Basic Analytical Training

October 2022

BASIC

Borny **A**nalytical **S**ervices **I**nternational **C**onsulting

Introductions

Name

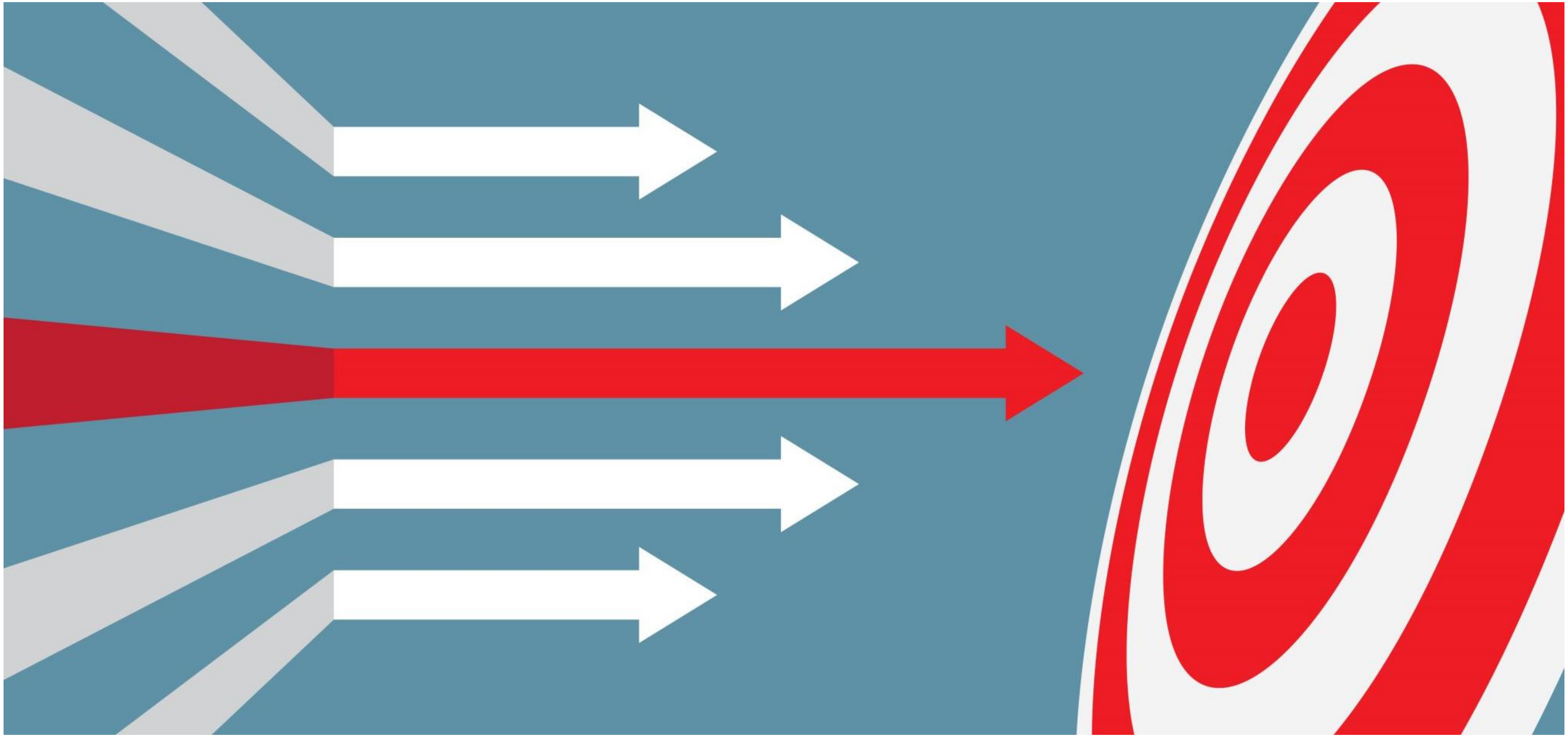
Background

Company

Type of Lab

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

ANALYTICAL GOALS

To Support:

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

ANALYTICAL GOALS

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

ADDITIONAL SAMPLING REQUIREMENTS

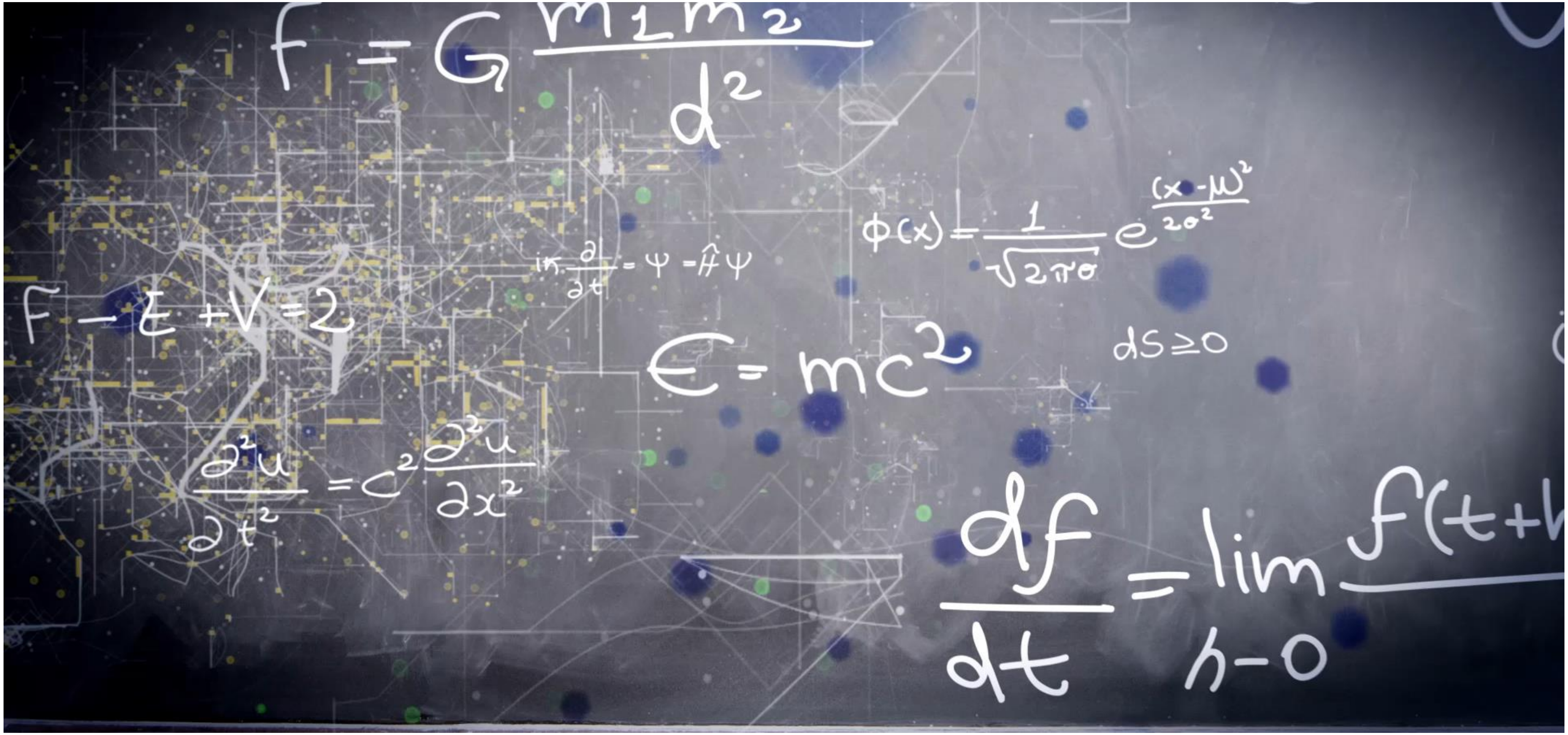
Document Source

- Description - Date - Time - Location

Storage

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

Analytical Methodology



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)

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

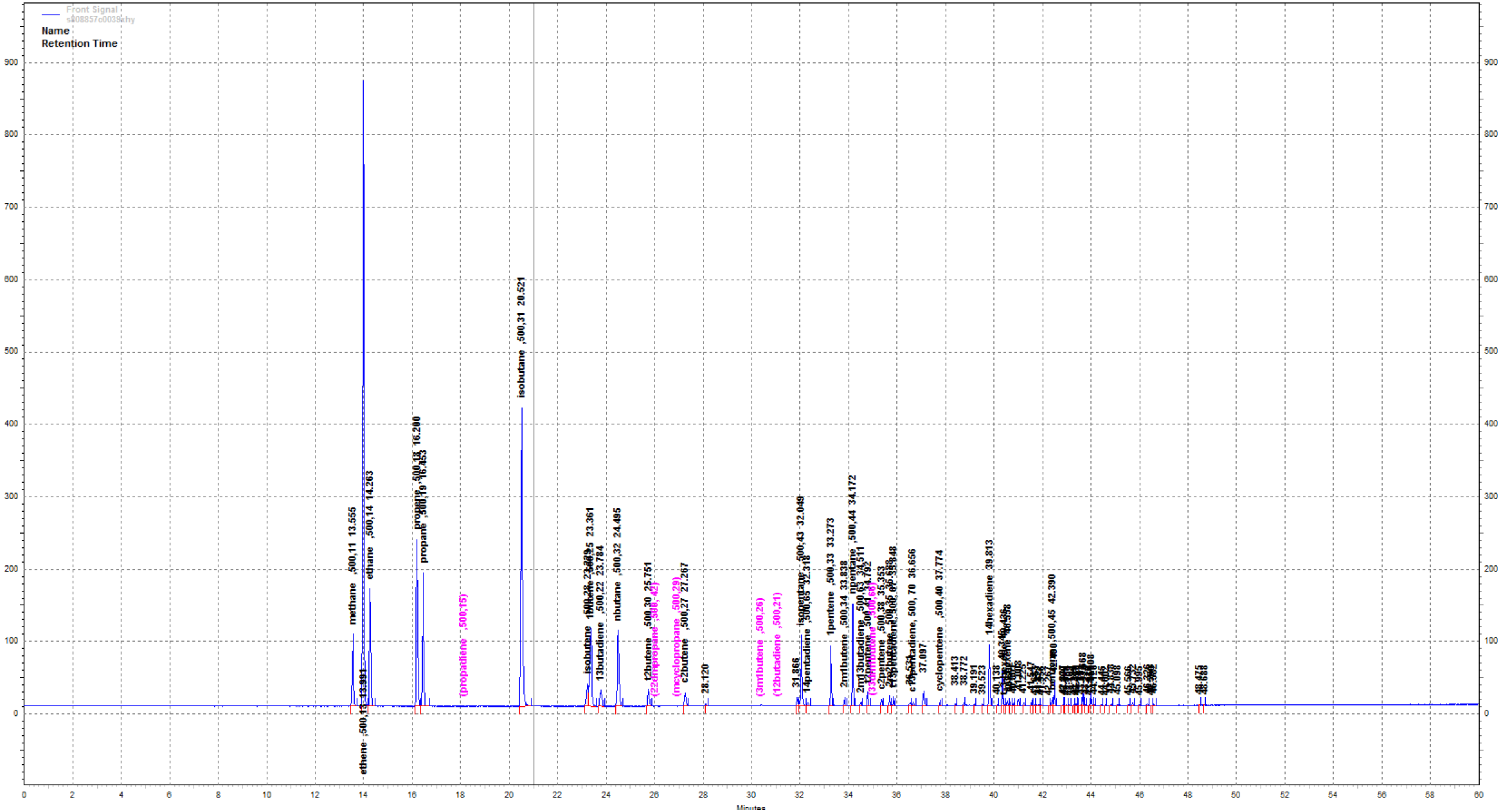
Phase (non-polar, polar, PLOT)

Outlet

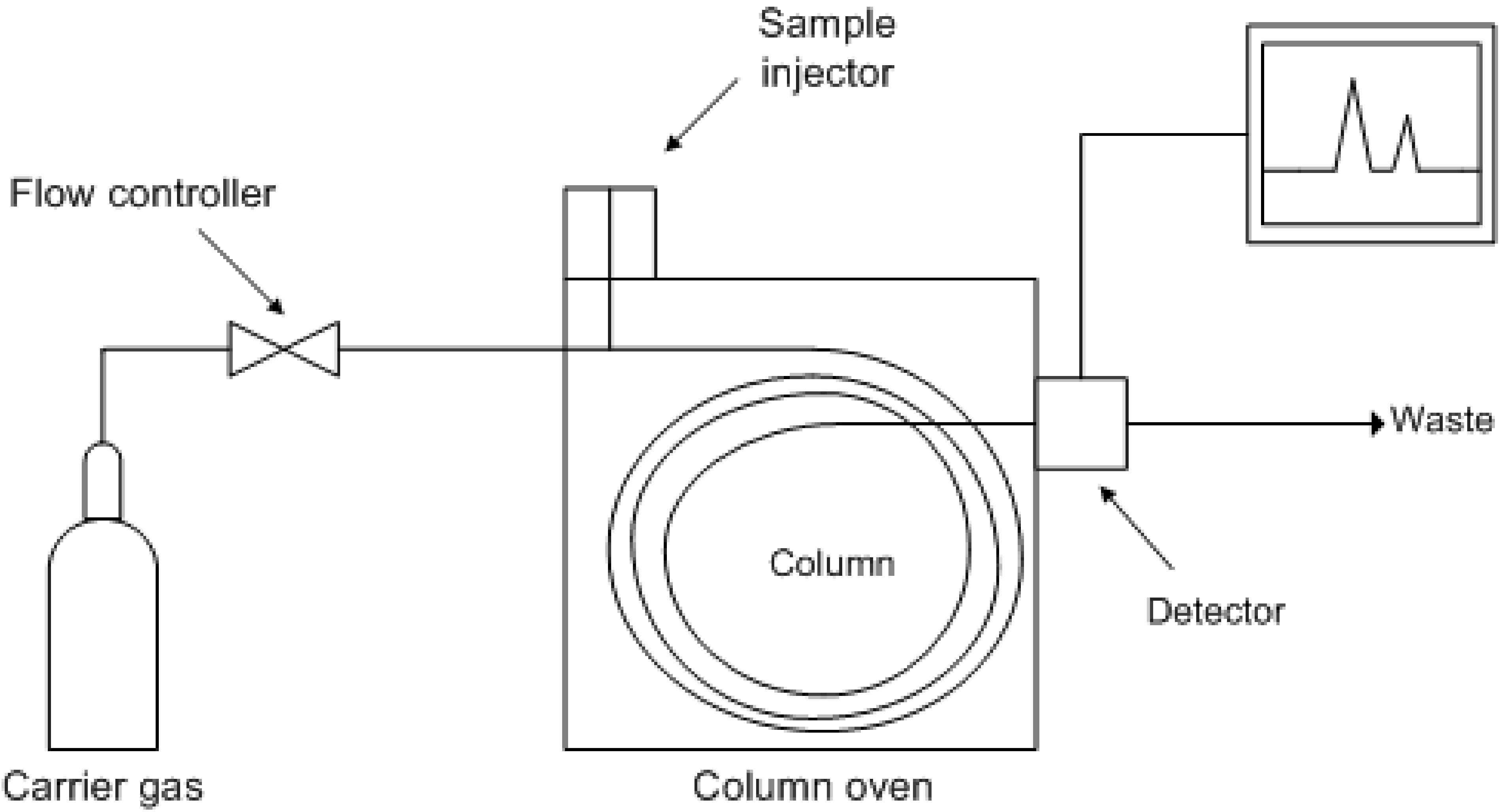
Detector

(FID, TCD, SCD,…)

Full Chromatogram



BASIC GC SYSTEM



GC TECHNOLOGY: THREE PRINCIPAL EVENTS

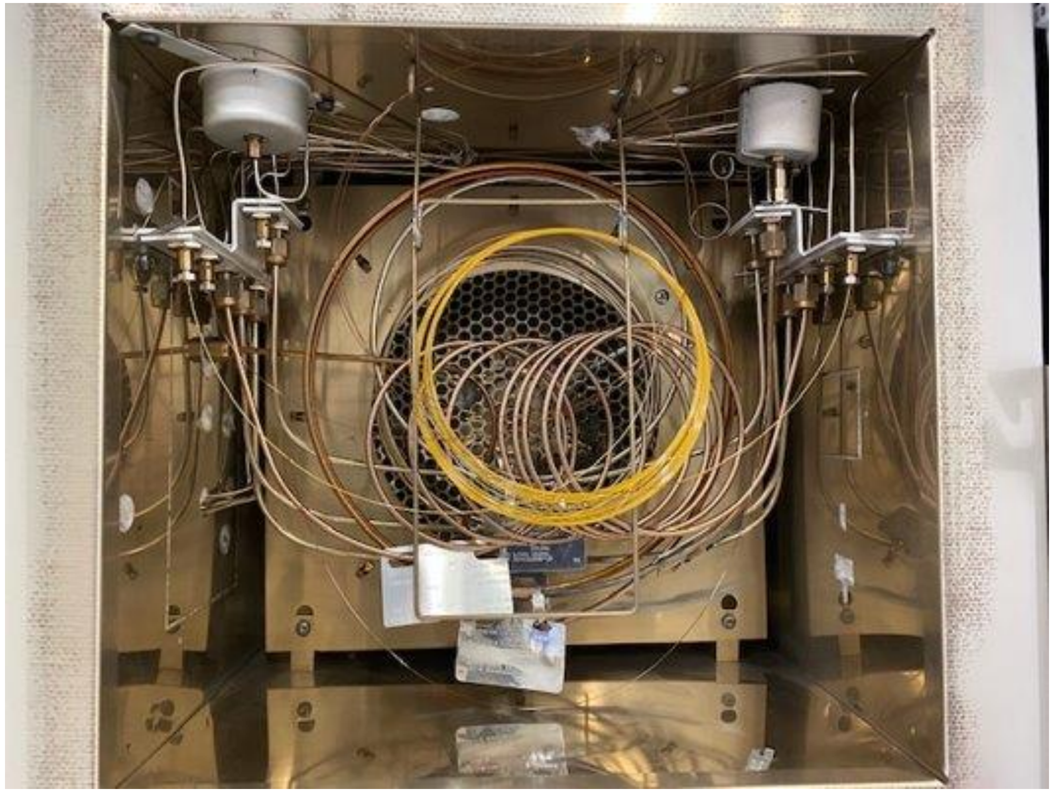
Injection

- Representative Sample
- Sample Size

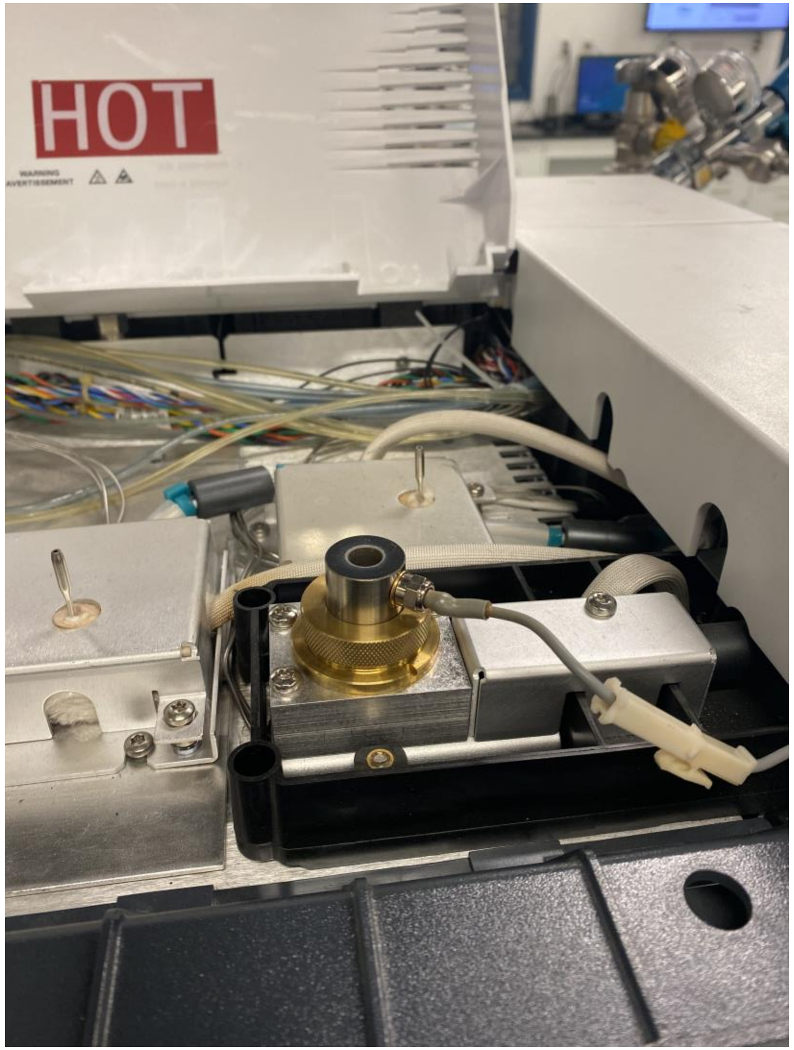
GC TECHNOLOGY: THREE PRINCIPAL EVENTS

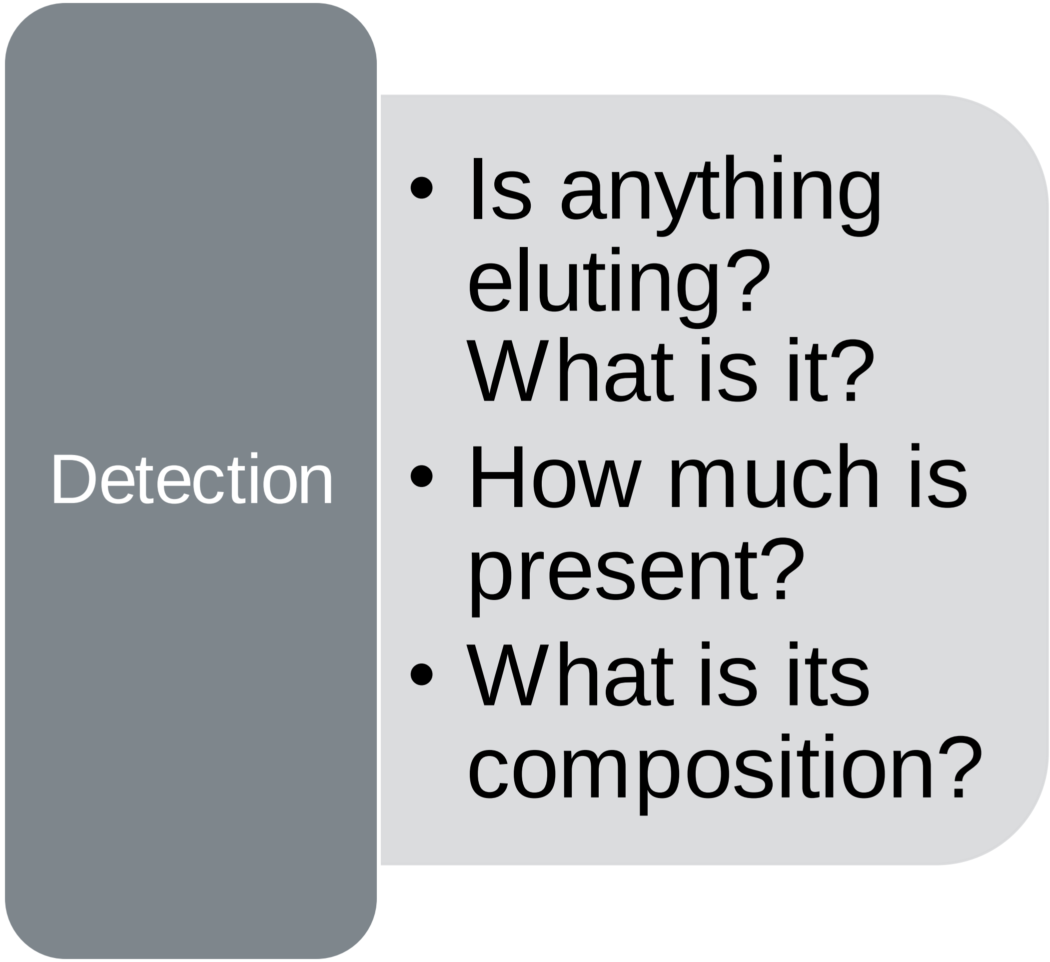
Separation

- 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)

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

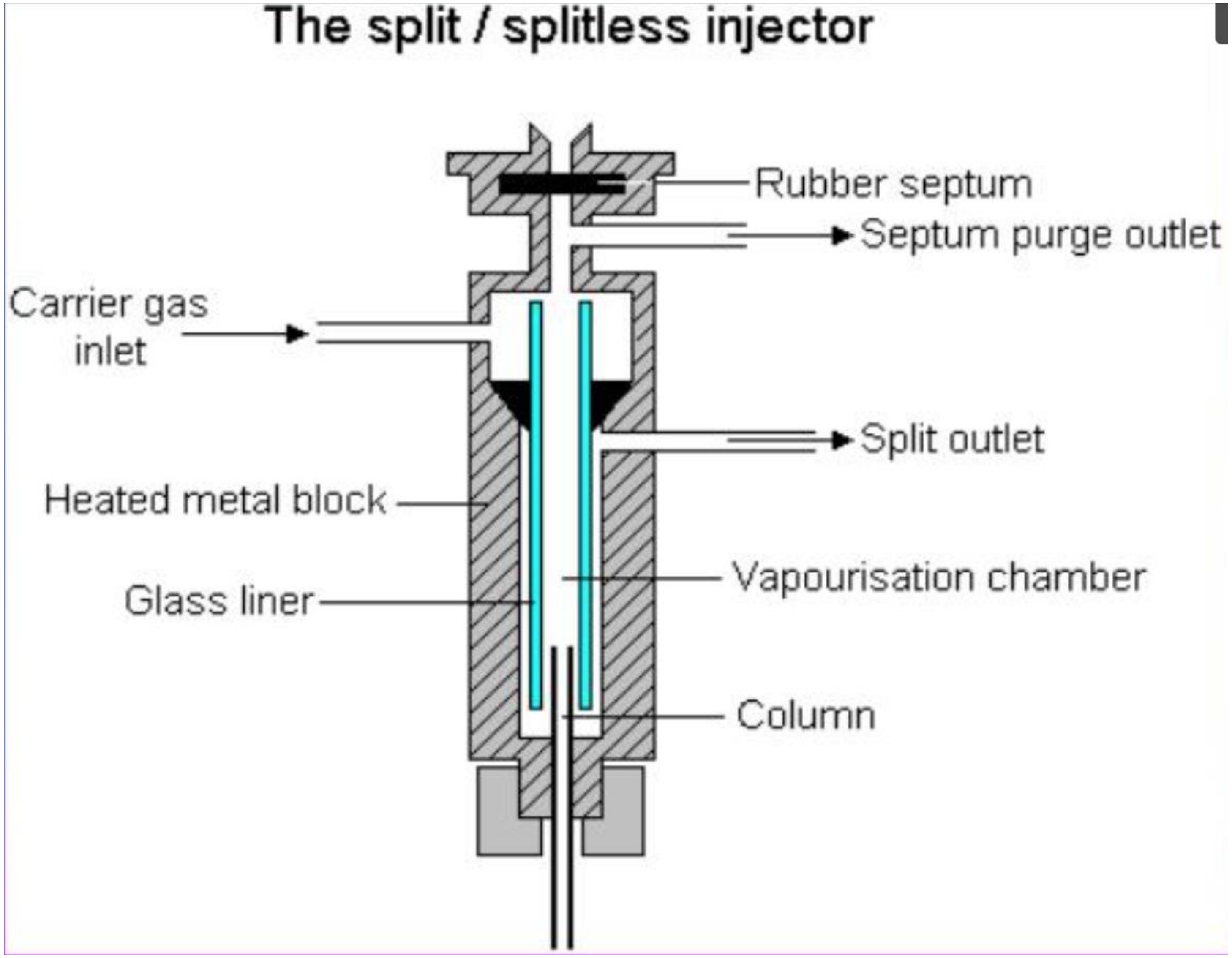
Cool on Column

- 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

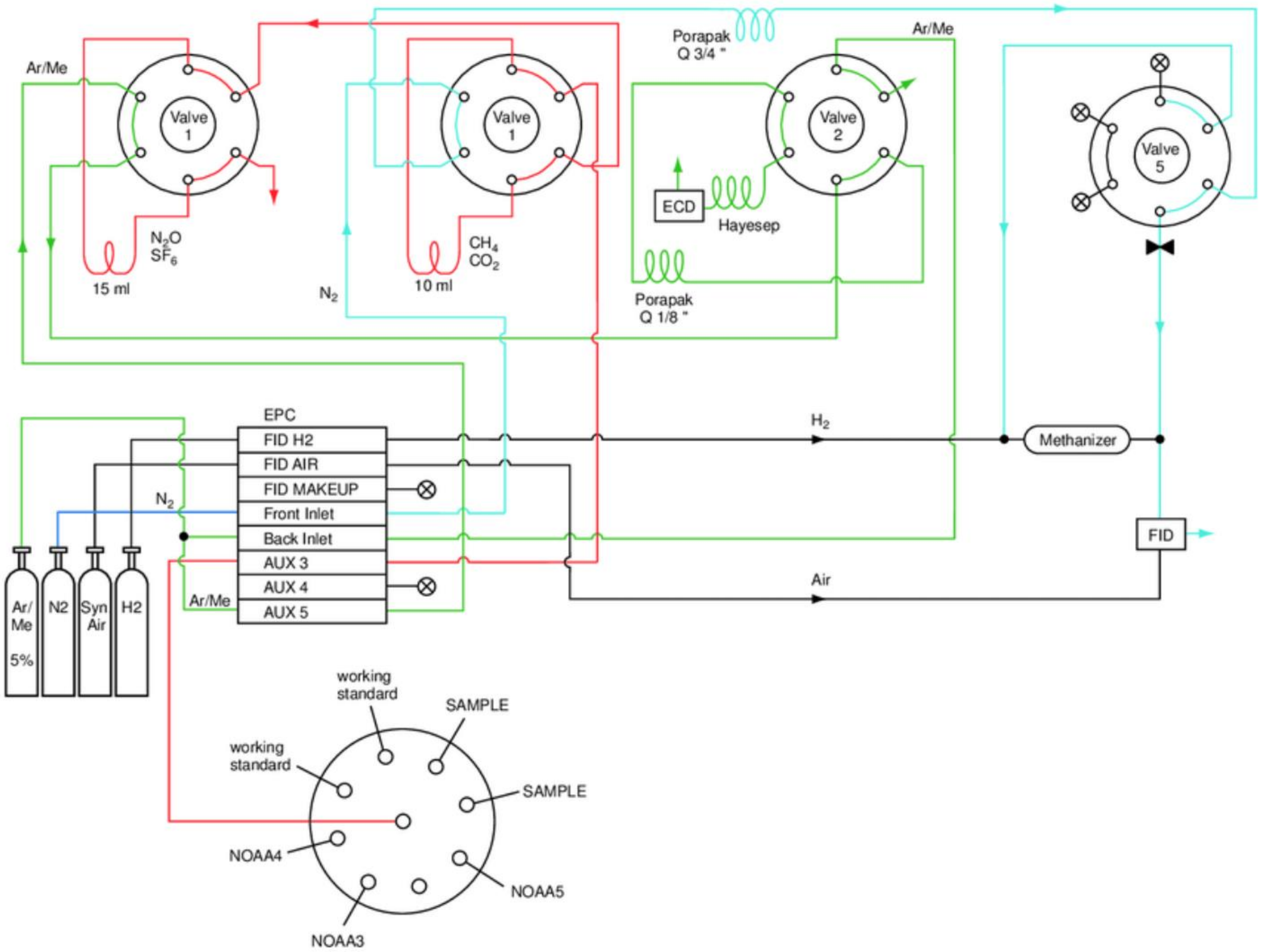
Direct on Column

- Gases (cc)
- Liquids (µL)

Split/Splitless



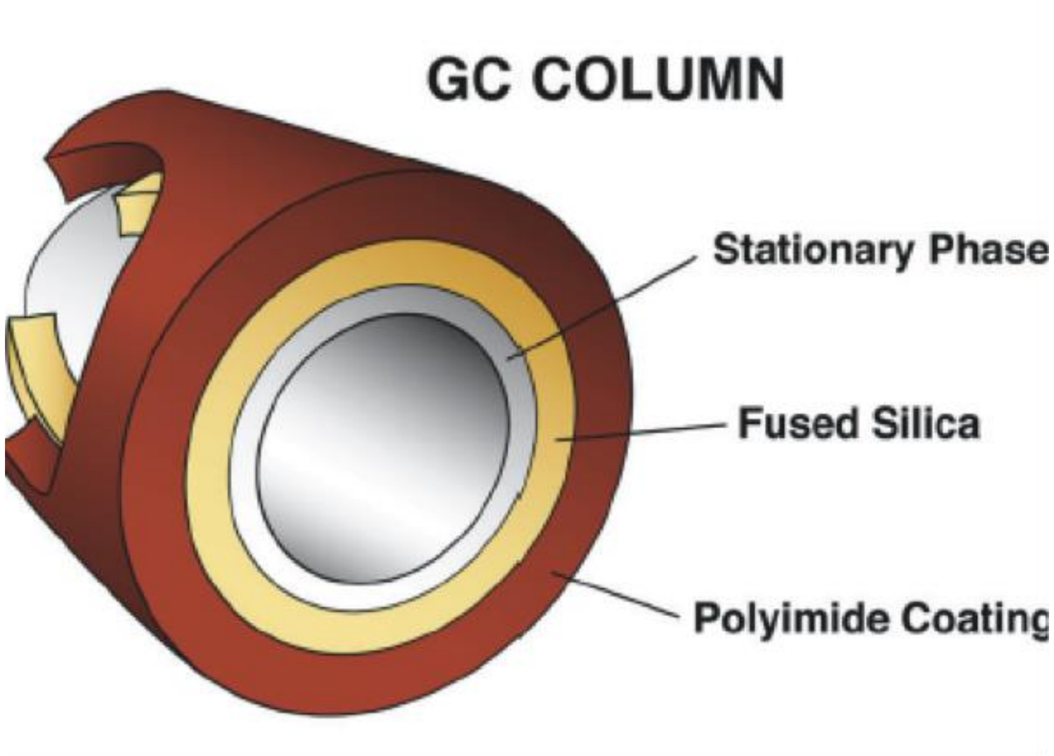
GC Valving Configuration



GC TECHNOLOGY: SEPARATION

Separation

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



GC TECHNOLOGY: COLUMNS

Separation

- Kováts Retention Index
- Boiling Point
- Polar
- PLOT

GC TECHNOLOGY: COLUMNS

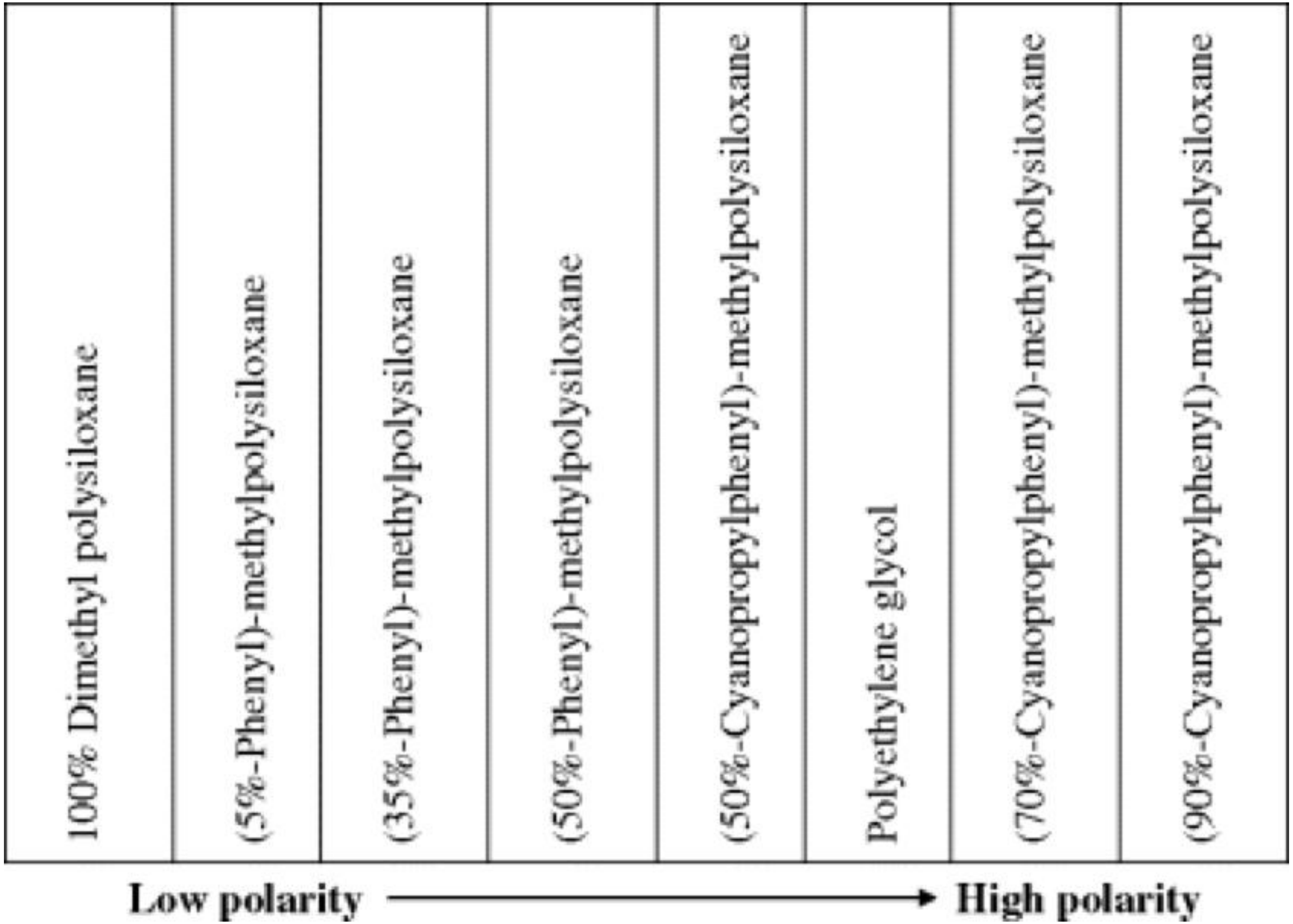
- The Kováts retention index (or Kováts index) of a compound is its retention time normalized to the retention times of adjacently eluting n-alkanes.
- It depends on the fact that log t ∝ n, where t is the retention time and n is the number of carbon atoms in the alkane.
- For an isothermal chromatogra 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



