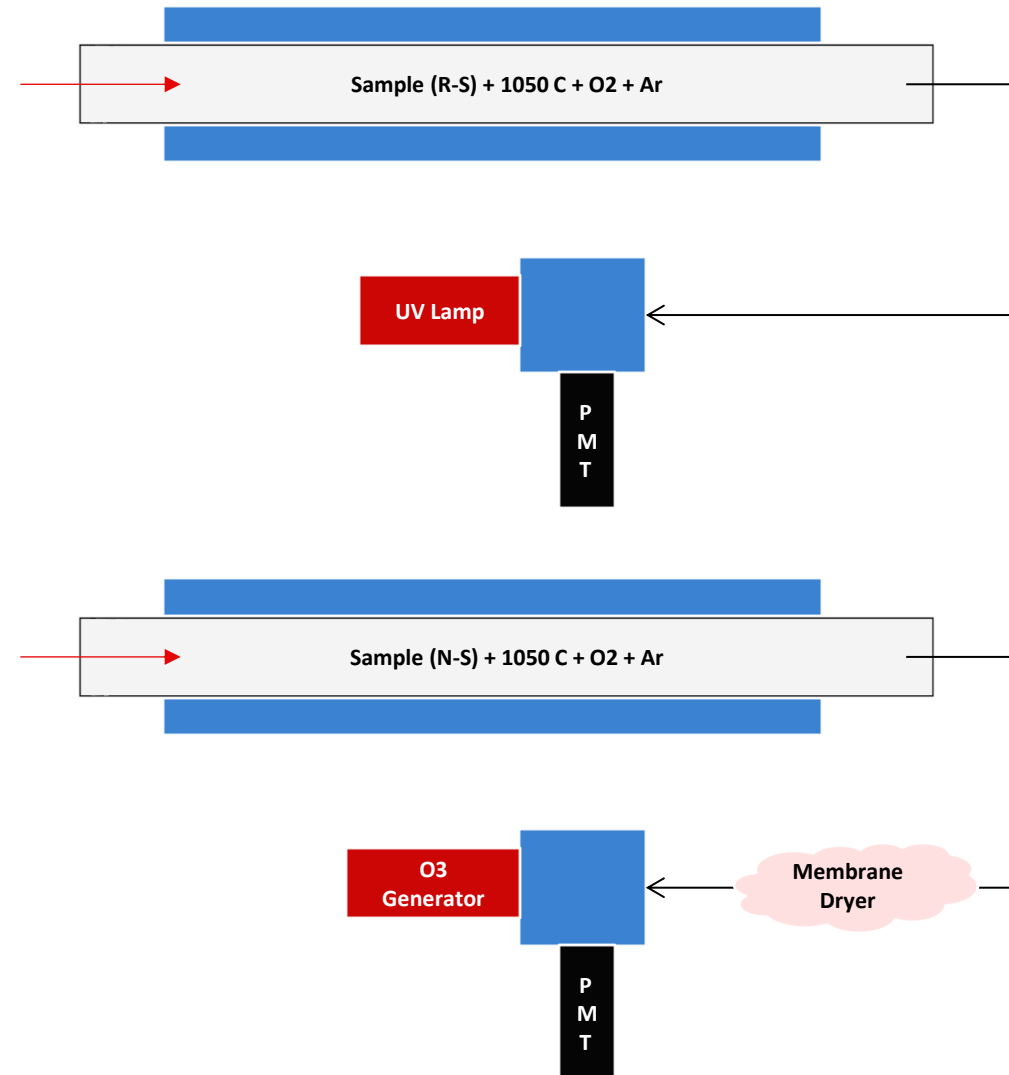
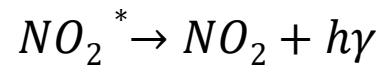
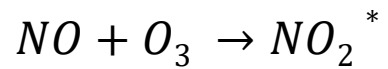
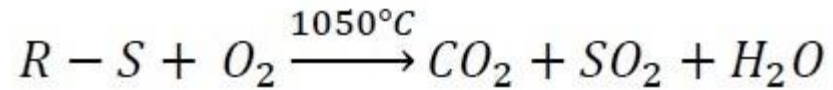
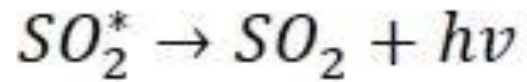
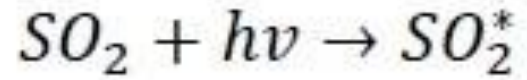


**Applications cover all
analyses**

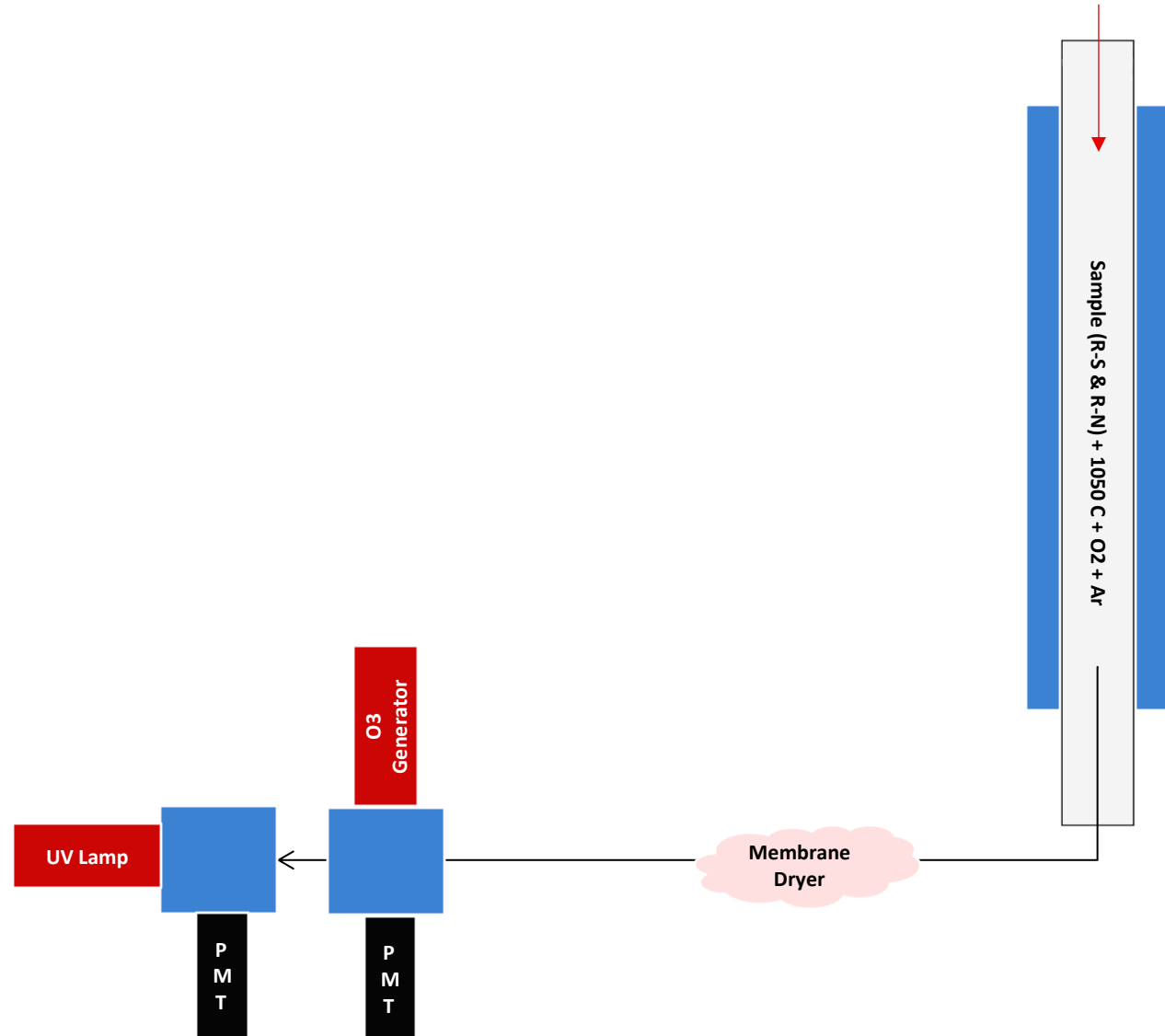
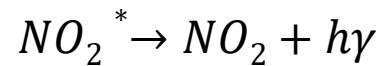
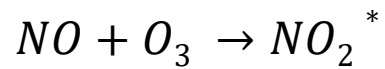
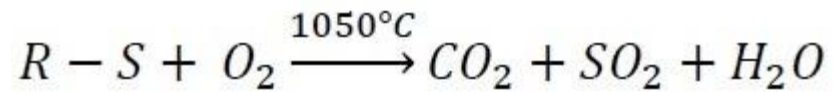
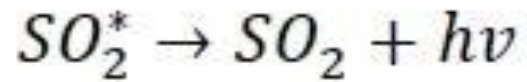
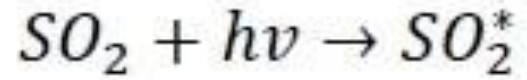
Total Oxygen
Densitometer
ICP and ICP-MS
Viscometer
XRD
XRF



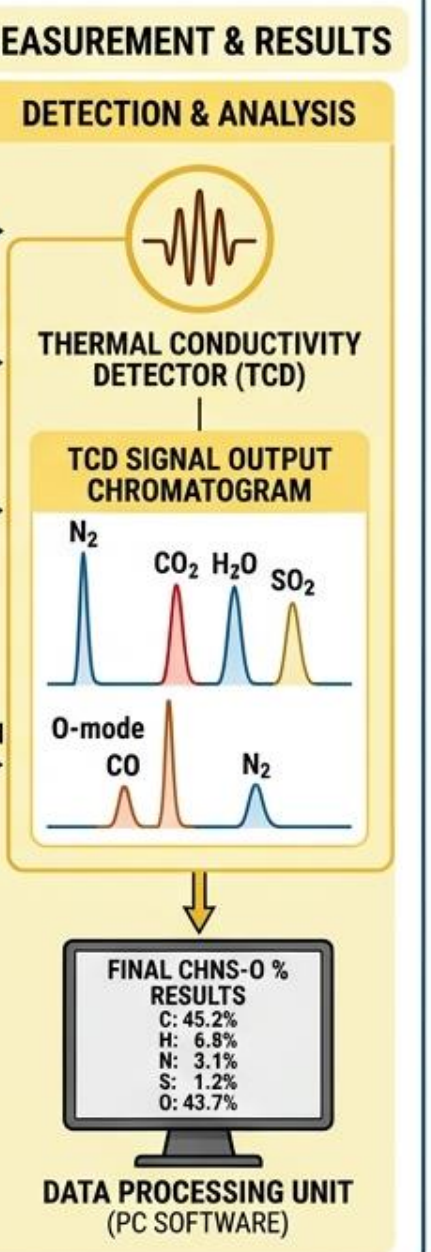
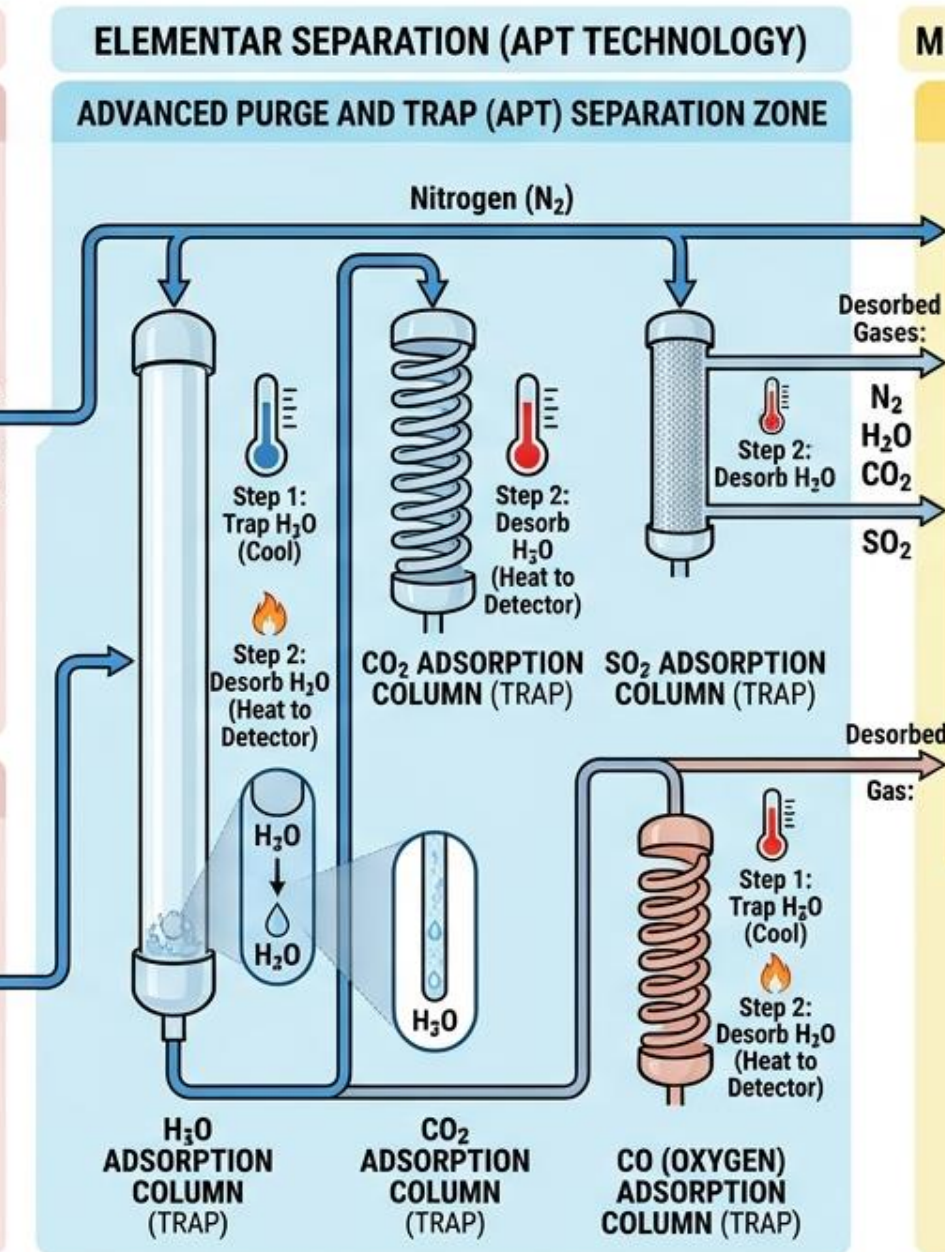
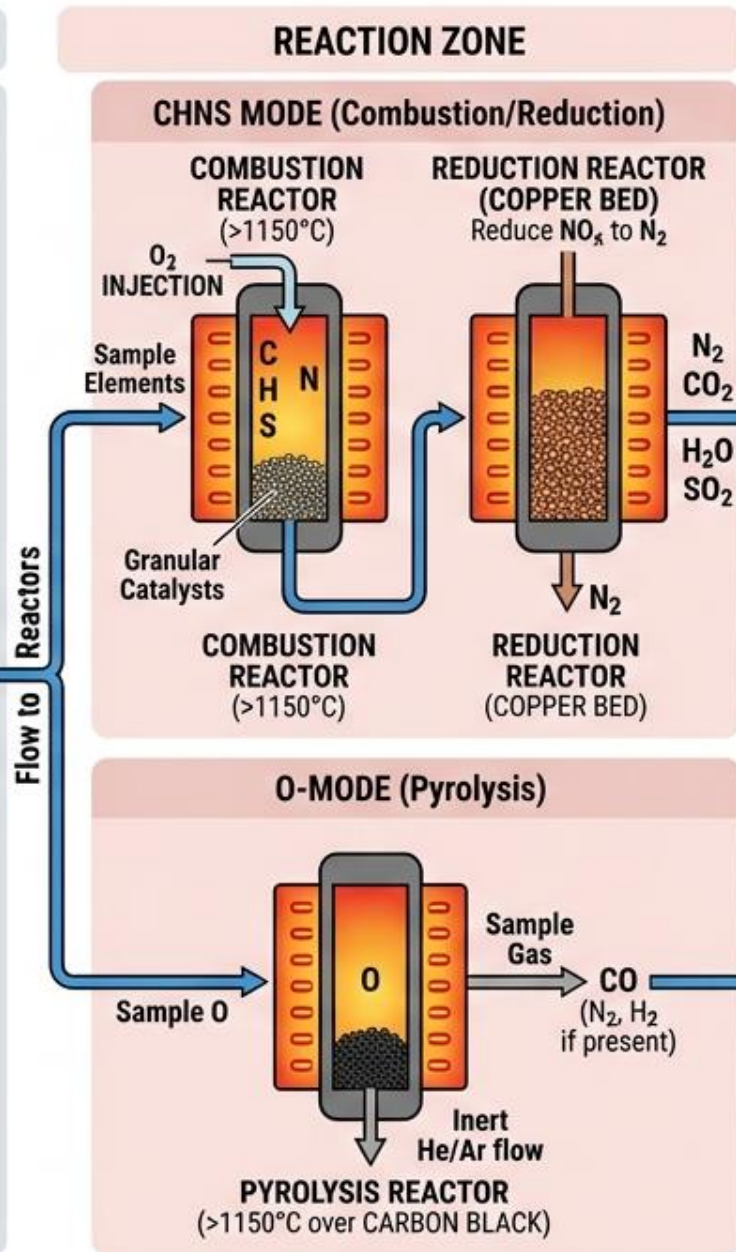
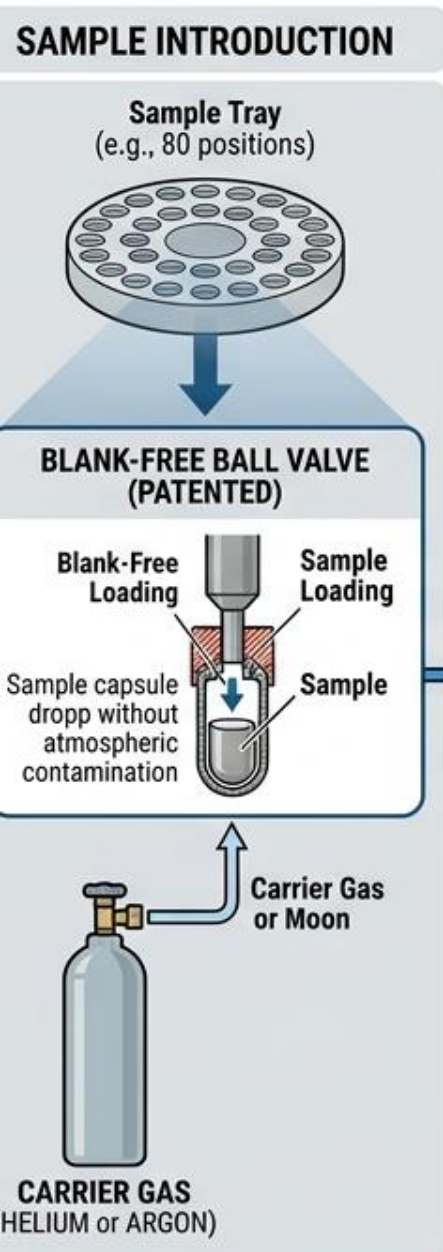
Total Sulfur & Nitrogen Analyzers



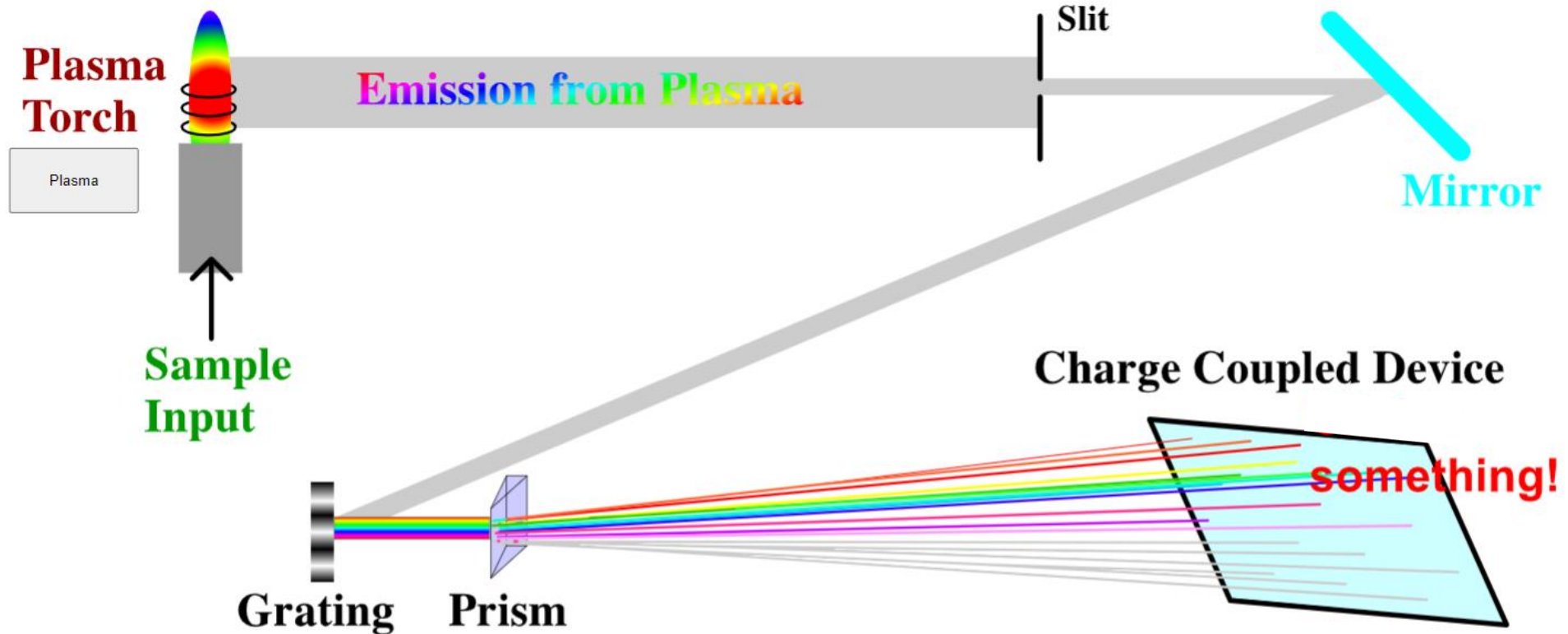
Total Sulfur & Nitrogen Analyzers



ELEMENTAR CHNS-O ANALYZER WORKFLOW SCHEMATIC (APT TECHNOLOGY)



Inductively Coupled Plasma



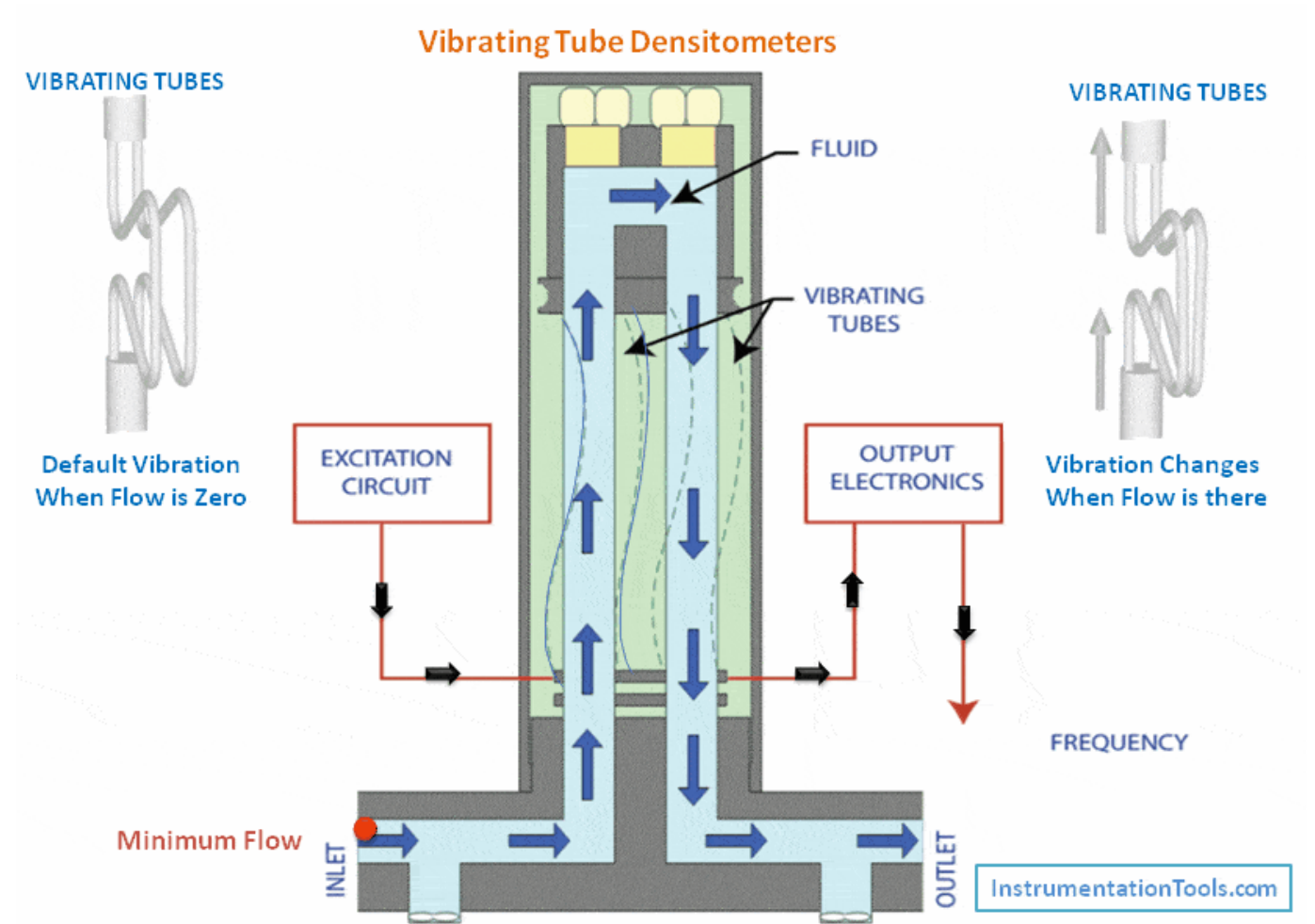
Two dispersion elements

Many of the dispersed light rays shown here are in the ultraviolet and, therefore, actually invisible.

Element	Cu	Mn	V	Mg	Cr	Fe
Primary λ , nm	327	294	291	285	267	238
Secondary λ	625	485	509	411	534	438
Tertiary λ	450	602	398	591	433	
Quaternary λ		403				

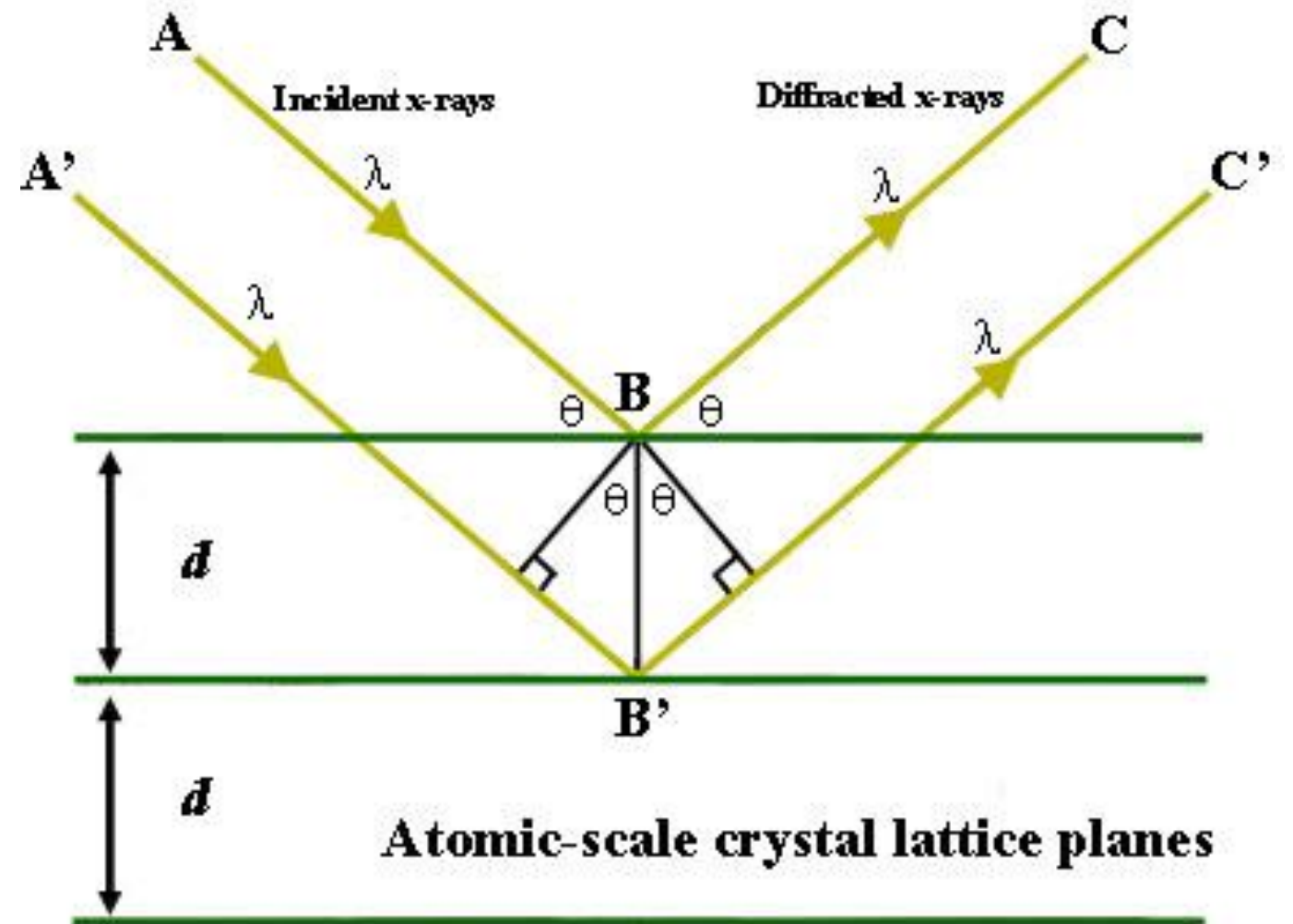
Densitometer Theory

- <https://instrumentationtools.com/densitometers-working-principle/>

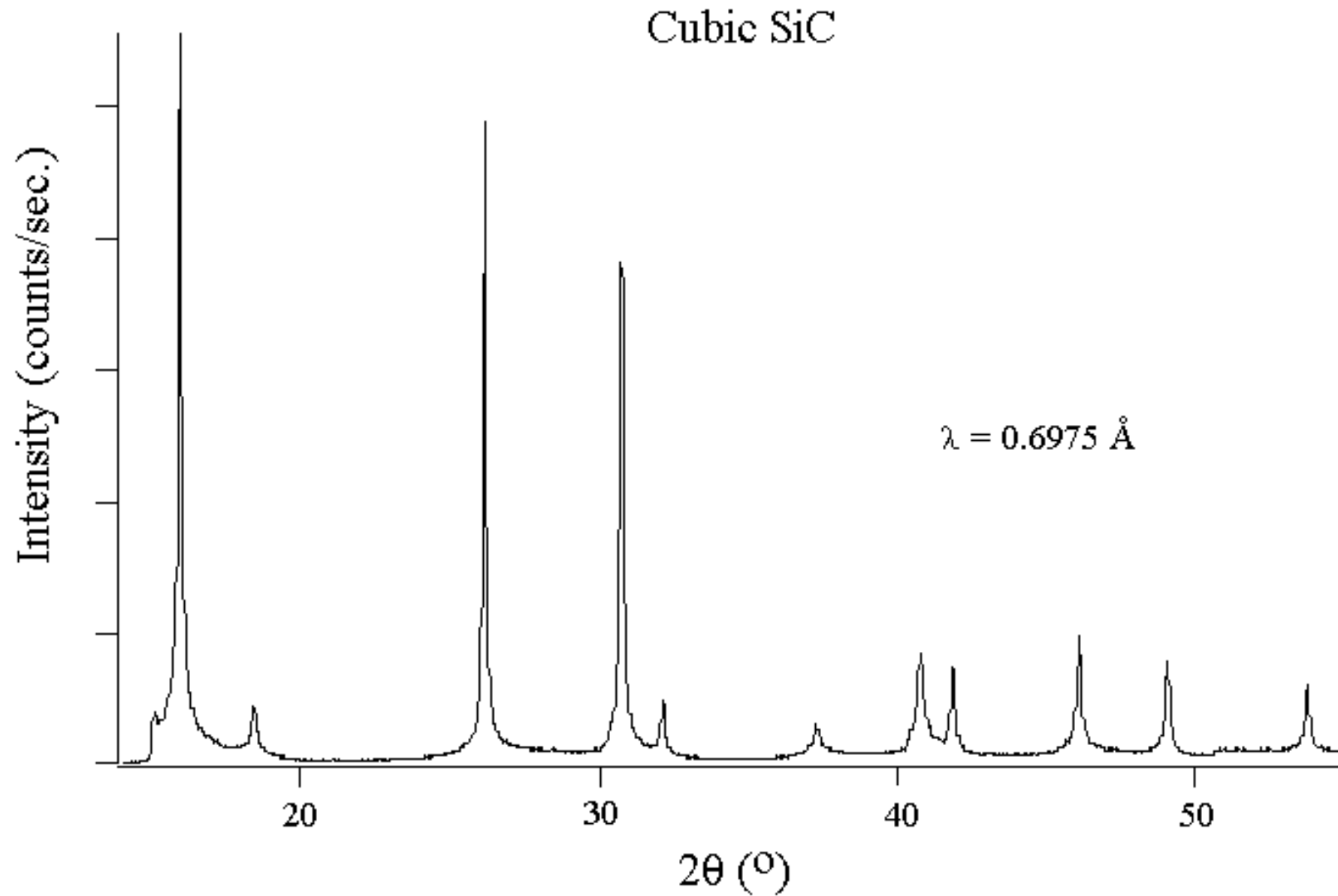


X-Ray Diffraction (XRD)

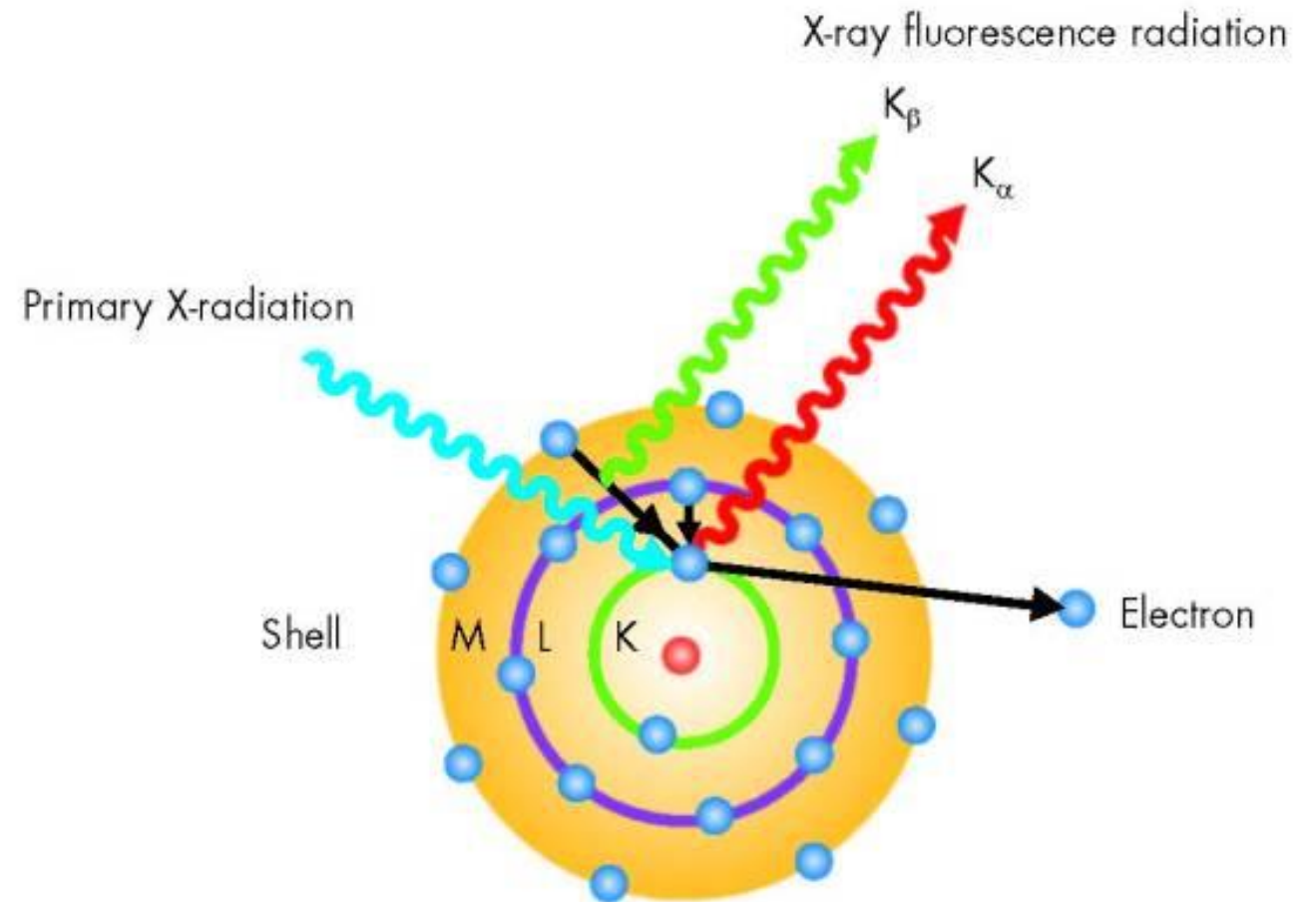
- Defined by Bragg's Law
- $n\lambda = 2d \sin\theta$