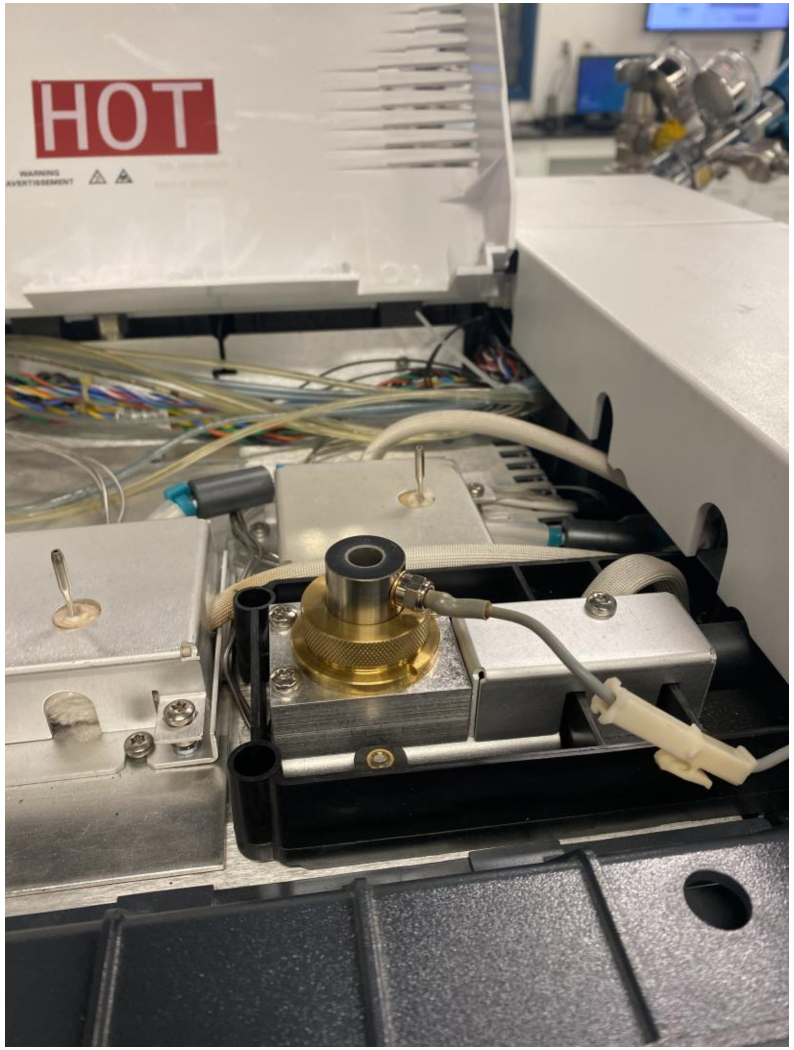
100% Dimethyl polysiloxane	(5%-Phenyl)-methylpolysiloxane	(35%-Phenyl)-methylpolysiloxane	(50%-Phenyl)-methylpolysiloxane	(50%-Cyanopropylphenyl)-methylpolysiloxane	Polyethylene glycol	(70%-Cyanopropylphenyl)-methylpolysiloxane	(90%-Cyanopropylphenyl)-methylpolysiloxane

Low polarity → **High polarity**

Types of Columns

Type of Solid Phase	Polarity	Separation Characteristics	Application	Operational Temperature Range (Approx.)
Methyl silicone DB-1	Non-polar	Boiling point order	Petroleum, solvents, high boiling point compounds	-60 to 360 °C
Phenylmethyl DB-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

GC TECHNOLOGY: DETECTION

Sensitivity

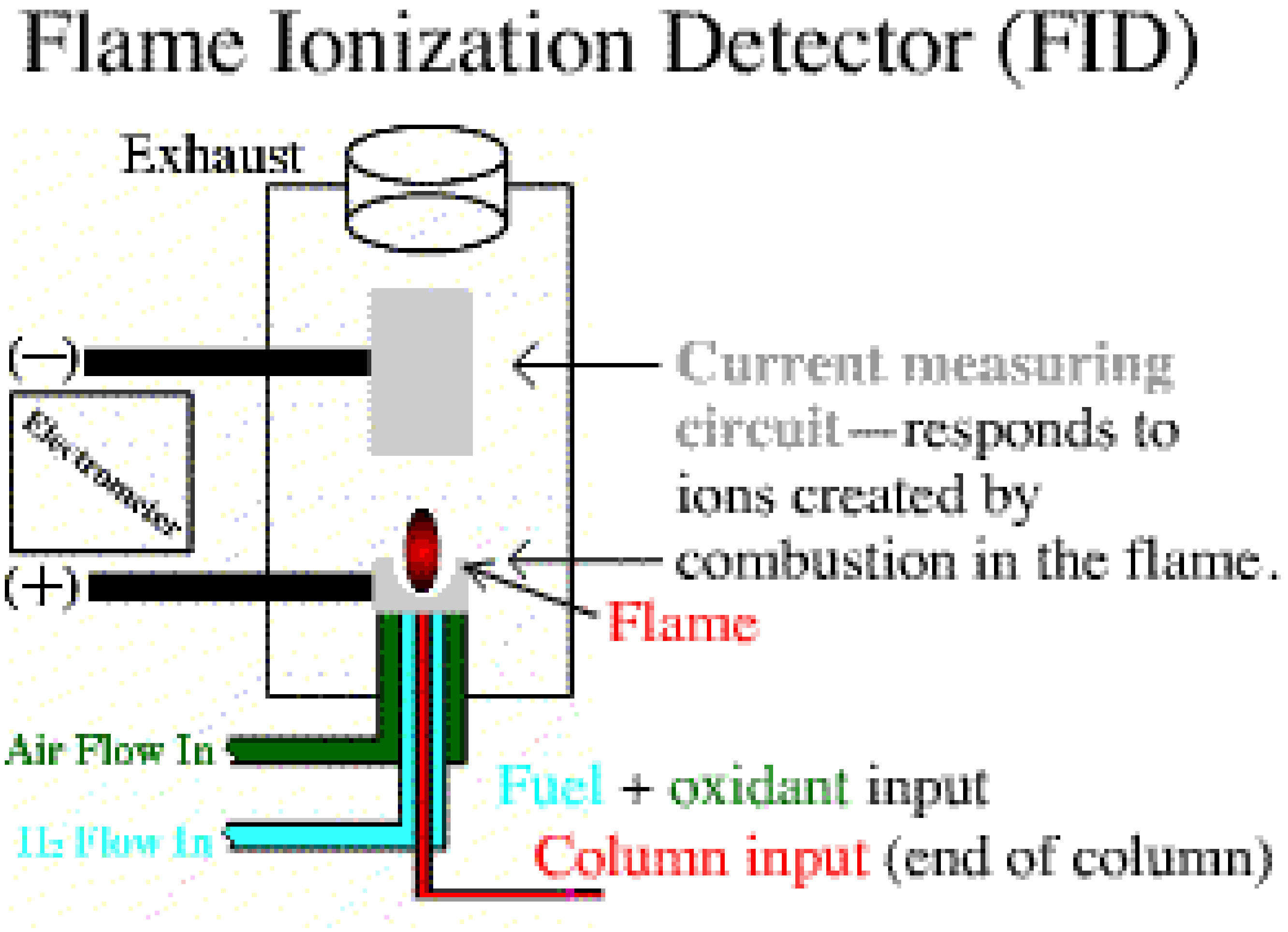
Selectivity & Speciation

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)

Current measuring circuit—responds to ions created by combustion in the flame.

FID Response factor calculations

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

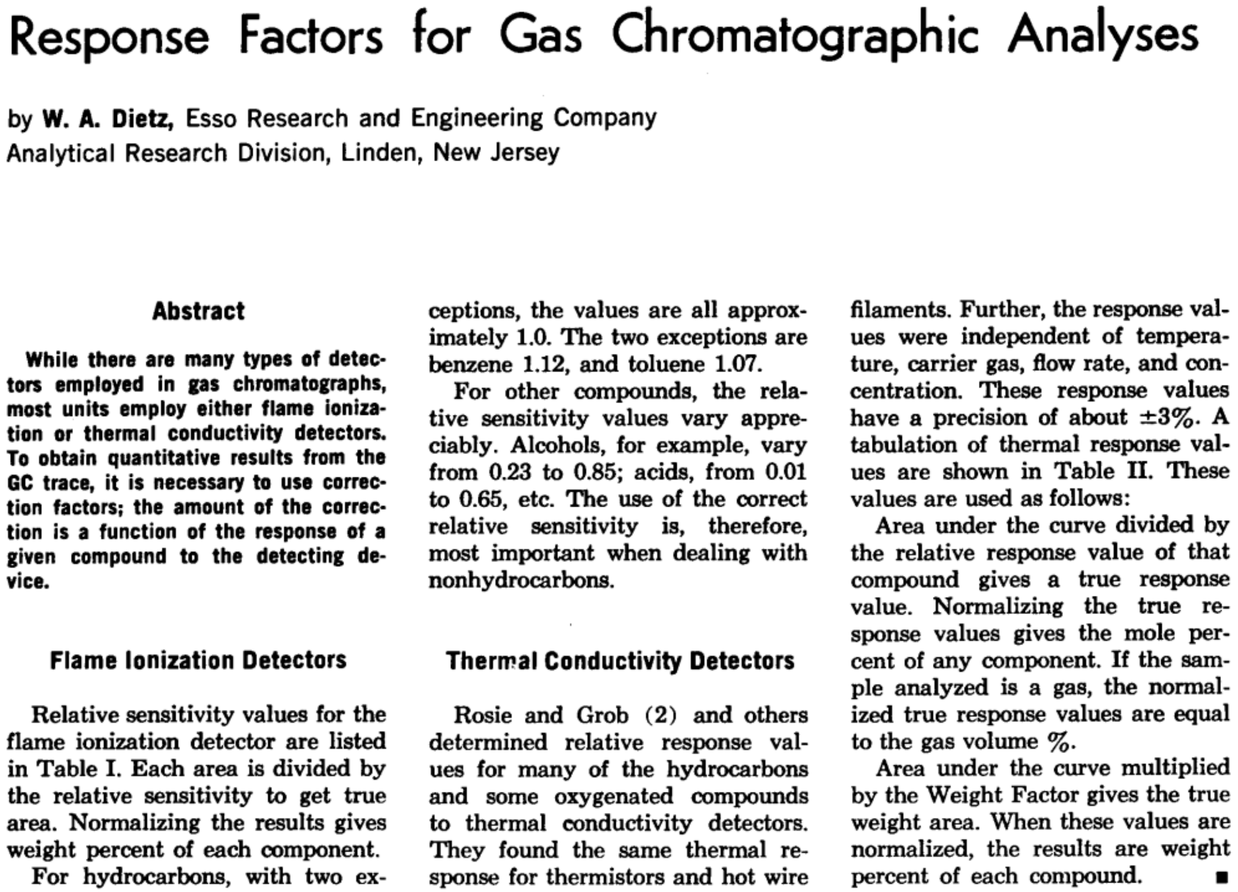
CH4 = $\frac{C}{MW} = \frac{12}{16}$ = 0.75 = 1.12

C4H8 = $\frac{C}{MW} = \frac{48}{56}$ = 0.86 = 0.98

C4H6 = $\frac{C}{MW} = \frac{48}{54}$ = 0.89 = 0.94

C7H16 = $\frac{C}{MW} = \frac{84}{100}$ = 0.84 = 1.00

CH3OH = $\frac{C}{MW} = \frac{12}{32}$ = 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 exceptions, 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 ±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 per cent 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

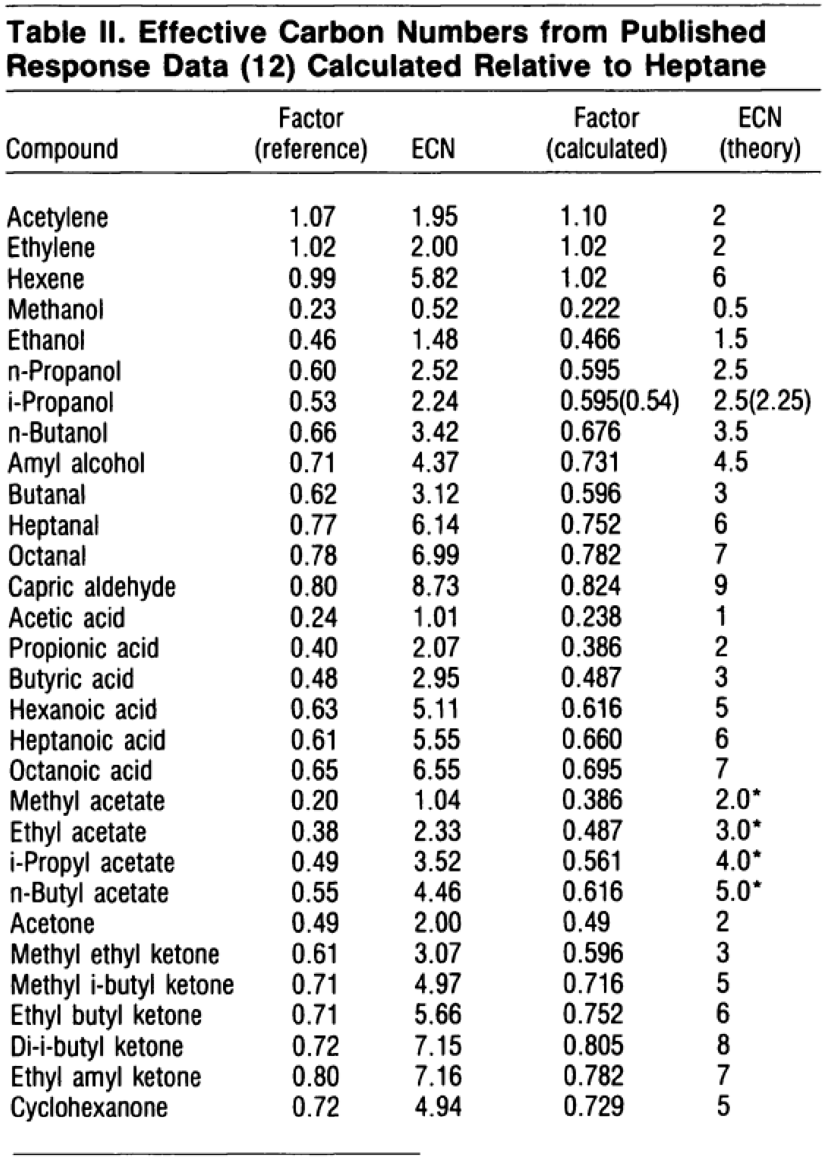
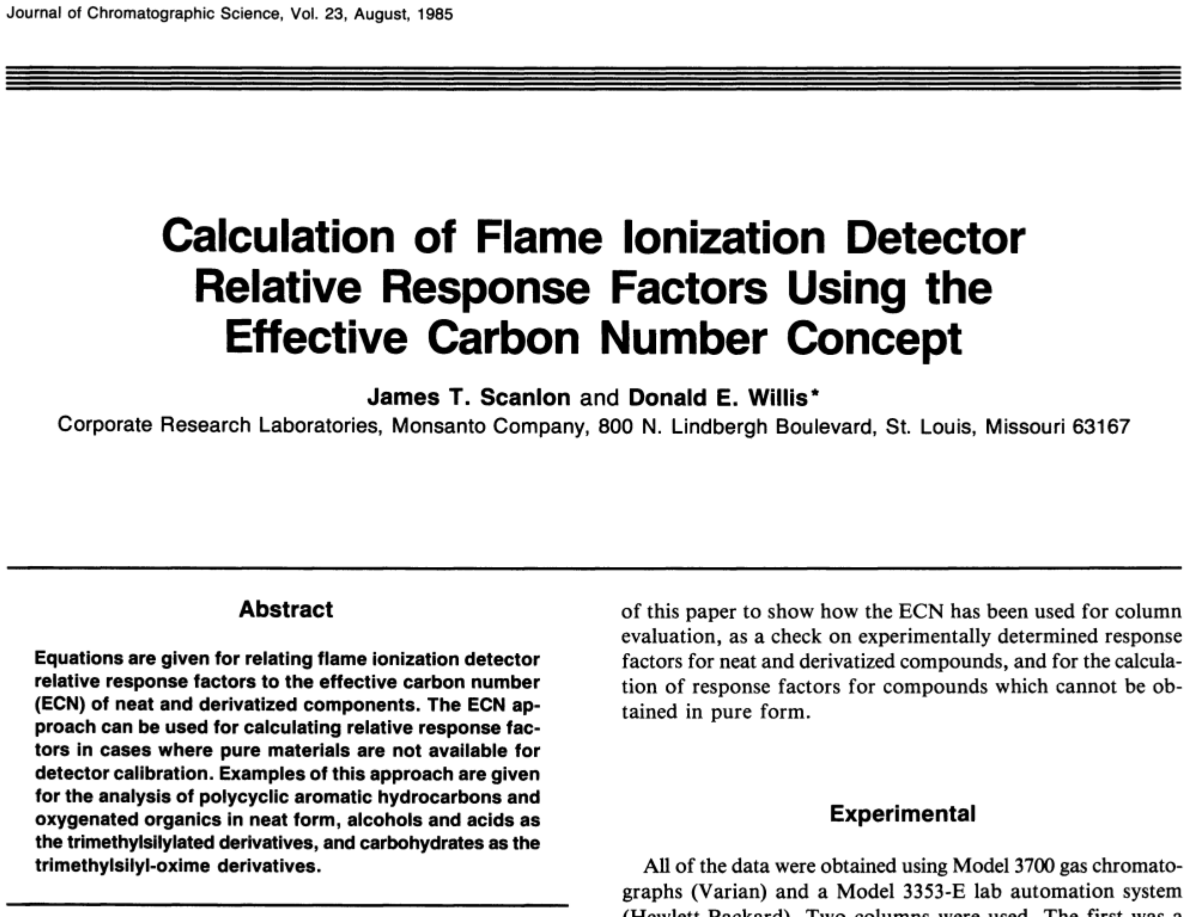


Table II. Effective Carbon Numbers from Published Response Data (12) Calculated Relative to Heptane

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

ASTM D5441

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.

INTERNATIONAL

Designation: D5441 – 98 (Reapproved 2017)

Standard Test Method for
Analysis of Methyl Tert-Butyl Ether (MTBE) by Gas Chromatography[1]

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 C_4 to C_{12} 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

mendations 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

ASTM D5441

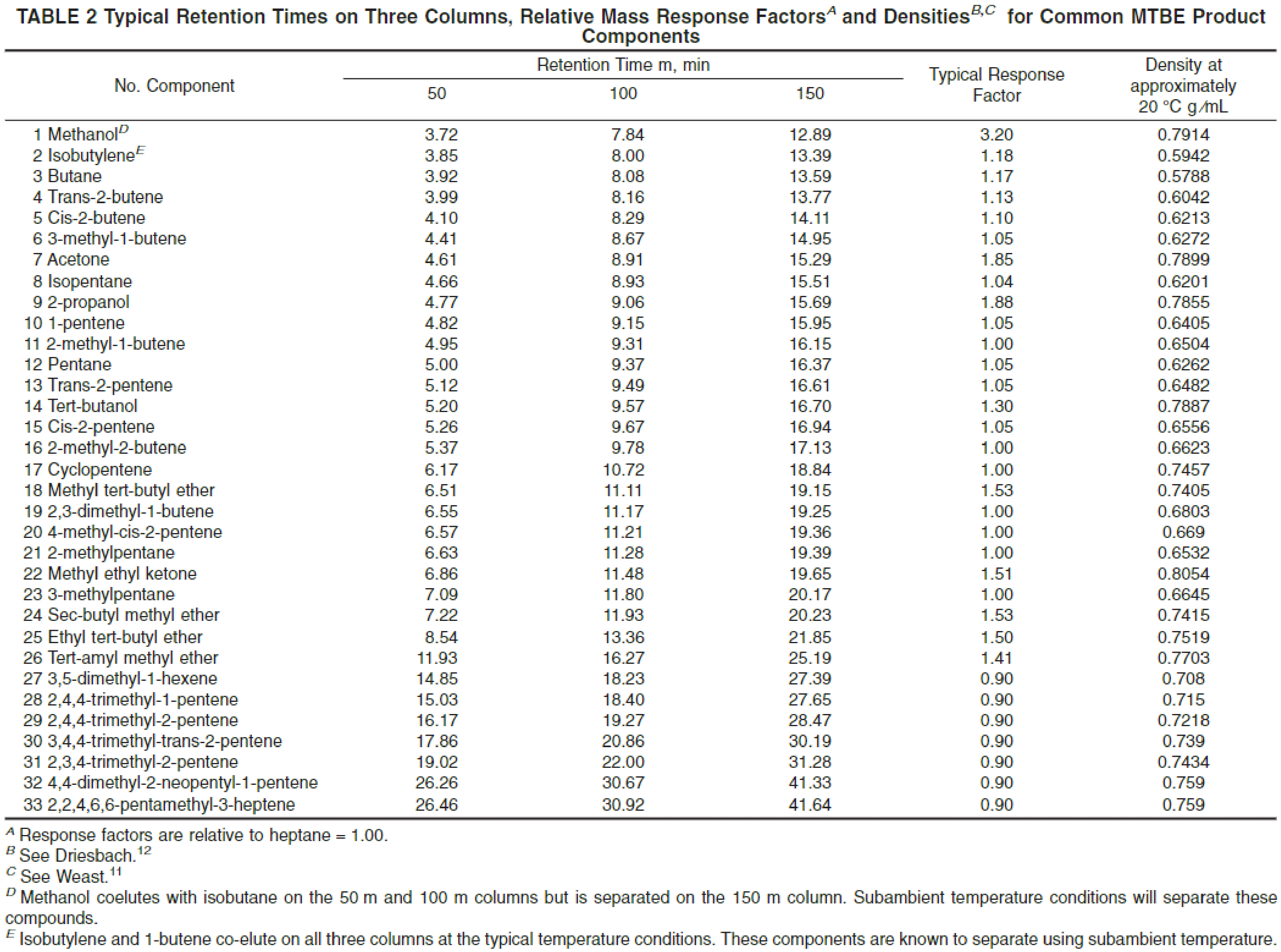


TABLE 2 Typical Retention Times on Three Columns, Relative Mass Response Factors[A] and Densities[B,C] for Common MTBE Product Components

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.

ASTM D6730

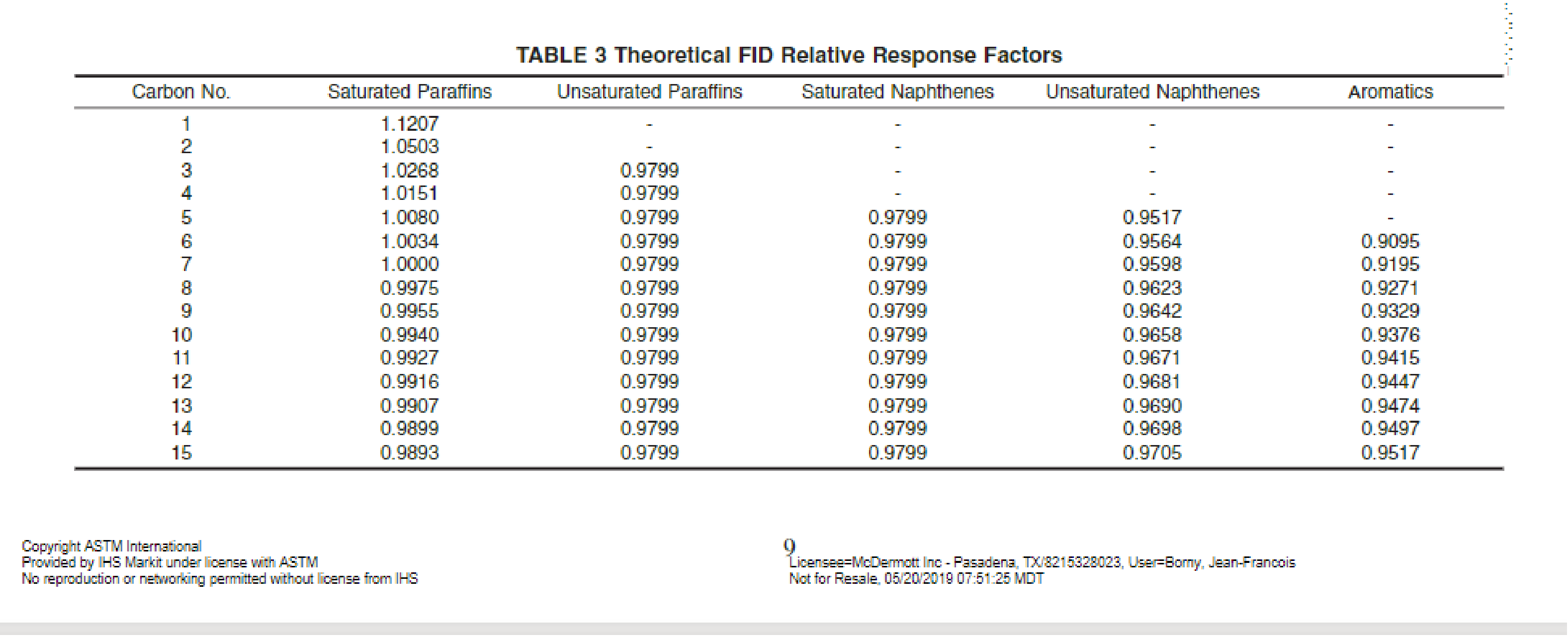
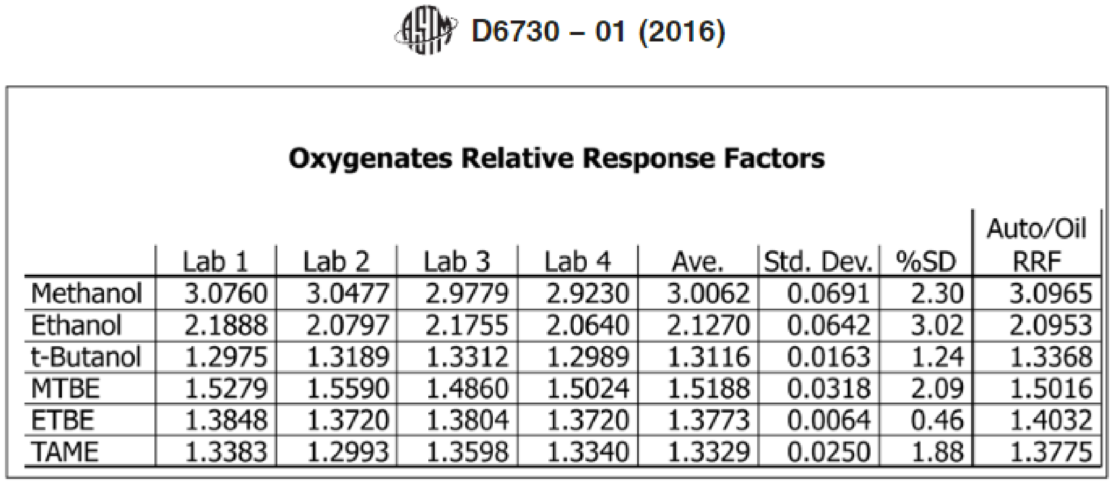


TABLE 3 Theoretical FID Relative Response Factors

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

9

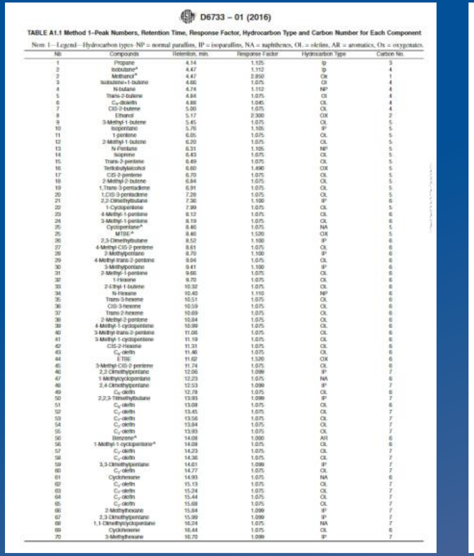
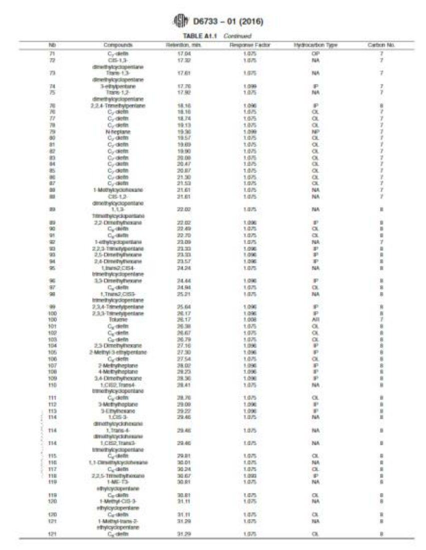
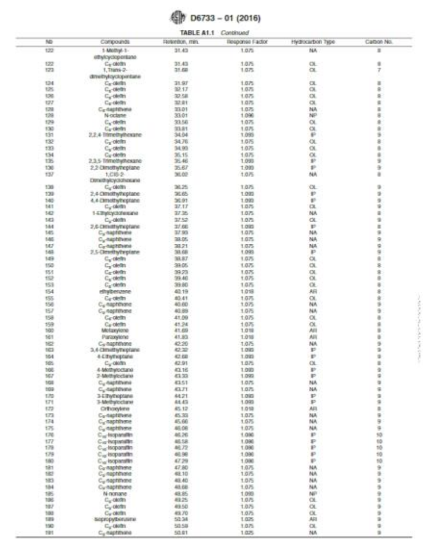
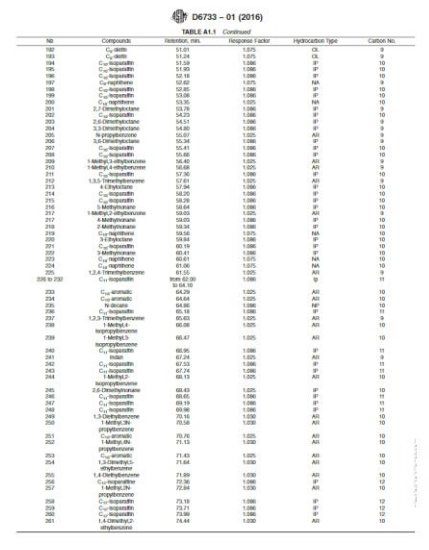
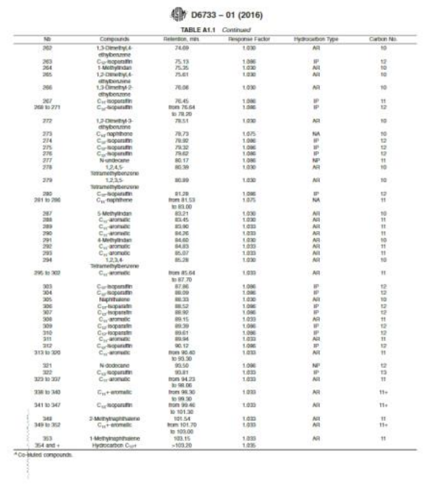
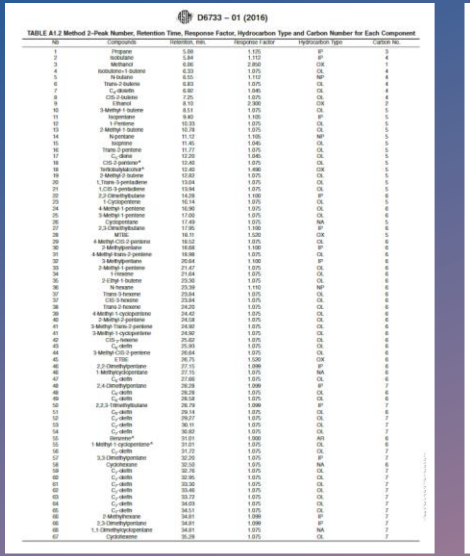
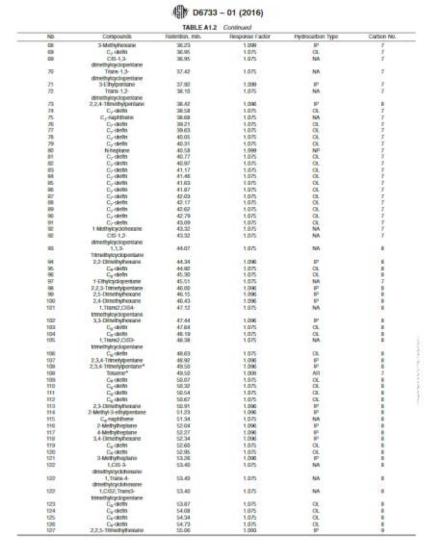
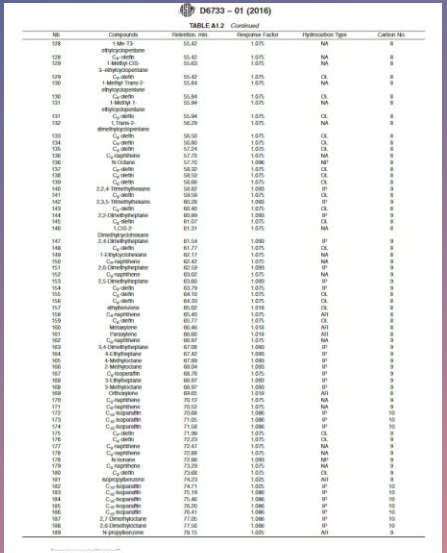
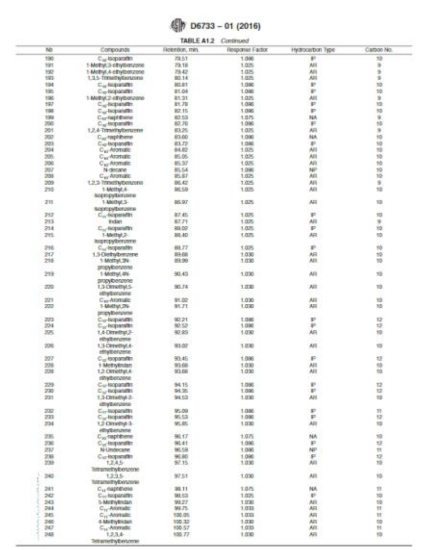
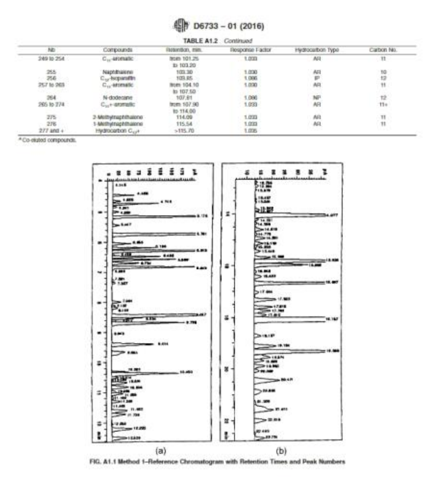