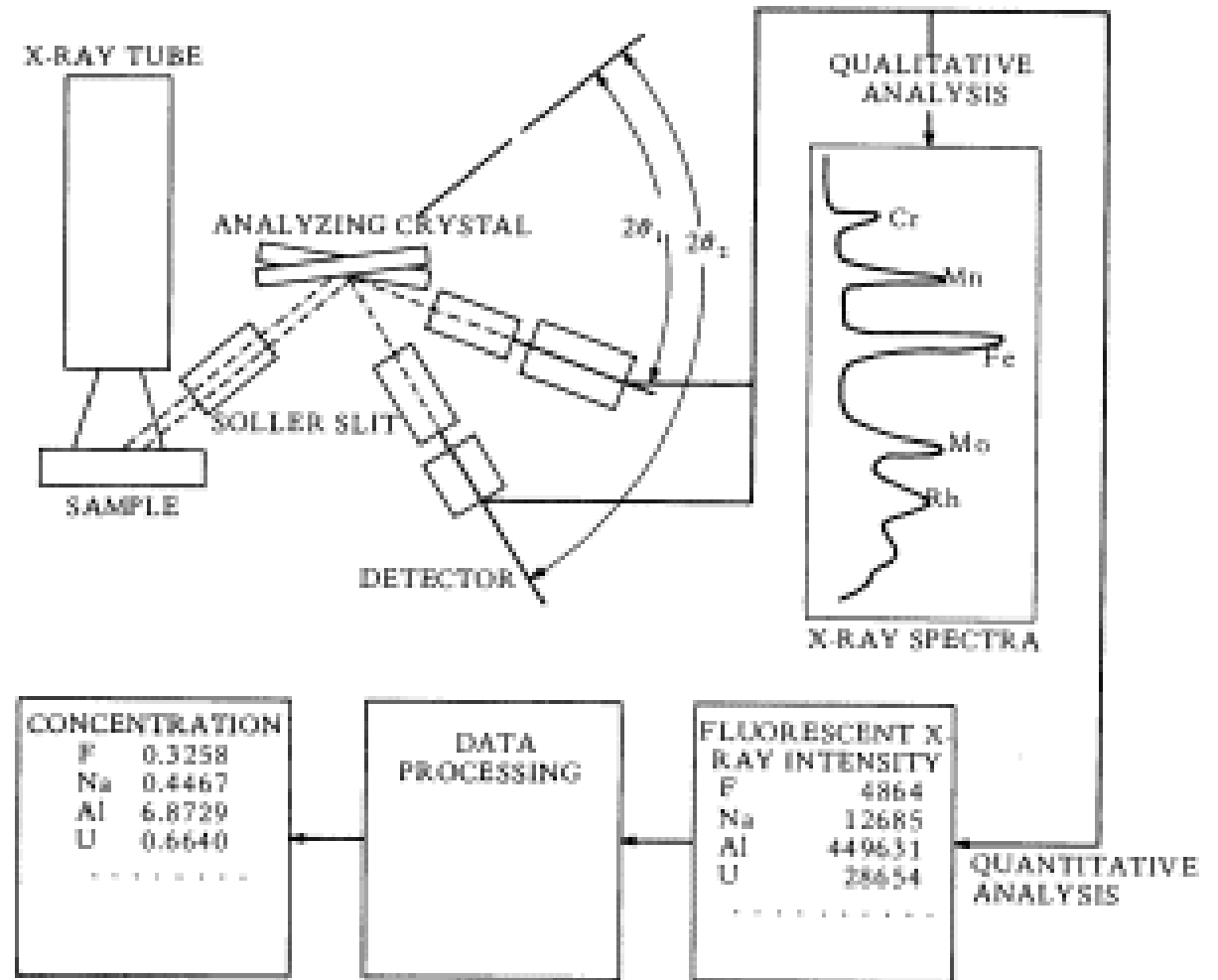
Example of XRD result



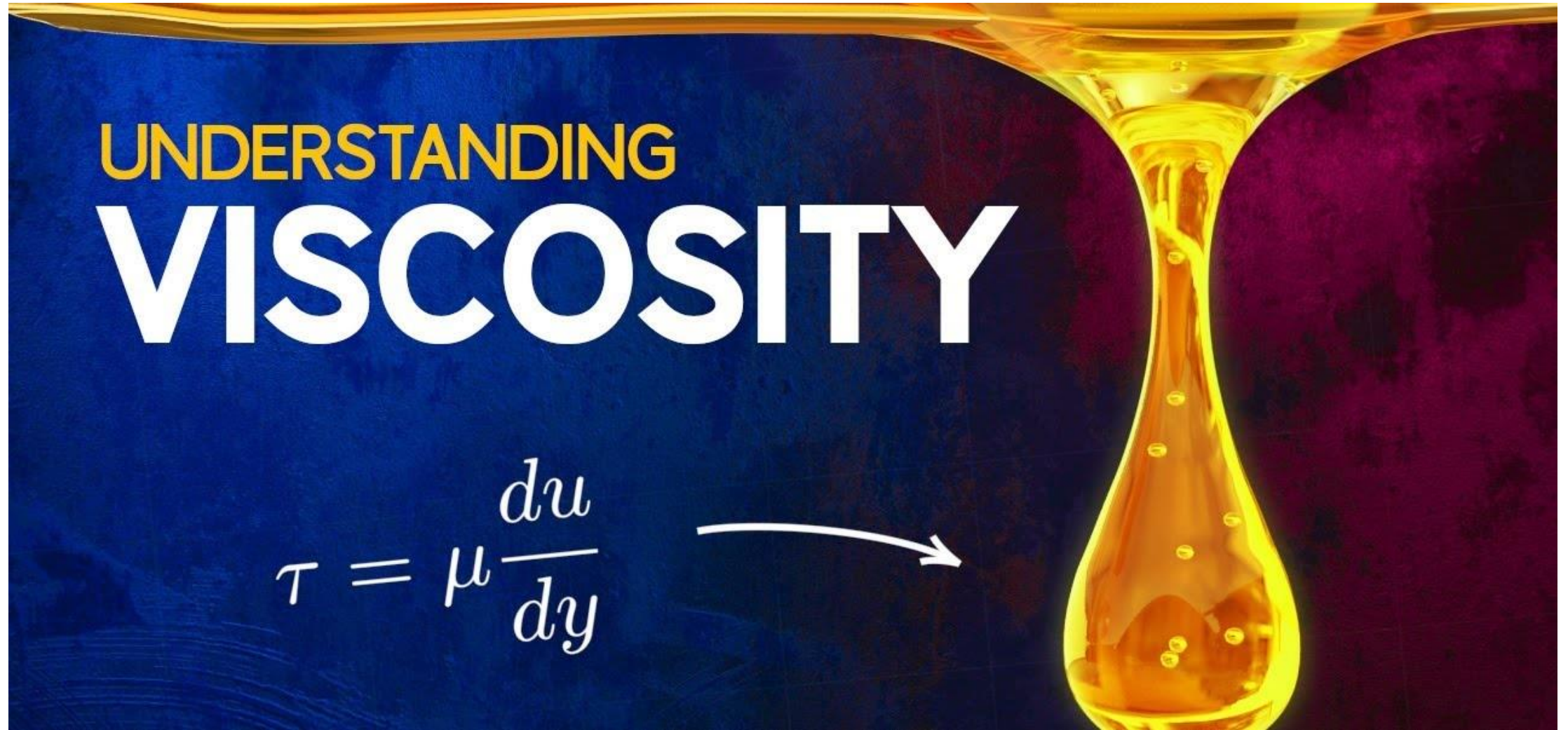
X-Ray Fluorescence (XRF)



X-Ray Fluorescence (XRF)



Viscosity Measurements: A Sticky Situation

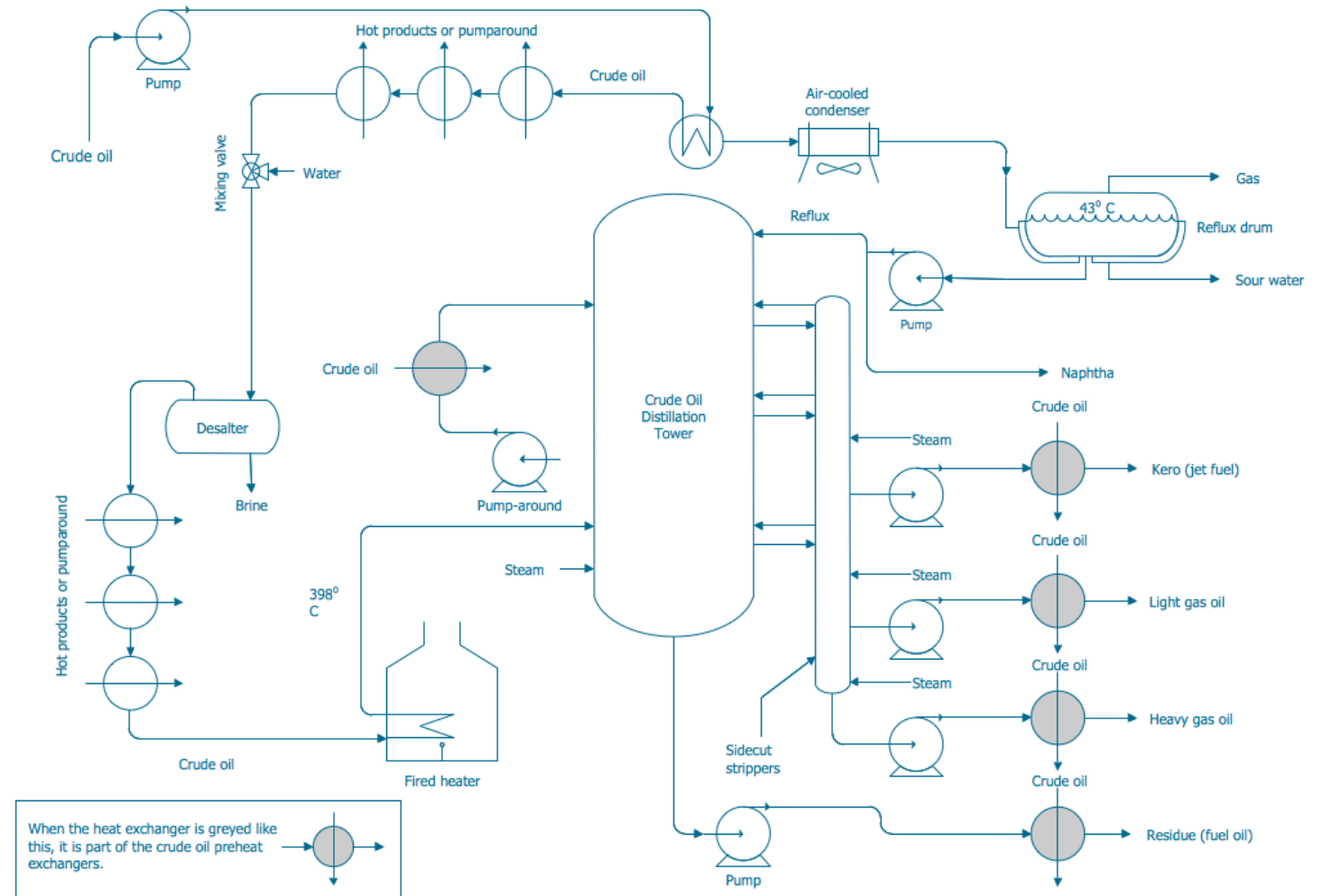


What is Viscosity

It is a property of fluid and a measure that describes a fluid's resistance to flow.

WHY DO WE CARE

Knowing how a material will behave affects the design of a process.

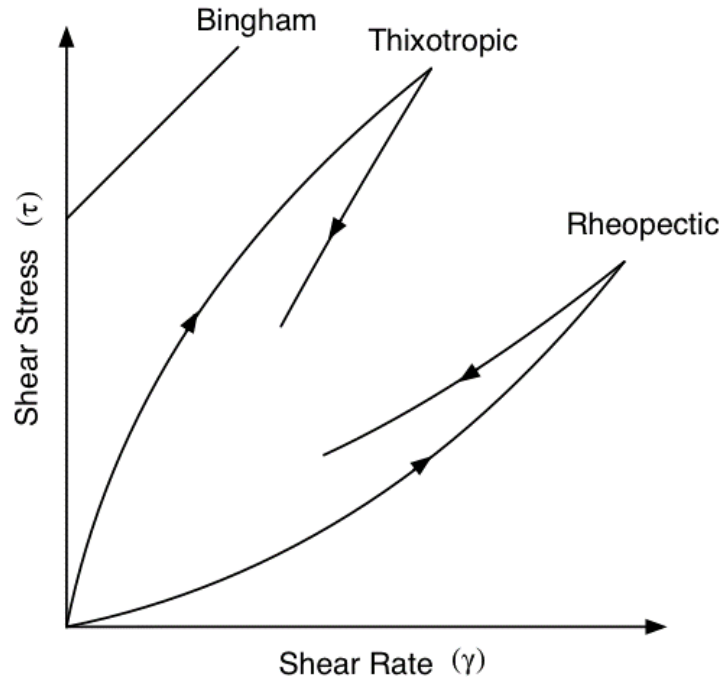


What affects viscosity

- Temperature
- Chemical composition-
size and shape
- Suspended materials
- Colloidal system

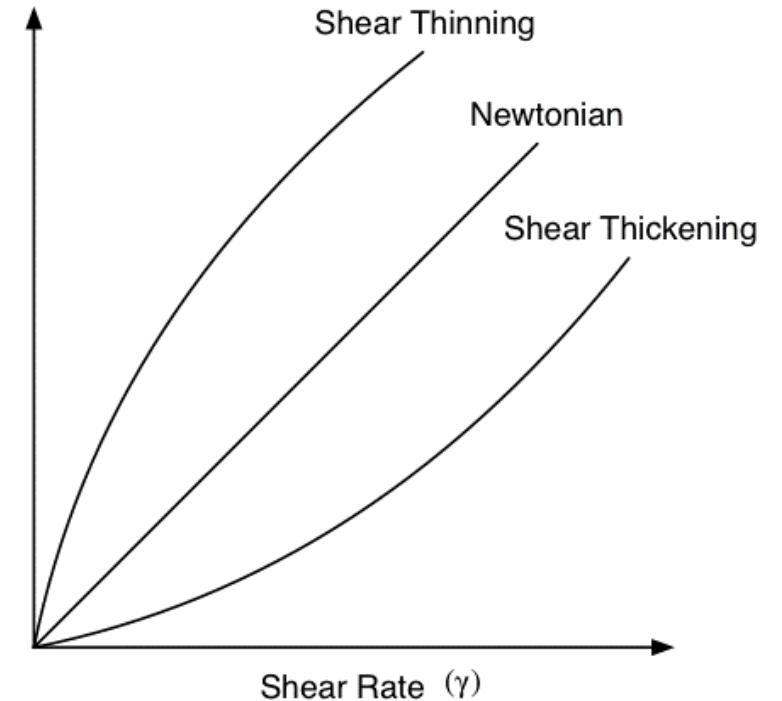


Newtonian vs Nonnewtonian



Nonnewtonian

The viscosity is not constant. It is dependent on the force being applied.

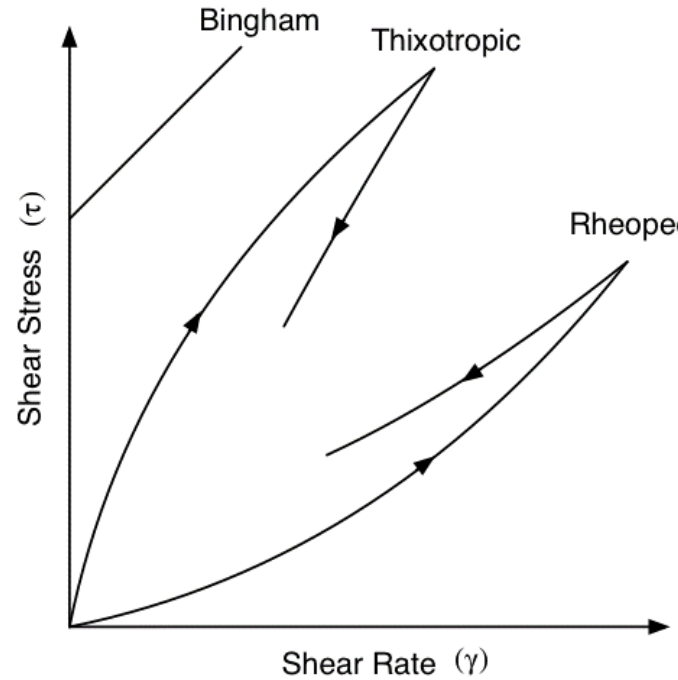


Newtonian

The viscosity is constant, no matter the force being applied.

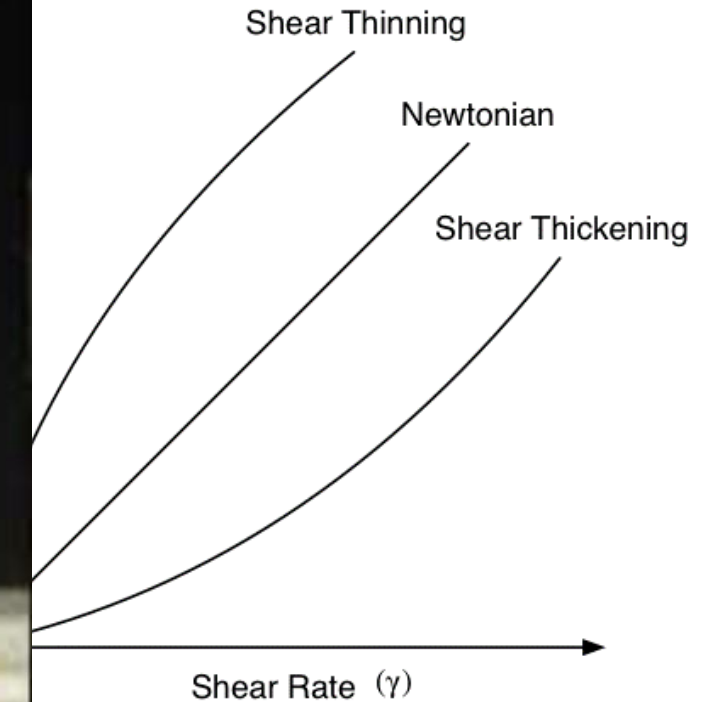
Newtonian

Newtonian



Nonnewtonian

The viscosity is not constant. It is dependent on the force being applied.



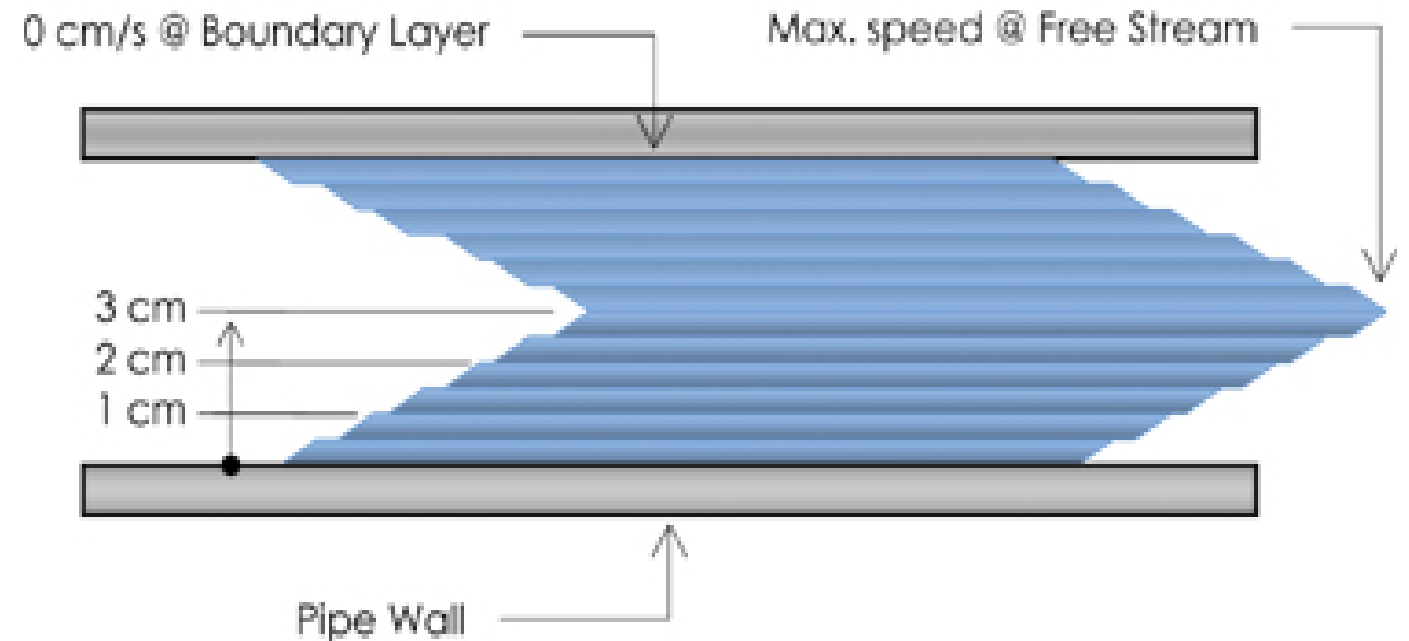
Newtonian

The viscosity is constant, no matter the force being applied.

The Force is Within

There are two **Forces** that play a role.

- The force required to push the fluid
- The internal resistive force of the fluid.



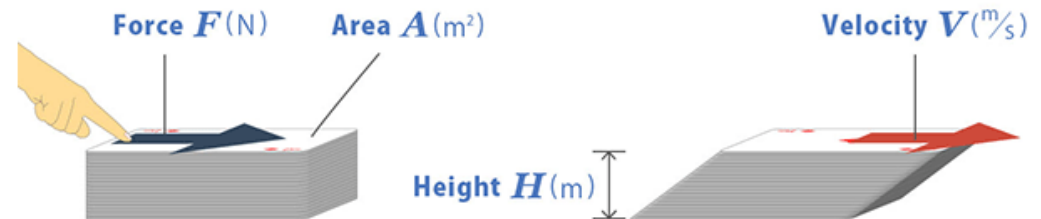
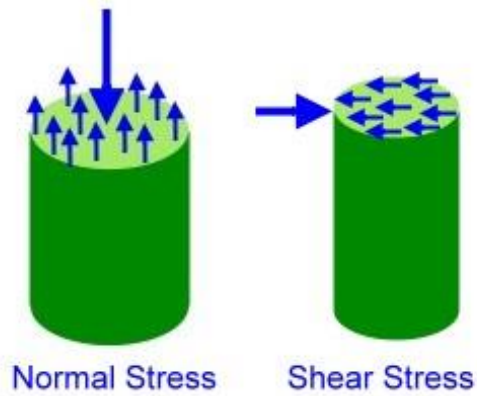
The Math Behind The Force

$$\text{Shear Stress} = \tau = \frac{\text{Force}}{\text{Area}} = \frac{\text{Force}}{\text{Length}^2}$$

$$\text{Shear Rate} = \frac{\Delta \text{Velocity}}{\Delta \text{Distance}} = \frac{\text{length}}{\text{time}} \times \frac{1}{\text{length}} = \frac{1}{\text{time}}$$

$$\frac{\frac{\text{Force}}{(\text{length})^2}}{\frac{1}{\text{time}}} = \frac{\text{Force} \times \text{time}}{(\text{length})^2}$$

$$\text{SI units} = \frac{\text{Ns}}{\text{m}^2} = \text{Pa} \cdot \text{s}$$





Who needs math...

Let the instrument do it for you

Viscosity Types

Kinematic Viscosity

- frequently measured using a capillary tube
- measuring units are $[\text{cm}^2/\text{s}]$ or $[\text{cSt}]$
- measures internal resistance to flow under gravitational forces
- density dependant
- do not run fluids with suspended solids

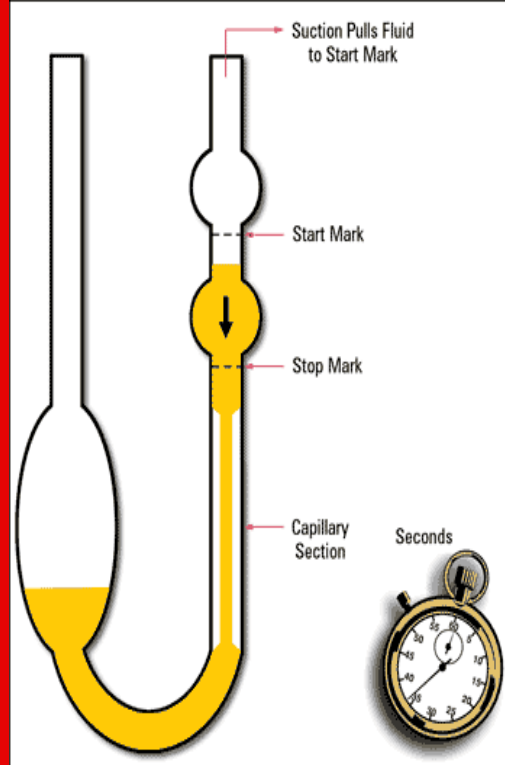
Dynamic Viscosity (aka Absolute viscosity)

- frequently measured using a spindle
- measuring units are $[\text{cP}]$ or $[\text{dyns/cm}]$
- measures internal resistance to flow with an external force
- Not density dependant
- suspended solids are ok

What are the differences

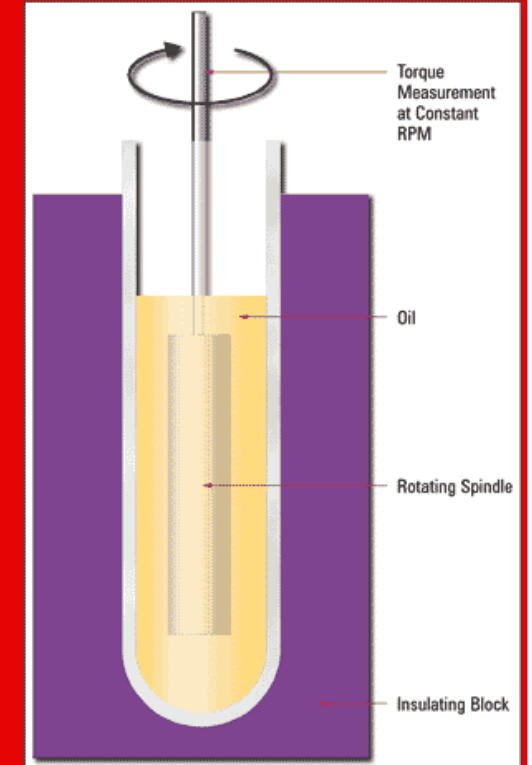
Kinematic

ASTM D445
Viscosity is measured by noting the time it takes the oil to travel through the orifice of a capillary under the force of gravity.



Rotational

ASTM D2983
Viscosity is measured as the resistance to flow with an external force, such as a spindle.



What are the limits



Max Temp
150 °C

Min Temp
40 °C

No
suspended
solids

Max Temp
300 °C

Min Temp
40 °C

OK with
suspended
solids



TYPICAL METHOD SOURCES

ASTM: American Society for Testing & Materials

IP: Institute of Petroleum, London

UOP: Universal Oil Products

Gas Processors Association

Open literature

Vendor technology

Documented Modifications

ASTM D2163-14

Standard Test Method for Determination of Hydrocarbons in Liquefied Petroleum (LP) Gases and Propane/Propene Mixtures by Gas Chromatography

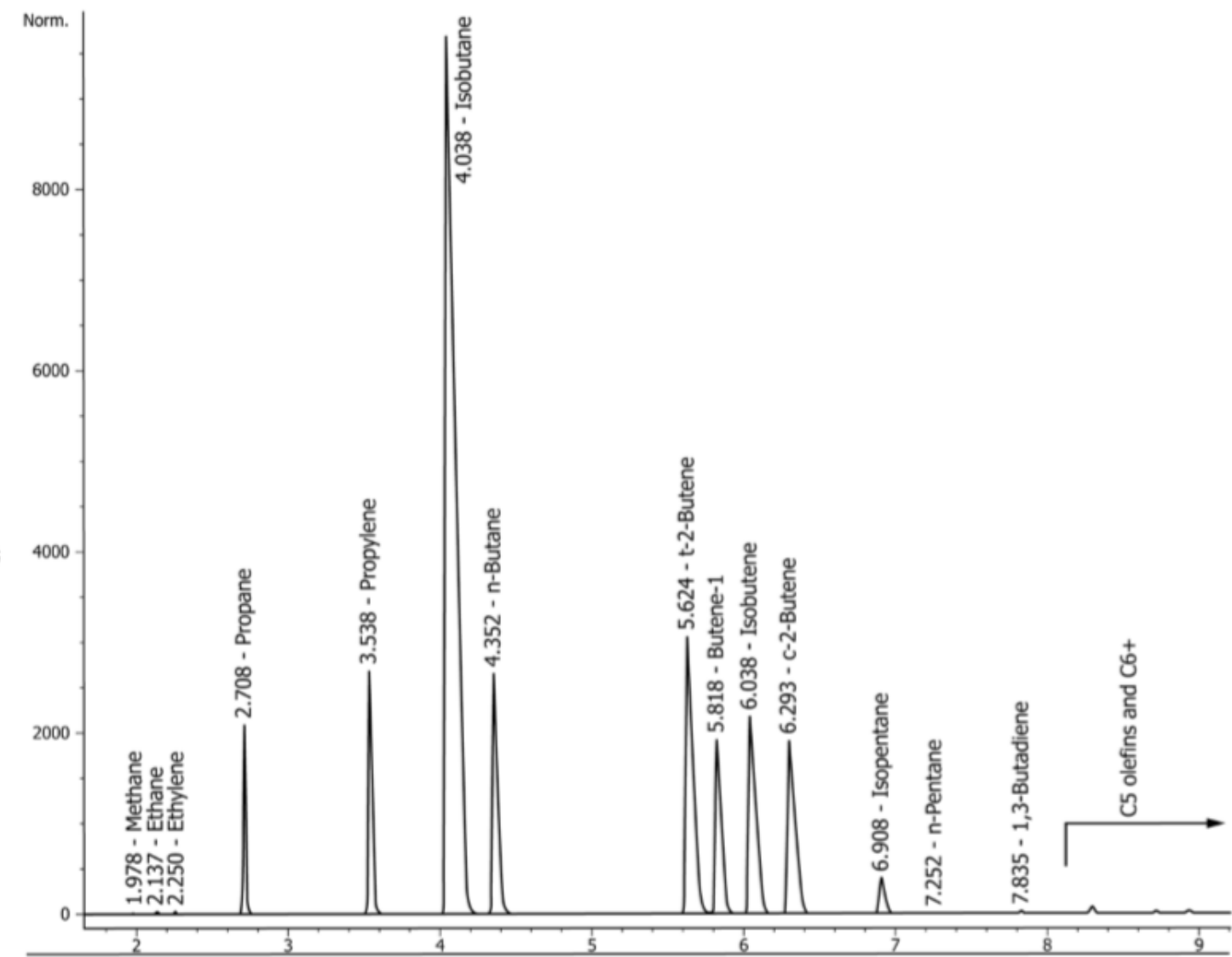
- 1. Scope
 - 1.1 This test method covers the quantitative determination of individual hydrocarbons in liquefied petroleum (LP) gases and mixtures of propane and propene, excluding high-purity propene in the range of C1 to C5. Component concentrations are determined in the range of 0.01 to 100 volume percent.
 - 1.2 This test method does not fully determine hydrocarbons heavier than C5 and non-hydrocarbon materials, and additional tests may be necessary to fully characterize an LPG sample.

ASTM D2163-14

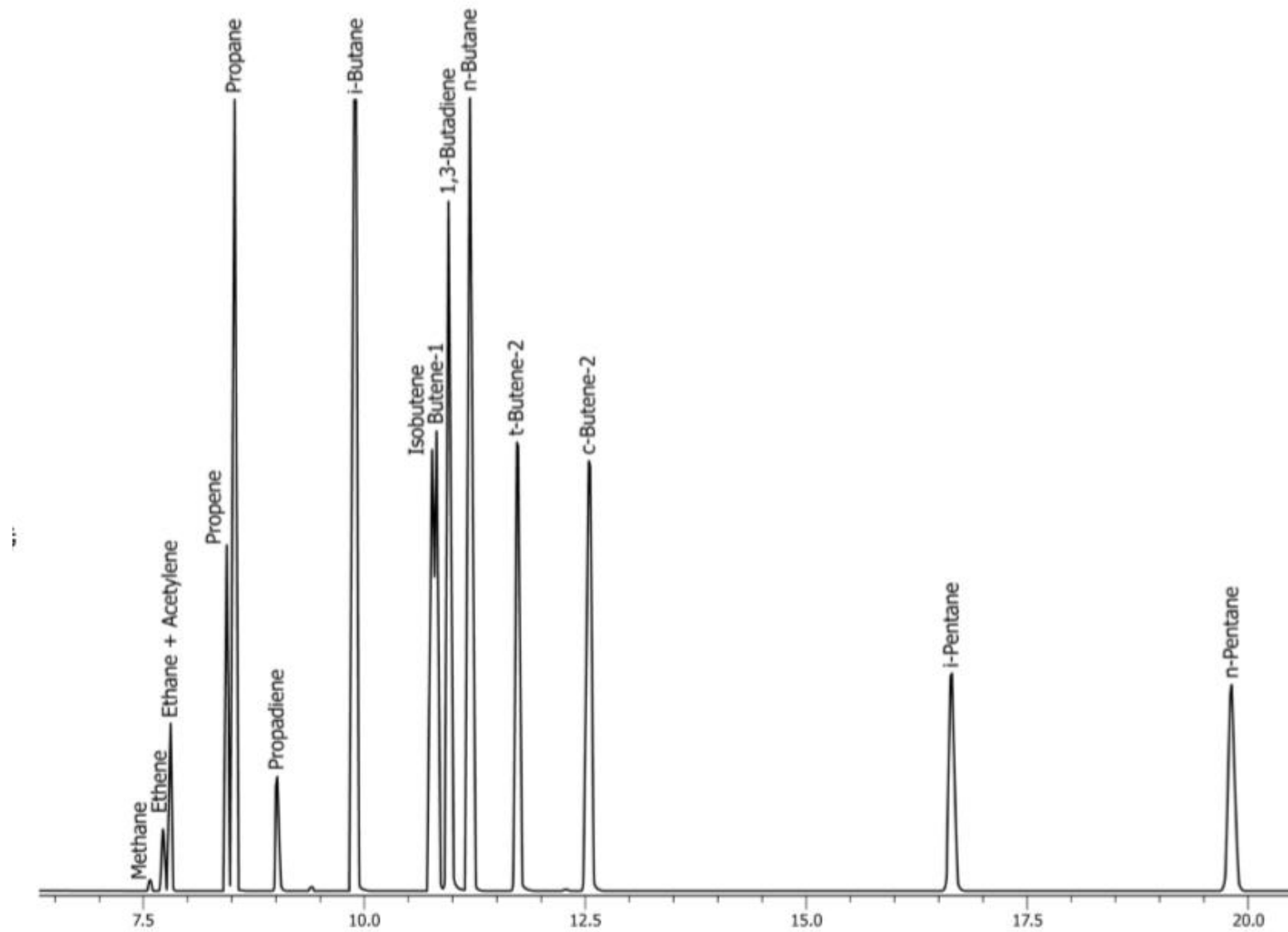
Standard Test Method for Determination of Hydrocarbons in Liquefied Petroleum (LP) Gases and Propane/Propene Mixtures by Gas Chromatography

- Summary of Test Method
 - An LPG sample is analyzed via either liquid or gas sampling valves by gas chromatography and compared to corresponding components separated under identical operating conditions from a reference standard mixture of known composition or from use of pure hydrocarbons. The chromatogram of the sample is interpreted by comparing peak retention times and areas with those obtained for the reference standard mixture or pure hydrocarbons.
- Apparatus
 - Gas Chromatograph
 - Detector — FID
 - Liquid Sampling Valve (recommended)
 - Gas Sampling Valve

Example Chromatogram Using the PLOT Column



Example Chromatogram Using the Dimethylpolysiloxane Column



Theoretical Mass Relative Response Factors

Component	RRF _i	Component	RRF _i
Methane	1.0	1-butene	0.874
Ethane	0.937	2-methylpropene (isobutene)	0.874
Ethene (Ethylene)	0.874	cis-2-butene	0.874
Propane	0.916	2,2-dimethyl propane (neopentane)	0.895
Propene (Propylene)	0.874	2-methyl butane (isopentane)	0.899
Cyclopropane	0.874	propyne (methyl acetylene)	0.834
2-Methylpropane (Isobutane)	0.906	cyclopentane	0.849
Ethyne (Acetylene)	0.813	n-pentane	0.899
Propadiene	0.834	1,3-butadiene	0.843
Butane	0.906	C ₅ ⁼ /C ₆ ⁺ composite (backflush only)	0.885
Trans-2-Butene	0.874	>nC ₅ (C ₅ ⁼ and heavier)	0.885

^ARF values obtained from Test Method **D6729**.

All response factors are relative to that of methane according to the following equation:

$$RRF_i = (MW_i / NC_i) \times (1 / MW_{methane})$$

where:

- RRF_i = relative response factor of each component with respect to methane,
- MW_i = the molecular weight of the component,
- NC_i = the number of carbon atoms in the component molecule, and
- $MW_{methane}$ = the molecular weight of methane.

Quality Control and Statistical Quality Assurance



What is SQC? Why do we do SQC?

• *There were three degrees of untruth – a fib, a lie, and statistics*

Charles Dilke



Measure each test, each method, each instrument, each analyst



Measure overall lab performance



How is an instrument behaving (Is it out of control?)



SQC can provide a deep insight into an issue

Yet, carelessness or duplicity can generate misleading results

What is SQC? Why do we do SQC?

SQC uses three scientific techniques

- sampling inspection
- analysis of the data
- control charting

Can be divided into following three broad categories

- descriptive statistics
- statistical process control
- acceptance sampling

Define Quality for Your Laboratory

- What does quality mean to your customers?
- Who are your customers?
- Precision of results

How good is good enough?

- Accuracy of 99%
 - 10 errors per 1,000 test
 - Typical lab analyze >200,000 test a year = **2,000 ERRORS!**
- Accuracy of 99.99%
 - Typical lab analyze >200,000 test a year = **20 ERRORS**

Define Quality for Your Laboratory

- Our customer define what quality is

What is Quality?

- Has the notion of value, not just efficiency
- Difference between **efficiency** and **effectiveness** is the difference between **knowledge** and **wisdom**
- Directed toward what *you want*, not toward what *you don't want*

Peter Druker

- There is a difference between doing things right and doing the right things

Doing things right

Management

Doing the right things

Leadership

- **Efficiency** is doing things right, which is irrelevant if you are not doing the right things



Elements of Laboratory Quality

Test Quality

Sample Quality

Analyst Competence

Customer Satisfaction

Documentation

Reputation

Path of Workflow

Sampling

Laboratory Environment

Quality Control Procedures

Communications

Record Keeping

Competent and knowledgeable staff

Good quality reagents and equipment

Limit of Detection

- The lowest amount of analyte in a sample which can be detected but not necessarily quantitated as an exact value
- 1:3 S/N ratio

Limit of Quantitation

- The concentration at which quantitative results can be reported with a high degree of confidence
- 1:10 S/N ratio