D6730 – 01 (2016)

Oxygenates Relative Response Factors

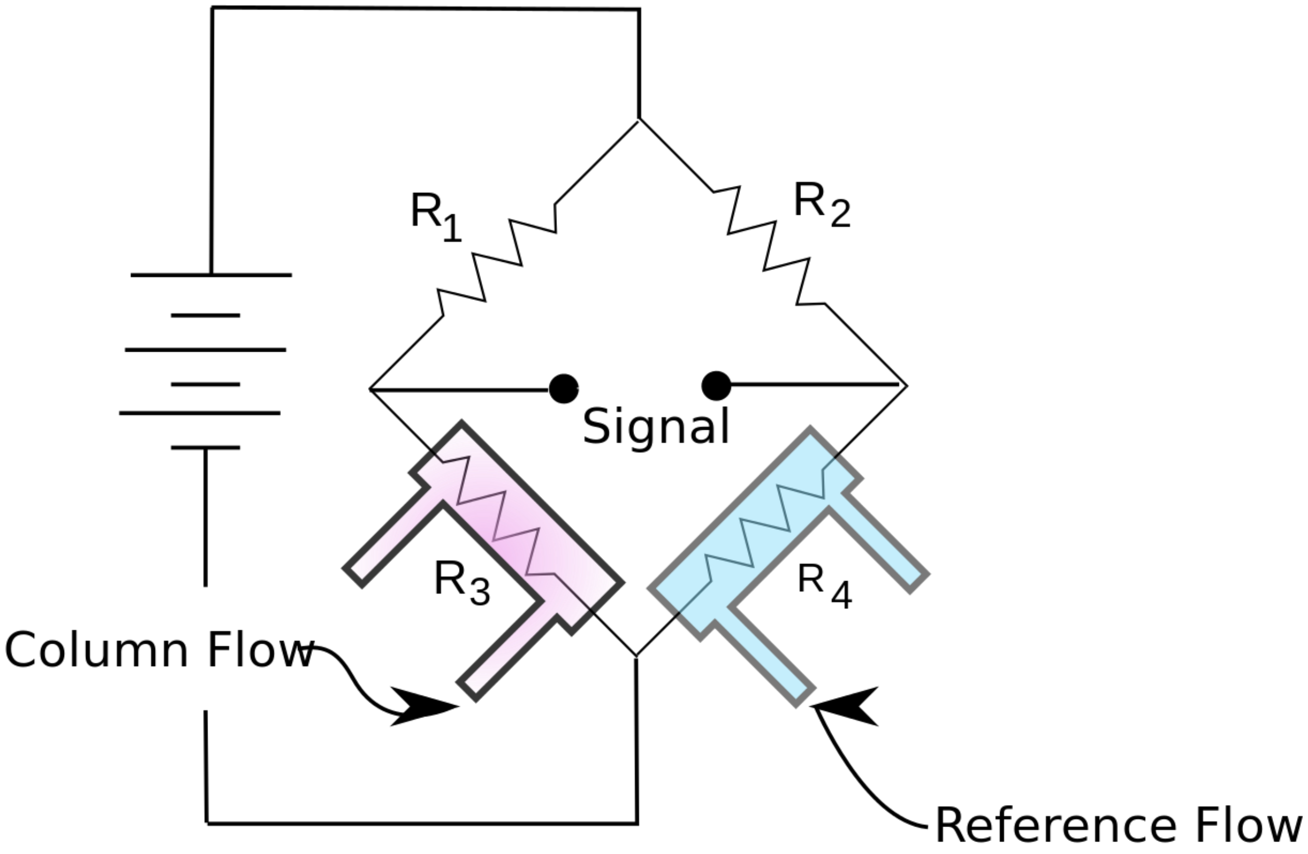
	Lab 1	Lab 2	Lab 3	Lab 4	Ave.	Std. Dev.	%SD	Auto/Oil RRF
Methanol	3.0760	3.0477	2.9779	2.9230	3.0062	0.0691	2.30	3.0965
Ethanol	2.1888	2.0797	2.1755	2.0640	2.1270	0.0642	3.02	2.0953
t-Butanol	1.2975	1.3189	1.3312	1.2989	1.3116	0.0163	1.24	1.3368
MTBE	1.5279	1.5590	1.4860	1.5024	1.5188	0.0318	2.09	1.5016
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

GC TECHNOLOGY: TCD

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



TCD Response factor

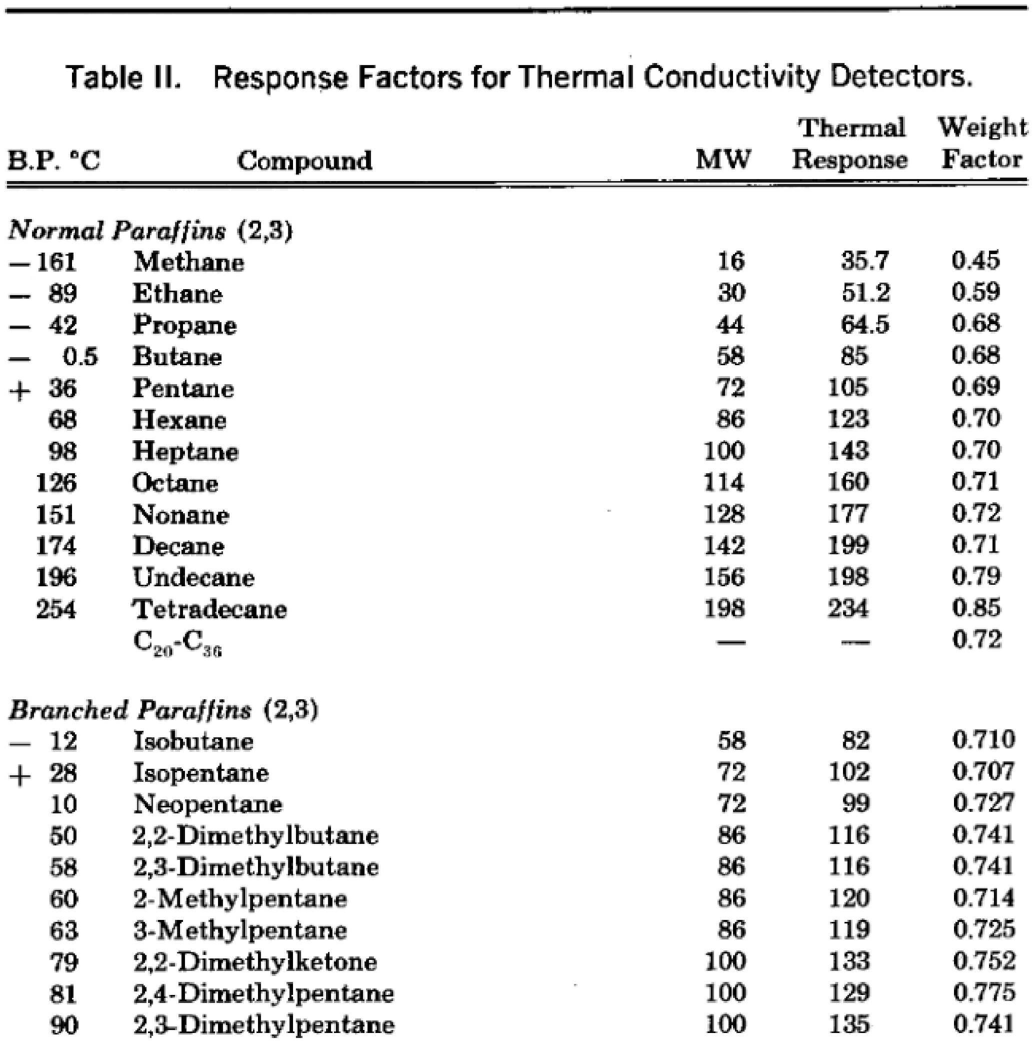
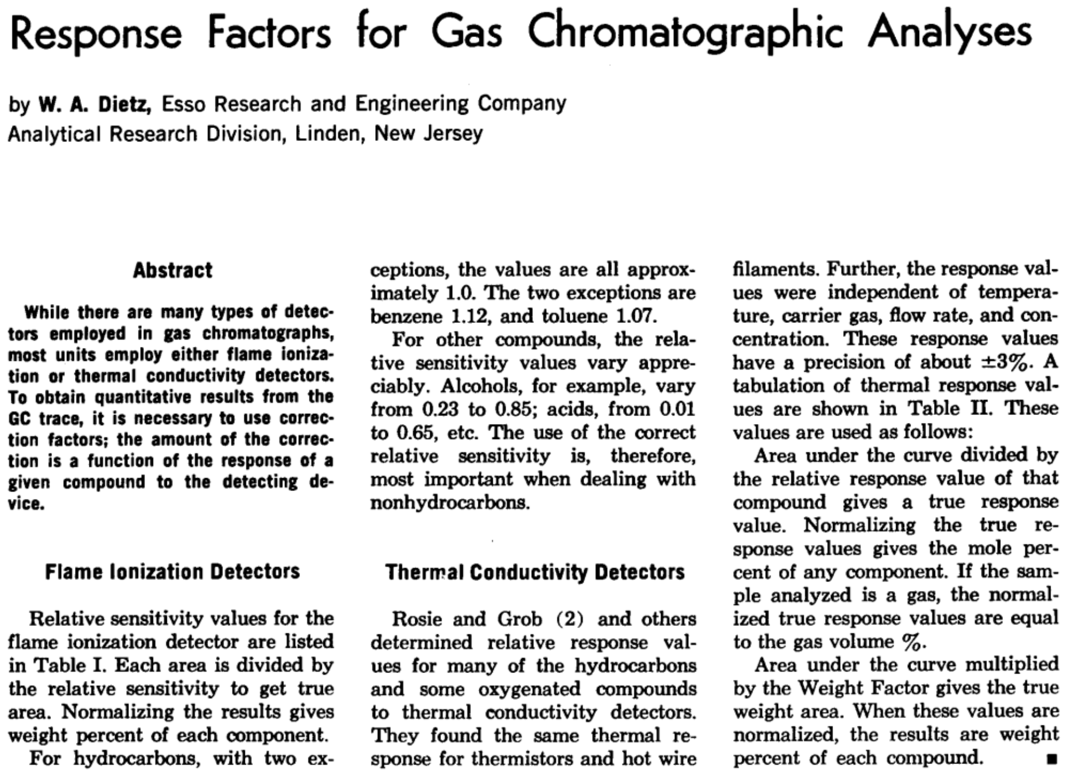


Table II. Response Factors for Thermal Conductivity Detectors.

B.P. °C	Compound	MW	Thermal Response	Weight Factor
Normal Paraffins (2,3)				
−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
Branched Paraffins (2,3)				
− 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

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 exceptions, 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 ±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

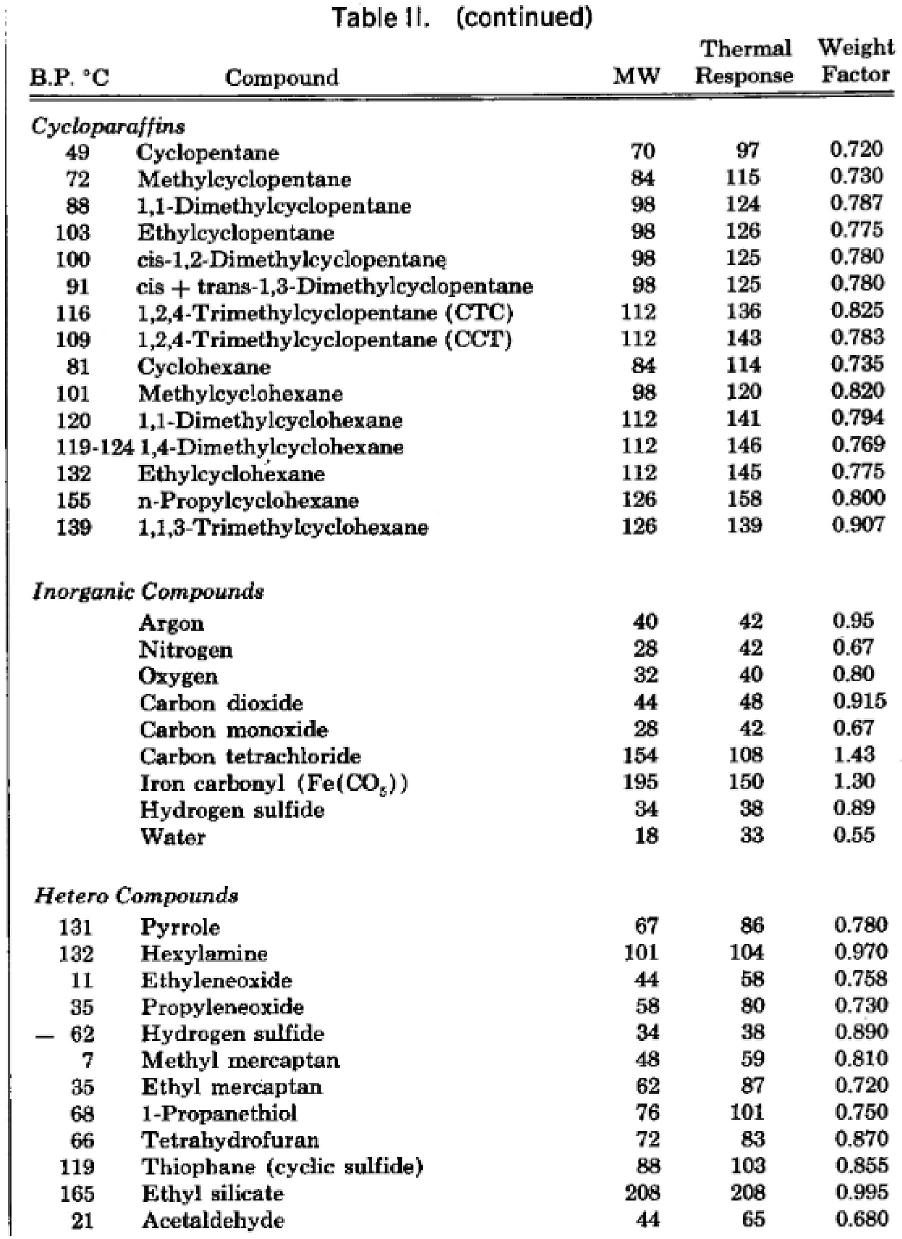
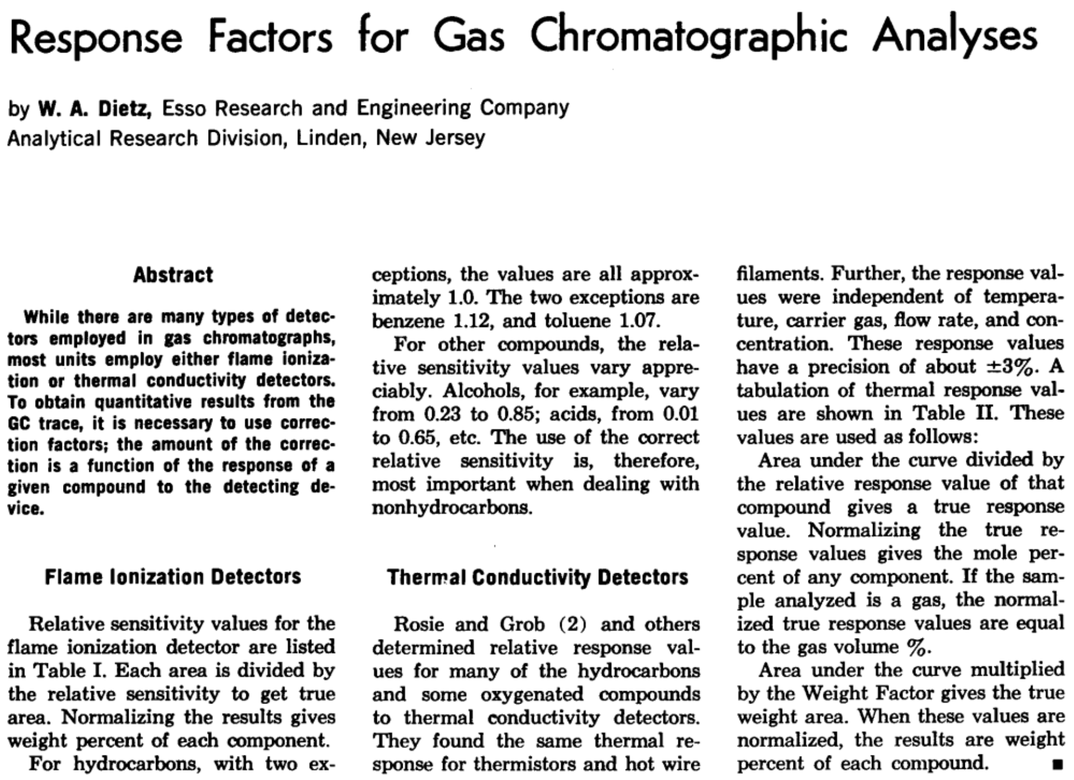


Table II. (continued)

B.P. °C	Compound	MW	Thermal Response	Weight Factor
Cycloparaffins				
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
Inorganic Compounds				
	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
Hetero Compounds				
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



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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

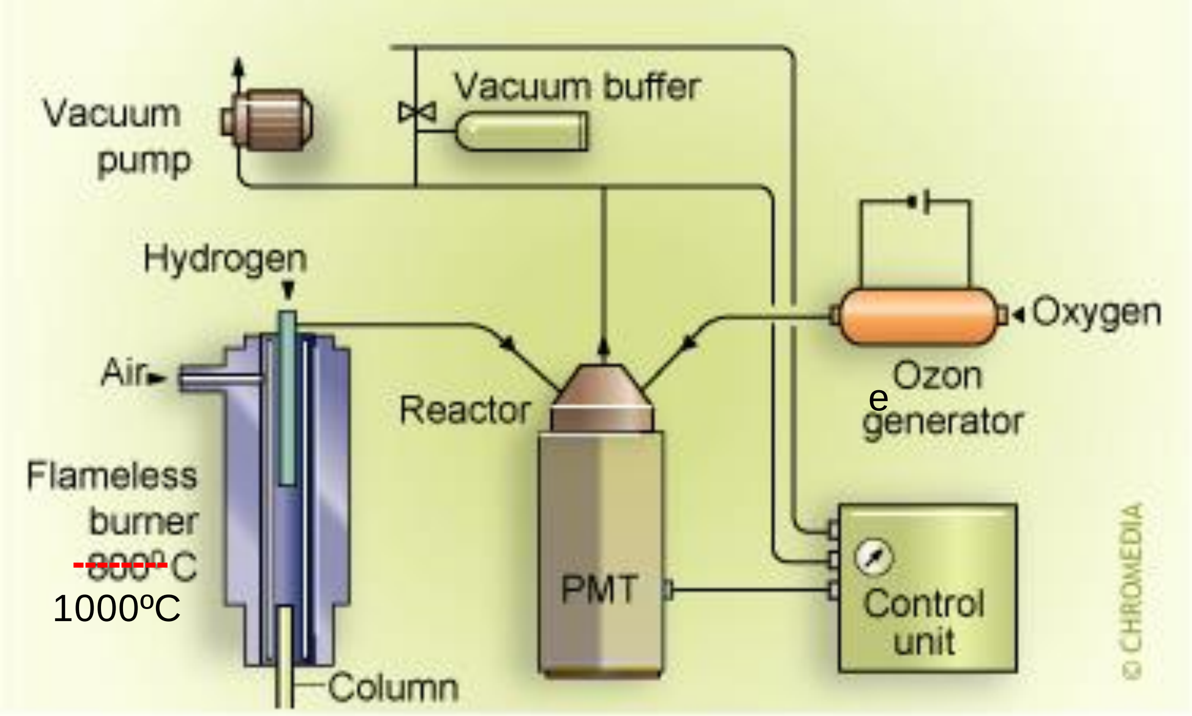
- Sulfur Chemiluminescence Detector
- Sulfur specific detector
- Response is equimolar for all sulfur
- External Standard calibration needed, but only one sulfur-containing compound necessary

- $R - S + O2 \rightarrow SO2 + CO2 + H2O$

- $SO2 + H2 \rightarrow H2S$

- $H2S + O3 \rightarrow SO2*$

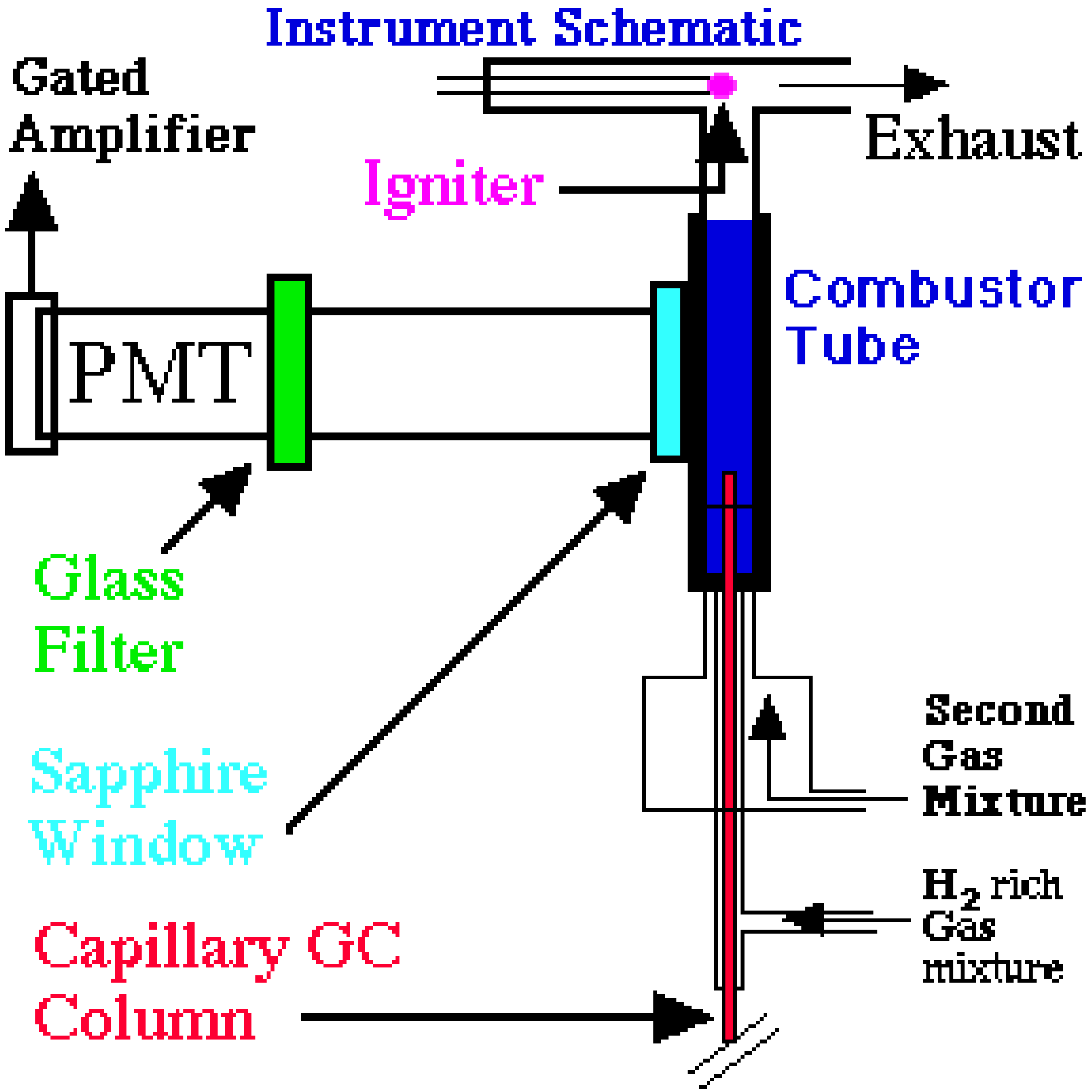
- $SO2* \rightarrow SO2 + h\gamma$



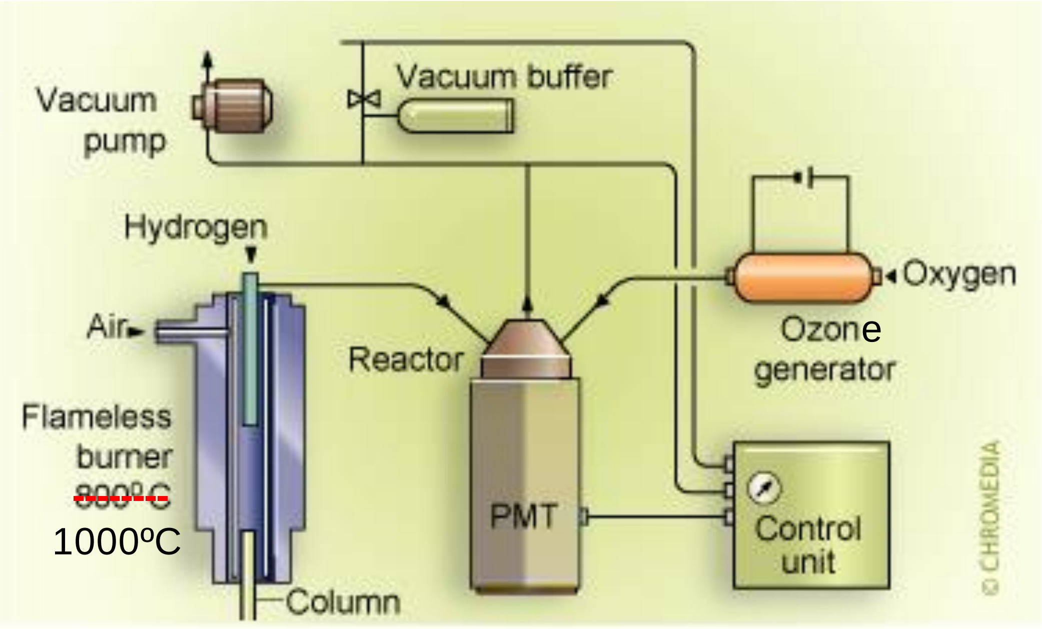
GC TECHNOLOGY: FPD/PFPD

- 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



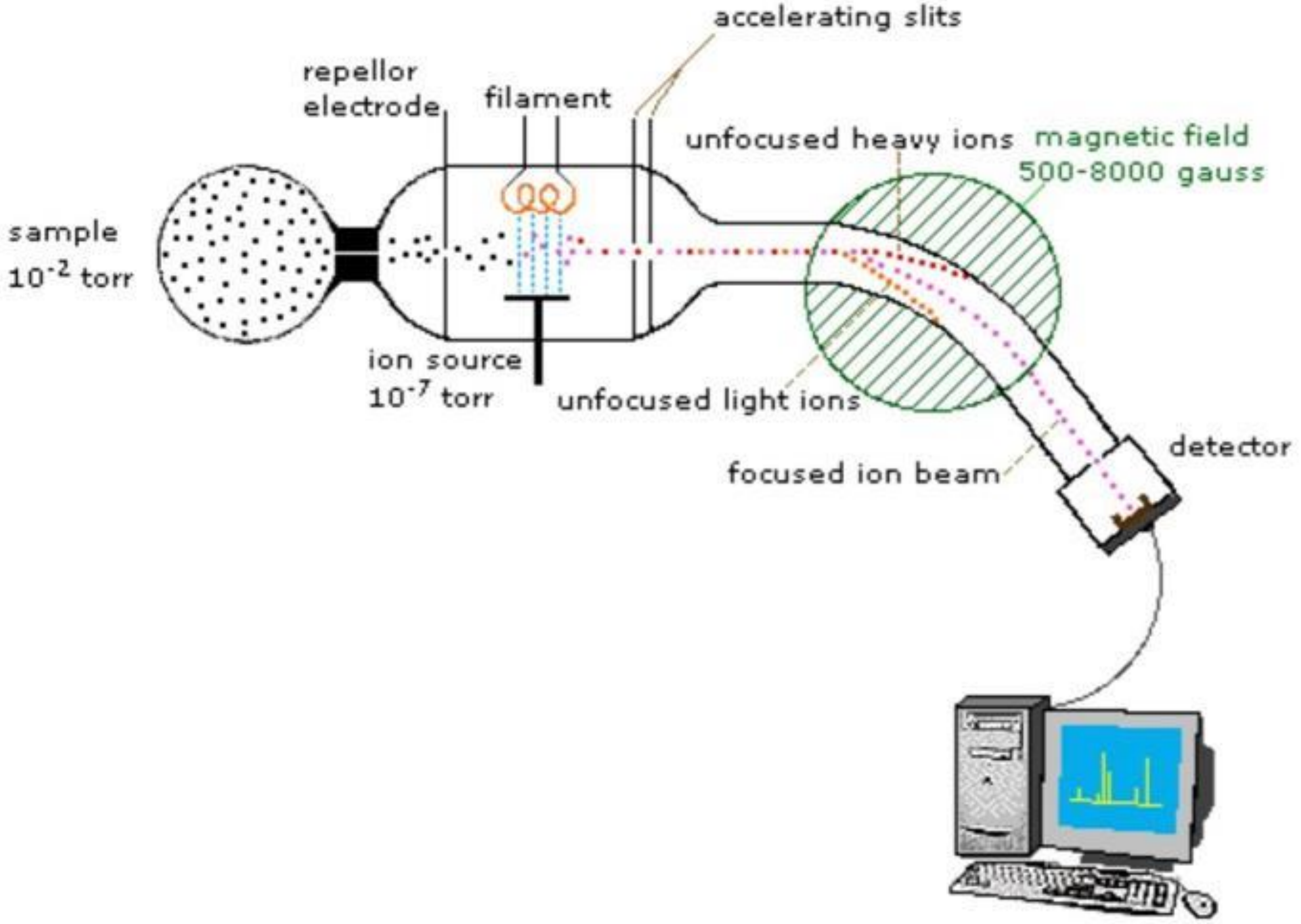
GC TECHNOLOGY: NCD



- Nitrogen Chemiluminescence Detector
- Nitrogen specific detector
- Response is equimolar for all nitrogen
- External standard needed but only one nitrogen-containing compound necessary
- $R - N + O2 + H2^{Opt} \rightarrow NO + CO2 + H2O$
- $NO + O3 \ \rightarrow NO2 *$
- $NO2 * \rightarrow NO2 + h\gamma$

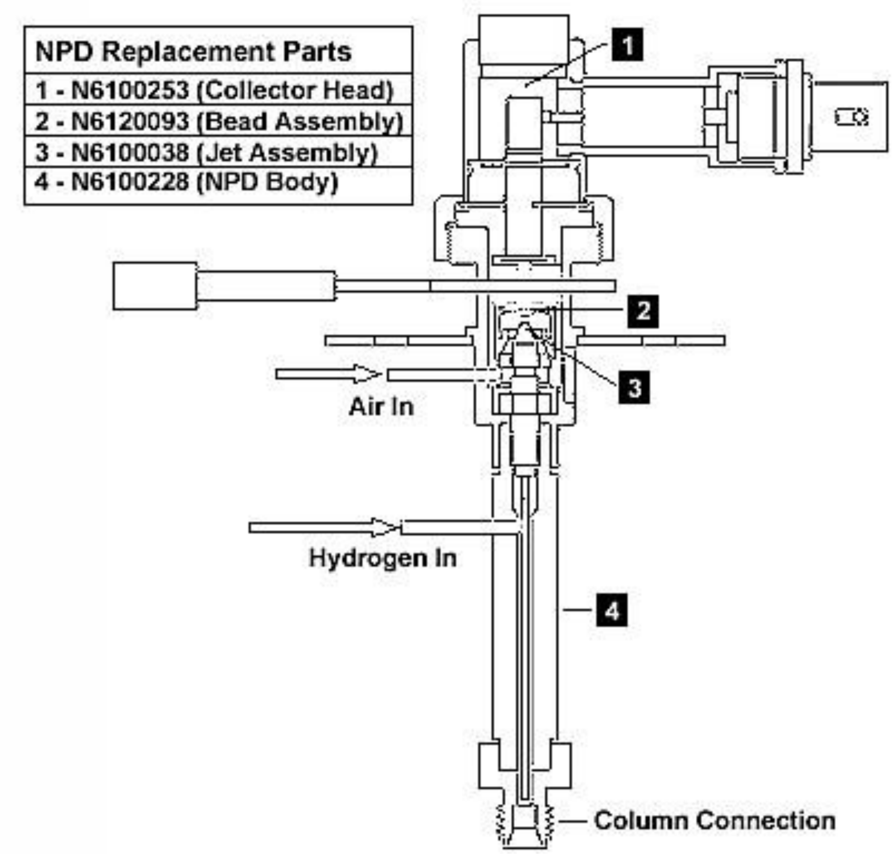
GC TECHNOLOGY: MS

- Mass Spectrometer Detector
- Mass selective detector
- Response is based on ionization