QA/QC - Instrument Performance Measures



Limit of Detection



Limit of Quantitation

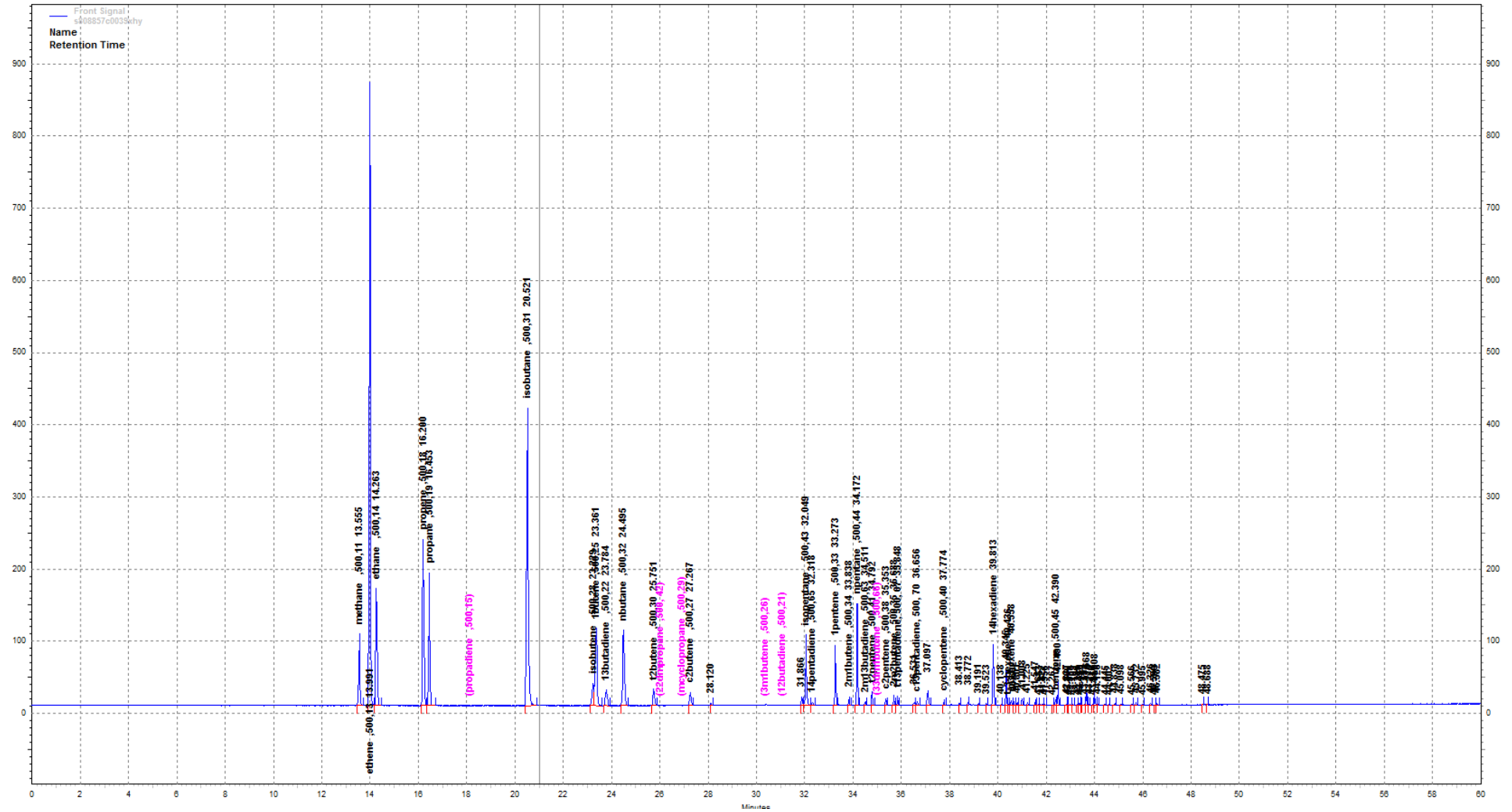


Sensitivity

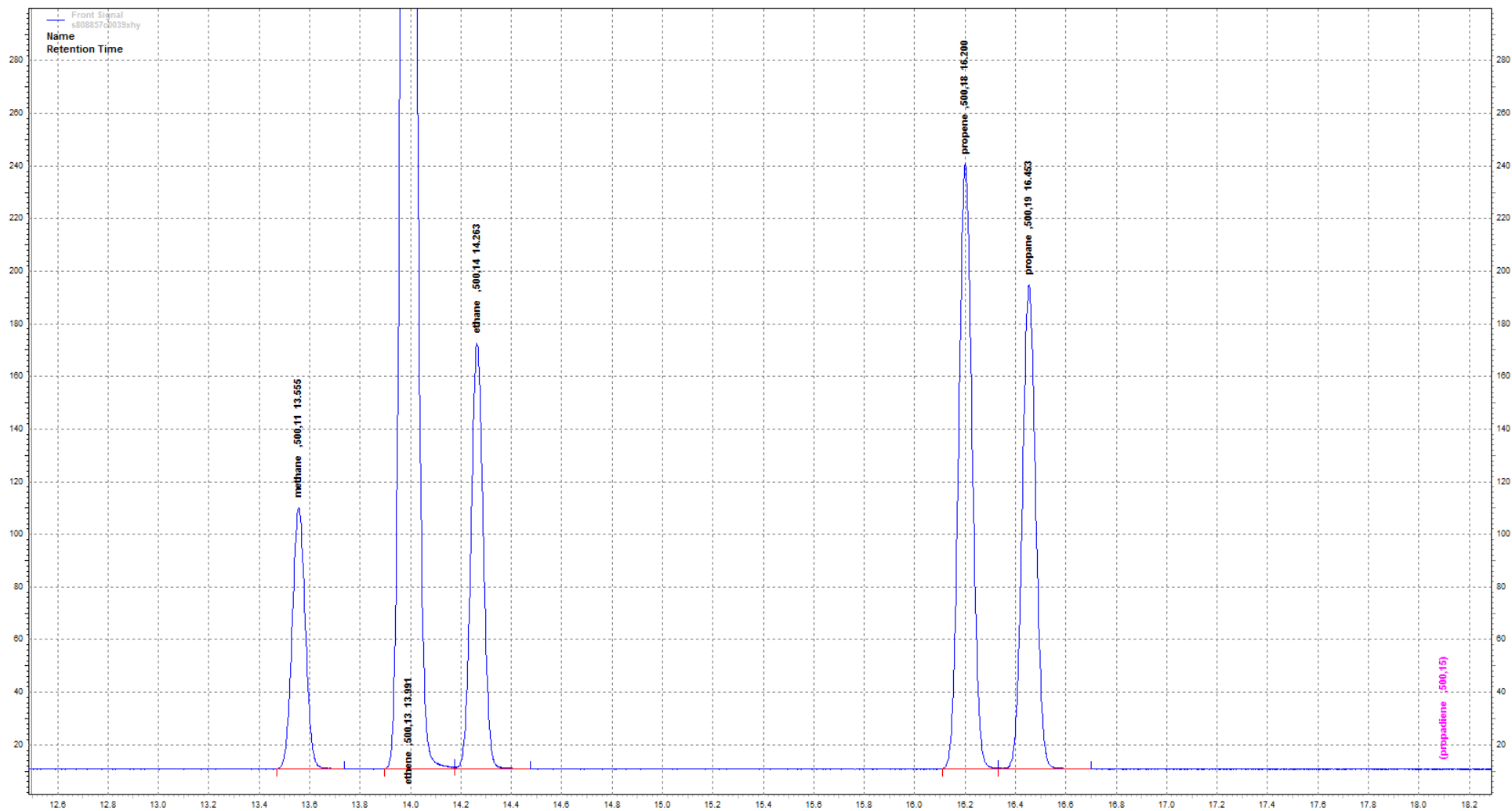


Stability

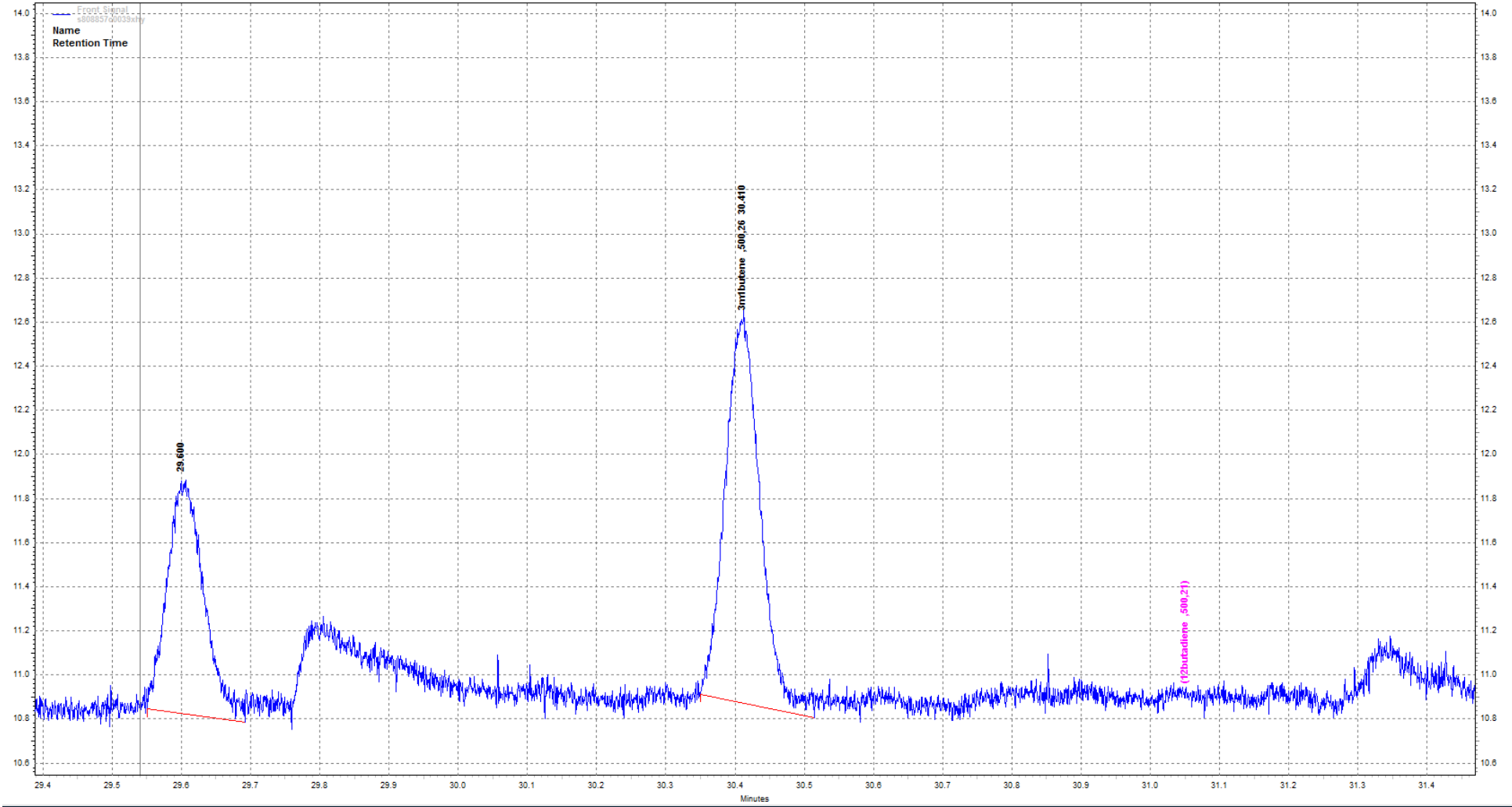
Full Chromatogram



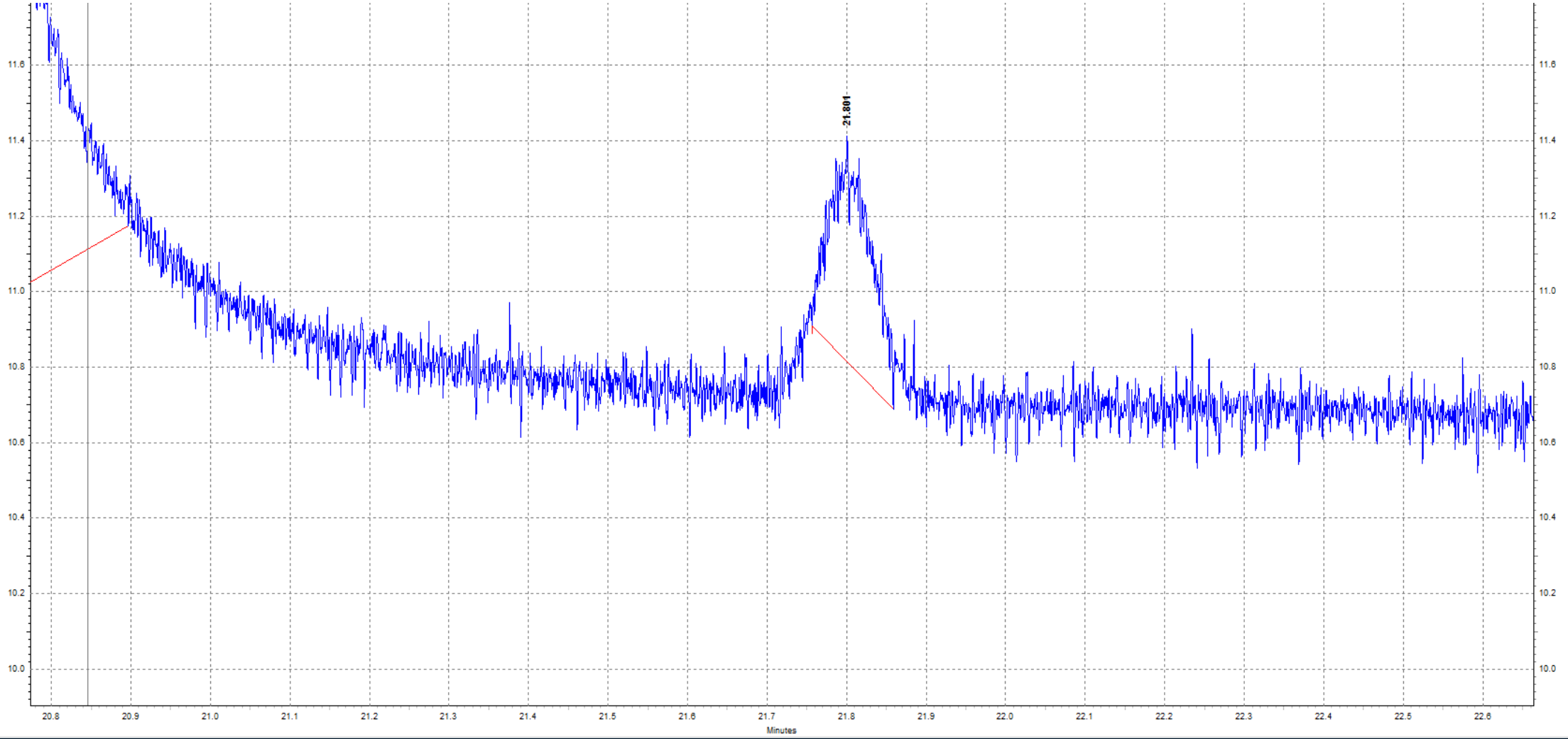
Expanded View



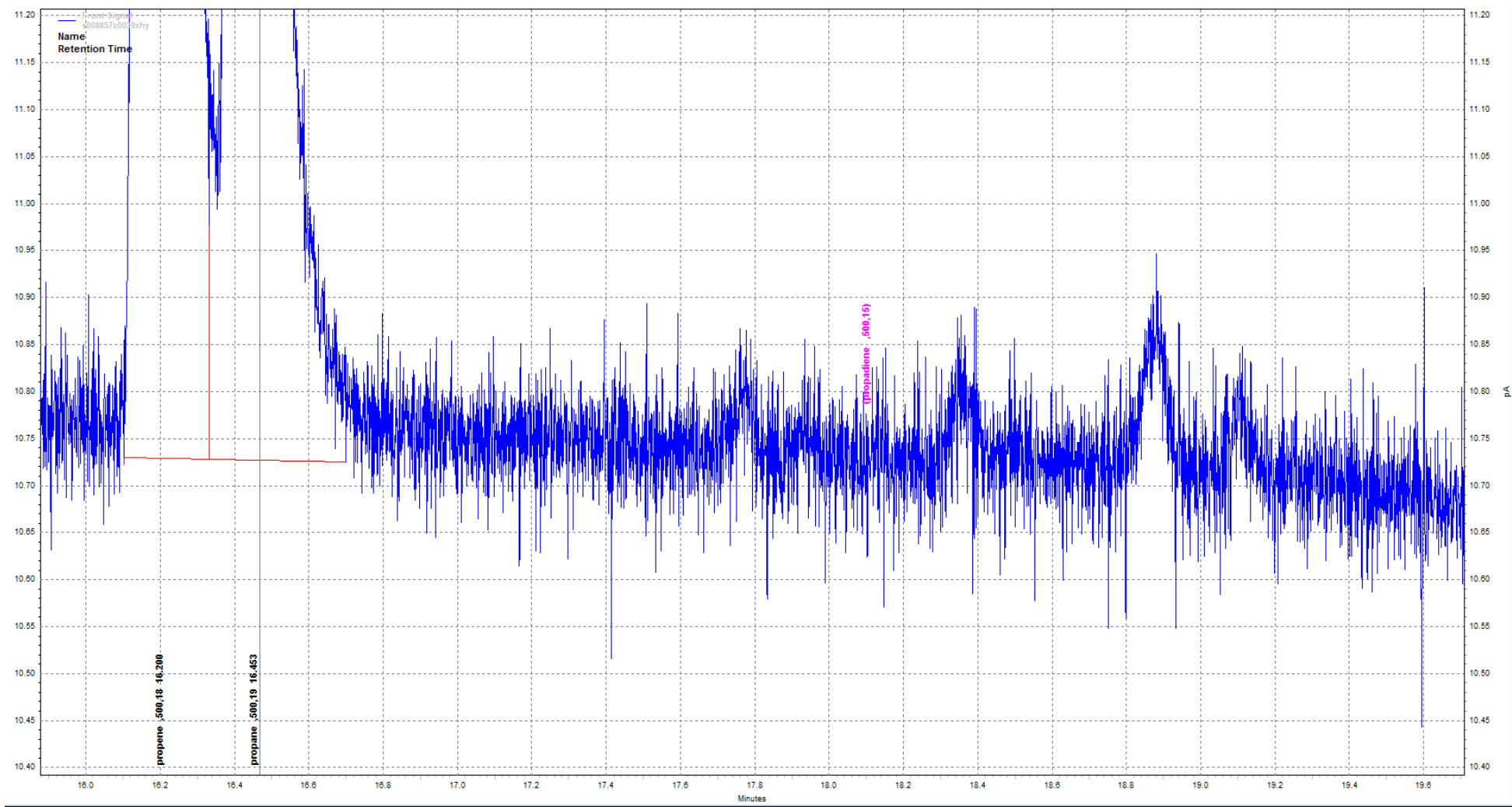
Quantitation Limit



Detection Limit



Below Detection Limit



QA/QC - Standards

Commercial Suppliers

- Very expensive; slow delivery
- Quality variable

Home Made Blends

- Customize as needed
- Dilute/Modify commercial references
- Cheaper than commercial

Working Samples

- Process Origins; contains typical impurities
- Must be stable; unreactive
- Good for trending
- Cheap

QA/QC - Calibration

Establish a mathematical function which describes the dependency of the system's parameter on the measured value

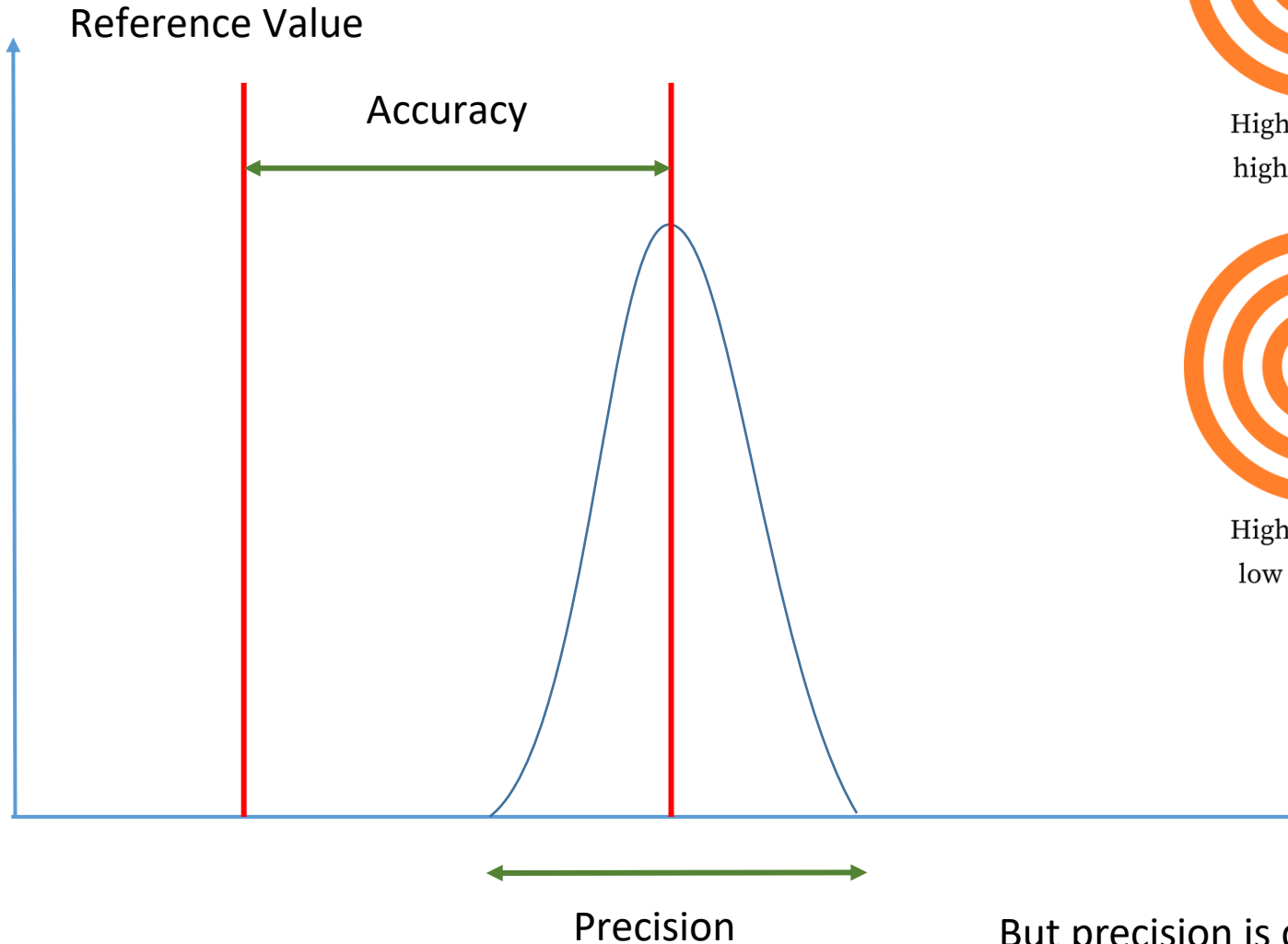
- Concentration
- Normalization vs External Standard

Gain statistical information of the analytical system

- Sensitivity
- Precision
- Accuracy

Accuracy vs Precision

Calibration adjusts to achieve accuracy



High accuracy,
high precision



Low accuracy,
high precision



High accuracy,
low precision



Low accuracy,
low precision

But precision is determined by the instrument

Repeatability and Reproducibility for Oxygenates (mg/kg)

NOTE 1—Where: X = the average individual oxygenate concentration of two results in mg/kg.

Analyte	Repeatability Limit (r)	Reproducibility Limit (R)
Acetone†	$(0.1821)(X^{0.5985})$	$(0.4424)(X^{0.5985})$
Acetaldehyde	$0.2595(X + 0.0001)^{0.595}$	$1.0439(X + 0.0001)^{0.595}$
Diethyl Ether	$0.1869(X + 0.0001)^{0.5981}$	$0.5966(X + 0.0001)^{0.5981}$
Dimethyl Ether	$0.05321(X + 0.0001)^{0.9273}$	$0.2784(X + 0.0001)^{0.9273}$
DIPE	$0.1188(X-0.6566)^{0.5889}$	$0.5219(X-0.6566)^{0.5889}$
ETBE	$(0.06778)(X^{0.8512})$	$(0.3613)(X^{0.8512})$
Ethanol	$0.1626(X + 0.0001)^{0.7649}$	$0.6808(X + 0.0001)^{0.7649}$
Iso-Propanol	$(0.2458)(X^{0.5108})$	$(1.1222)(X^{0.5108})$
MEK	$(0.2009)(X^{0.5094})$	$(0.7171)(X^{0.5094})$
Methanol	$(0.2870)(X^{0.4887})$	$(1.9695)(X^{0.4887})$
MTBE	$(0.1261)(X^{0.6368})$	$(0.2861)(X^{0.9442})$
n-Butanol	$(0.1179)(X^{0.9278})$	$(0.3890)(X^{0.9278})$
Sec-Butanol	$(0.1063)(X^{0.8057})$	$(0.5578)(X^{0.8057})$
TAME	$0.2812(X + 0.0001)^{0.4011}$	$0.9946(X + 0.0001)^{0.4011}$

†Editorially corrected.

Risk of being out of tolerance

Cost of calibration

Accuracy requirements

Experience with equipment and methods

Manufacturer recommendations

QA/QC - Common Sources of Analytical Error

Temperature and humidity variations

Weighing errors

Sampling errors

Instrument precision

Calibration standard error

Rounding error

Human error

Contamination

Reading error

Non-linearity

Flow rate variations

SOURCES OF ERRORS

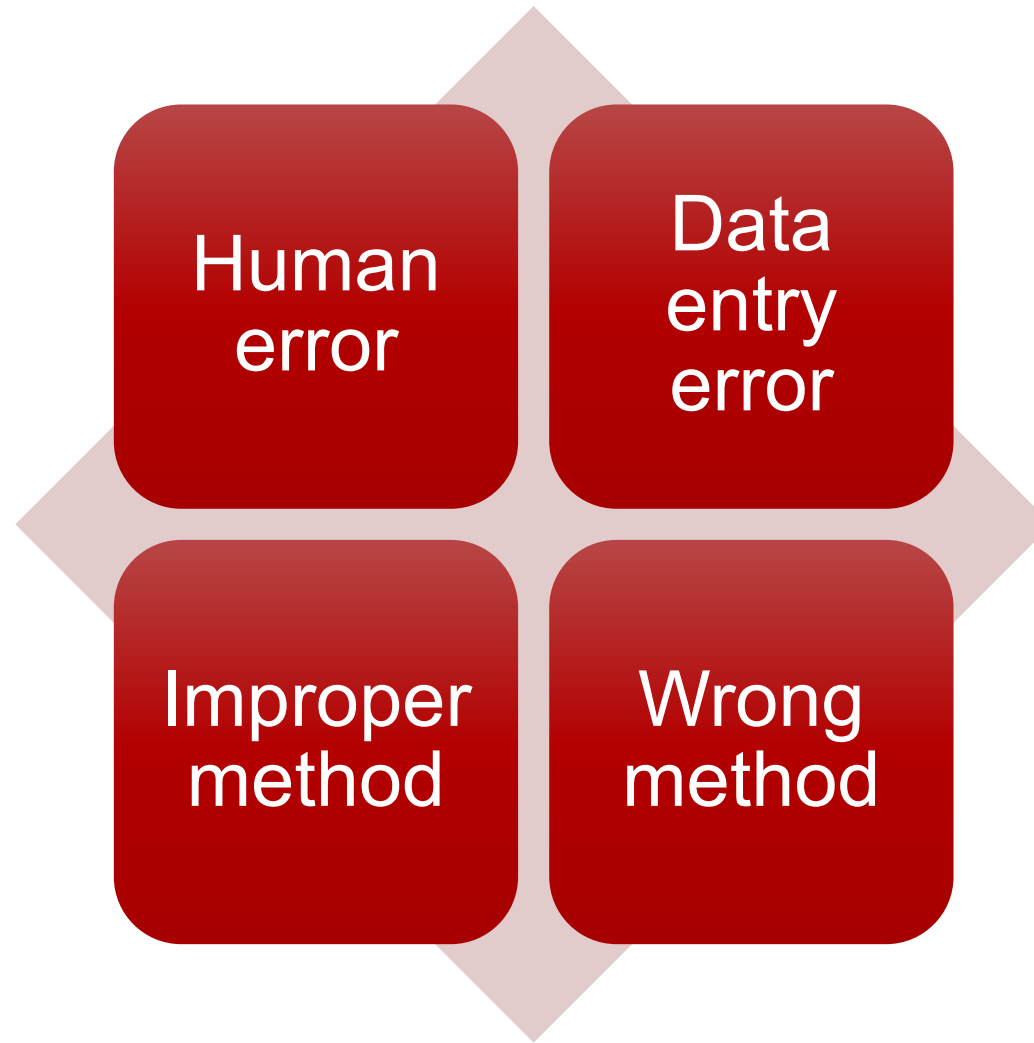
Systematic Errors

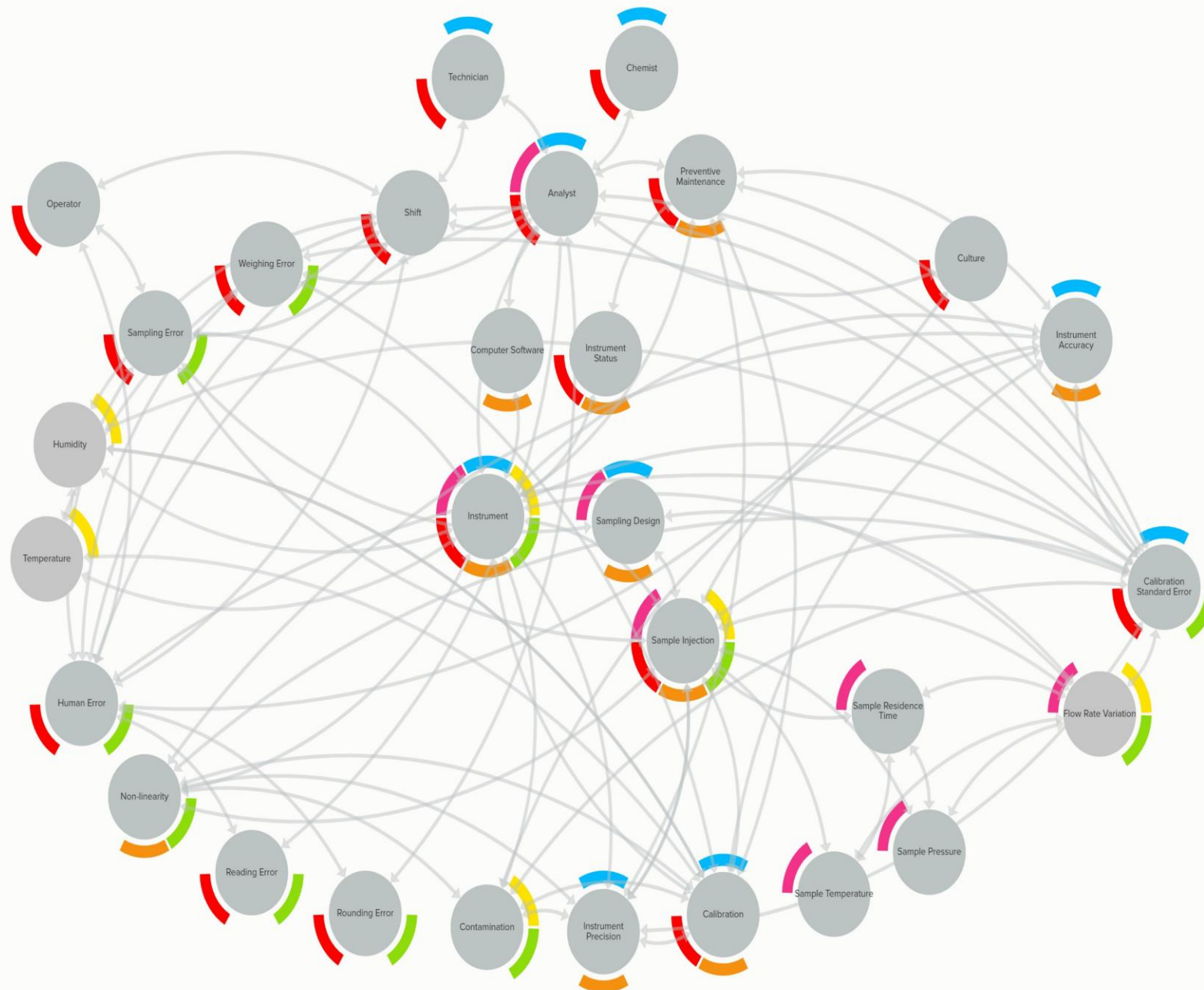
- Method limits
- Bias
- Mathematical correction

Random Errors

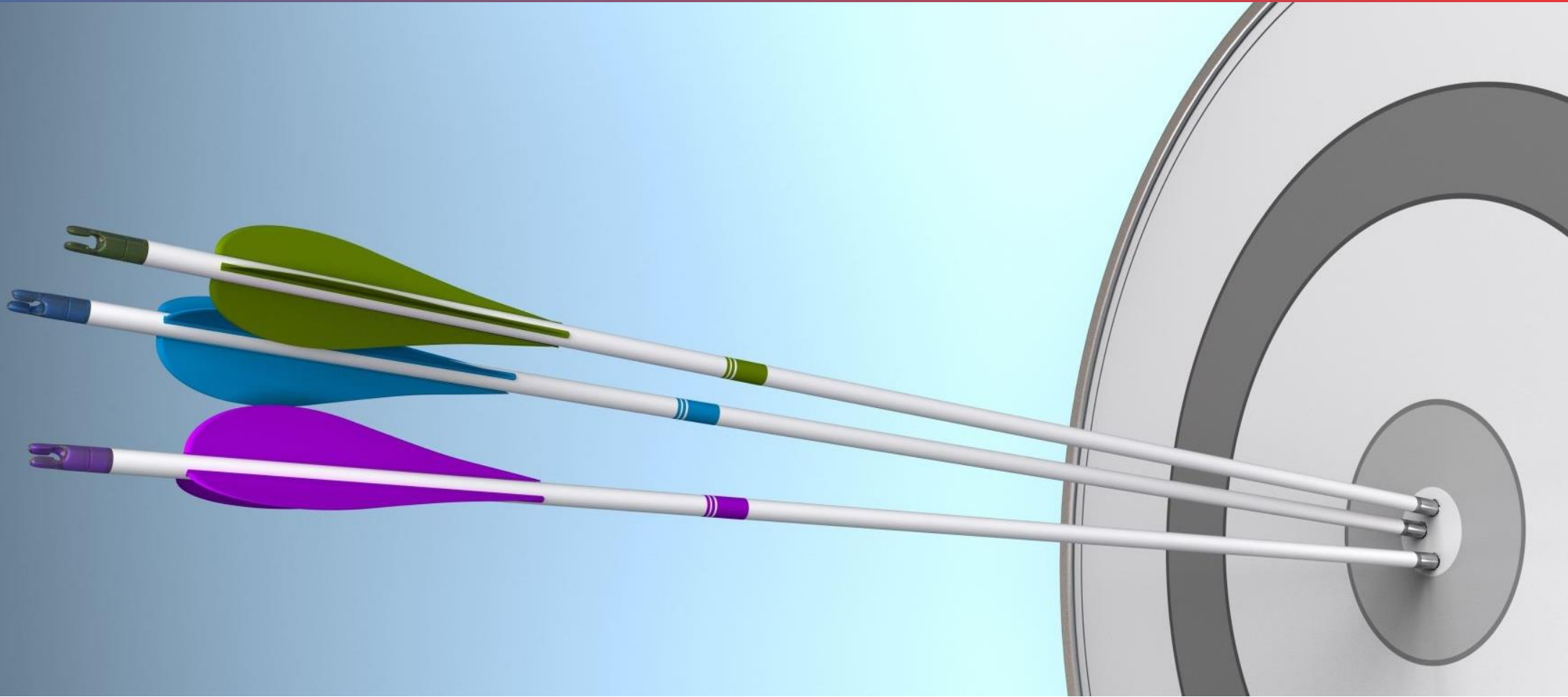
- Normal variations
- Statistical

SOURCES OF ERRORS - MISTAKES





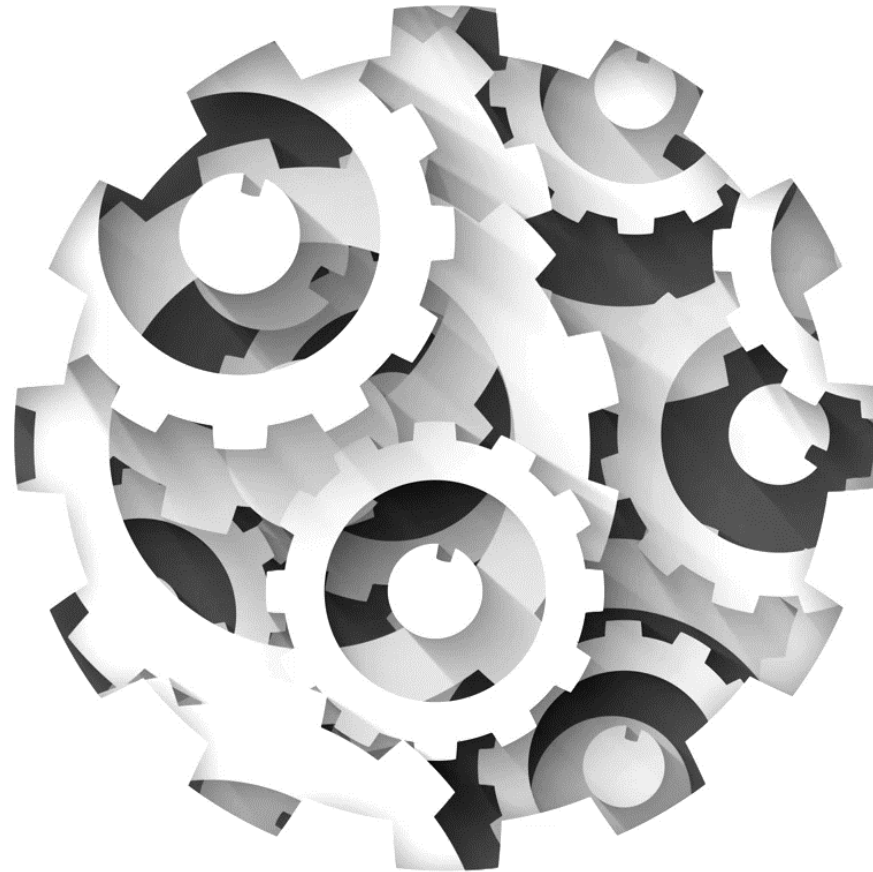
- SQC Systems



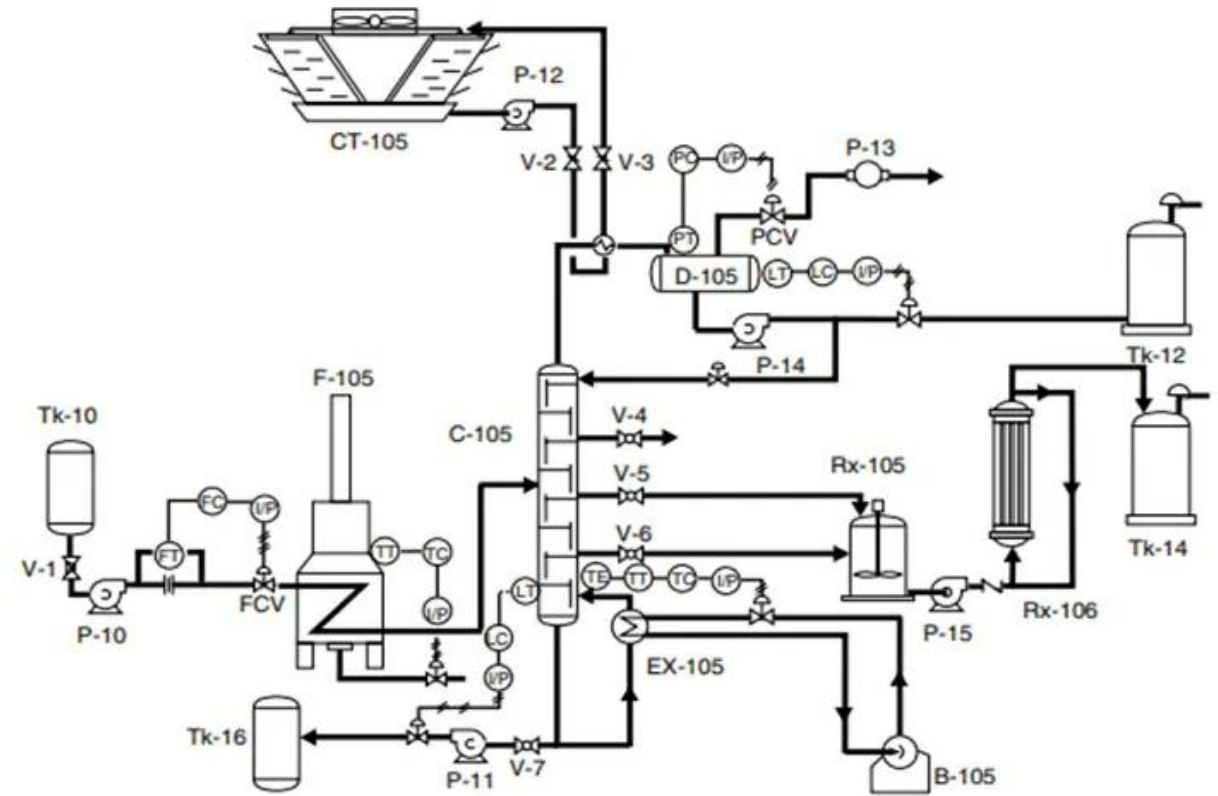
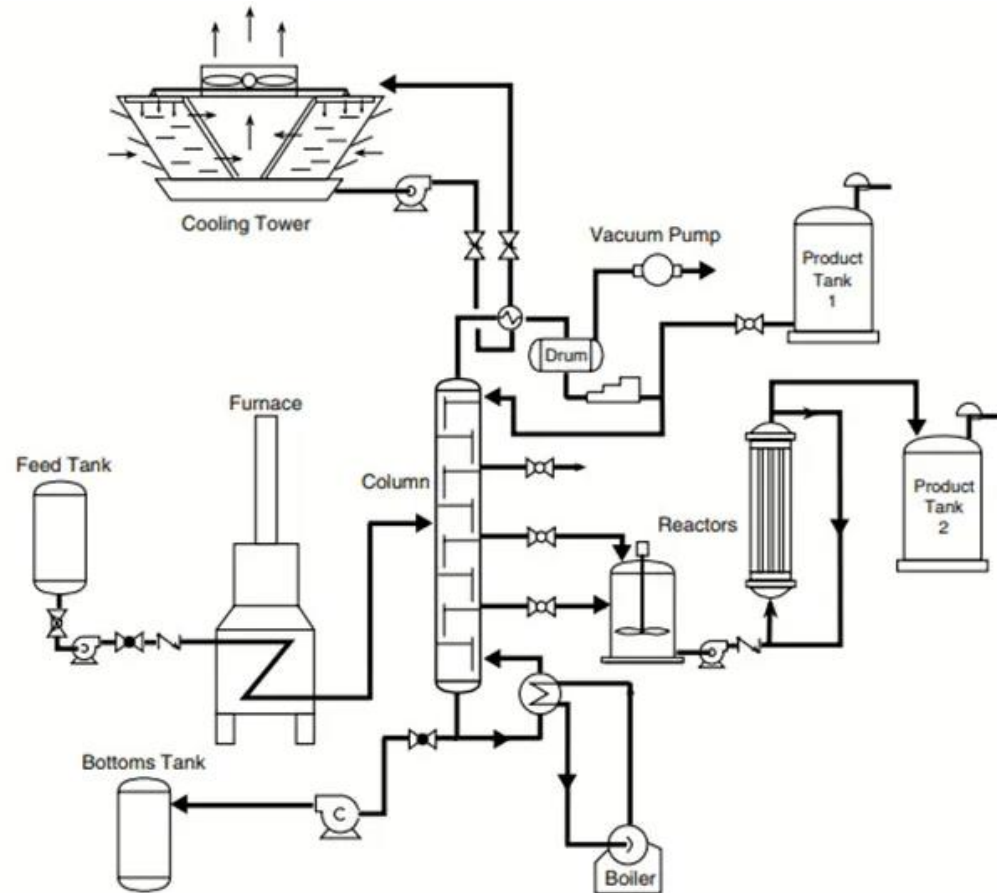
QA/QC – Customer Satisfaction