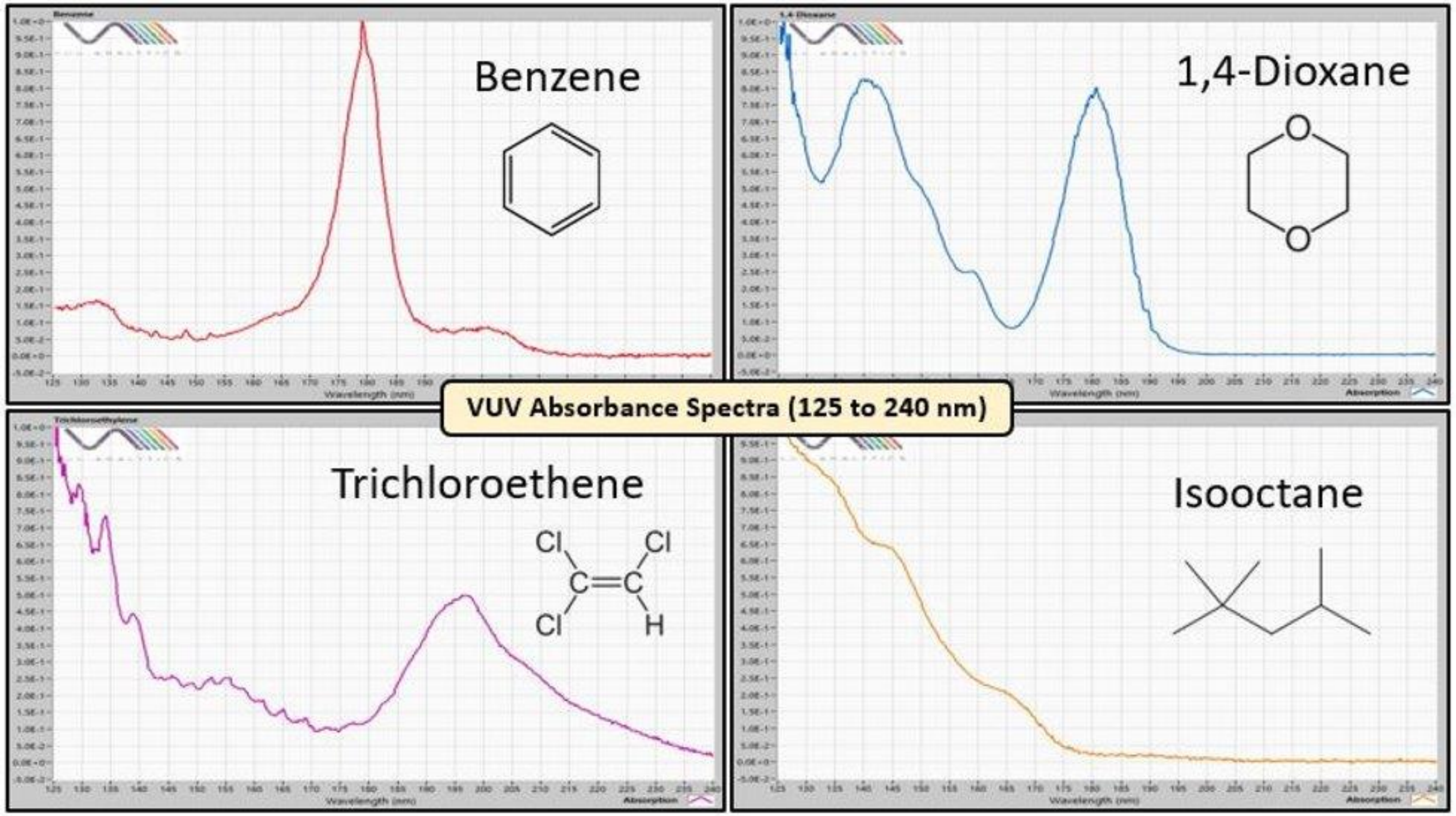
GC TECHNOLOGY: TSD/NPD

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



GC TECHNOLOGY: VUV

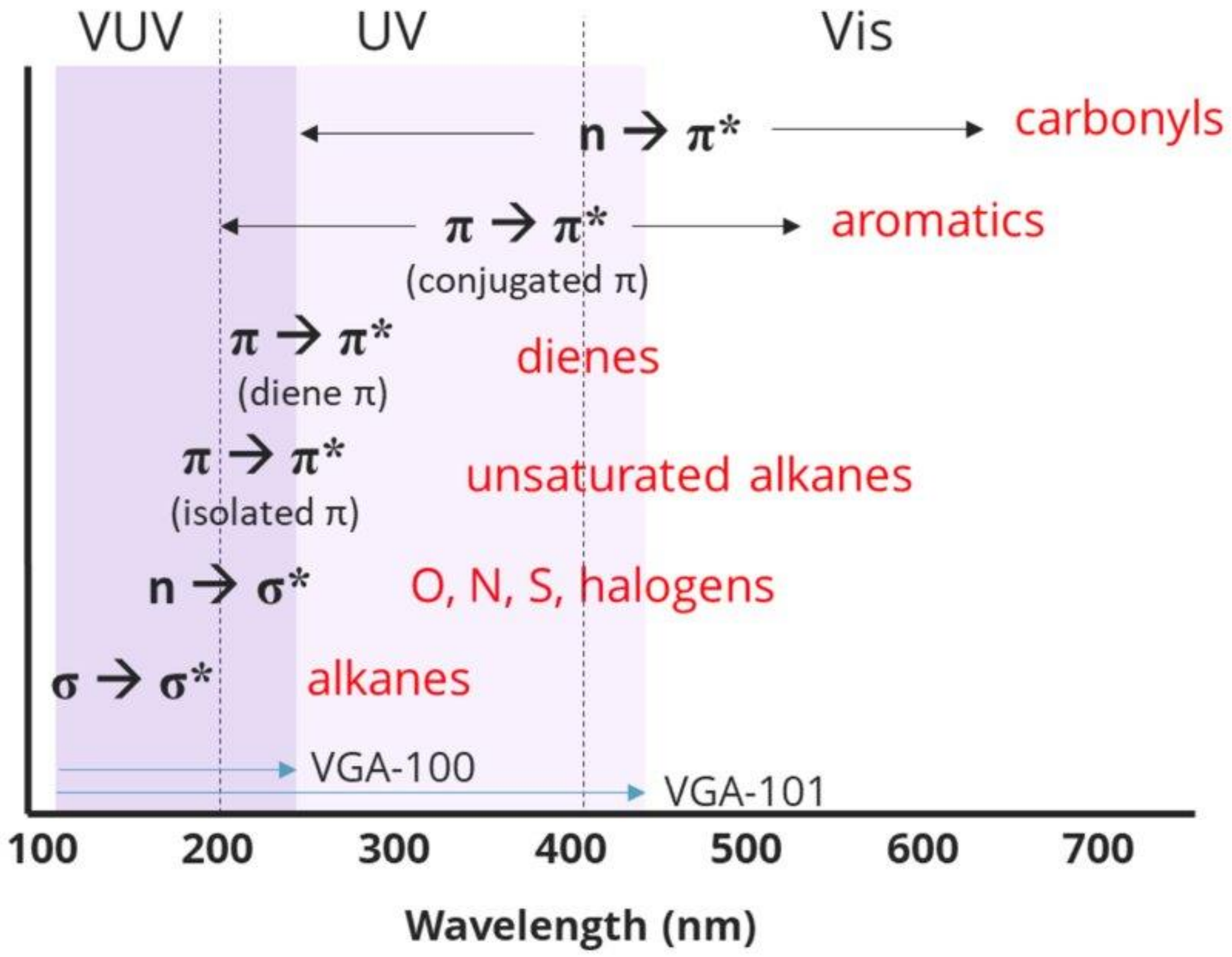
- Vacuum Ultraviolet Detector
- Nearly Universal Detector

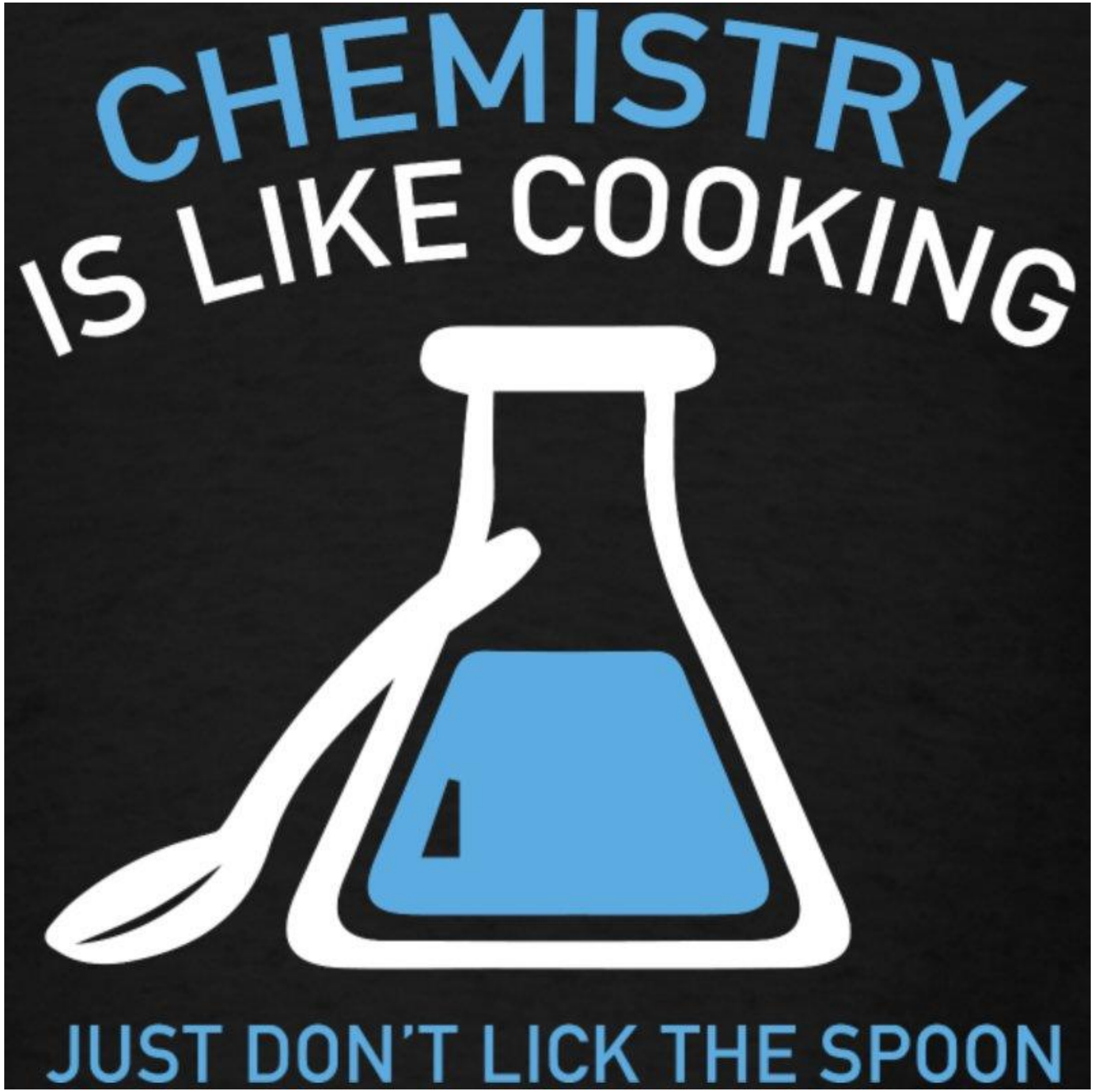


VUV Absorbance Spectra (125 to 240 nm)

GC TECHNOLOGY: VUV

- Vacuum Ultraviolet Detector
- Nearly Universal Detector




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 know 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.

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.

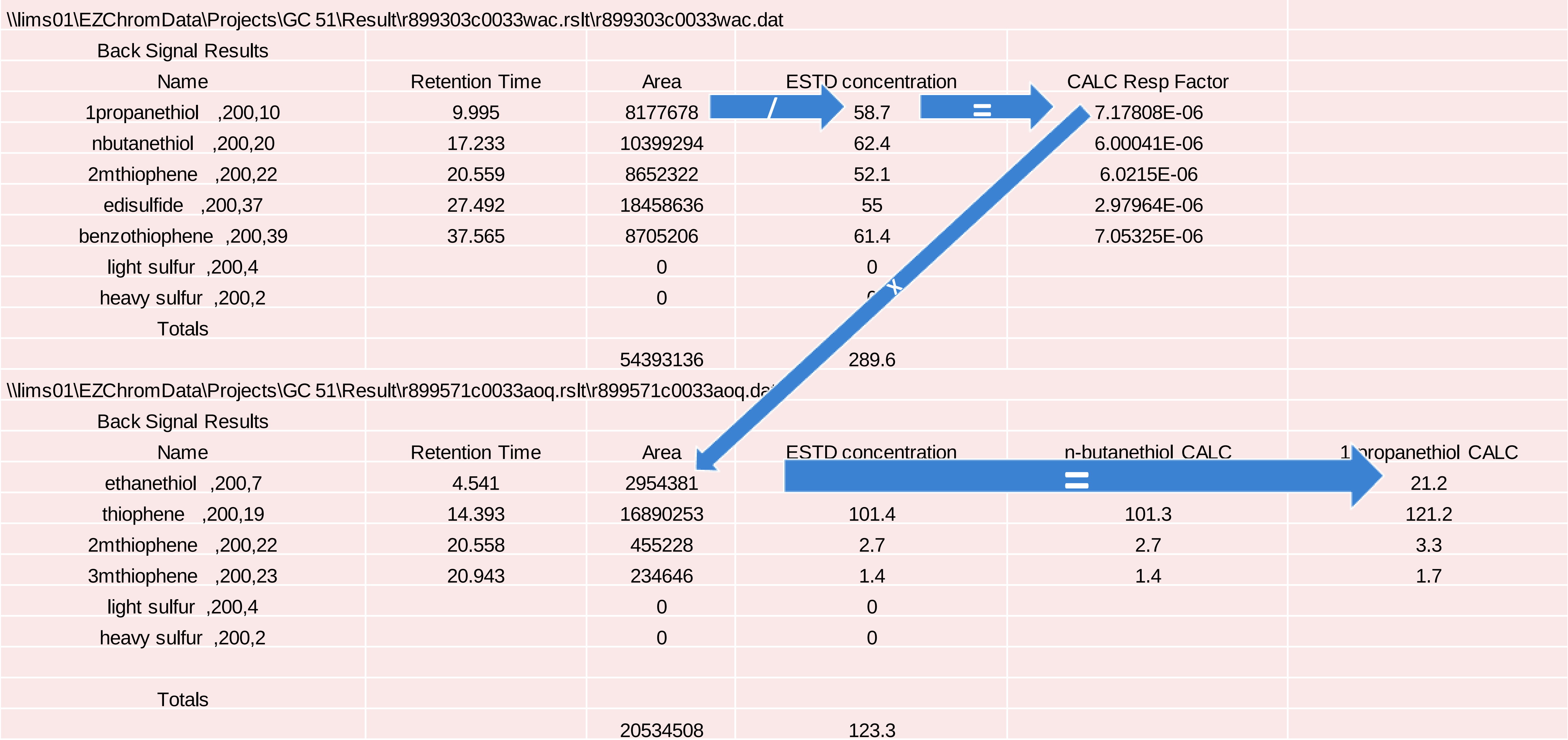
ESTD Response Factor Calculation:

$RF = (A_x) / (C_x)$

A_x = Area of the compound

C_x = Concentration of the compound

SCD – External Standard



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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		

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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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Totals					
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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:

$$\% X = \frac{Ax.fx}{\Sigma Af}\ x\ 100 \qquad \frac{Ax\ is\ Area\ .fx\ is\ response\ factor}{\Sigma Af\ is\ Sum\ of\ all\ RF\ modified\ areas}\ x\ 100$$

FID - Normalization

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

FID - Normalization

\\lims01\EZChromData\Projects\GC 46\Result\r898280c0039udk.rslt\r898280c0039udk.dat					
Back Signal Results					
Name	Retention Time	Area	RRF	NORM Area	NORM concentration
ethene ,100,28	13.233	197236	0.966	190529.976	[redacted]
		24383	1	24383	[redacted]
propane ,100,34	15.875	4542	1.01	4587.42	[redacted]
isobutane ,100,48	20.313	146189	1	146189	[redacted]
1butene ,100,40	23.303	10481868	0.966	10125484.49	[redacted]
		8852	1	8852	[redacted]
nbutane ,100,49	24.515	122391584	1	122391584	[redacted]
		16738	1	16738	[redacted]
t2butene ,100,45	25.868	155159516	0.966	149884092.5	[redacted]
		226016	1	226016	[redacted]
22dmpropane ,100, 69	26.562	21733	0.994	21602.602	[redacted]
c2butene ,100,42	27.484	69035406	0.966	66688202.2	[redacted]
isopentane ,100,71	32.432	4068	0.994	4043.592	[redacted]
2m2butene ,100,62	36.172	13229	0.966	12779.214	[redacted]
3m1pentene ,100,63	38.591	5458209	0.965	5267171.685	[redacted]
		41	1	41	[redacted]
23dm-butane ,100,106	39.045	6435	0.994	6396.39	[redacted]
2m-pentane ,100,107	39.279	35130	0.994	34919.22	[redacted]
3m-pentane ,100,93	40.034	99455	0.994	98858.27	[redacted]
1-hexene ,100,84	40.317	1830098	0.966	1767874.668	[redacted]
n-hexane ,100,109	40.823	16327607	0.966	15772468.36	[redacted]
		6327414	1	6327414	[redacted]
t-3-hexene ,100,102	40.937	8337254	0.966	8053787.364	[redacted]
c-3-hexene ,100,95	41.005	1219428	0.966	1177967.448	[redacted]
t-2-hexene ,100,101	41.065	17768128	0.966	17164011.65	[redacted]
				405415994	100.0000

FID - Normalization

\\lims01\EZChromData\Projects\GC 46\Result\r898280c0039udk.rslt\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

Separation Process

- Capillary Column
- Packed Column
- Multi-Valve/Column

Component Detection

- Flame “FID”
- Thermal “TCD”
- Sulfur “SCD”, “FPD”
- Many Others

Data Handling

- References
- Calibration
- Quantification

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?

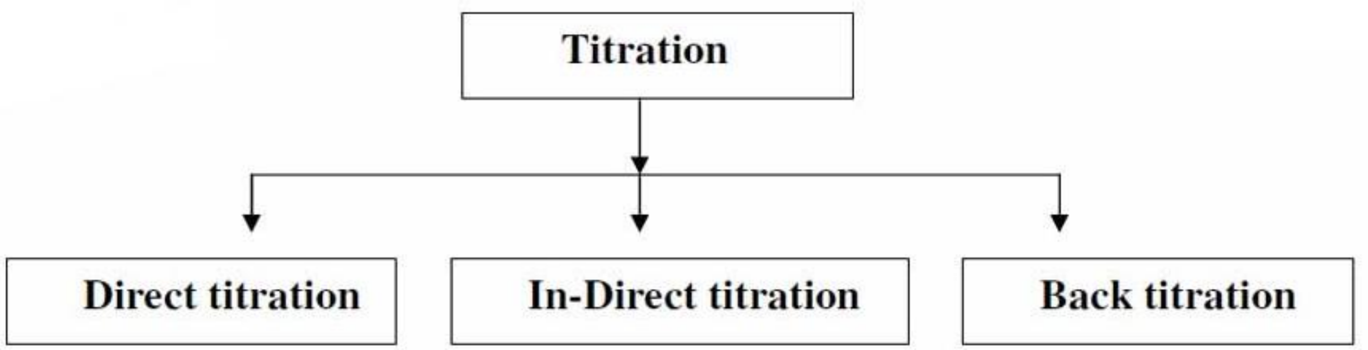
- *A technique where a solution of known concentration is used to determine the concentration of an unknown solution.*
- *Typically, the titrant (the known solution) is added from a burette to a known quantity of the analyte (the unknown solution) until the reaction is complete.*
- *Knowing the volume 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 (CH_3COOH) by titration with sodium hydroxide (NaOH)*

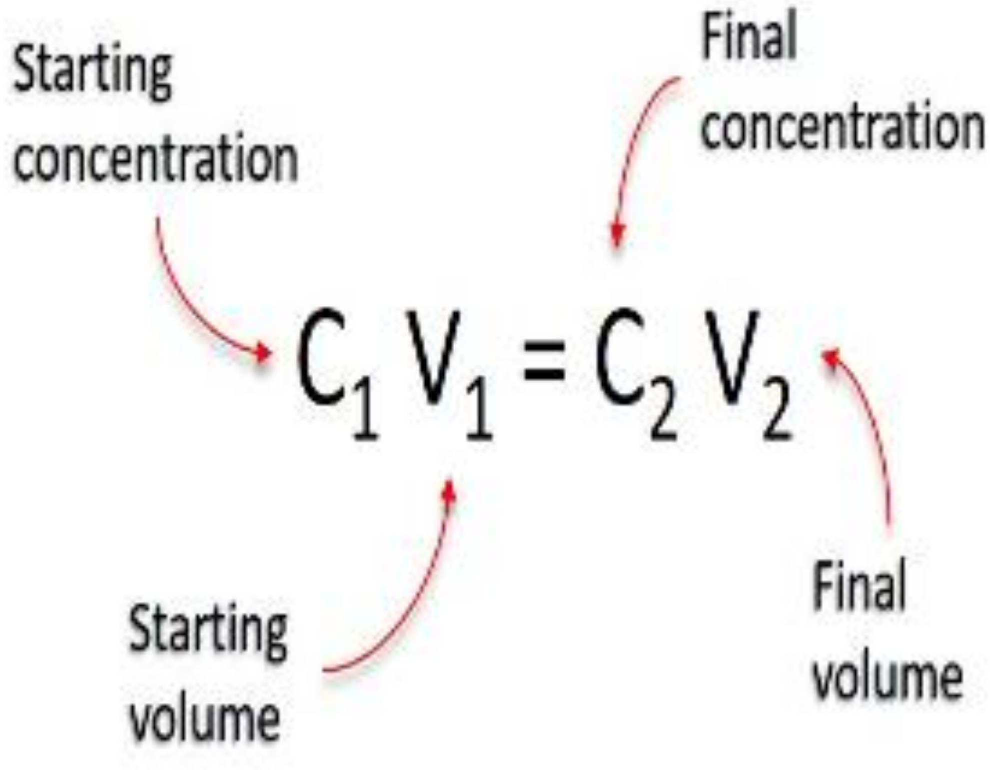
$$\underset{\text{(analyte)}}{CH_3COOH} + \underset{\text{(titrant)}}{NaOH} \longrightarrow \underbrace{CH_3COONa + H_2O}_{\text{(reaction products)}}$$

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

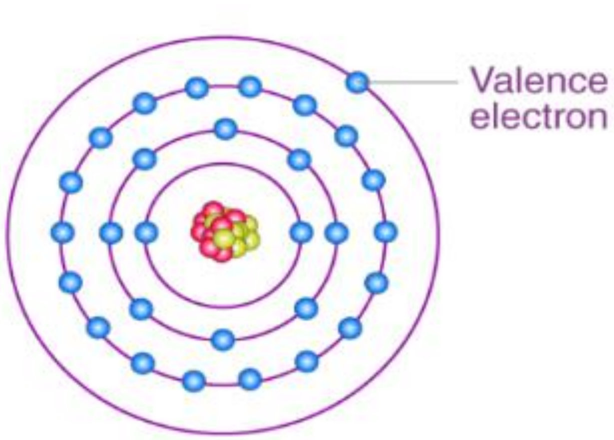
- **Advantages of Titration:**
  - There are several reasons why titration is used in laboratories worldwide:
    - Titration is an established analytical technique.
    - It is fast.
    - It is a very accurate and precise technique.
    - A high degree of automation can be implemented.
    - Titration 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.

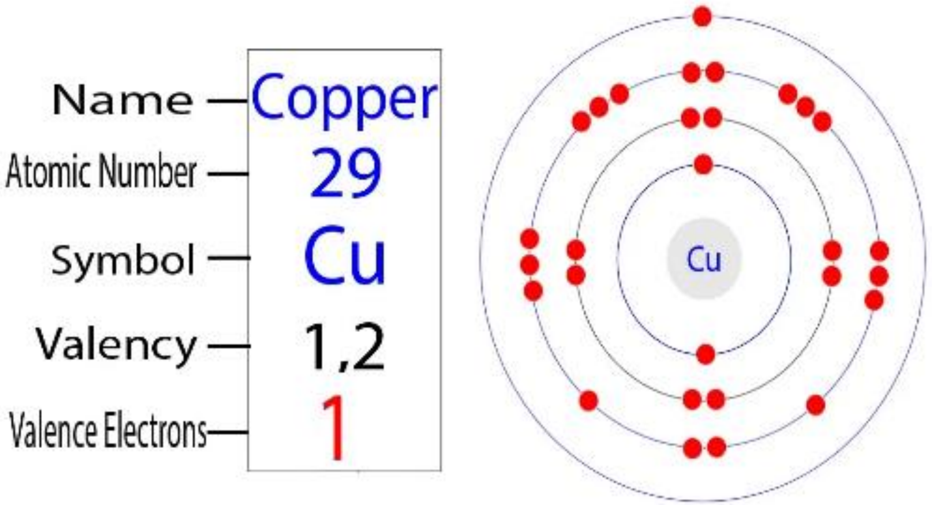
Terminology and Definitions

- **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

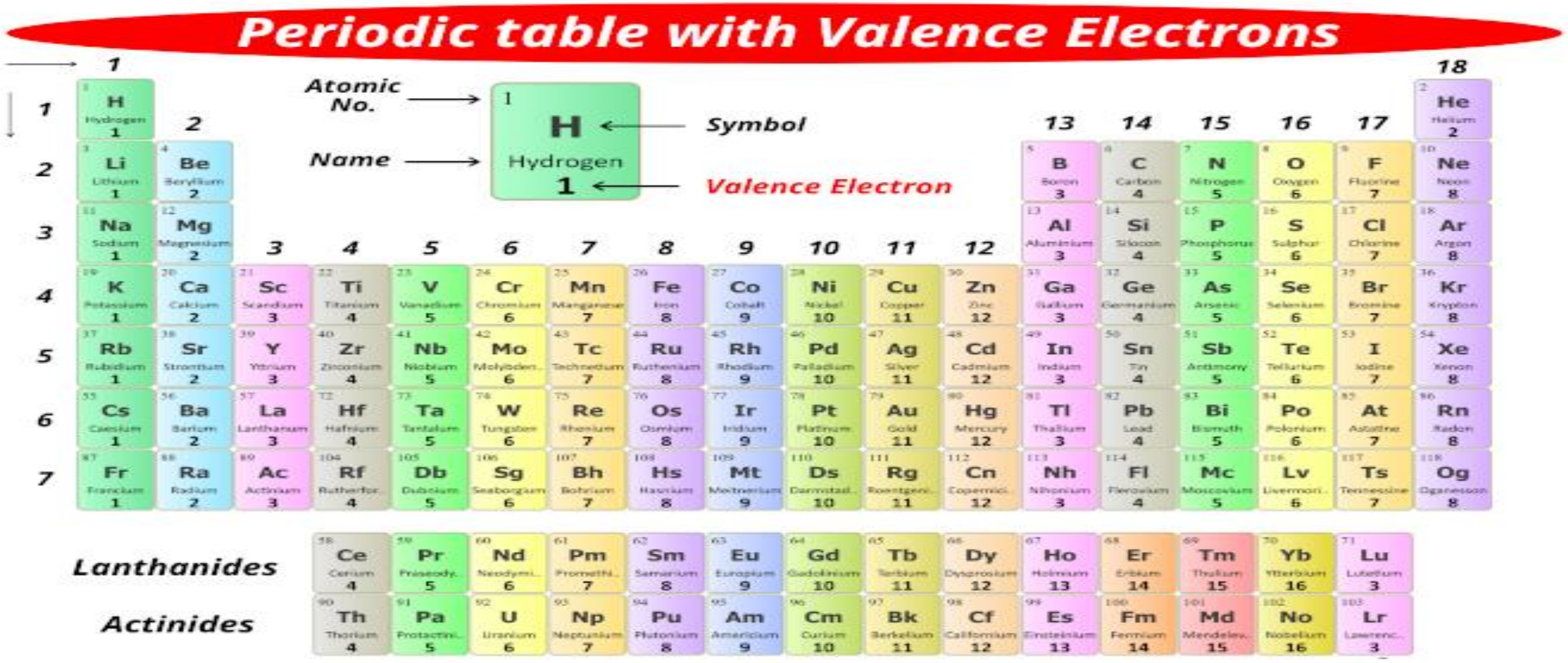
- **Valence Electrons:**
  - Valence electrons are electrons located in the outermost electron shell of an atom.
  - These electrons, being the furthest from the nucleus and thus the least tightly held by the atom, are the electrons that participate in bonds and reactions.
  - The number of valence electrons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





Terminology and Definitions

- **Valence Electrons Continued:**



Periodic table with Valence Electrons

Atomic No. → 1

H ← Symbol

Name → Hydrogen

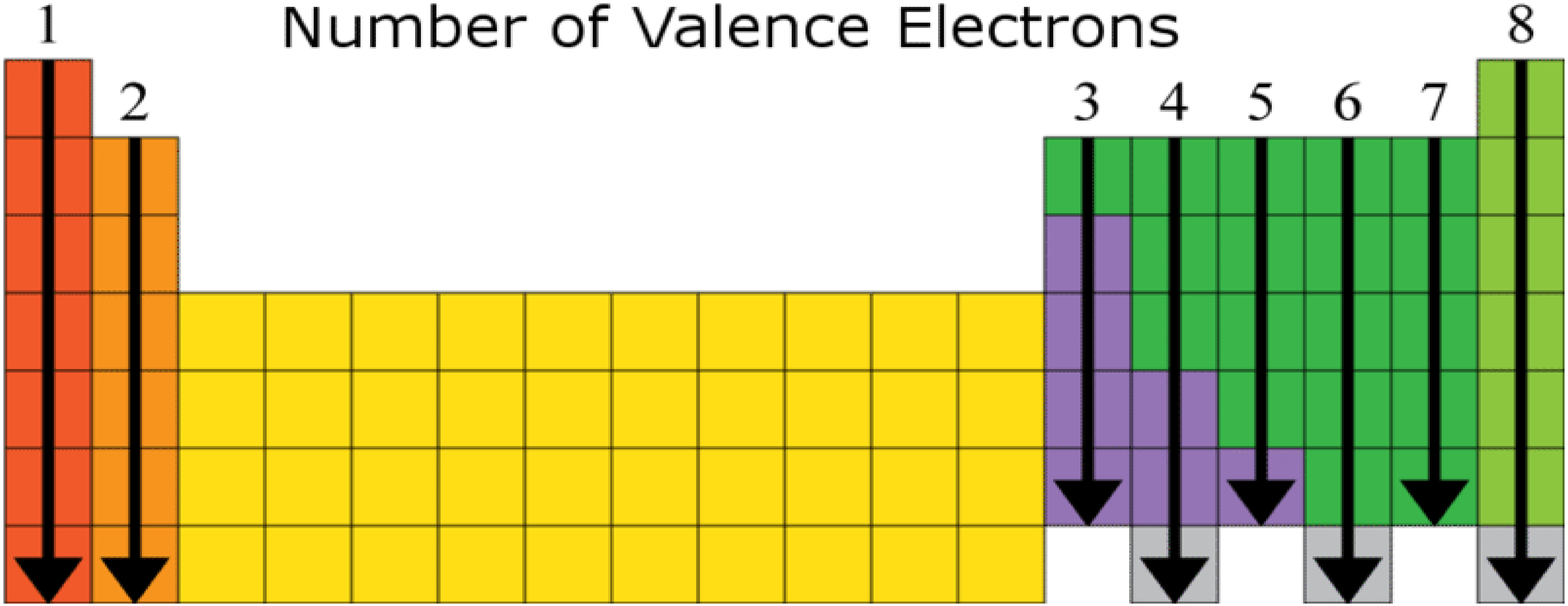
1 ← Valence Electron

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H Hydrogen 1																	2 He Helium 2
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
3	11 Na Sodium 1	12 Mg Magnesium 2											13 Al Aluminium 3	14 Si Silicon 4	15 P Phosphorus 5	16 S Sulphur 6	17 Cl Chlorine 7	18 Ar Argon 8
4	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
5	37 Rb Rubidium 1	38 Sr Strontium 2	39 Y Yttrium 3	40 Zr Zirconium 4	41 Nb Niobium 5	42 Mo Molybden... 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
6	55 Cs Caesium 1	56 Ba Barium 2	57 La Lanthanum 3	72 Hf Hafnium 4	73 Ta Tantalum 5	74 W Tungsten 6	75 Re Rhenium 7	76 Os Osmium 8	77 Ir Iridium 9	78 Pt Platinum 10	79 Au Gold 11	80 Hg Mercury 12	81 Tl Thallium 3	82 Pb Lead 4	83 Bi Bismuth 5	84 Po Polonium 6	85 At Astatine 7	86 Rn Radon 8
7	87 Fr Francium 1	88 Ra Radium 2	89 Ac Actinium 3	104 Rf Rutherfor... 4	105 Db Dubnium 5	106 Sg Seaborgium 6	107 Bh Bohrium 7	108 Hs Hassium 8	109 Mt Meitnerium 9	110 Ds Darmstad... 10	111 Rg Roentgeni... 11	112 Cn Copernici... 12	113 Nh Nihonium 3	114 Fl Flerovium 4	115 Mc Moscovium 5	116 Lv Livermori... 6	117 Ts Tennessine 7	118 Og Oganesson 8

Lanthanides	58 Ce Cerium 4	59 Pr Praseody... 5	60 Nd Neodymi... 6	61 Pm Prometh... 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
Actinides	90 Th Thorium 4	91 Pa Protactini... 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 Mendelev... 15	102 No Nobelium 16	103 Lr Lawrenc... 3

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 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

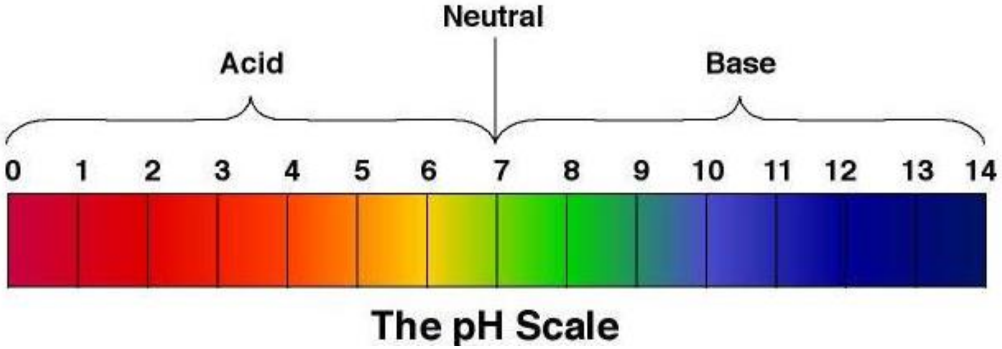
- **Molarity/Normality Conversions Examples:**
  - **NaOH Example:**
    - To go from 0.1 molarity to normality:
      - valence = 1
      - Molarity = 0.1
      - Therefore (1 valence) x (0.1 molarity) = 0.1 Normality.
    - To go from 0.1 normality to molarity:
      - valence = 1
      - Molarity = 0.1
      - Therefore (0.1 normality) / (1 valence) = 0.1 Molarity

Terminology and Definitions

- **Molarity Normality Conversions Examples Continued:**
  - **H_2SO_4 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) = 0.5 Molarity

Terminology and Definitions

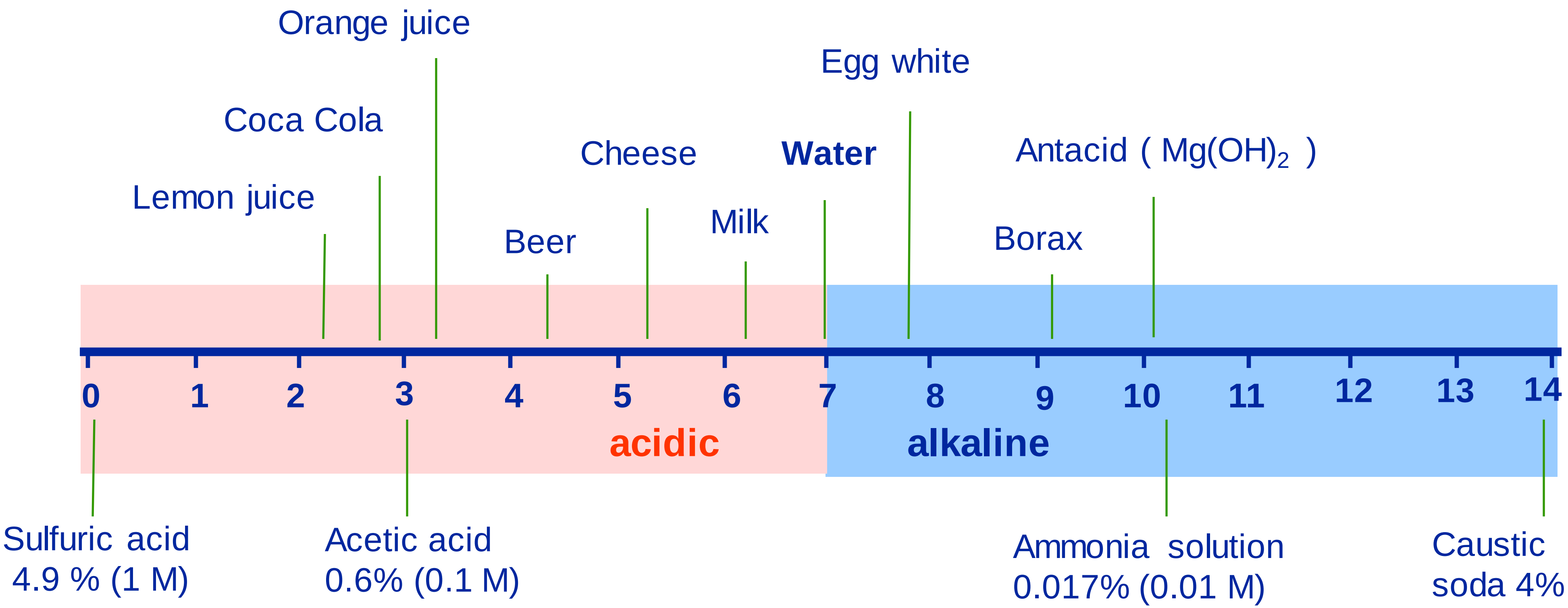
- **pH:** The negative logarithm of H+ ion concentration. (pH = -log [H^+])
- **pH Scale:**



- ***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.