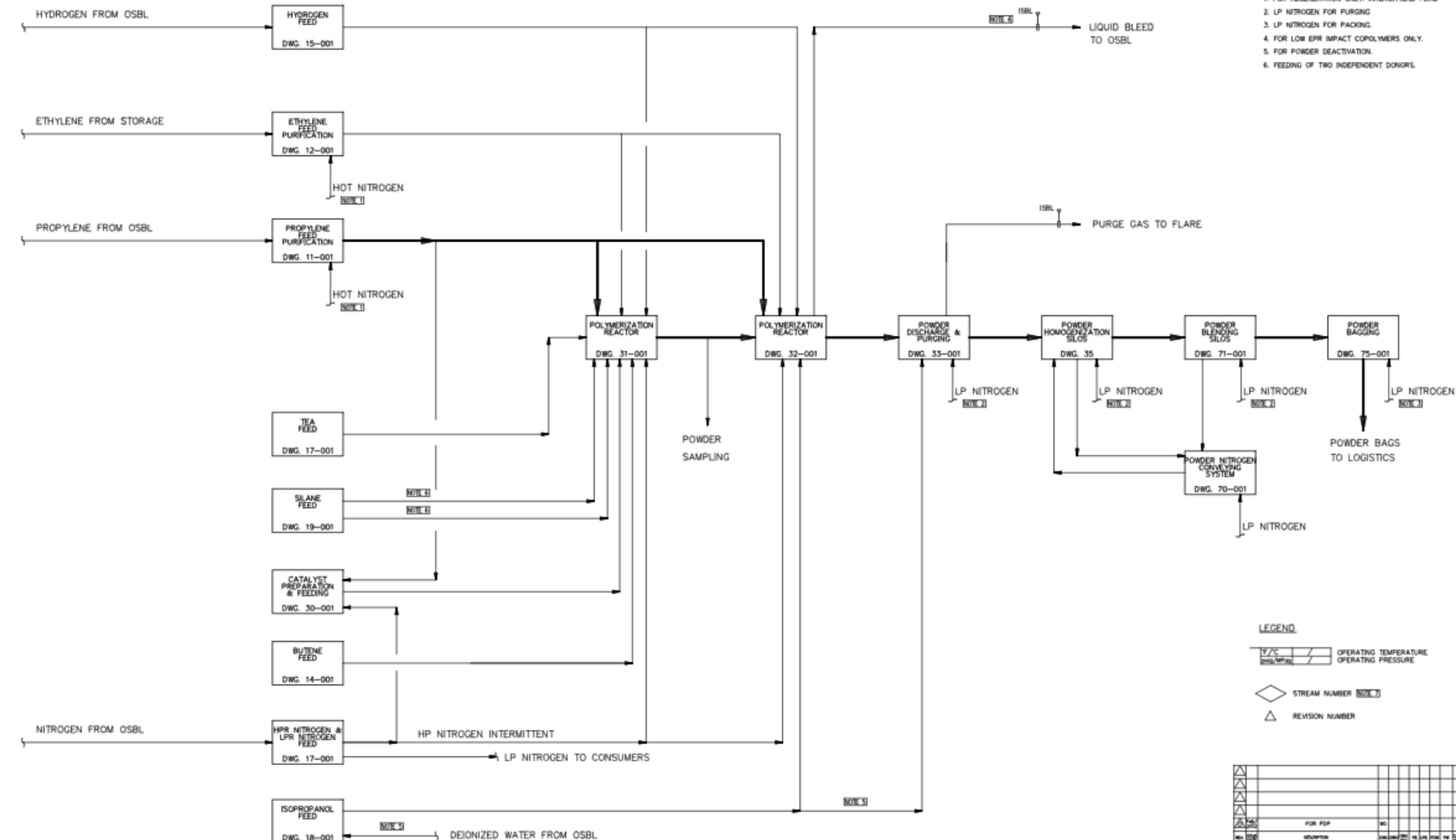
Meets or exceeds customer requirements

Process Basics



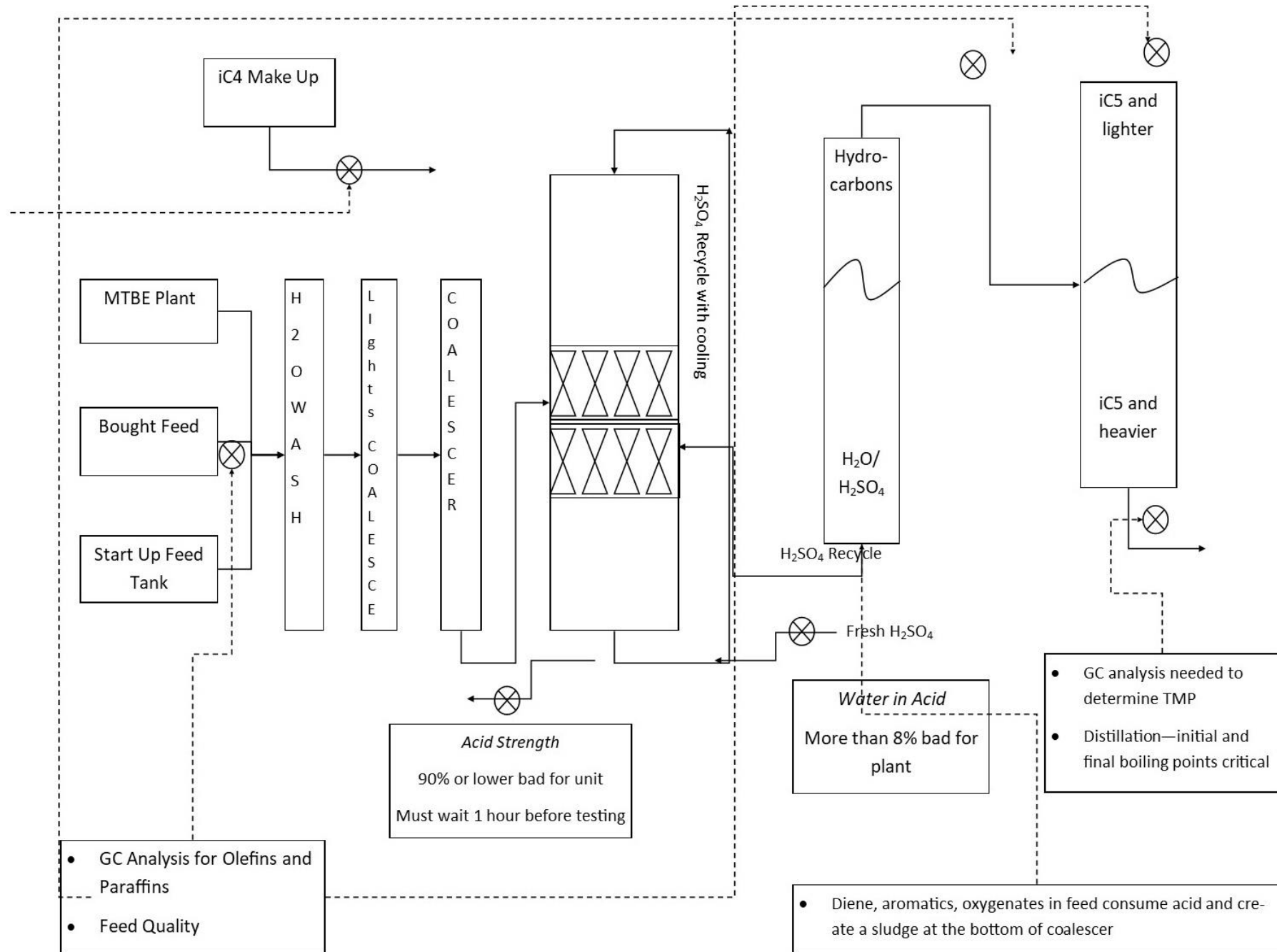
Process Basics



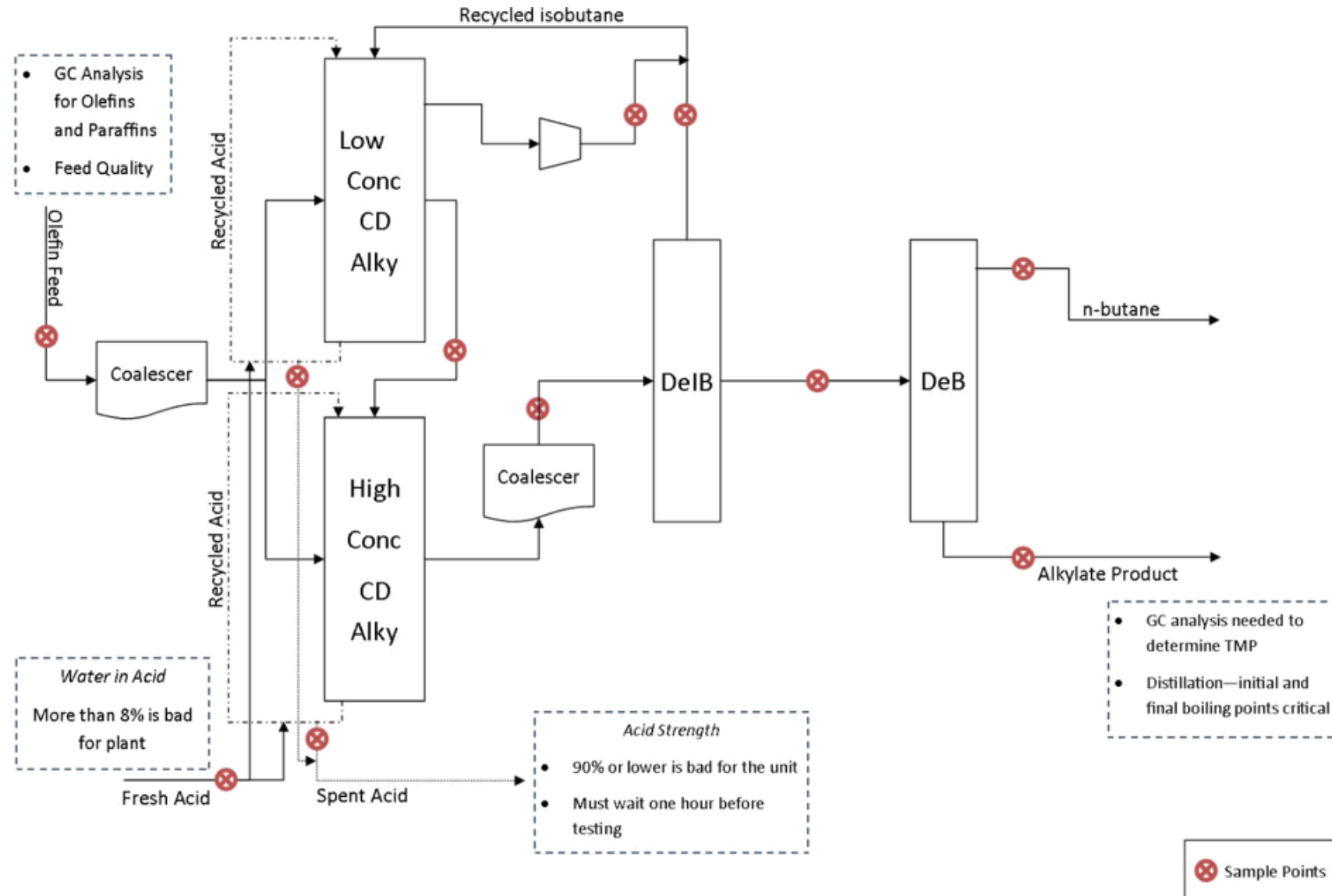


BLOCK FLOW DIAGRAM

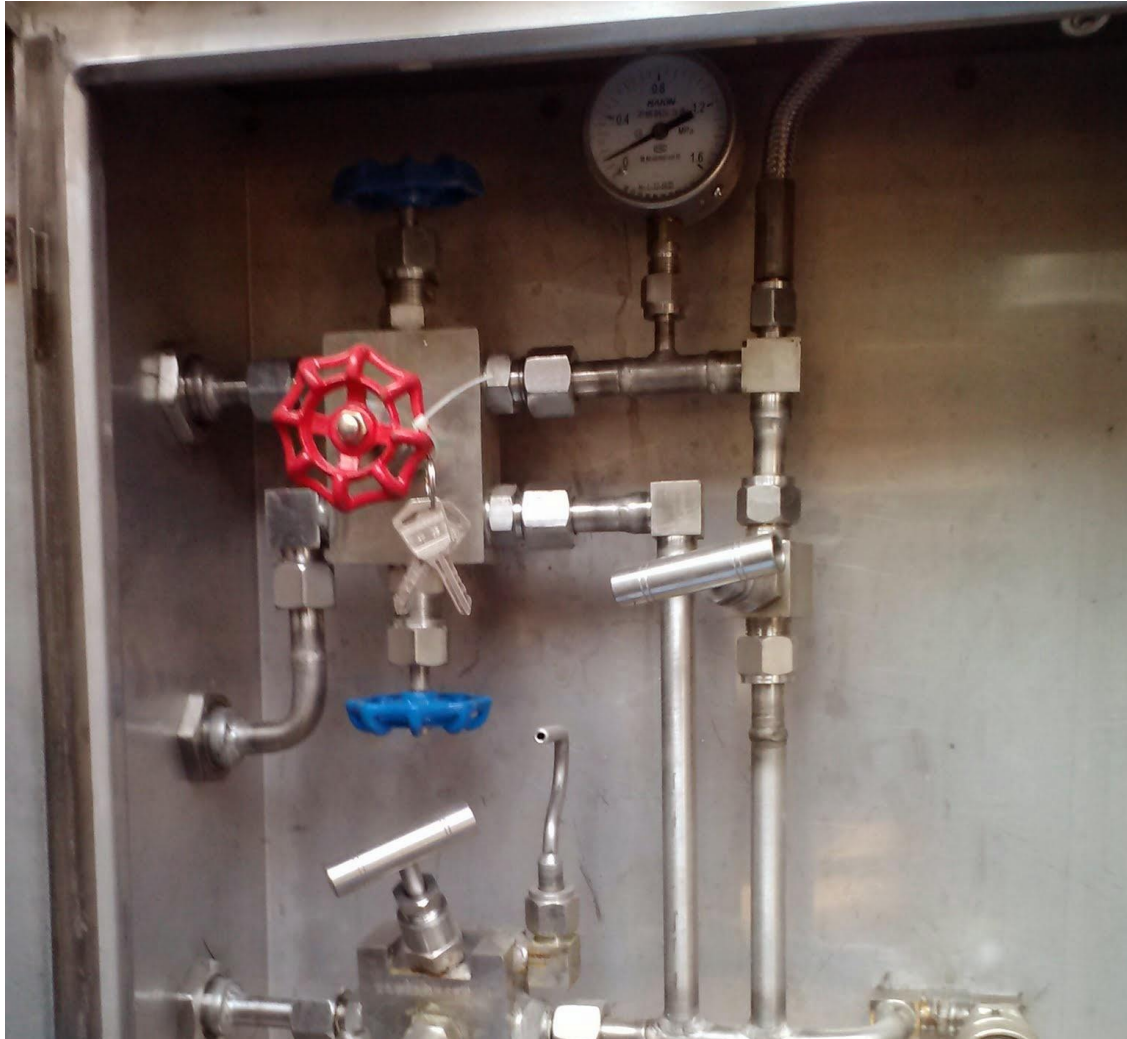
Flow Diagram



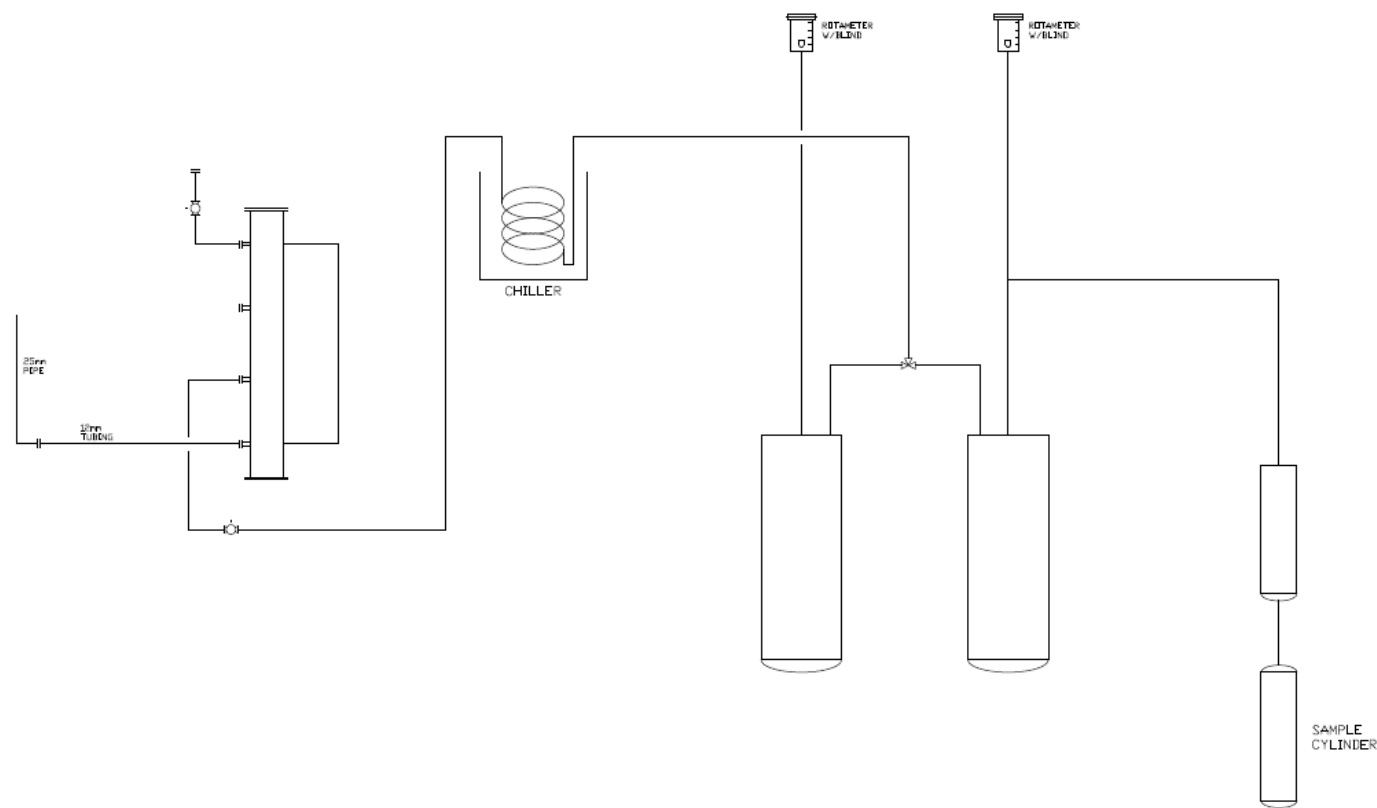
Simplified Flow Diagram



Process Basics

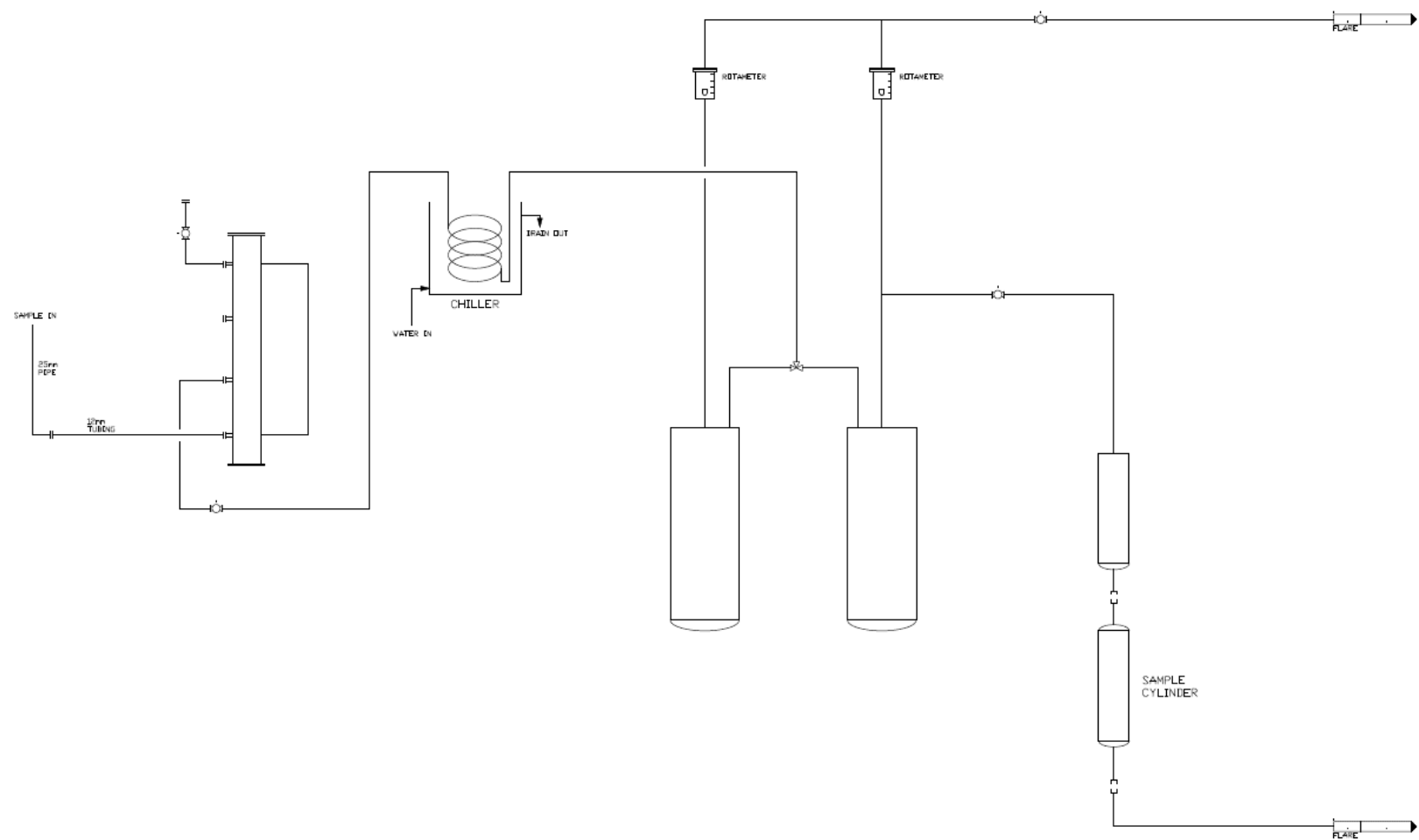


Sample Point Design

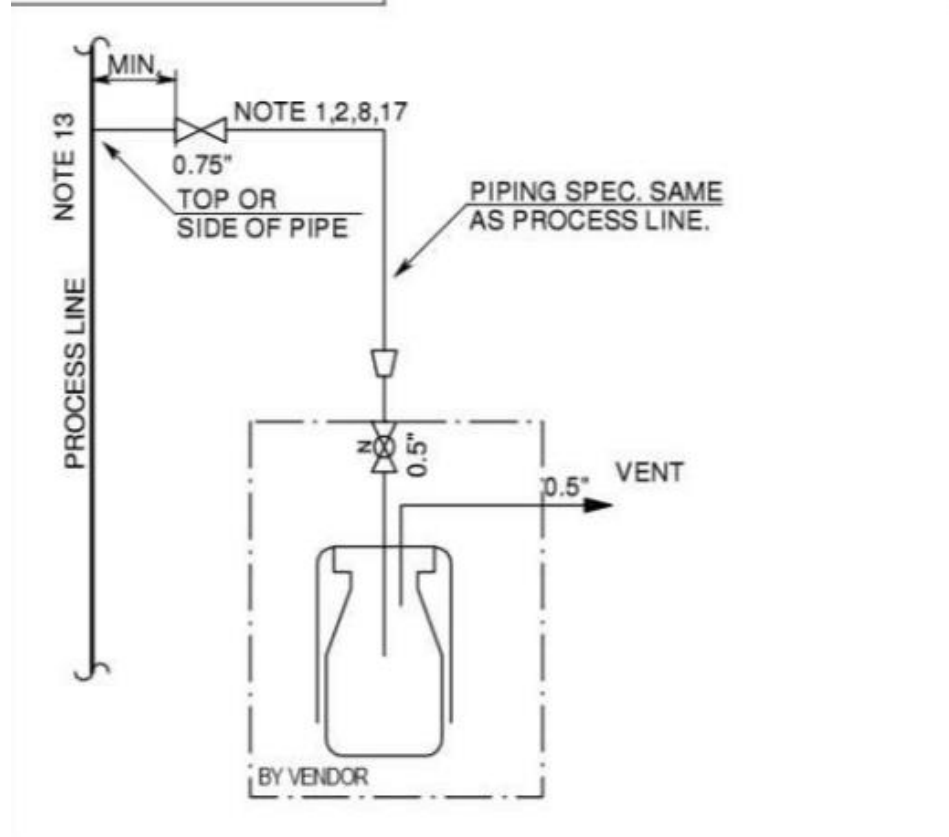
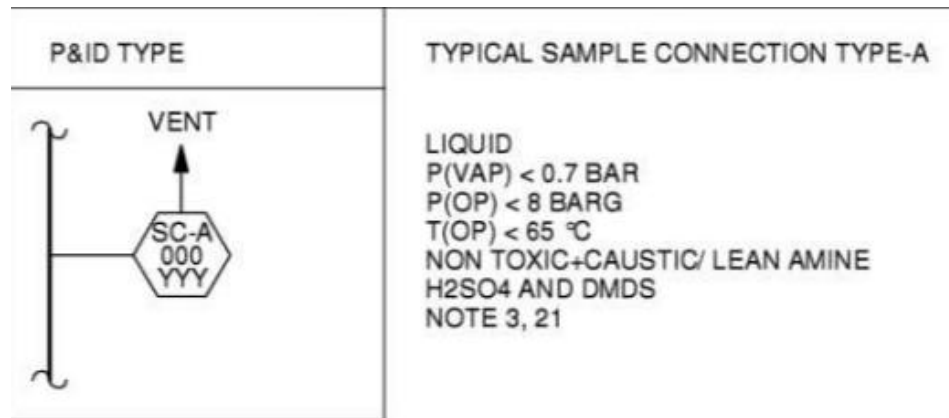


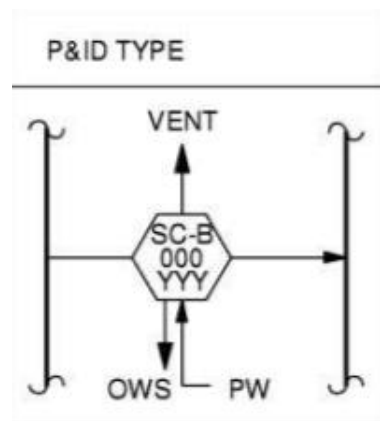
HEATER
EFFLUENT
SAMPLE POINT
EXISTING

Sample Point Design



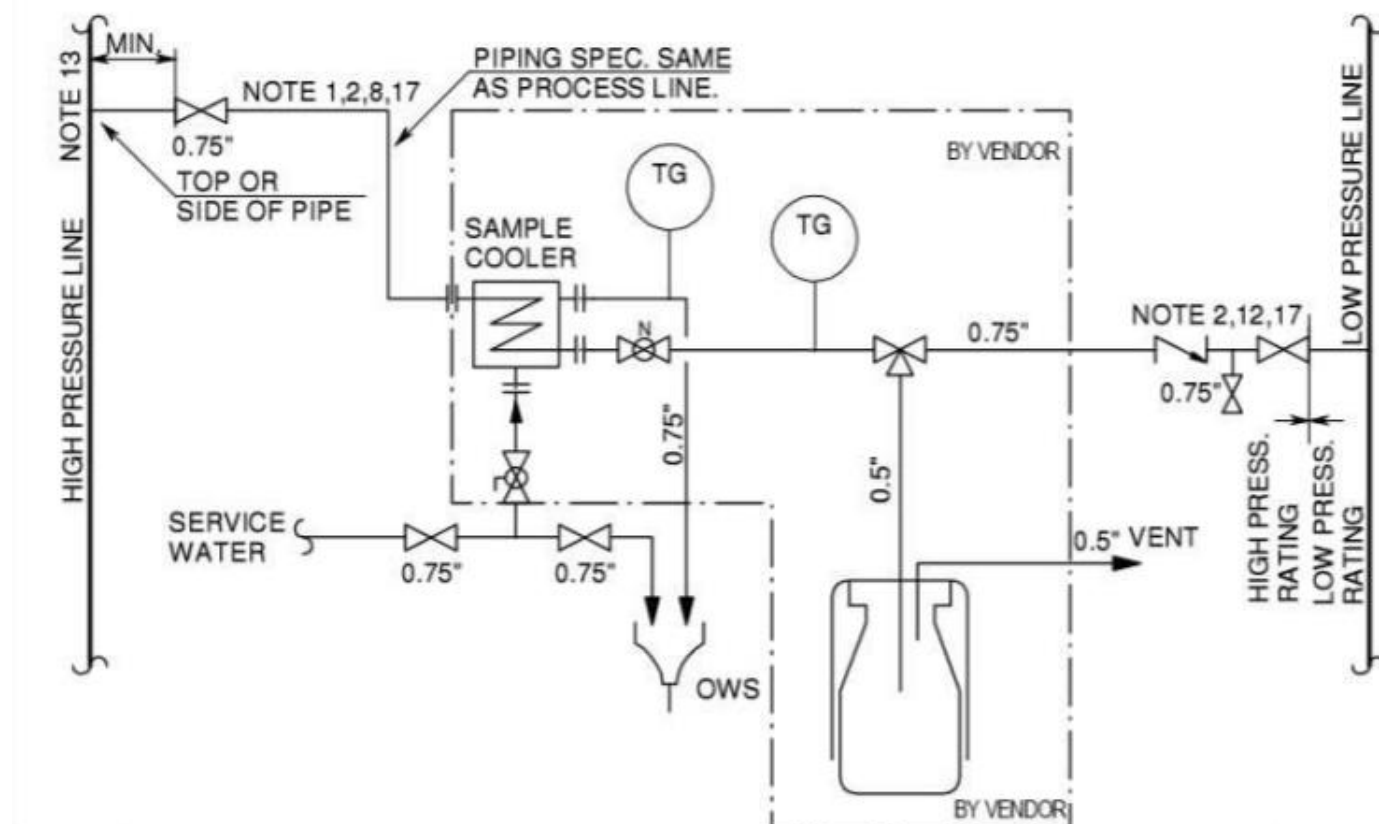
HEATER
EFFLUENT
SAMPLE POINT
PROPOSED

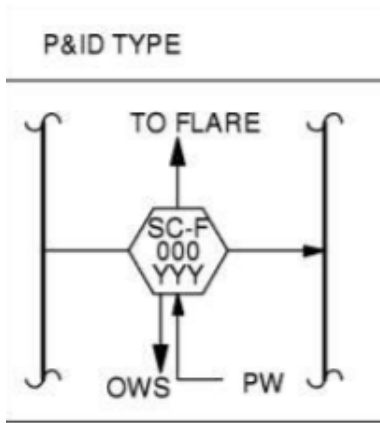




TYPICAL SAMPLE CONNECTION TYPE-B

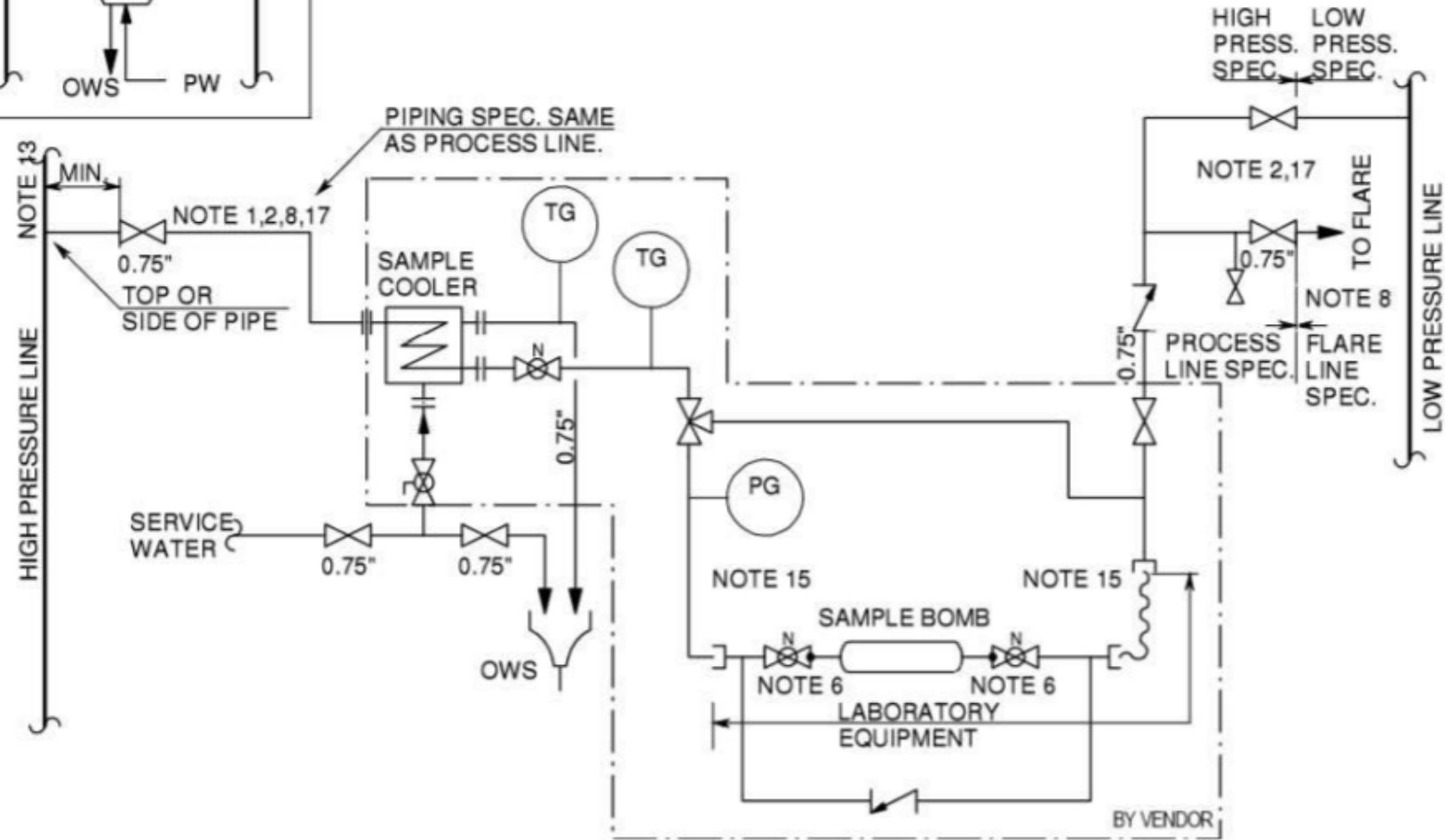
LIQUID
 $P(VAP) < 0.7 \text{ BAR}$
 $P(OP) < 8 \text{ BARG}$
 $T(OP) \geq 65 \text{ }^{\circ}\text{C}$
 NON TOXIC+CAUSTIC/ LEAN AMINE/ H_2SO_4 AND DMDS
 NOTE 3, 21





TYPICAL SAMPLE CONNECTION TYPE-F

VAPOUR / GAS
 $T(OP) \geq 65^\circ C$
 NON TOXIC
 NOTE 3, 21



Sampling System Fundamental

What do we need to know	What are our Requirements	Sample Extraction	Time Delay	Phase Fundamentals	Sample Conditioning
• Why Measure? • Inputs to Design	• Representative • Timeliness • Compatibility	• Sample Tap • Probe Consideration	• Fundamentals • Liquids vs Gases • Complicating Factors	• Phase Behavior & Diagrams • Phase Calculation • Condensation • Vaporization	• Fundamentals of Filtration • Liquid Removal • Stream Switching

Why Measure?

Accounting / Custody Transfer

- Accuracy is critical
- Speed not important

Environmental Compliance

- Regulatory
- Accuracy and Validation is Critical

Direct Process Control

- Specific and Reliable

Process Monitoring

- Reliable

Process Safety

- Speed and Accuracy
- Reliable
- Critical Alarms

Requirements

Representative

- Must be useful for its intended purpose
- Must provide the information needed to make decisions

Speed of Response

- Must respond quickly enough to provide the information needed to make a decision
- Must be able to achieve the goal of the analysis

Compatibility

- Material of construction can handle the process fluid
- Must be design to handle pressure, temperature, flow rates and other physical parameters

Summary in three points

Chemists

- Analyze the samples they receive to the best ability of the analytical equipment available to them

Engineers

- Utilize the analytical results provided to them to alter, improve, or change the process

Scientists

- We are all scientists, but we focus of different aspect of science

Any final questions or
comments?

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BnSIC

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