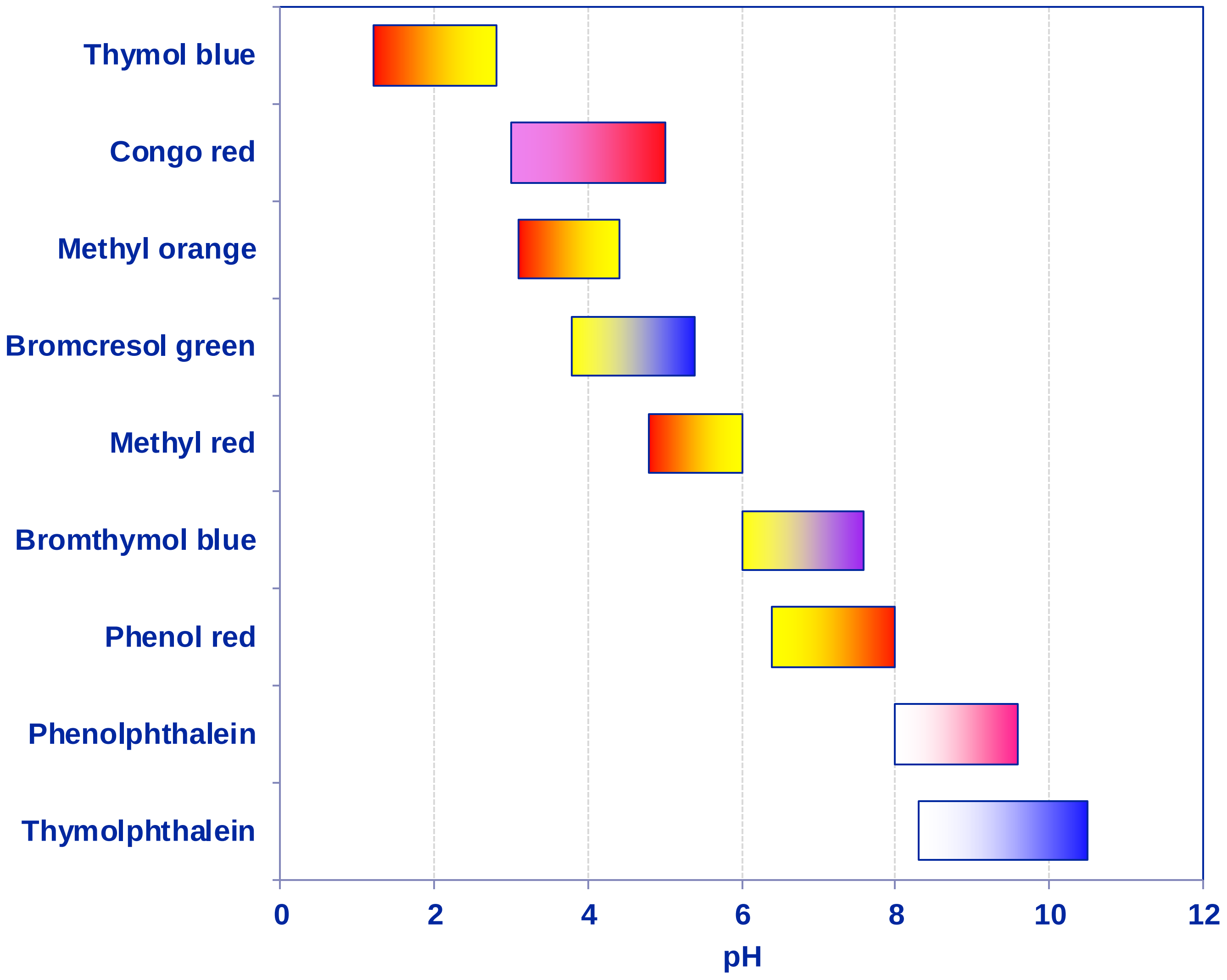
Terminology and Definitions

- 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

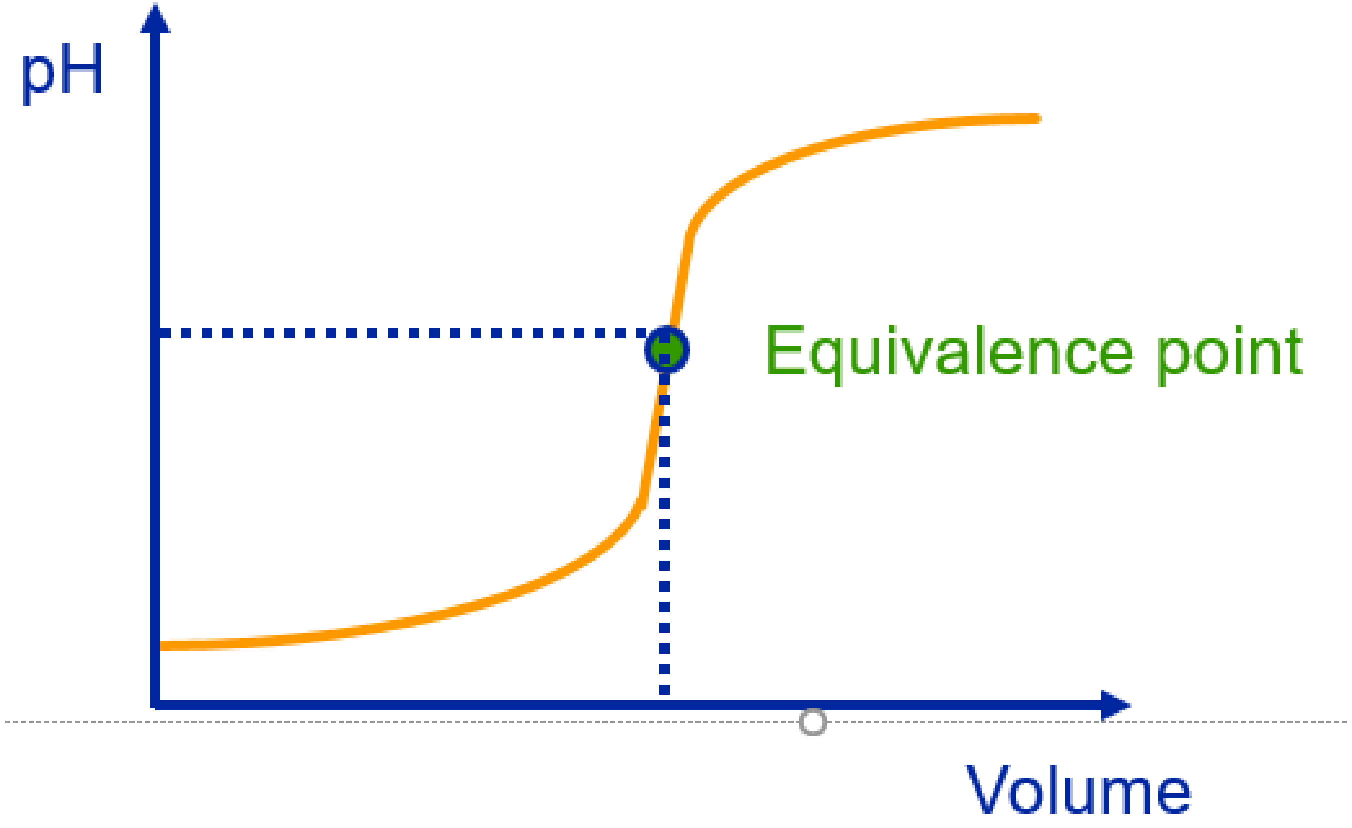
  Continued:

  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

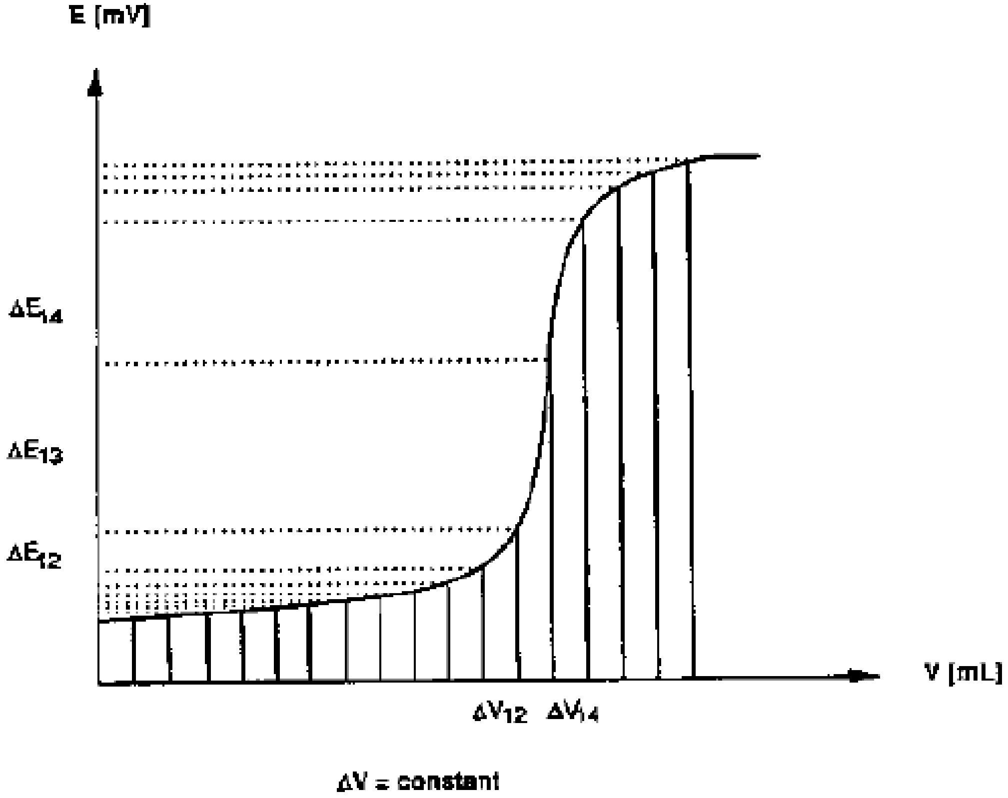
- **Equivalence Point (Inflection Point):**
  - The point when enough reagent is added to <u>react completely</u> with the analyte.
  - At the equivalence point, the number of moles of the titrant are equal to the number of moles of analyte.
  - It occurs before the endpoint.
  - It does not indicate 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, $AgNO_3$, $Na_2S_2O_3$) which are needed for the reaction with one mole of analyte.

Terminology and Definitions

- Equivalence Point (Inflection Point)

INFLECTION

INCREMENT: CONSTANT SIZE LARGE

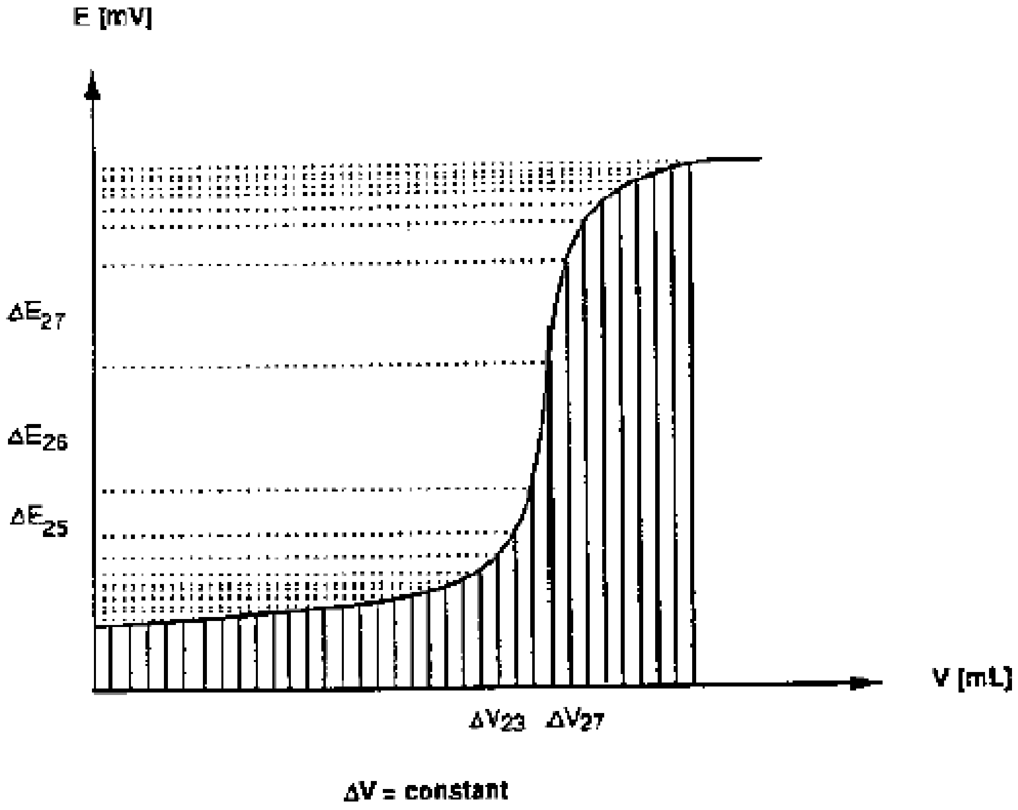


Terminology and Definitions

- Equivalence Point (Inflection Point)

INFLECTION

INCREMENT: CONSTANT SIZE SMALL

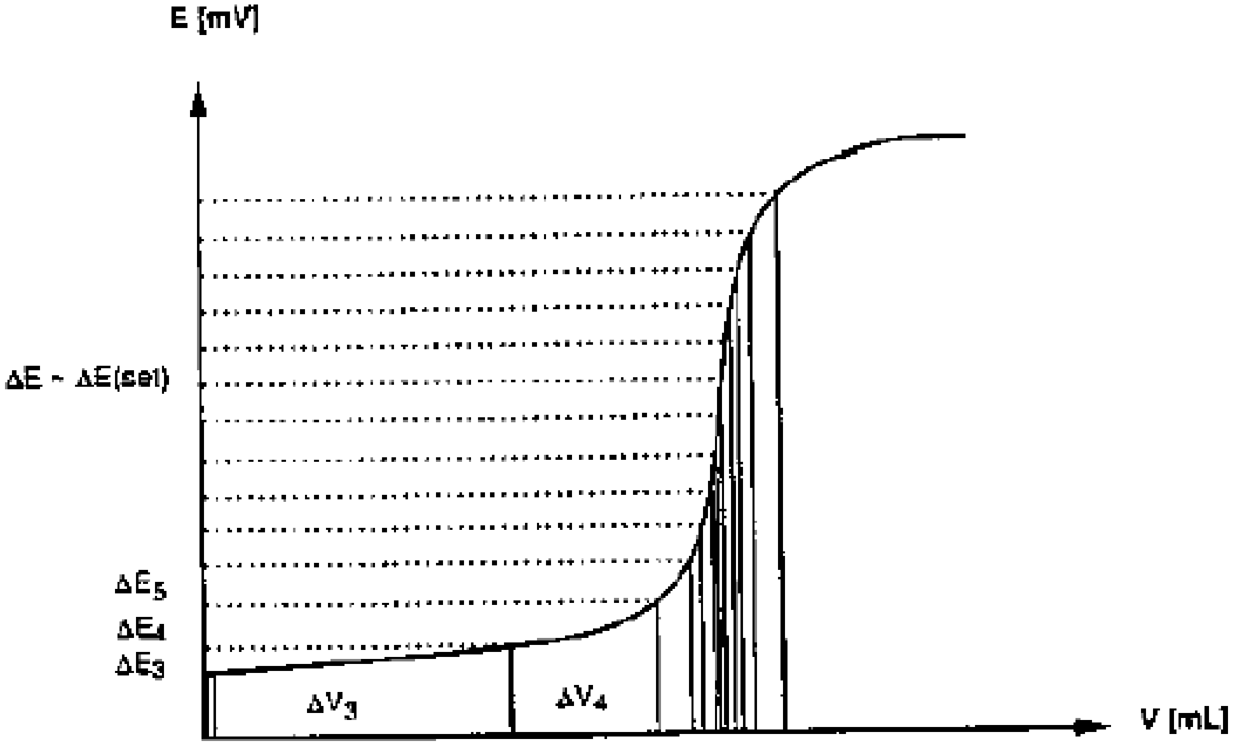


Terminology and Definitions

- Equivalence Point (Inflection Point)

INFLECTION

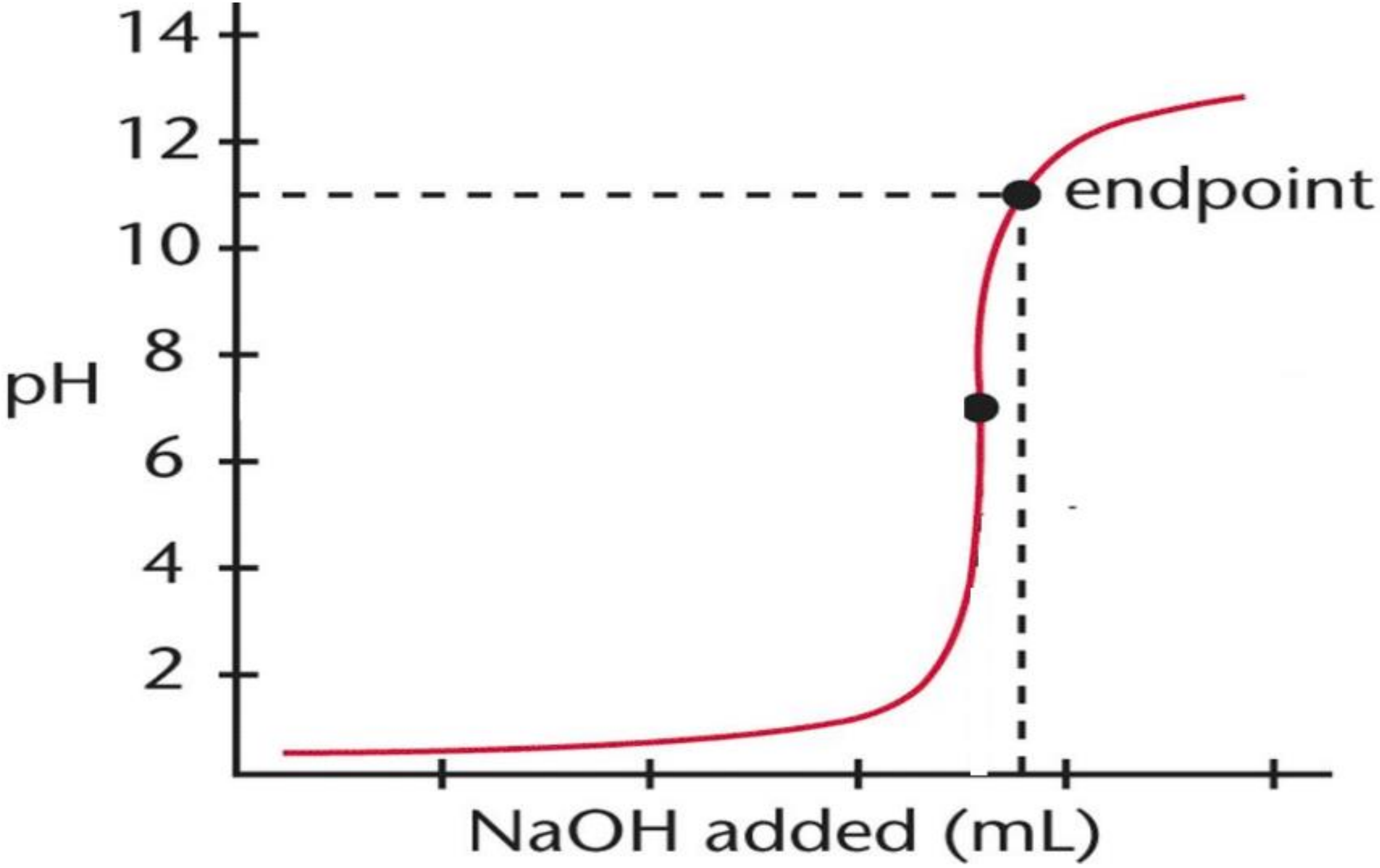
INCREMENT: DYNAMIC VARIABLE



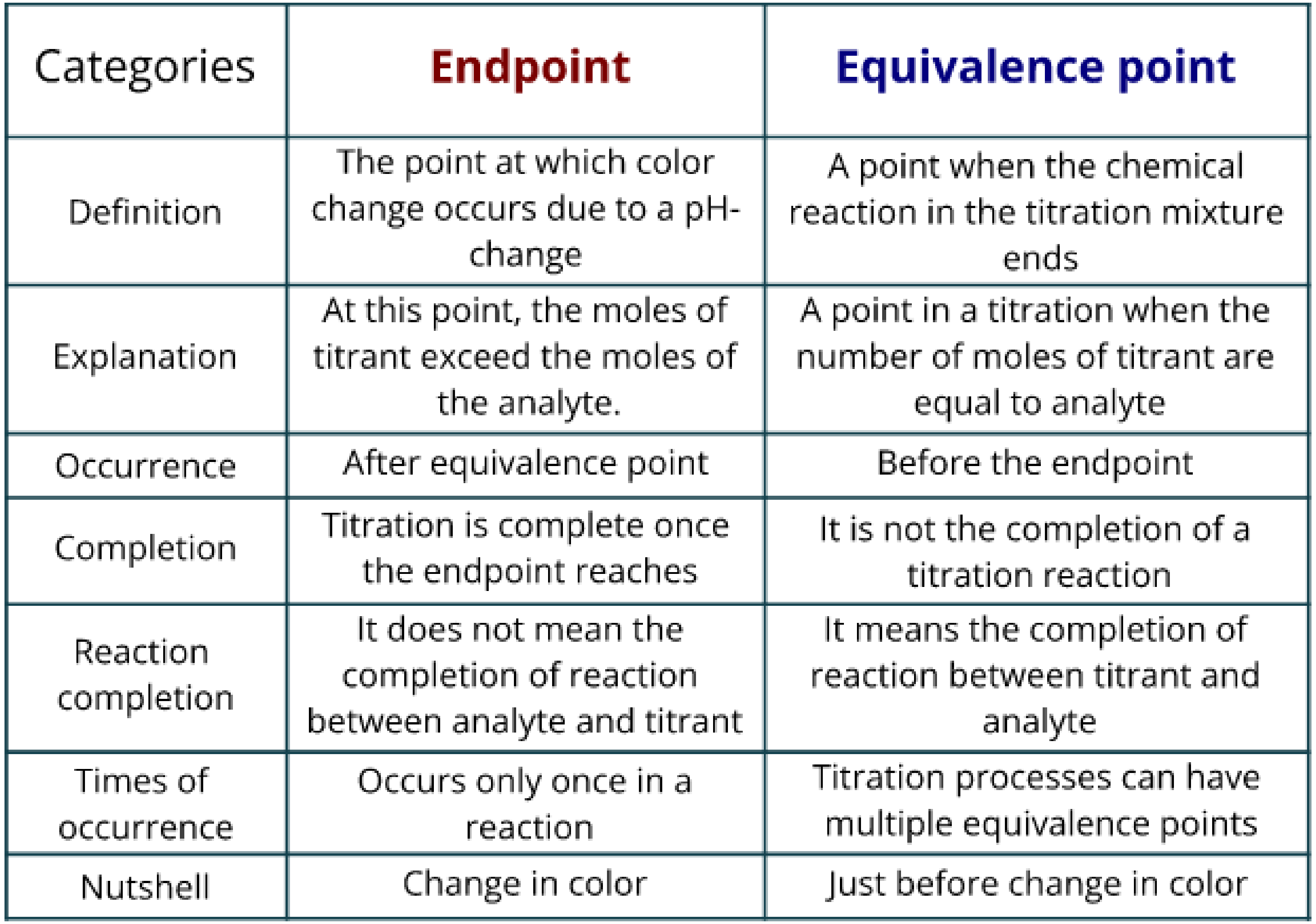
Terminology and Definitions

- **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

$$\mathrm{HCl} + \mathrm{NaOH} \longrightarrow \mathrm{NaCl} + \mathrm{H_2O}$$

$$\mathrm{ACID} + \mathrm{BASE} \longrightarrow \mathrm{SALT} + \mathrm{WATER}$$

Types of Titration Reactions

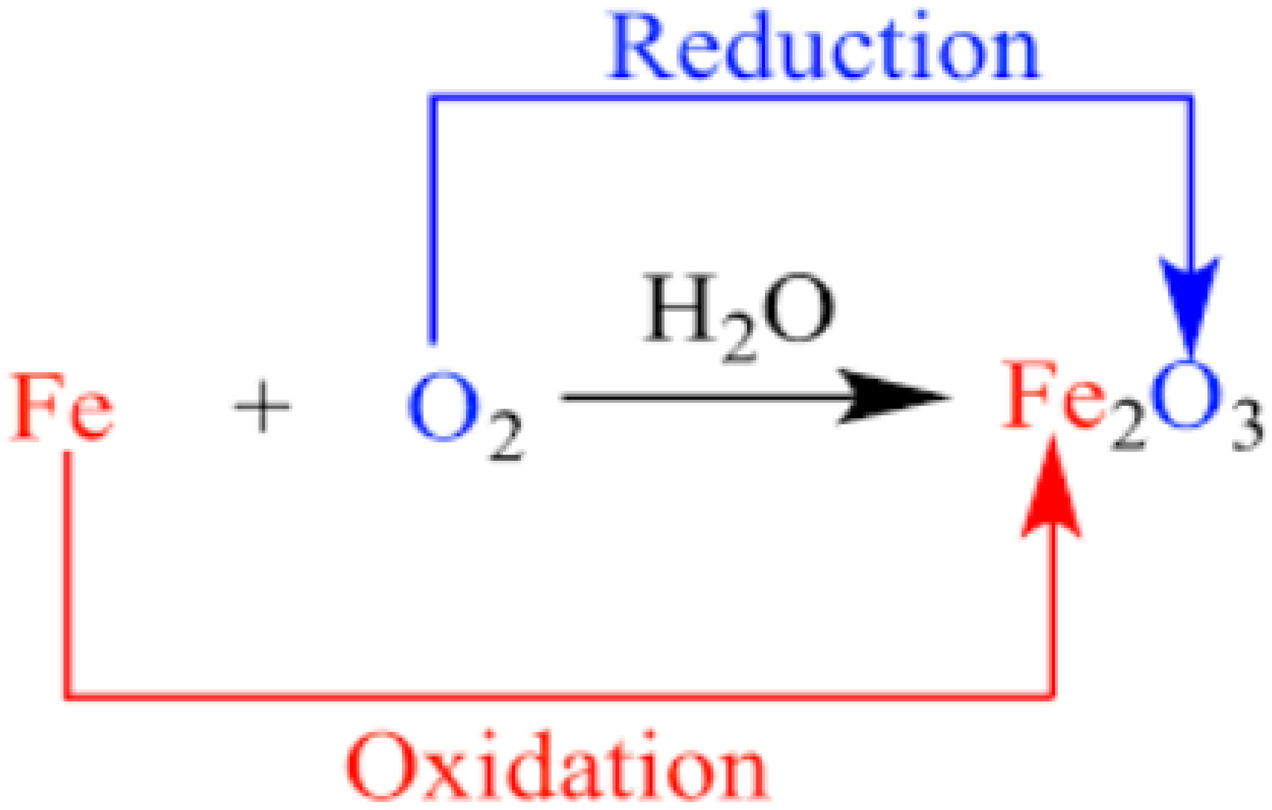
- Oxidation-Reduction Reaction (Redox):

  What is a Redox Reaction (Oxidation-Reduction)?

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

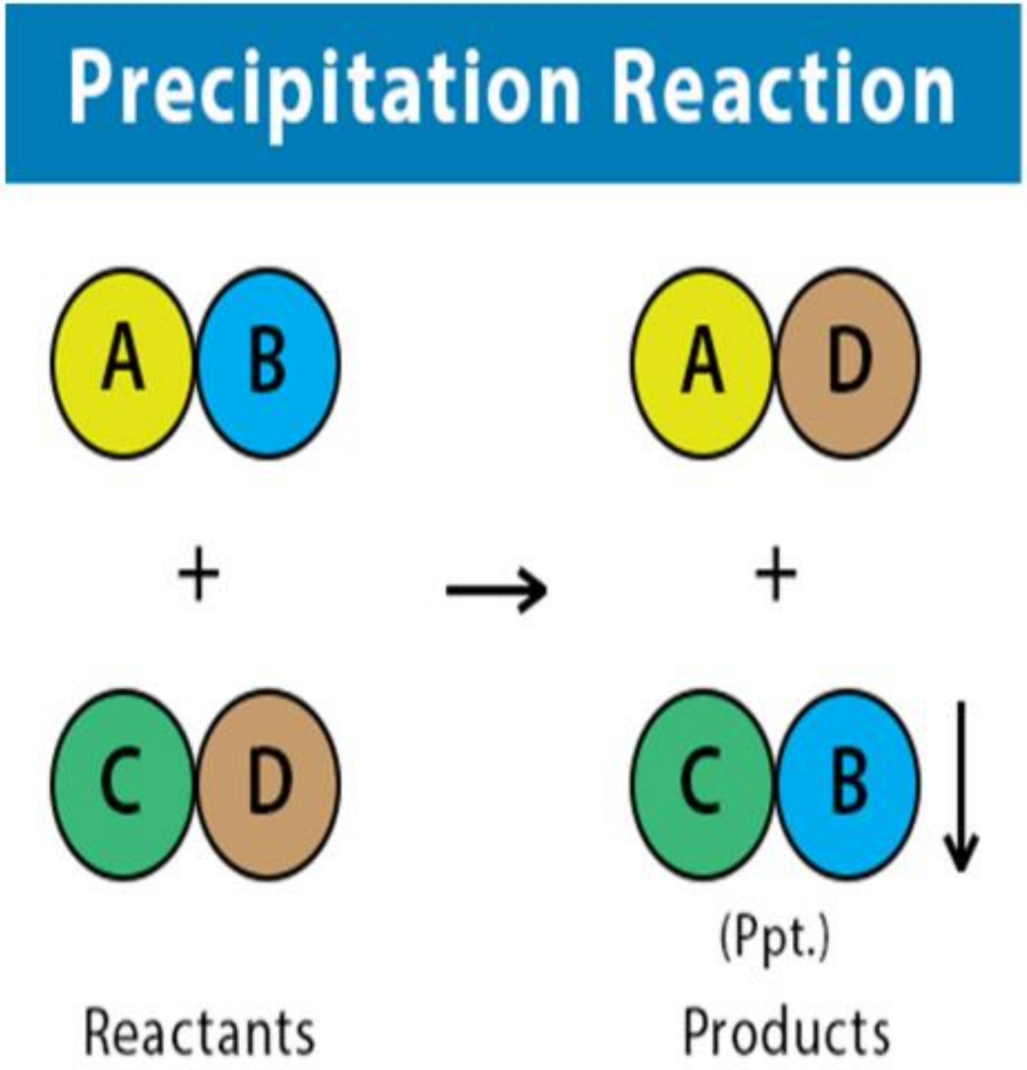
  The oxidation number of a molecule, atom, or ion changes by gaining or losing an electron.

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



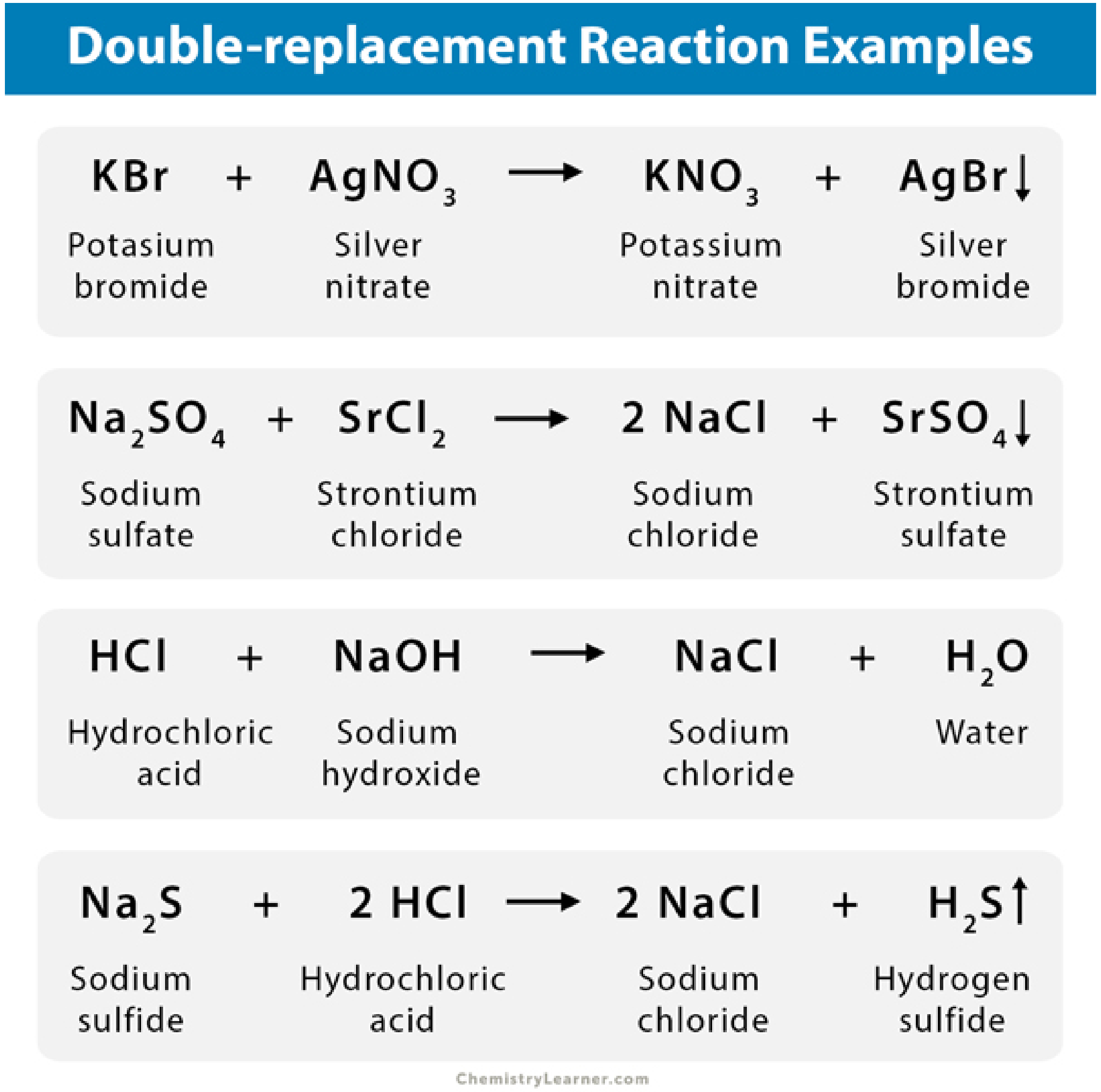
Types of Titration Reactions

- 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.



Types of Titration Reactions

- Examples of Precipitation Reactions:



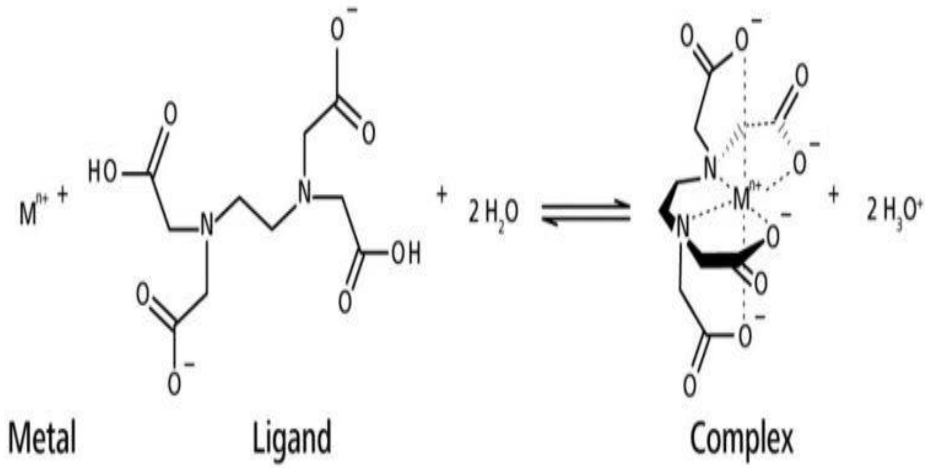
Double-replacement Reaction Examples

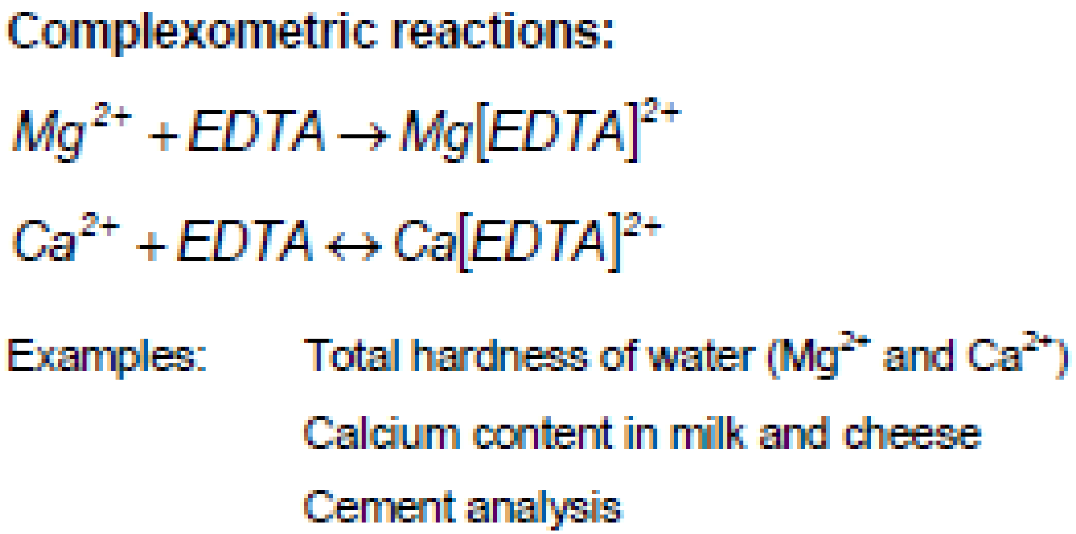
KBr	+	$AgNO_3$	$\longrightarrow$	KNO_3	+	$AgBr\downarrow$
Potasium bromide		Silver nitrate		Potassium nitrate		Silver bromide
Na_2SO_4	+	$SrCl_2$	$\longrightarrow$	$2\ NaCl$	+	$SrSO_4\downarrow$
Sodium sulfate		Strontium chloride		Sodium chloride		Strontium sulfate
HCl	+	$NaOH$	$\longrightarrow$	$NaCl$	+	H_2O
Hydrochloric acid		Sodium hydroxide		Sodium chloride		Water
Na_2S	+	$2\ HCl$	$\longrightarrow$	$2\ NaCl$	+	$H_2S\uparrow$
Sodium sulfide		Hydrochloric acid		Sodium chloride		Hydrogen sulfide

ChemistryLearner.com

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:

$$Mg^{2+} + EDTA \rightarrow Mg[EDTA]^{2+}$$

$$Ca^{2+} + EDTA \leftrightarrow Ca[EDTA]^{2+}$$

Examples: Total hardness of water (Mg^{2+} and Ca^{2+})

Calcium content in milk and cheese

Cement analysis

Calculations

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

- 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)

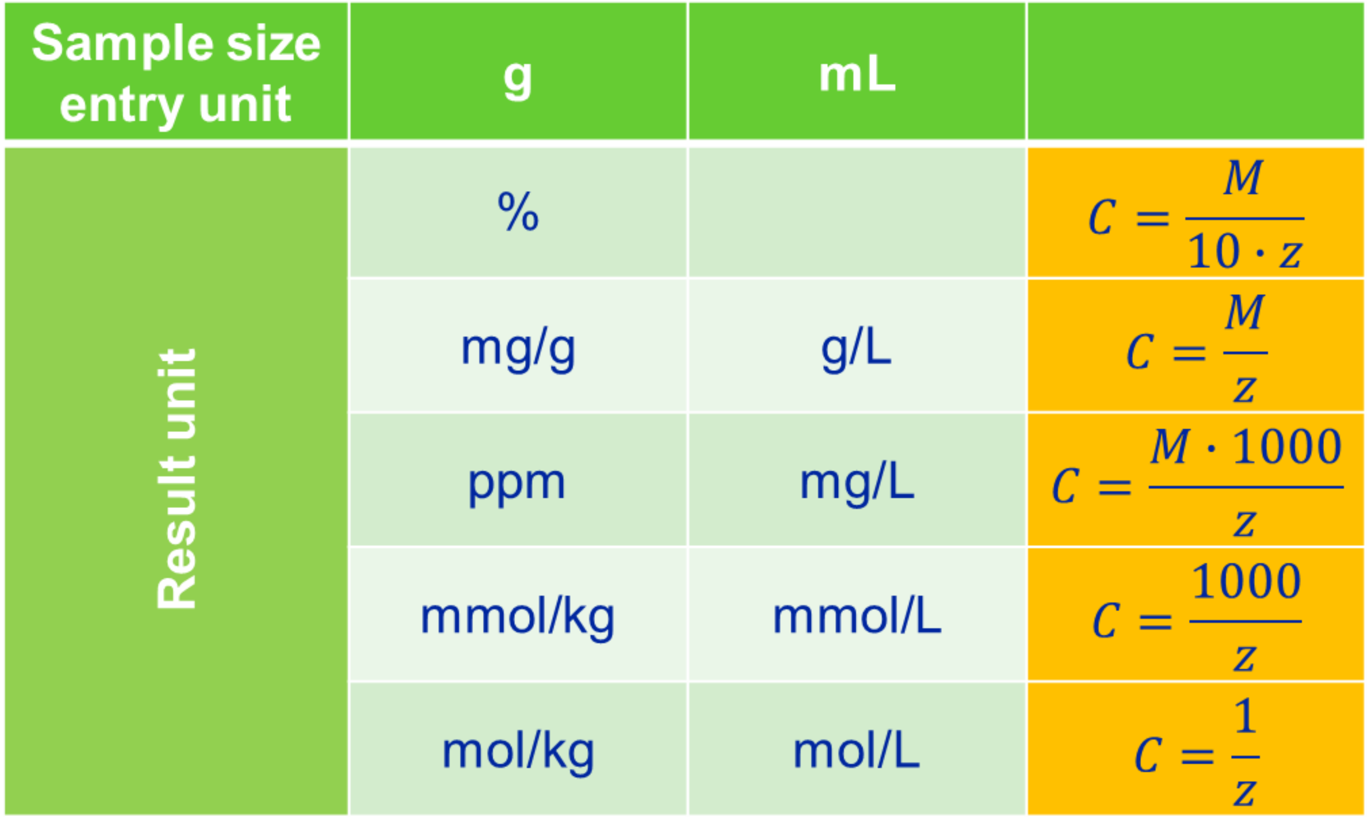
  - The constant *C* is dependent on the result unit wanted and on the unit of the sample size

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 g/mol) in a 1 g sample of vinegar, 5 mL sodium hydroxide (c = 0.1 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:

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

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

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:

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

  - 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 g/mol) was used as a solid titer standard to determine the titer of sodium hydroxide (c = 0.1 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:*

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

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

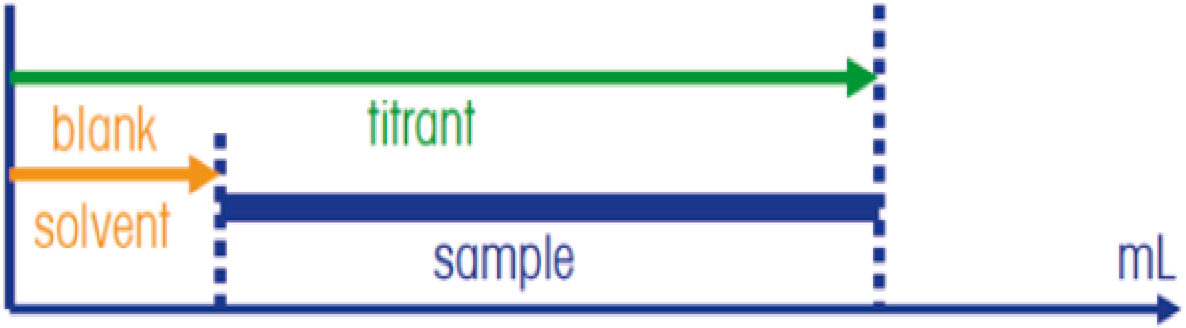
Calculations - Blanks

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.

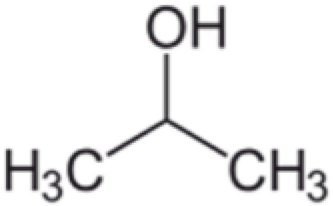
To determine the blank value a titration of the **solvent without any sample** has to be performed. The blank value is the volume of the titrant used until the equivalence or endpoint is reached.

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

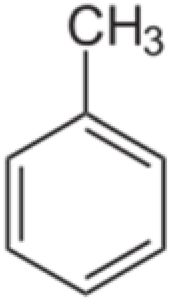


Calculations - Blanks

- 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.*



2-propanol



Toluene

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)

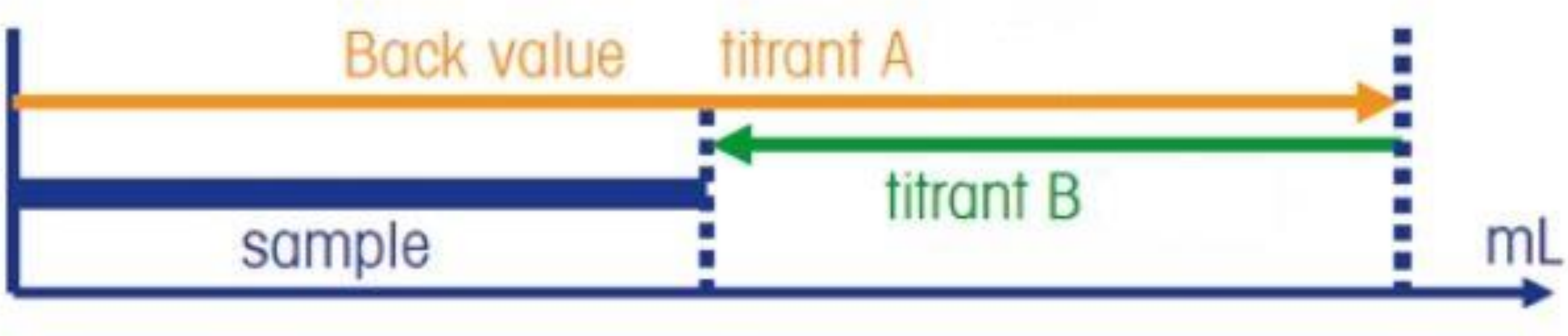
C = Constant for unit conversion

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).*

$$\underset{\text{(analyte)}}{5\,NO_2^-} + \underset{\text{(titrant A)}}{2\,MnO_4^-} + 6\,H^+ \rightleftharpoons 2\,Mn^{2+} + 5\,NO_3^- + 3\,H_2O$$

$$\underset{\text{(titrant A)}}{MnO_4^-} + \underset{\text{(titrant B)}}{5\,Fe^{2+}} + 8\,H^+ \rightleftharpoons Mn^{2+} + 5\,Fe^{3+} + 4\,H_2O$$

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.

$$H_2SO_4 + 2\,NaOH \rightleftharpoons Na_2SO_4 + 2\,H_2O \qquad z = 2$$

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

$$Cr^{6+} + 3\,e^- \longrightarrow Cr^{3+} \qquad z = 3$$

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:

$$c(1/\mathrm{z}\ \mathrm{A}) = c(\mathrm{A}) \cdot z$$

  - Example 1: Sulphuric acid (c(H2SO4) = 0.05 mol/L) as titrant:

$$H_2SO_4 \longrightarrow SO_4^{2-} + 2\ H^+$$

$$c(1/2\ \mathrm{H_2SO_4}) = c(\mathrm{H_2SO_4}) \cdot z = 0.05\,\frac{\mathrm{mol}}{\mathrm{L}} \cdot 2 = 0.1\,\frac{\mathrm{mol}}{\mathrm{L}}$$

  - Example 2: Potassium permanganate (c(KMnO4) = 0.02 mol/L) as titrant:

$$KMnO_4 + 8\ H^+ + 5\ e^- \longrightarrow Mn^{2+} + 4\ H_2O + K^+$$

$$c(1/5\ \mathrm{KMnO_4}) = c(\mathrm{KMnO_4}) \cdot z = 0.02\,\frac{\mathrm{mol}}{\mathrm{L}} \cdot 5 = 0.1\,\frac{\mathrm{mol}}{\mathrm{L}}$$

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.

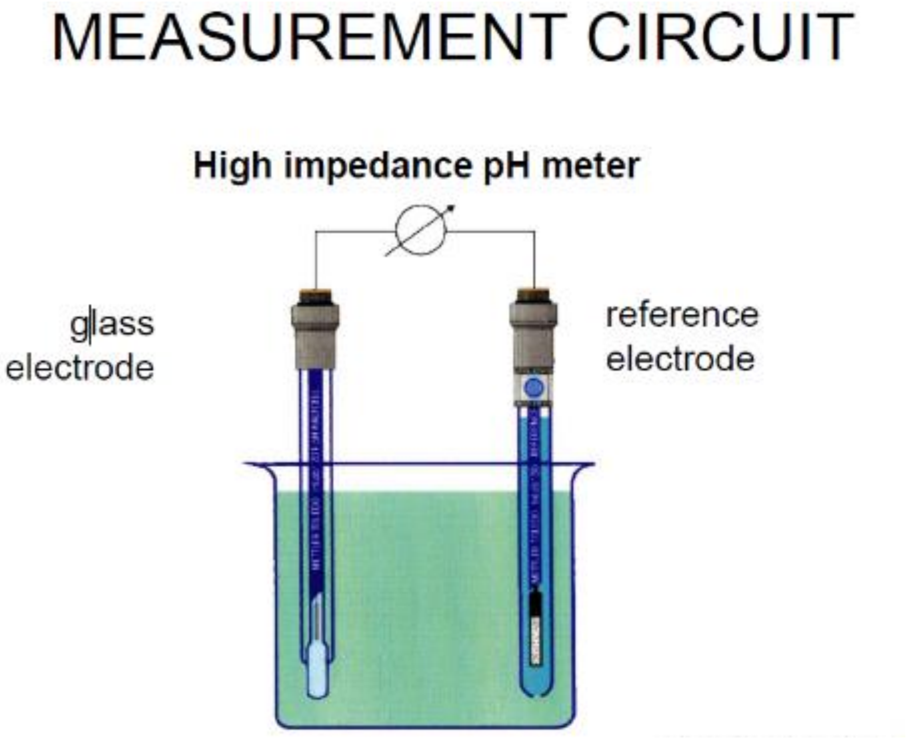
$$\mathrm{KOOC\text{-}C_6H_4\text{-}COOH} + \mathrm{NaOH} \longrightarrow \mathrm{KOOC\text{-}C_6H_4\text{-}COONa} + \mathrm{H_2O}$$

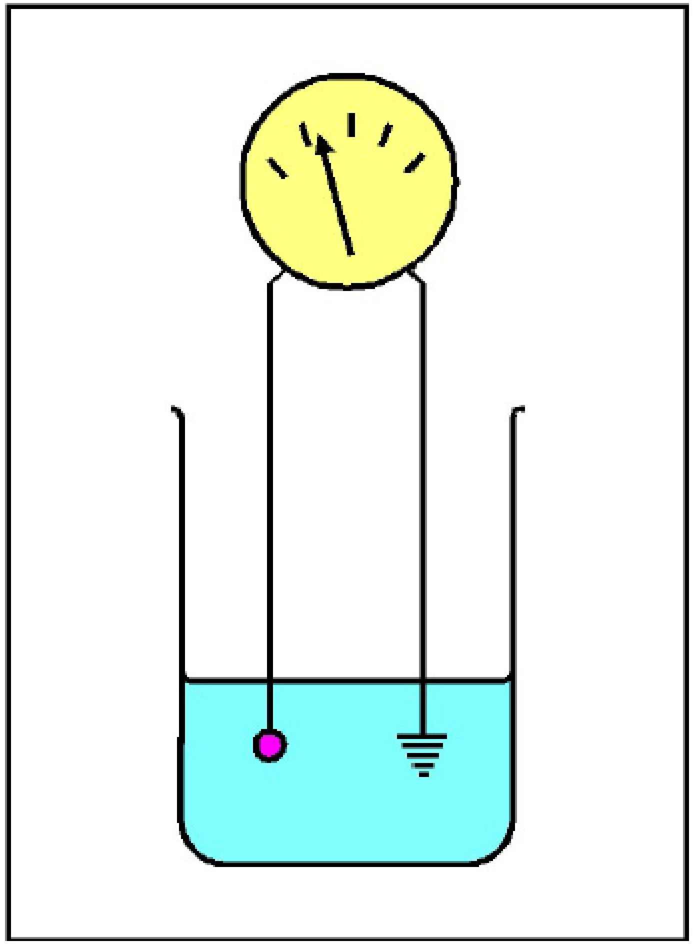
- The actual titrant concentration (cact) is the nominal concentration (cnom) times the titer (t)

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

Probes

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





Probes – Reference vs Indicator

- What is the difference between Reference Electrodes and Indicator Electr
  - 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)

$$Ag^0 \leftarrow\rightarrow Ag^+ + e^-$$

Probes – Reference vs Indicator

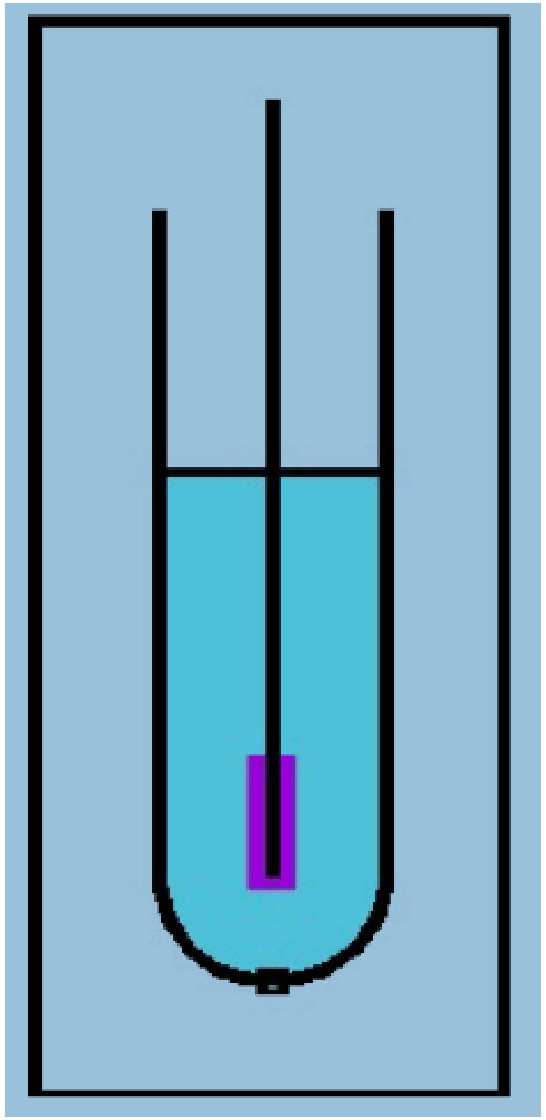
- Reference Electrode:

  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

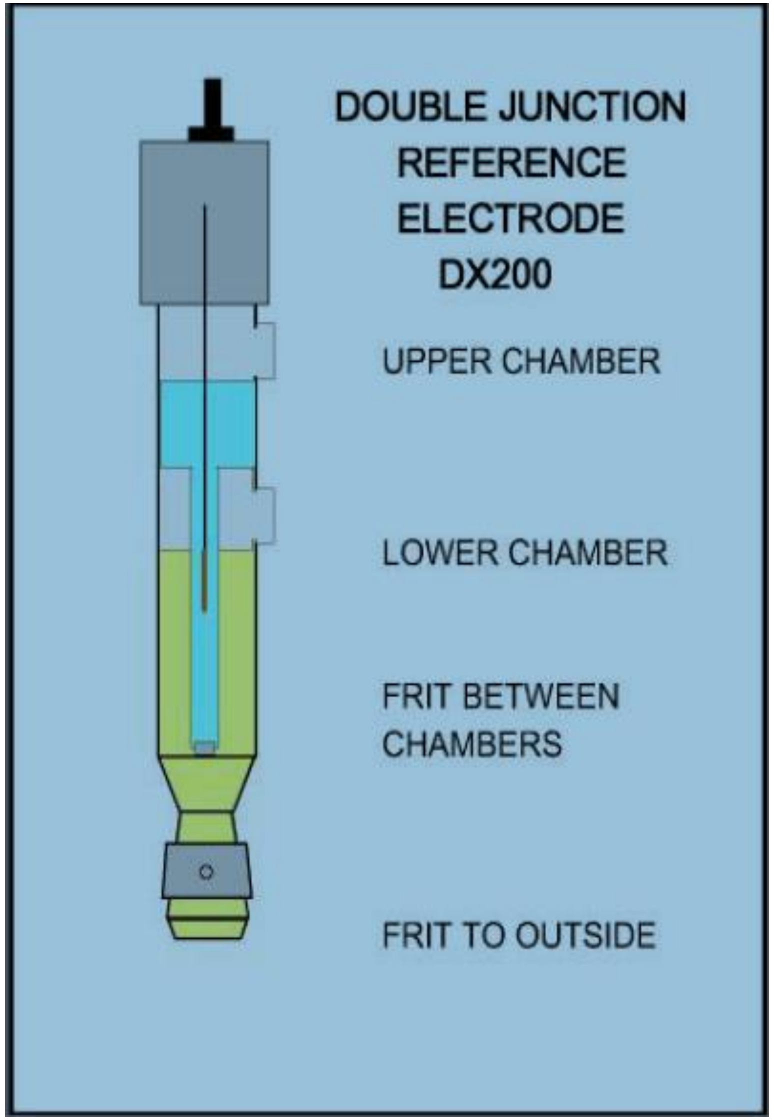
  1 M NaCl

  KNO3

  LiCl in EtOH

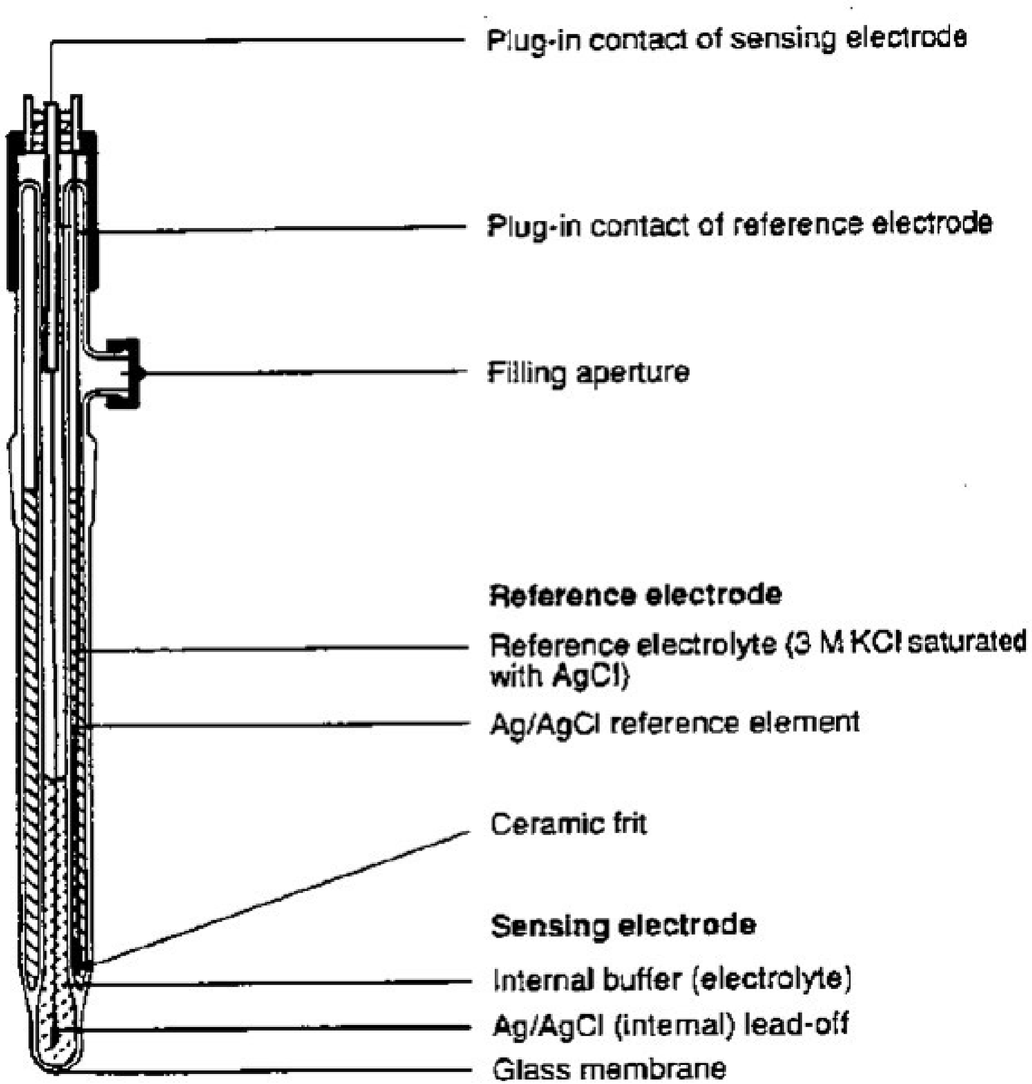
  LiCl in glacial acetic acid

  KClO4 in glacial acetic acid



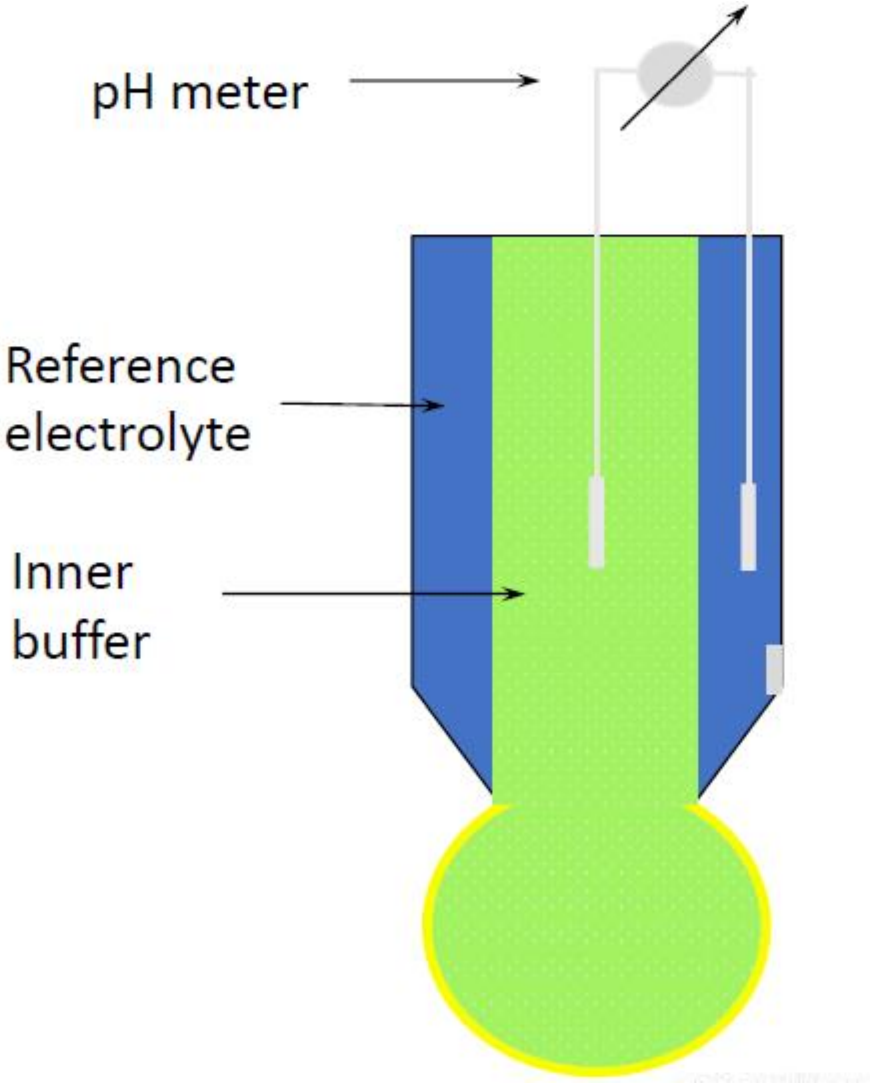
Probes

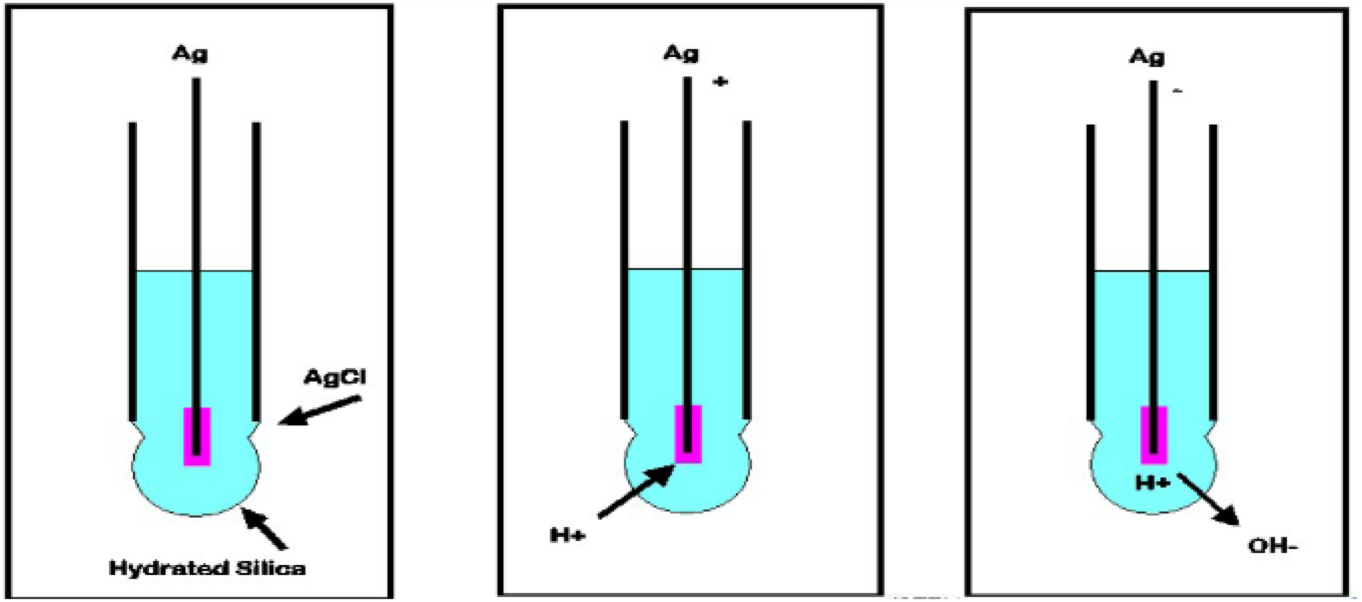
- Typical Combination pH Electrode



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 th potential changes.





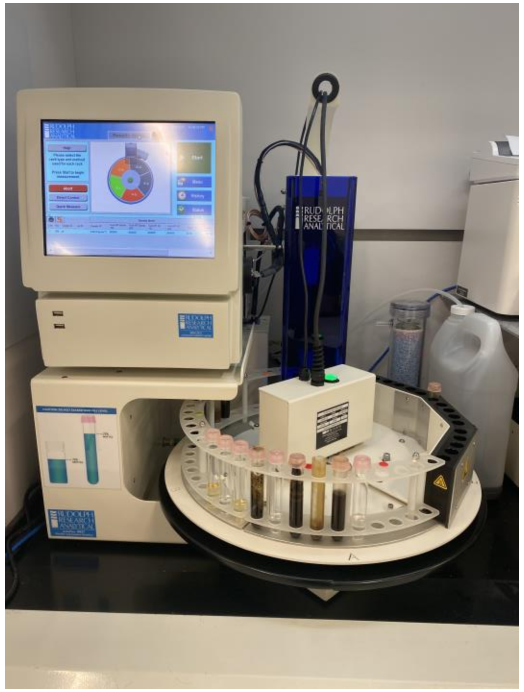
OTHER ANALYSES

Characterization of all aspect of a sample

Total Sulfur/Nitrogen
Analyzer
Total Chloride
Density
Metal Content
Viscosity

Applications cover all analyses

TNSA
Densitometer
ICP and ICP-MS
Viscometer
XRD
XRF



Total Sulfur & Nitrogen Analyzers

$$SO_2 + hv \rightarrow SO_2^*$$

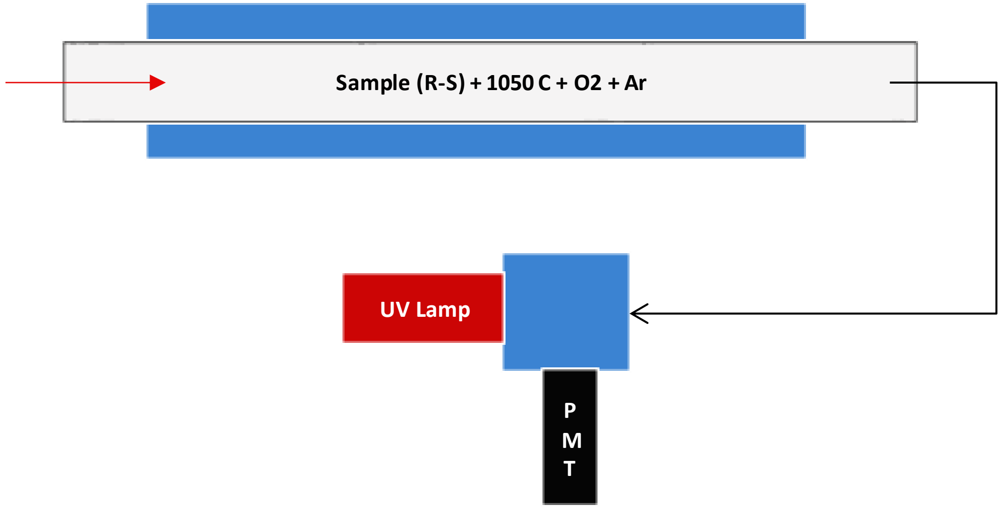
$$SO_2^* \rightarrow SO_2 + hv$$

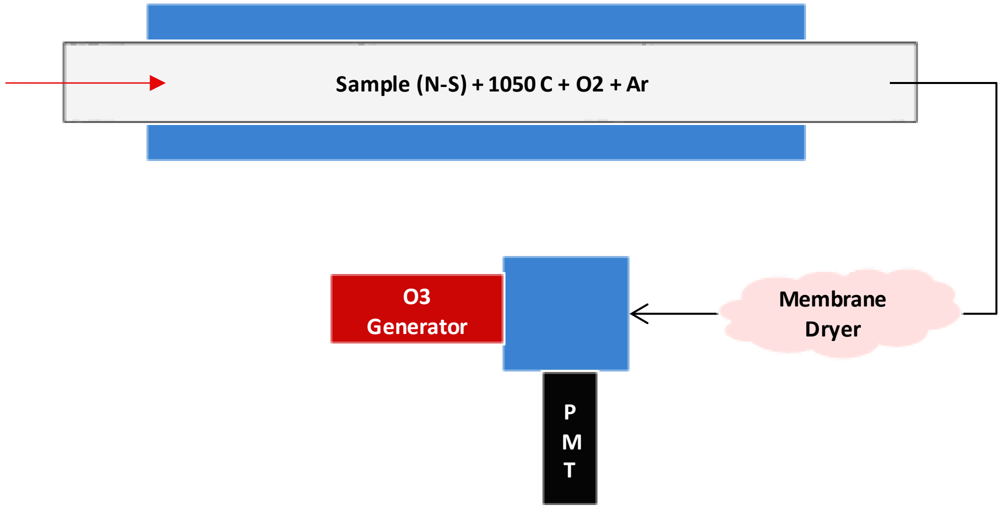
$$R - S + O_2 \xrightarrow{1050°C} CO_2 + SO_2 + H_2O$$

$$R - N + O_2 \rightarrow NO + CO_2 + H_2O$$

$$NO + O_3 \rightarrow NO_2{}^*$$

$$NO_2{}^* \rightarrow NO_2 + h\gamma$$





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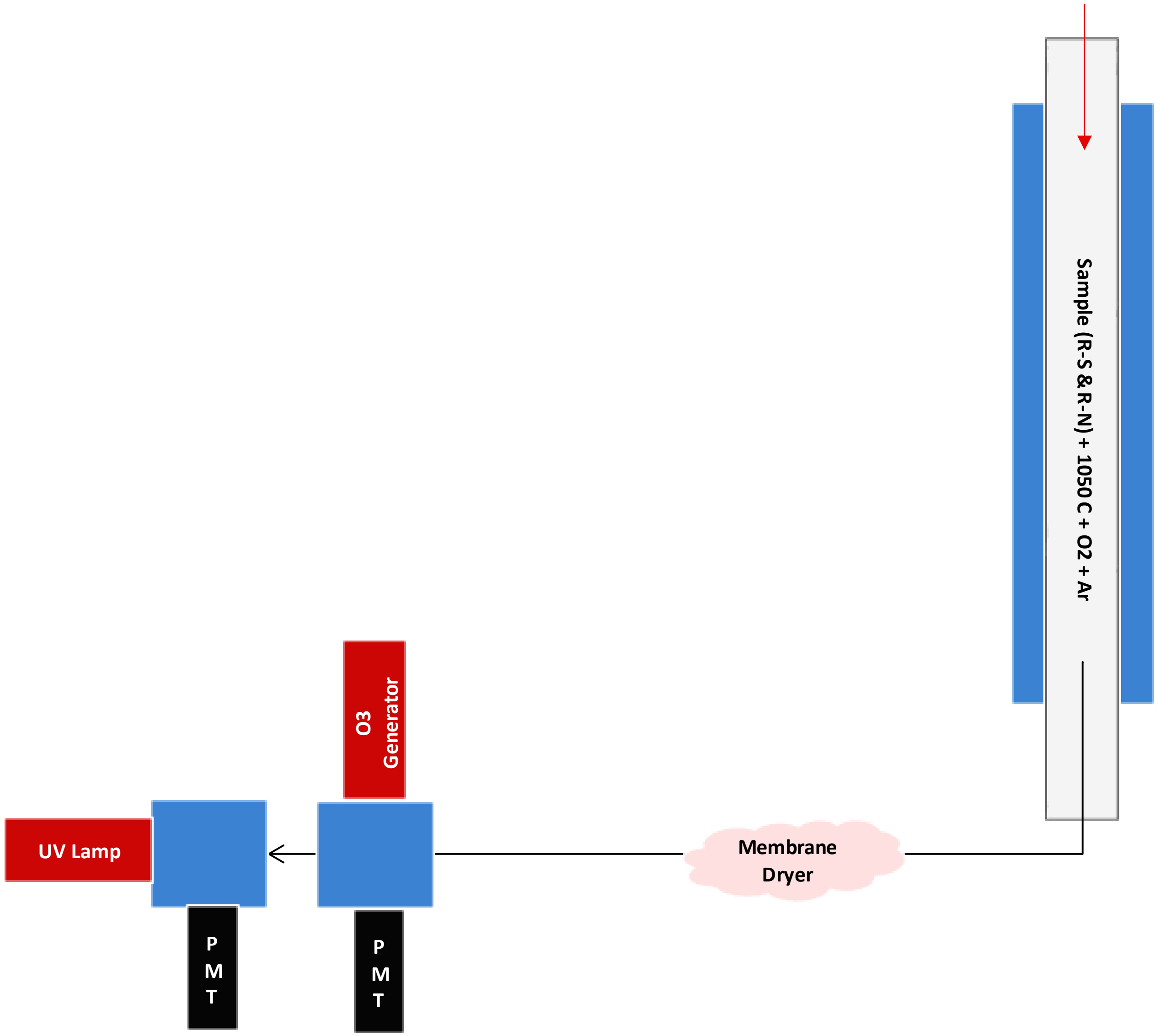
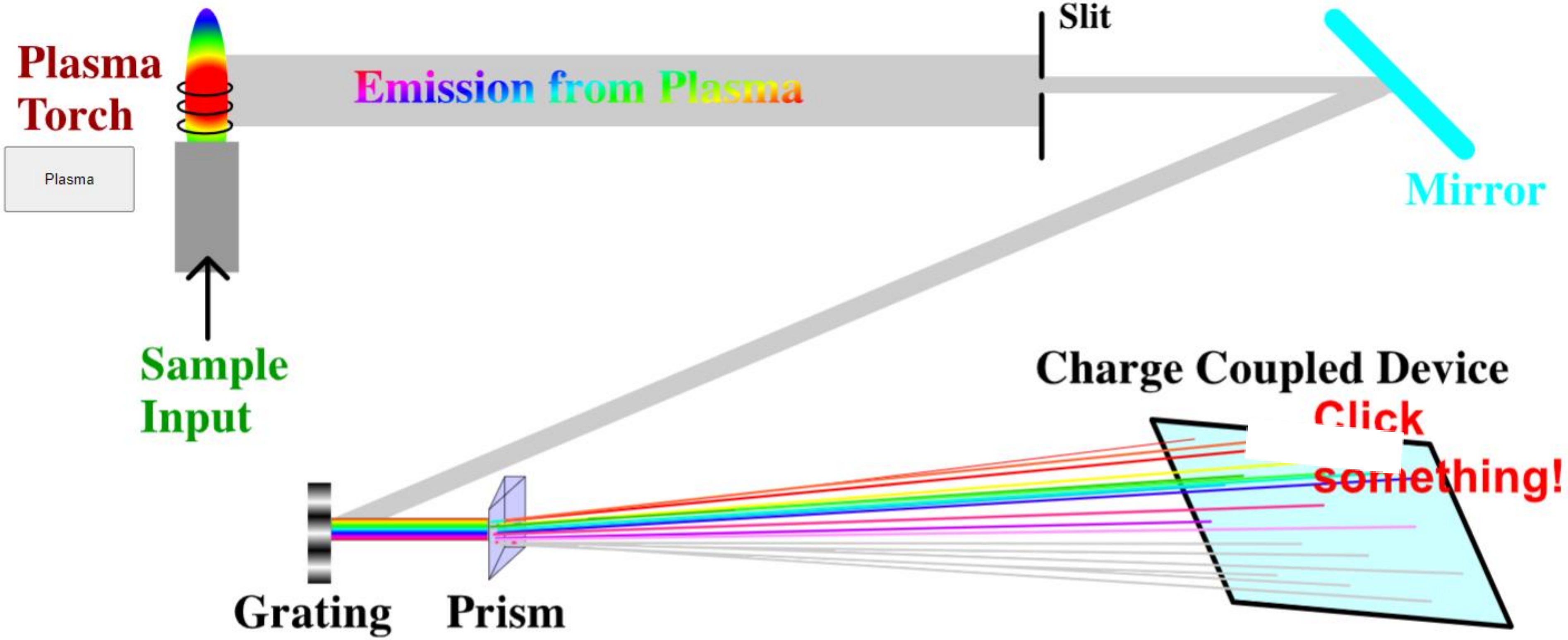


Inductively Coupled Plasma



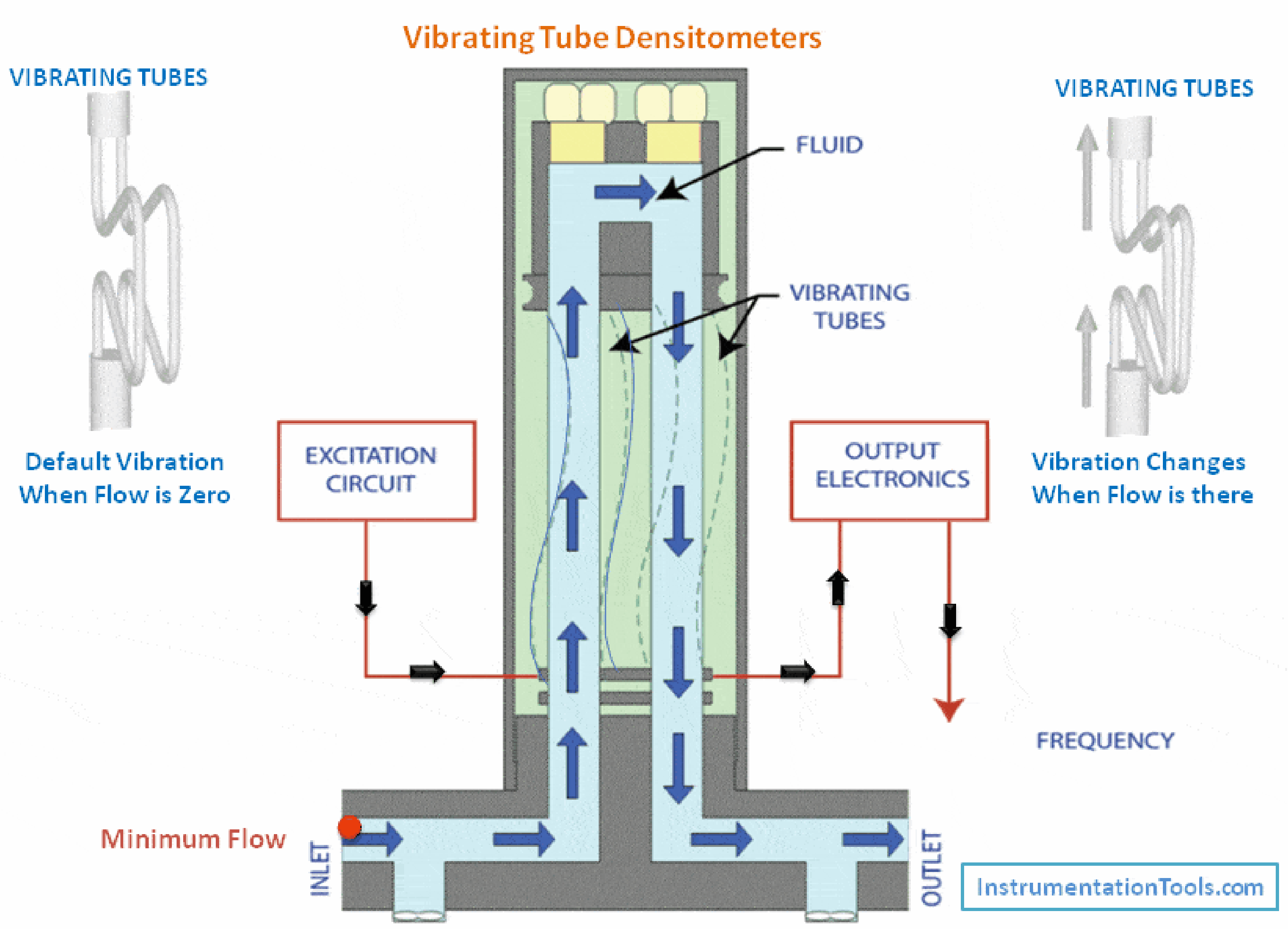
Two dispersion elements

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				

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

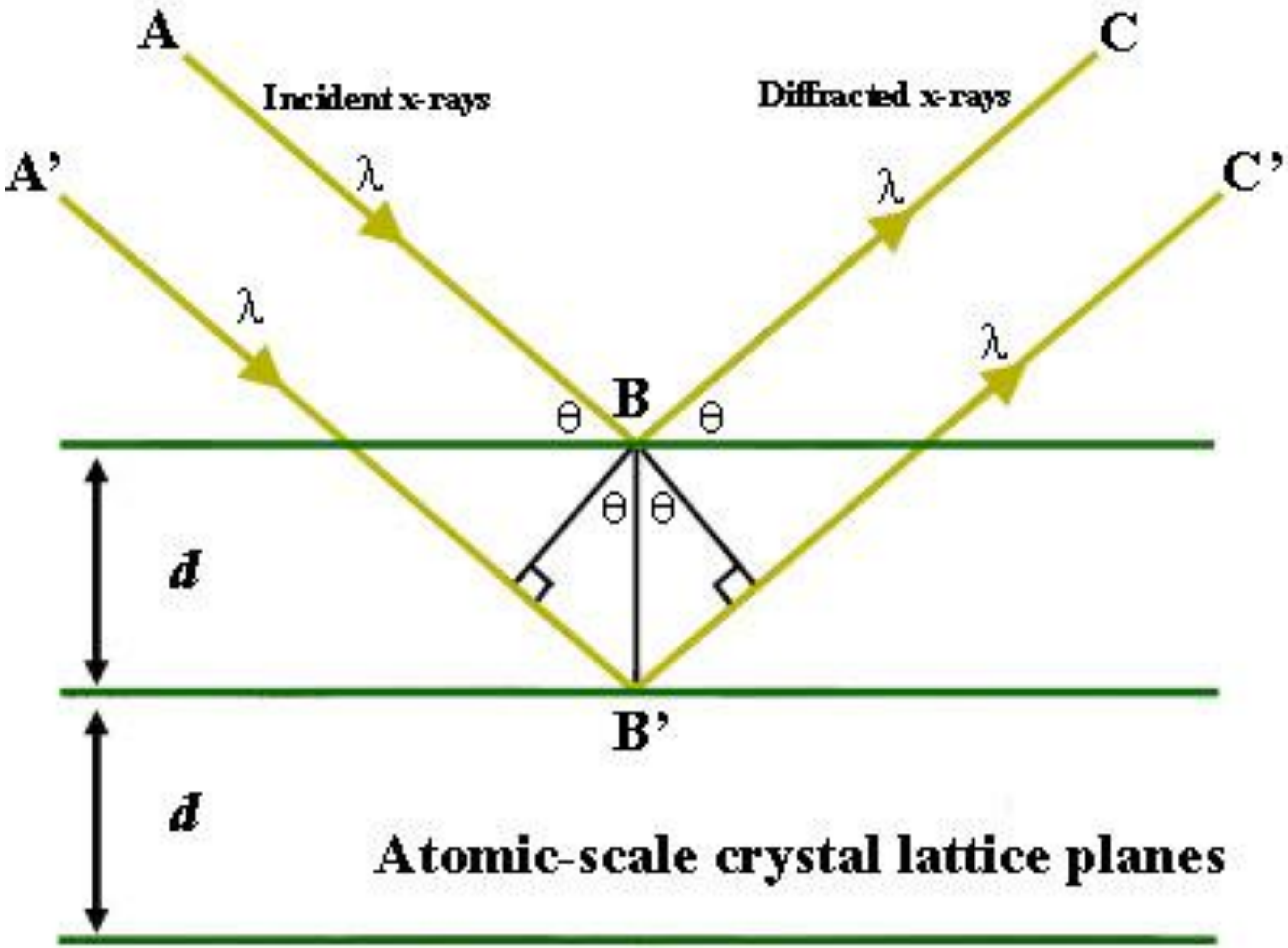
Densitometer Theory

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

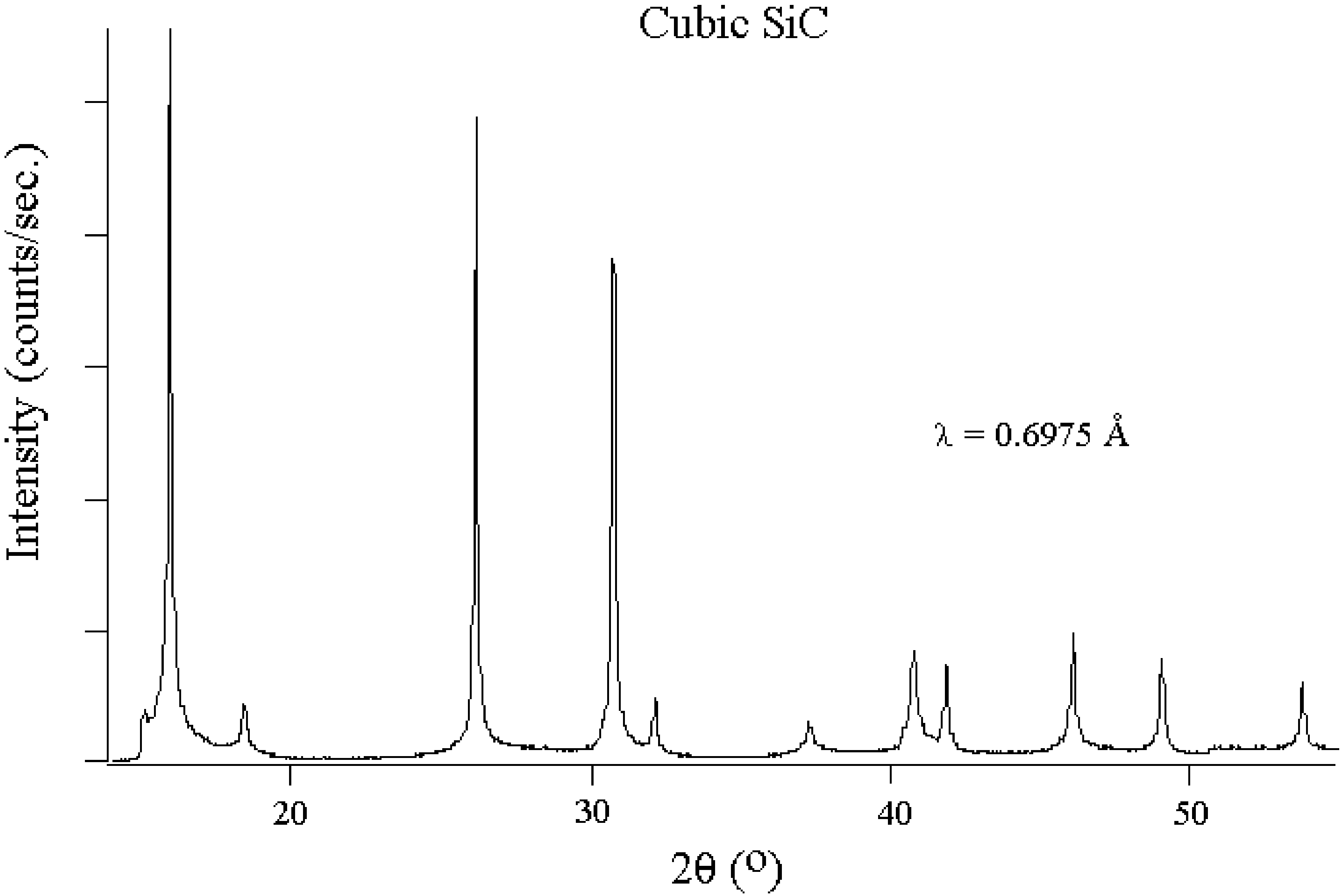


X-Ray Diffraction (XRD)

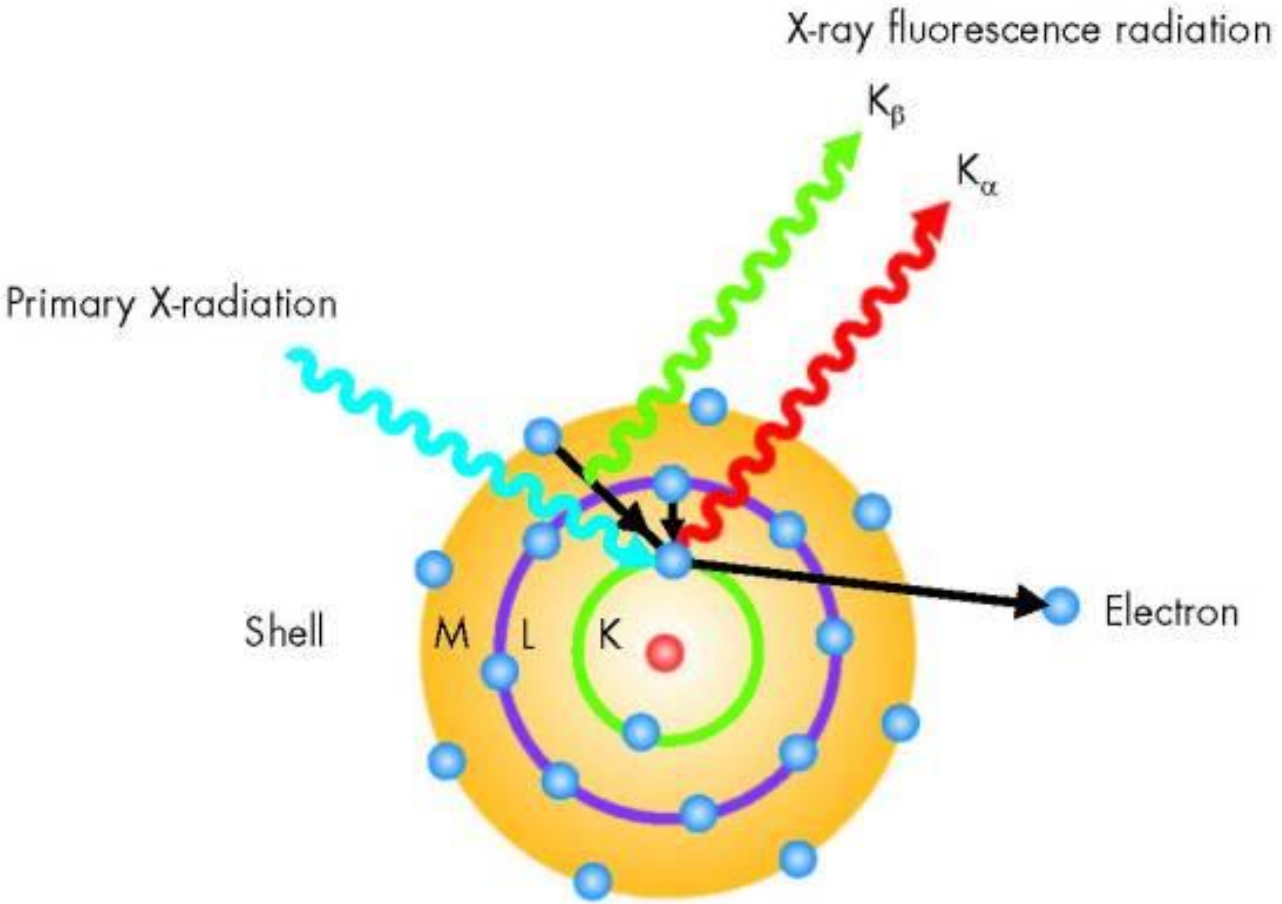
- Defined by Bragg's Law
- $n\lambda = 2d \sin\Theta$



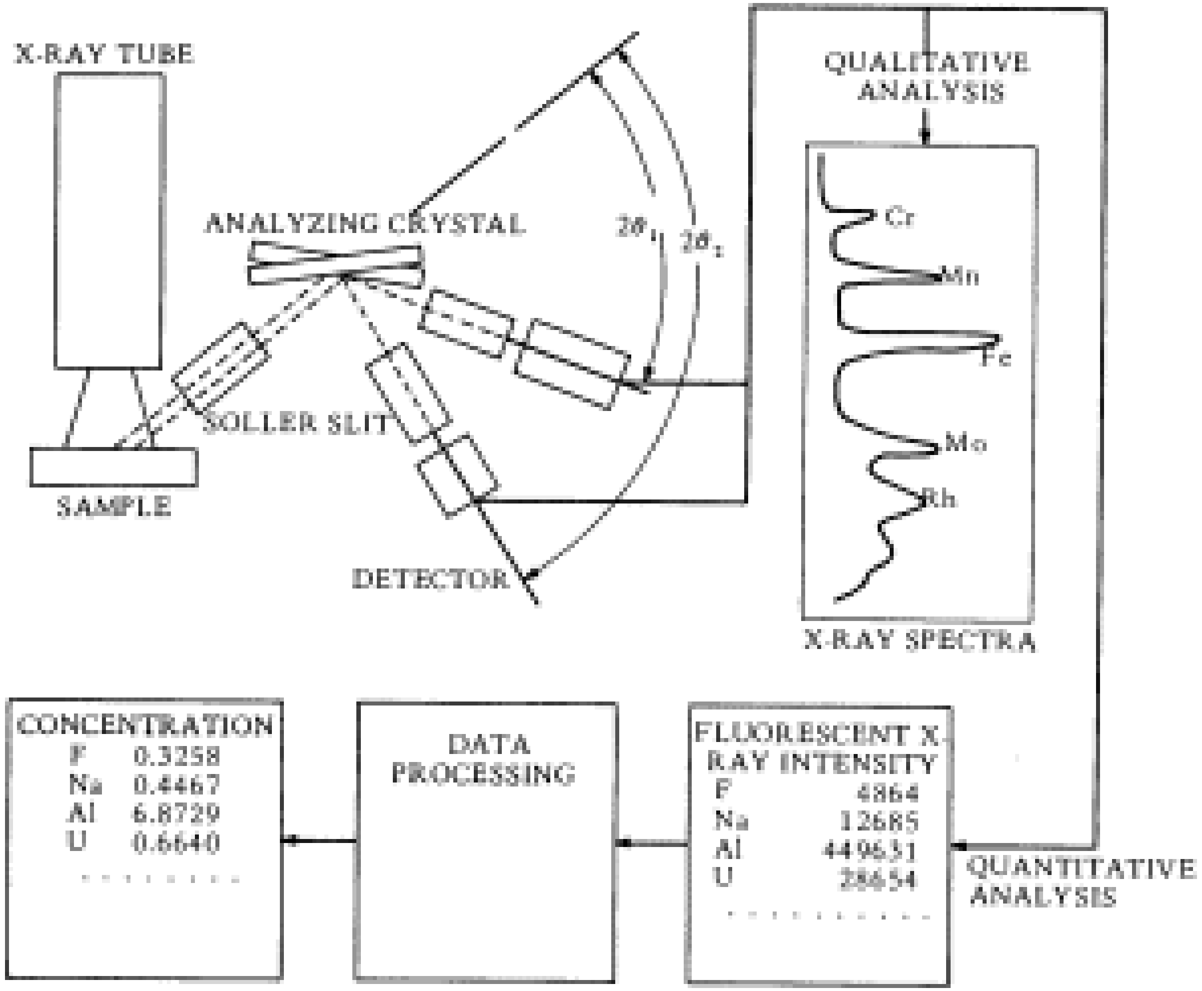
Example of XRD result



X-Ray Fluorescence (XRF)



X-Ray Fluorescence (XRF)



CONCENTRATION	
F	0.3258
Na	0.4467
Al	6.8729
U	0.6640
....	

FLUORESCENT X-RAY INTENSITY	
F	4864
Na	12685
Al	449631
U	28654
....	

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

Quality Control and Quality Assurance

QA/QC

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**

QA/QC

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

QA/QC - Instrument Performance Measures

- Limit of Detection
- Limit of Quantitation
- Sensitivity
- Stability

QA/QC - Limits

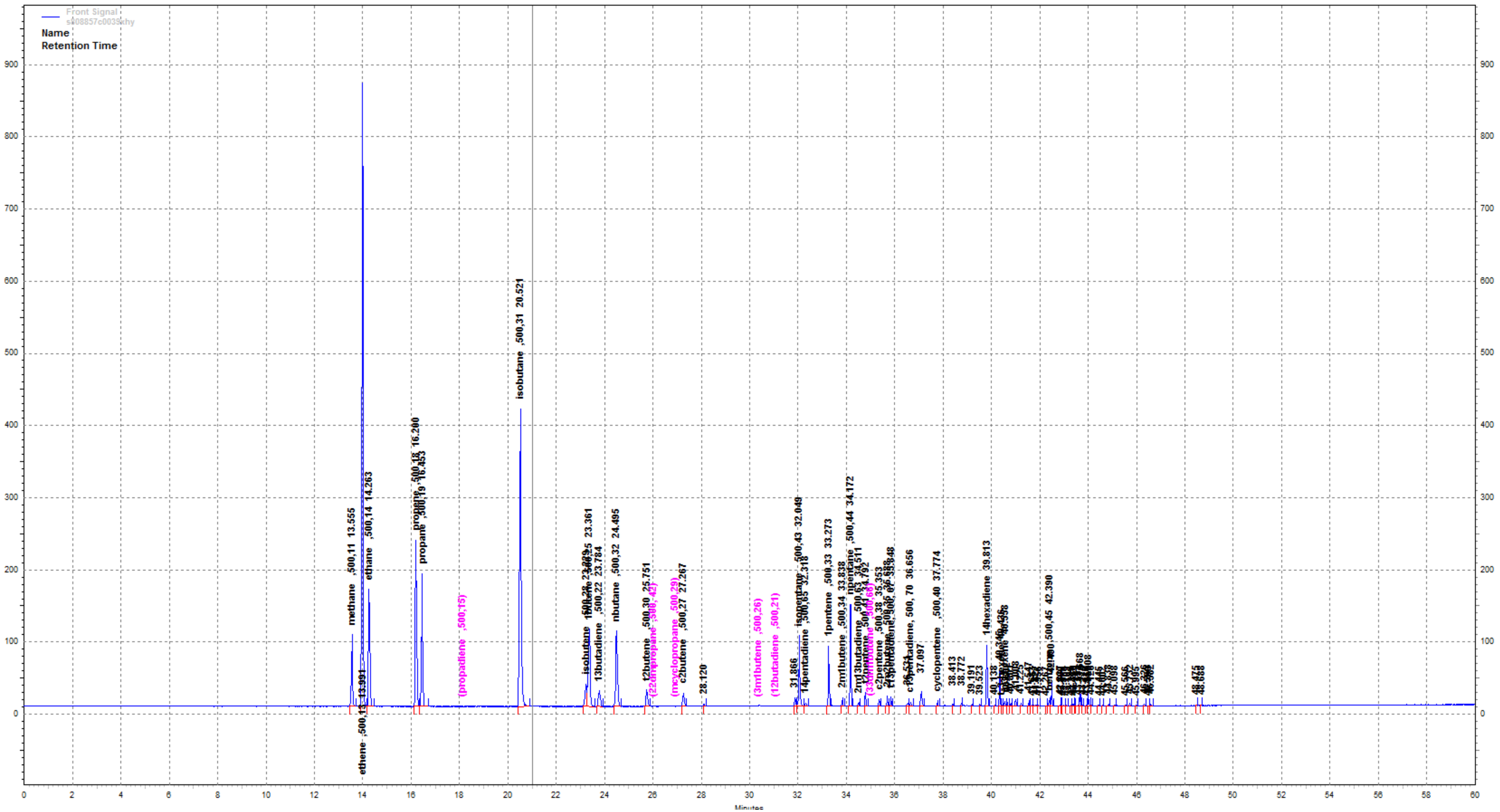
Limit of Detection

- 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

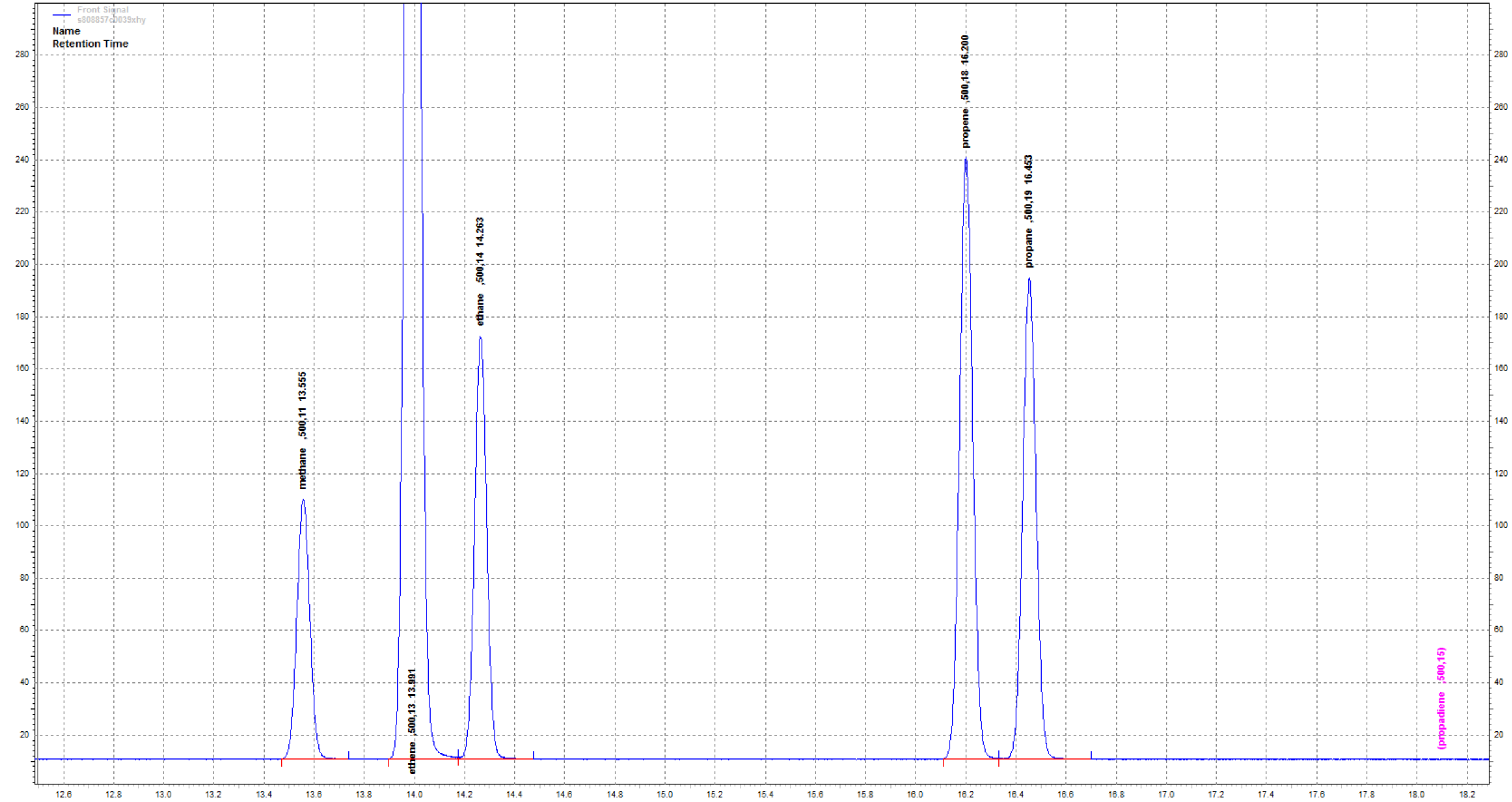
Limit of Quantitation

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

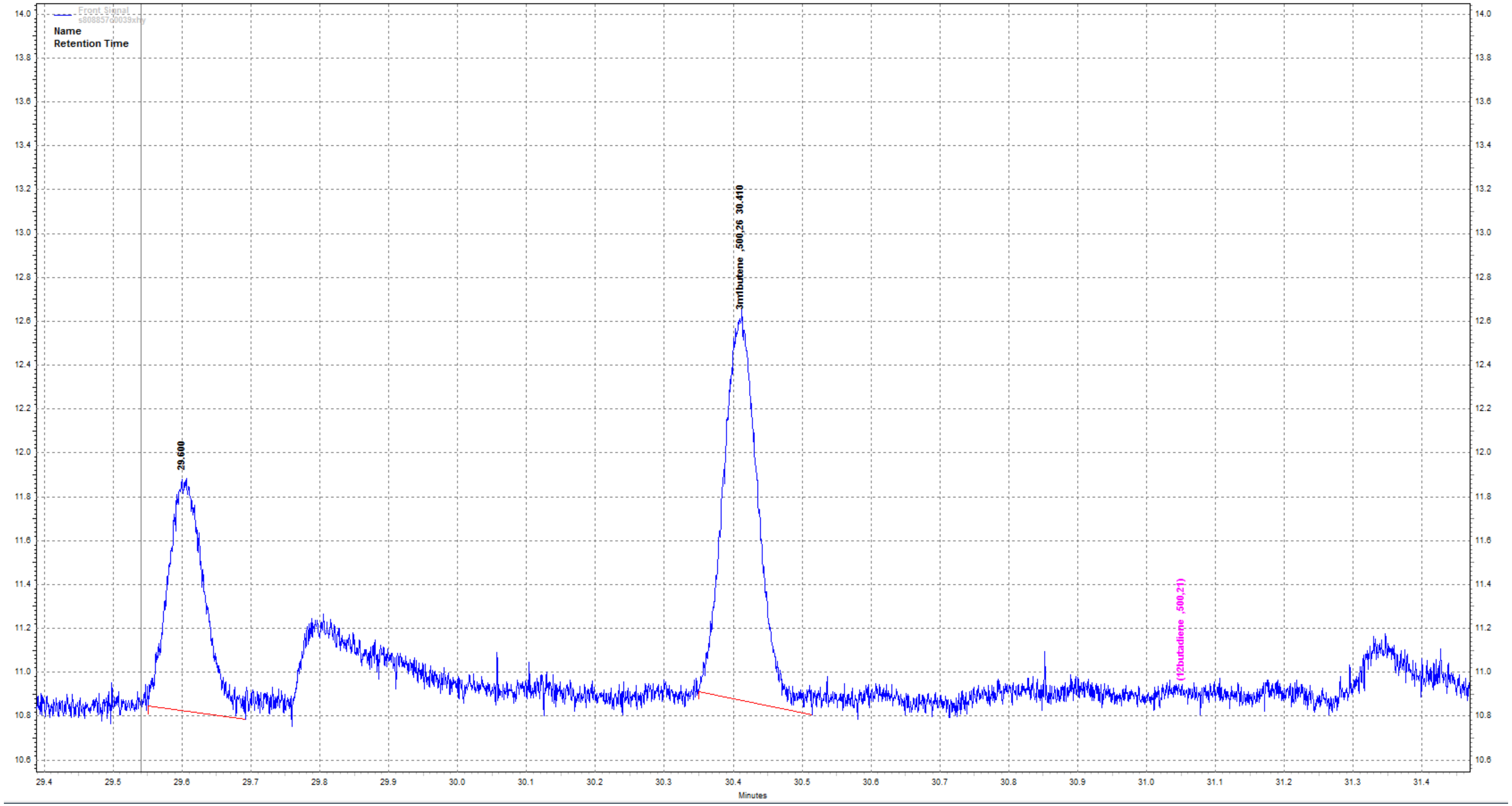
Full Chromatogram



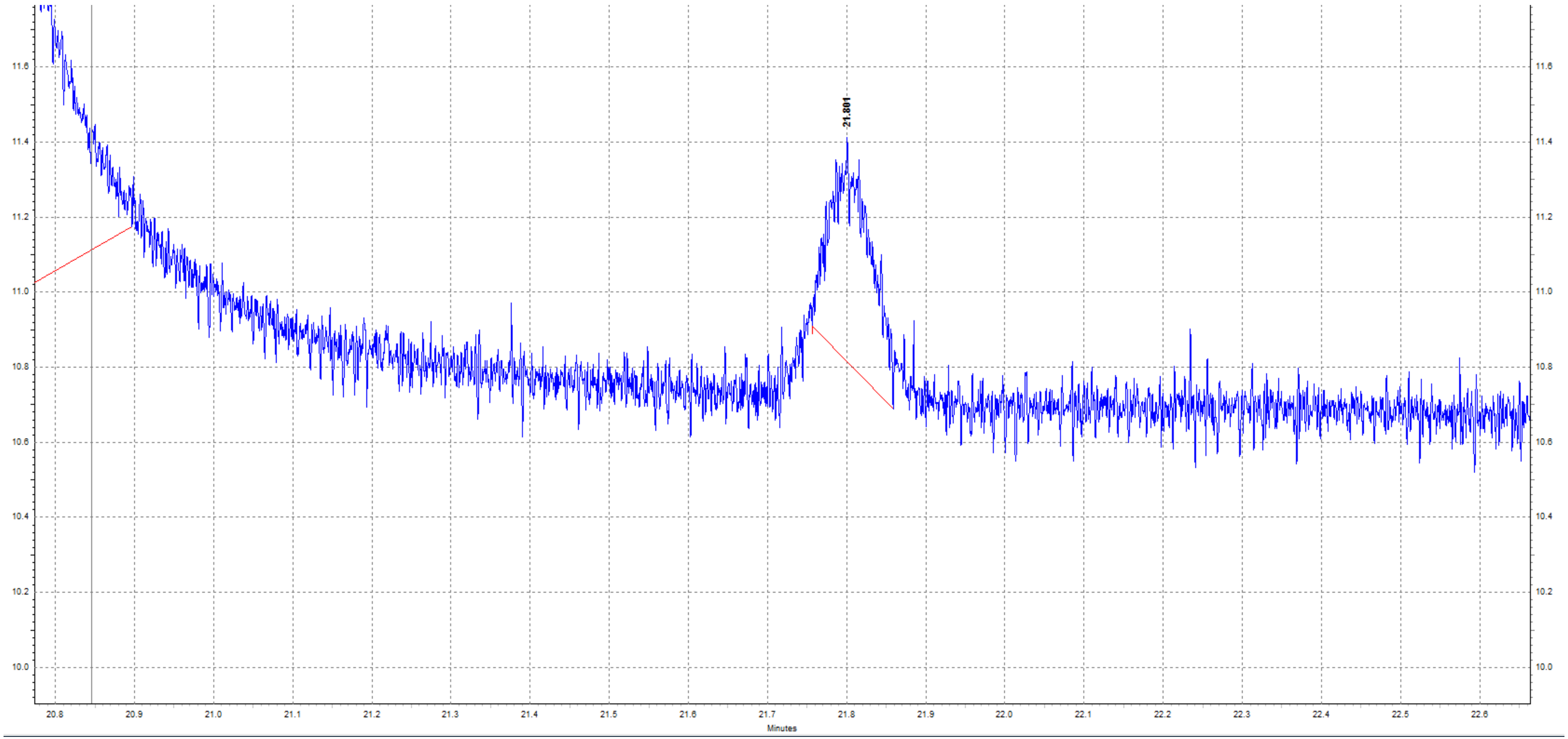
Expanded View



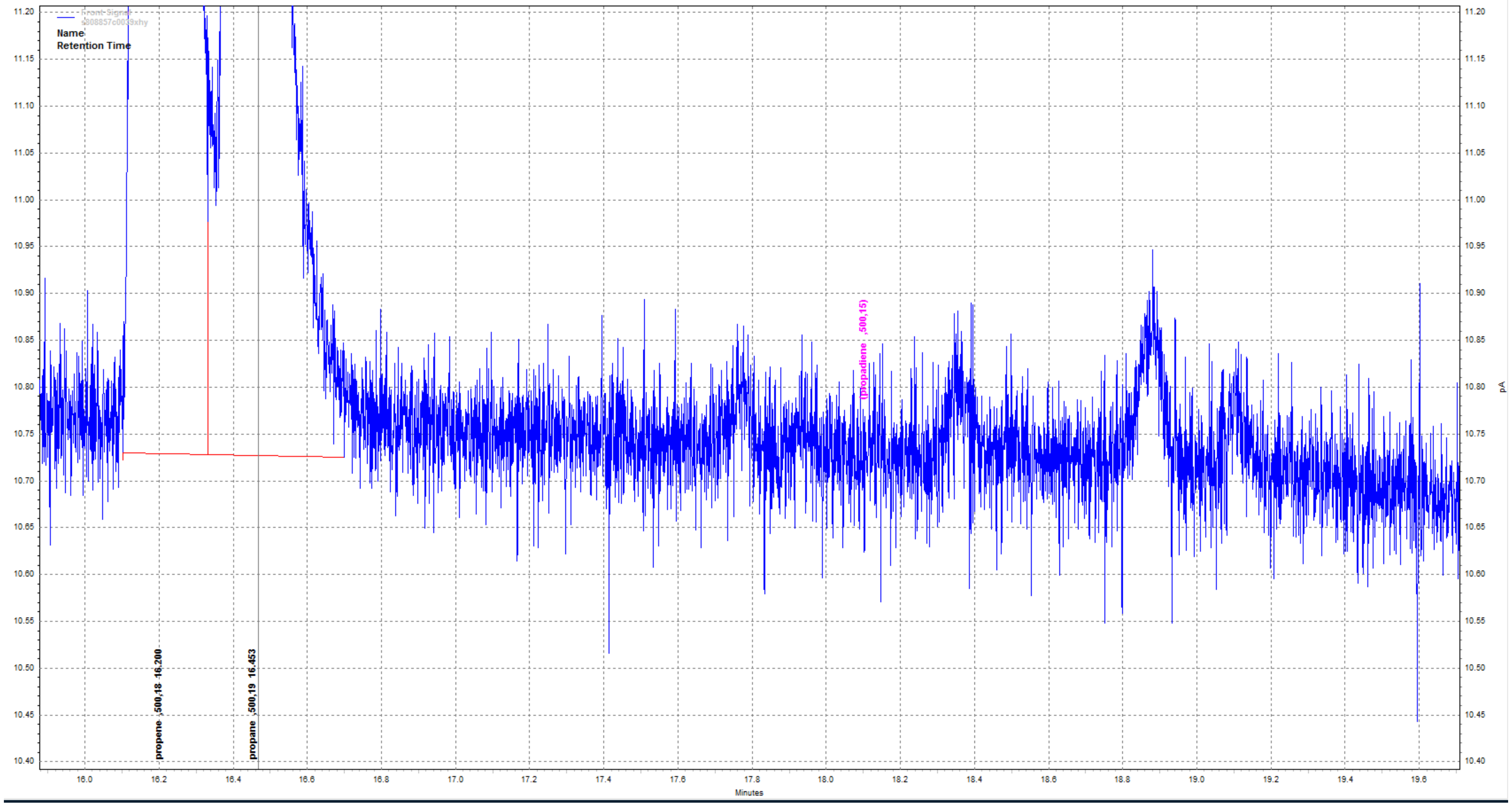
Quantitation Limit



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 depency of the system’s parameter on the measured value

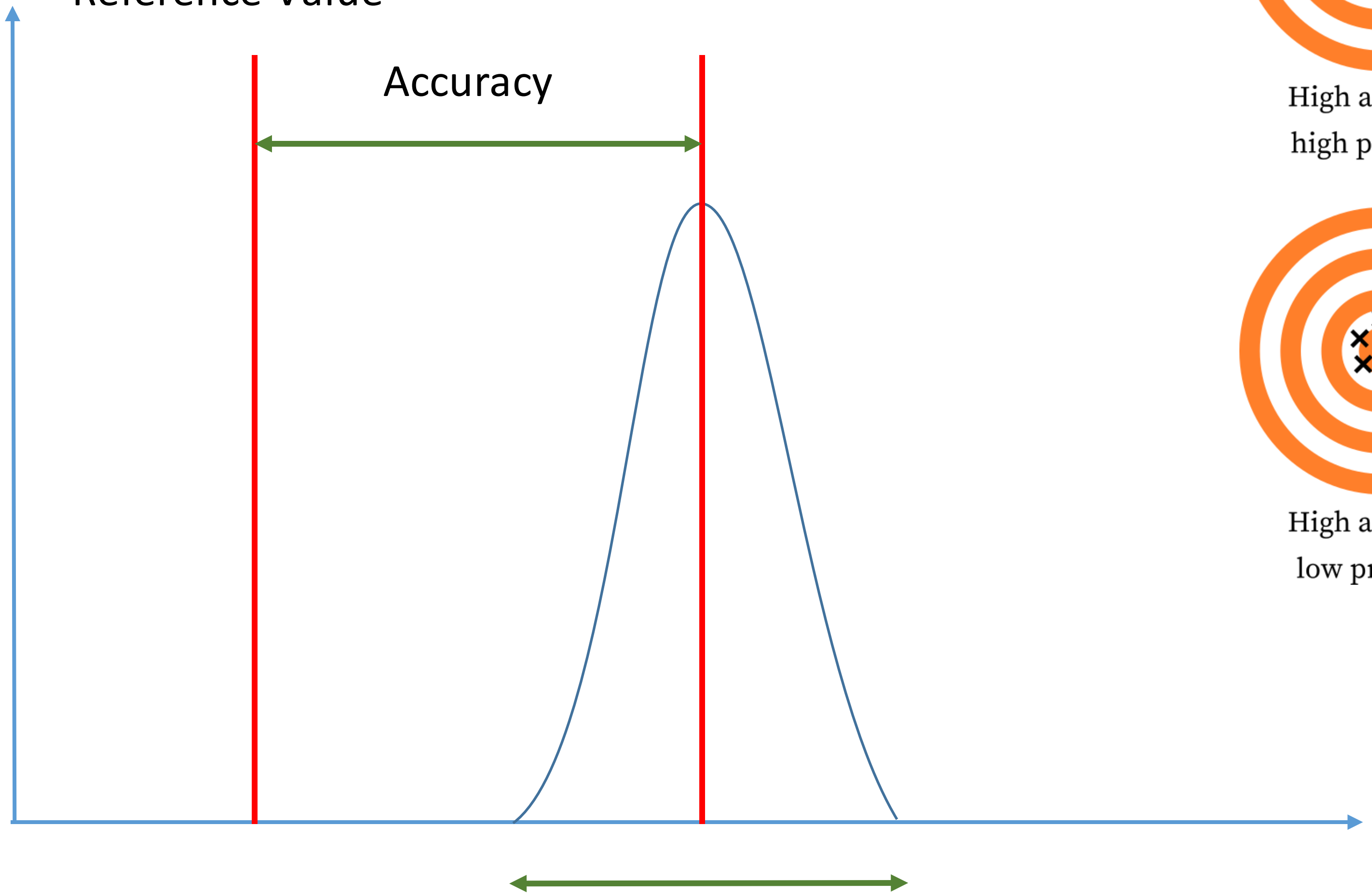
- Concentration
- Normalization vs External Standard

Gain statistical information of the analytical system

- Sensitivity
- Precision
- Accuracy

Accuracy vs Precision

Calibration adjusts to achieve accuracy



Reference Value

Accuracy

Precision

High accuracy,
high precision

Low accuracy,
high precision

High accuracy,
low precision

Low accuracy,
low precision

But, precision is determined by the instrument

QA/QC - Frequency of Calibration

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

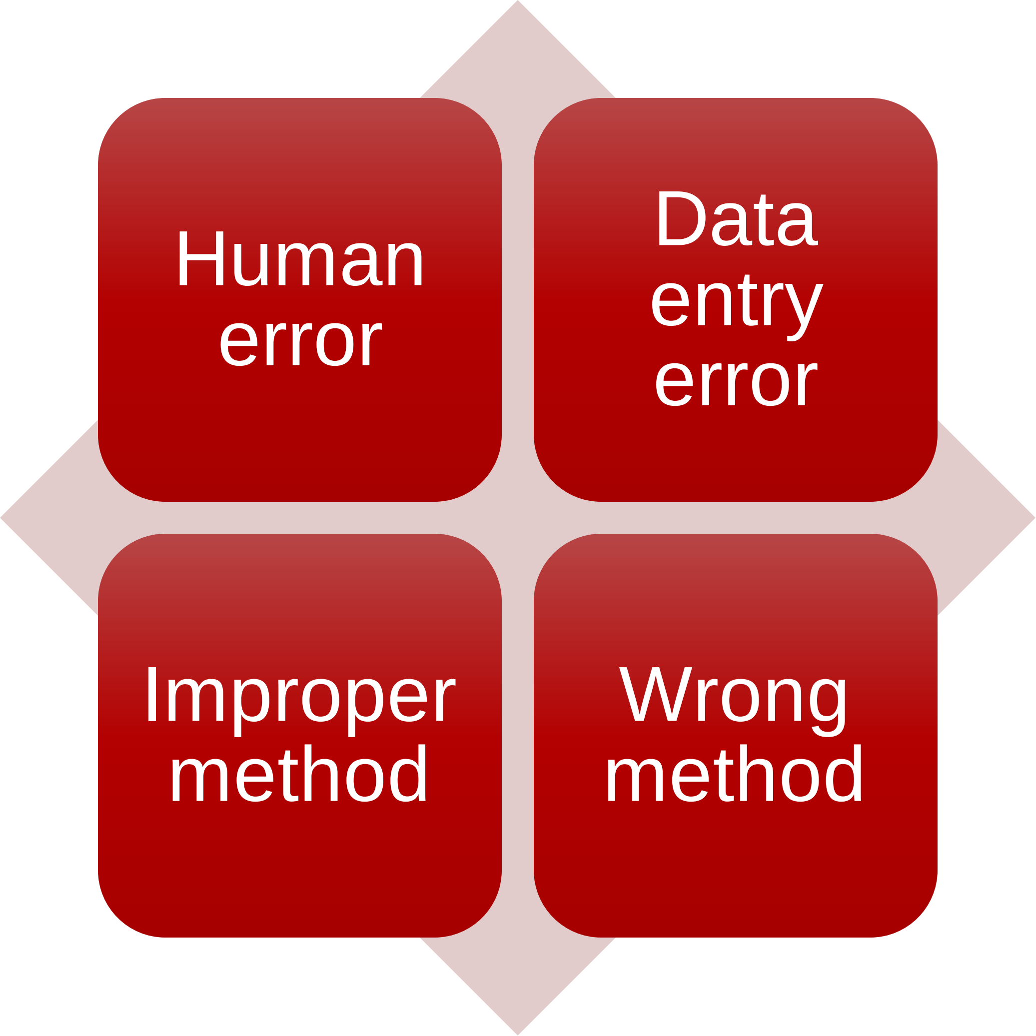
Systematic Errors

- Method limits
- Bias
- Mathematical correction

Random Errors

- Normal variations
- Statistical

SOURCES OF ERRORS - MISTAKES

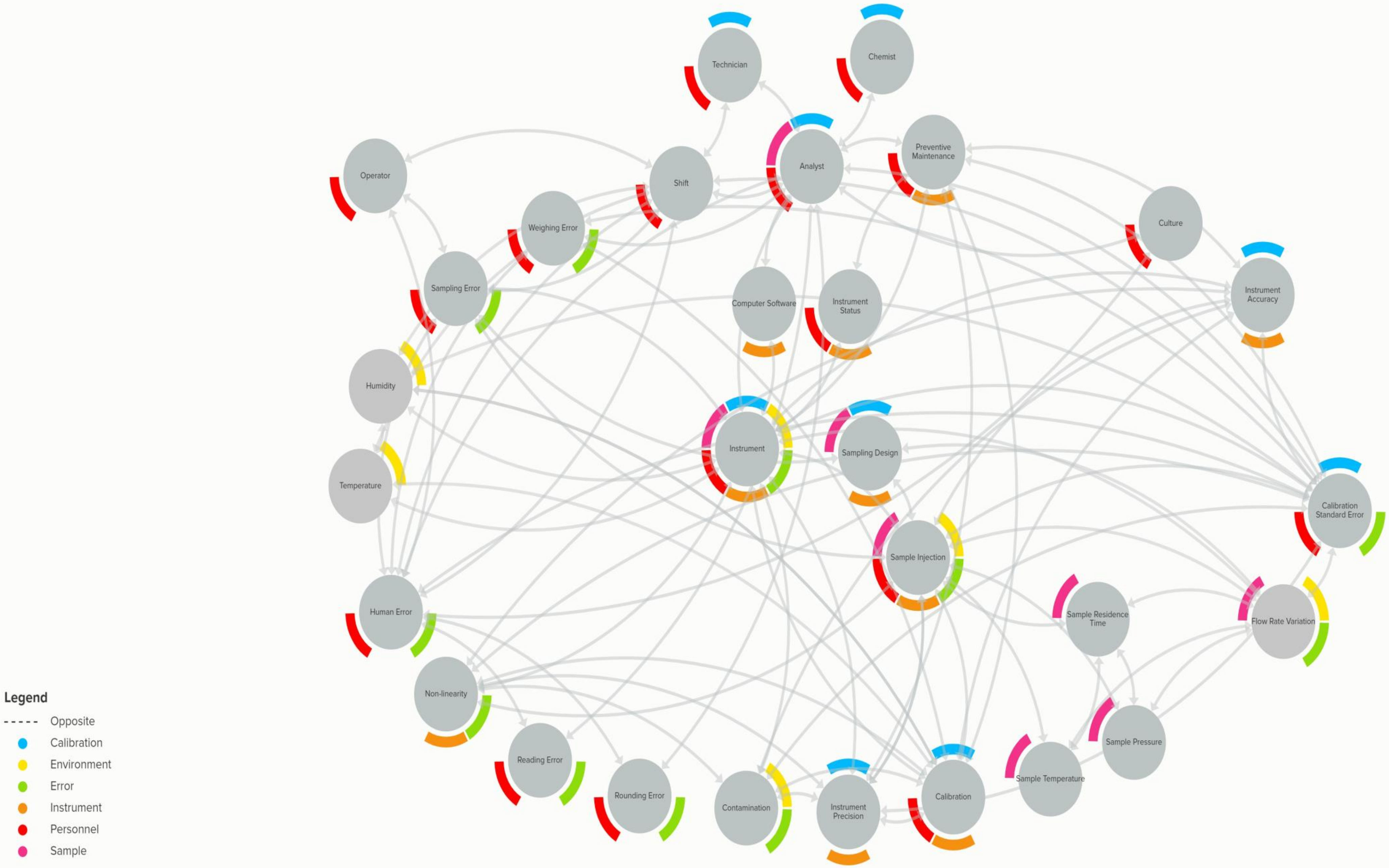


Human error

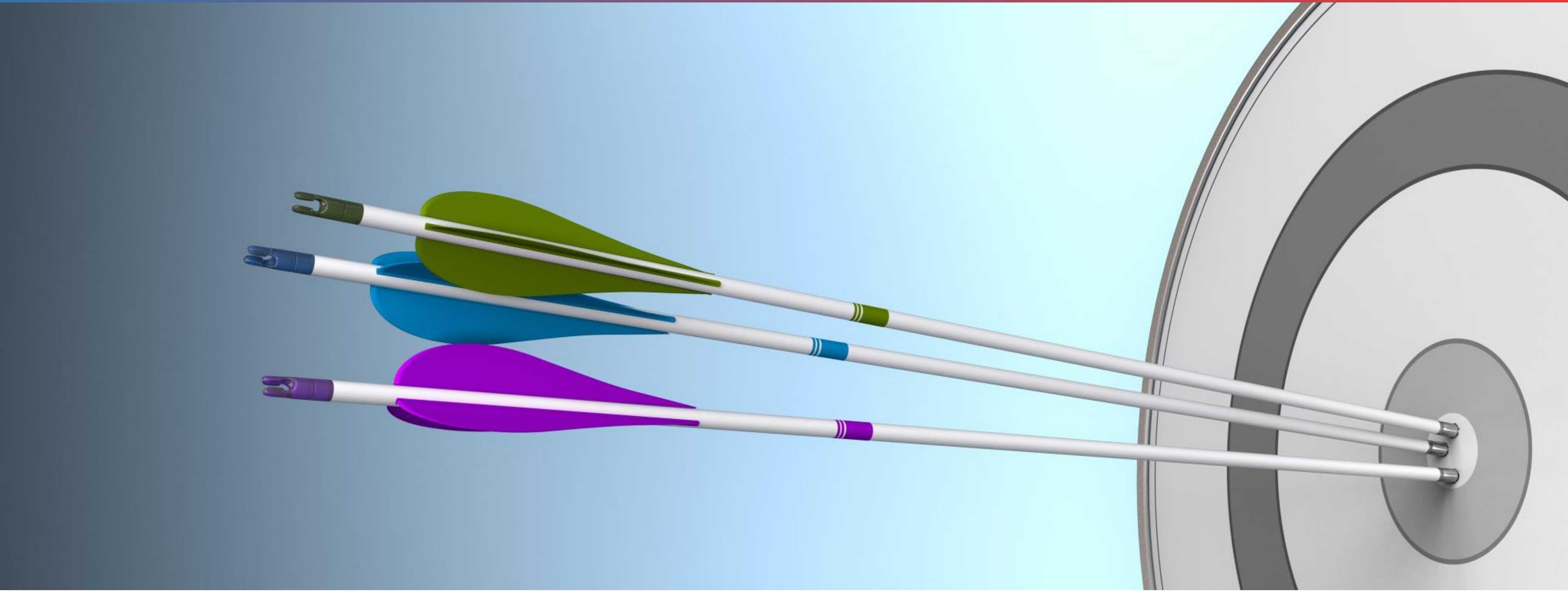
Data entry error

Improper method

Wrong method


Technician
Chemist
Analyst
Preventive Maintenance
Operator
Shift
Weighing Error
Culture
Sampling Error
Computer Software
Instrument Status
Instrument Accuracy
Humidity
Instrument
Sampling Design
Temperature
Calibration Standard Error
Sample Injection
Human Error
Sample Residence Time
Flow Rate Variation
Non-linearity
Sample Pressure
Reading Error
Rounding Error
Contamination
Instrument Precision
Calibration
Sample Temperature
Legend
- - - - - Opposite
● Calibration
● Environment
● Error
● Instrument
● Personnel
● Sample

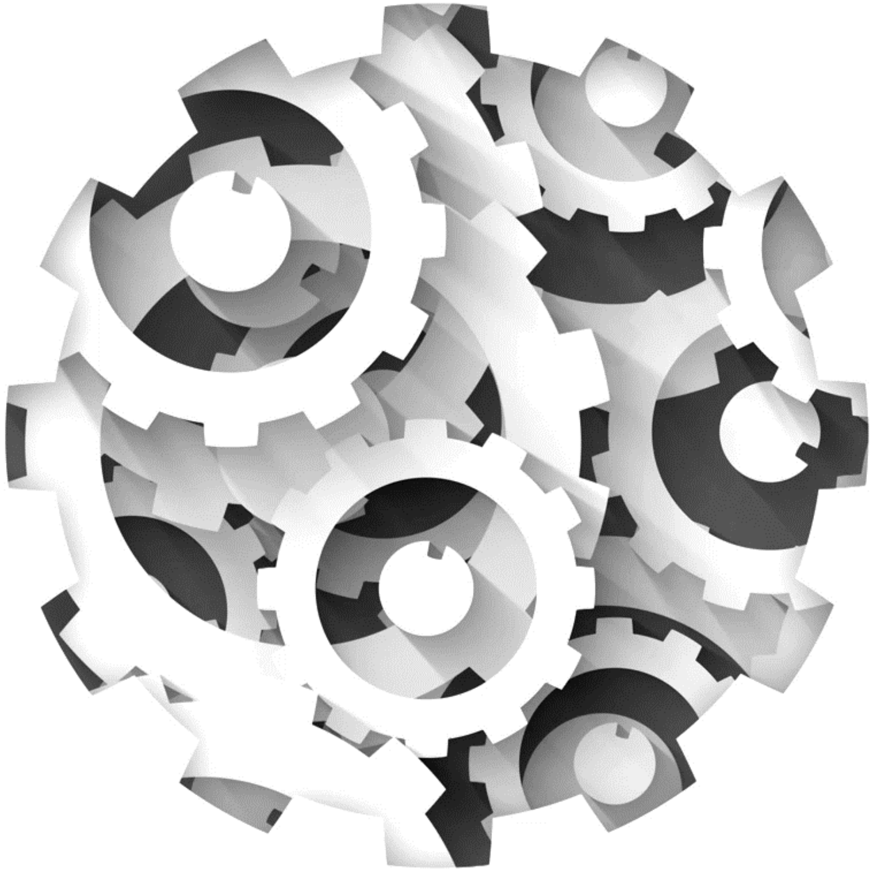
- SQC Systems



QA/QC – Customer Satisfaction

Meets or exceeds customer requirements

Process Basics



900-P-9309
CENTRIFUGAL PUMP
MOD 316 SS
.X.
POWER: 1/3 HP, 1725 RPM
CAP: 2 GPM @ 10' TDH

900-V-9309
ACID RECOVERY TANK
. X .
DP: 285 PSIG @
. @
MOD SA 106 GR.B

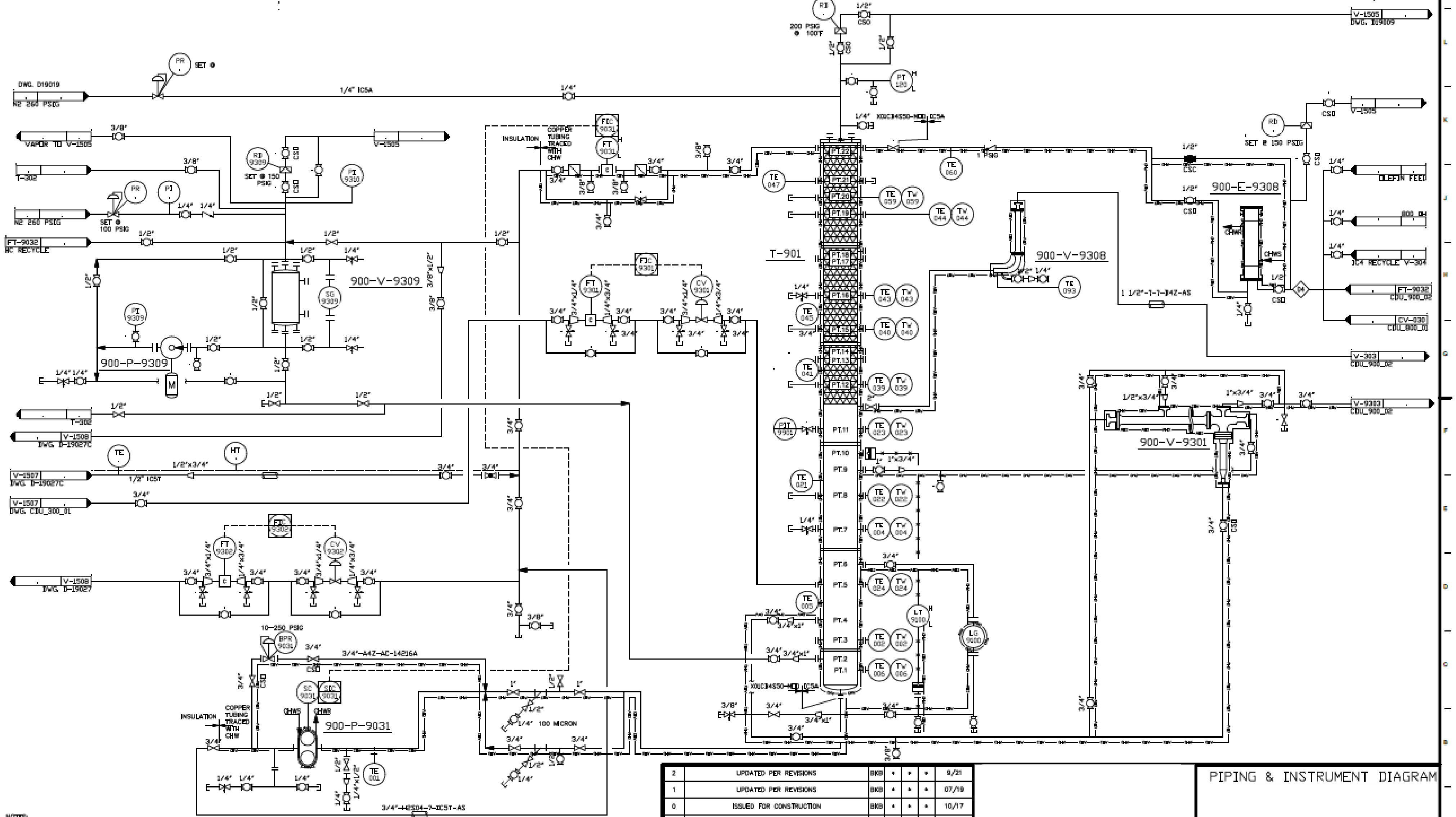
900-P-9031
ACID RECYCLE PUMP
MOD: ALLOY 20
.X.
POWER: 2HP, 1750RPM
CAP: 6 GPM

900-V-9308
SEPARATOR
. X .
. @
. @
A106 GR. B CS

T-901
TOWER
SHELL: . @.
TUBE: . @.
DT: 100°F

900-V-9301
LIQUID/LIQUID COALESCER 316SS
. X .
. @.
. @.

900-E-9308
RECYCLE COOLER
. X .
. @
. @
MOD: 316 S.S.



NOTES:
1. BOTH PNEUMATIC VALVES TO OPERATE OFF OF DISCRETE-IN ON DELTA-V.
2. NEED MANUAL OPERATOR OVERRIDE.
3. NEED INTERLOCK W/LT-100 & LOSS IN P0-031 POWER.
4. ALL INSTRUMENTATION HAVE PREFIX OF "900".

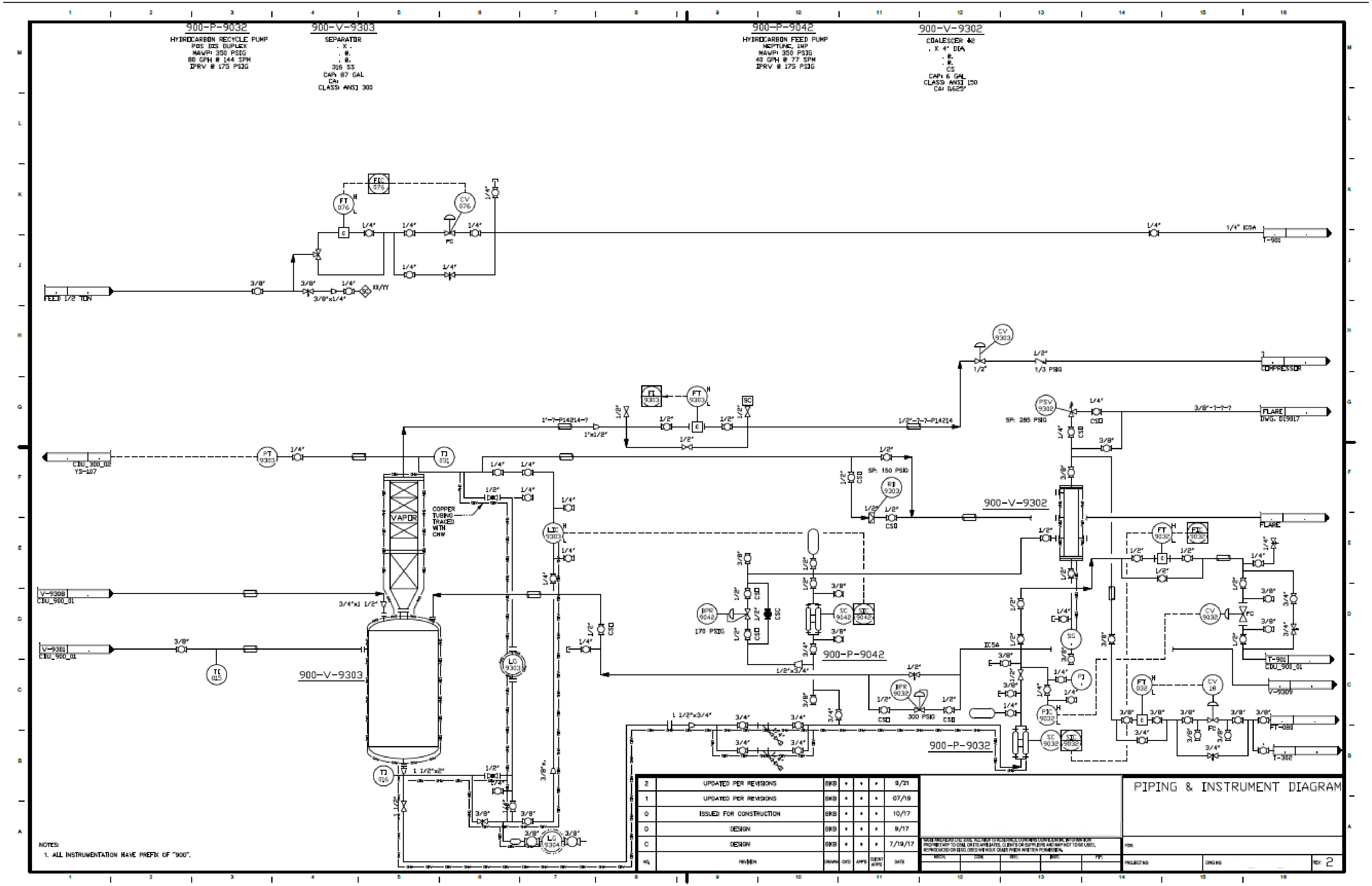
NO.	REVISION	DRAWN	CKD	APPD	CLIENT APPD	DATE
2	UPDATED PER REVISIONS	BKB	•	•	•	9/21
1	UPDATED PER REVISIONS	BKB	•	•	•	07/19
0	ISSUED FOR CONSTRUCTION	BKB	•	•	•	10/17
D	DESIGN	BKB	•	•	•	9/17
C	DESIGN	BKB	•	•	•	7/19/17

MECH: CIVIL: STR: INST: PIP:

PIPING & INSTRUMENT DIAGRAM

FOR:

PROJECT NO:
DWG NO:
REV: 2



NOTES:
1. ALL INSTRUMENTATION HAVE PREFIX OF "900".

NO.	REVISION	DRAWN	CHD	APPD	CLIENT APPD	DATE
2	UPDATED PER REVISIONS	BKB	•	•	•	9/21
1	UPDATED PER REVISIONS	BKB	•	•	•	07/19
0	ISSUED FOR CONSTRUCTION	BKB	•	•	•	10/17
D	DESIGN	BKB	•	•	•	9/17
C	DESIGN	BKB	•	•	•	7/19/17

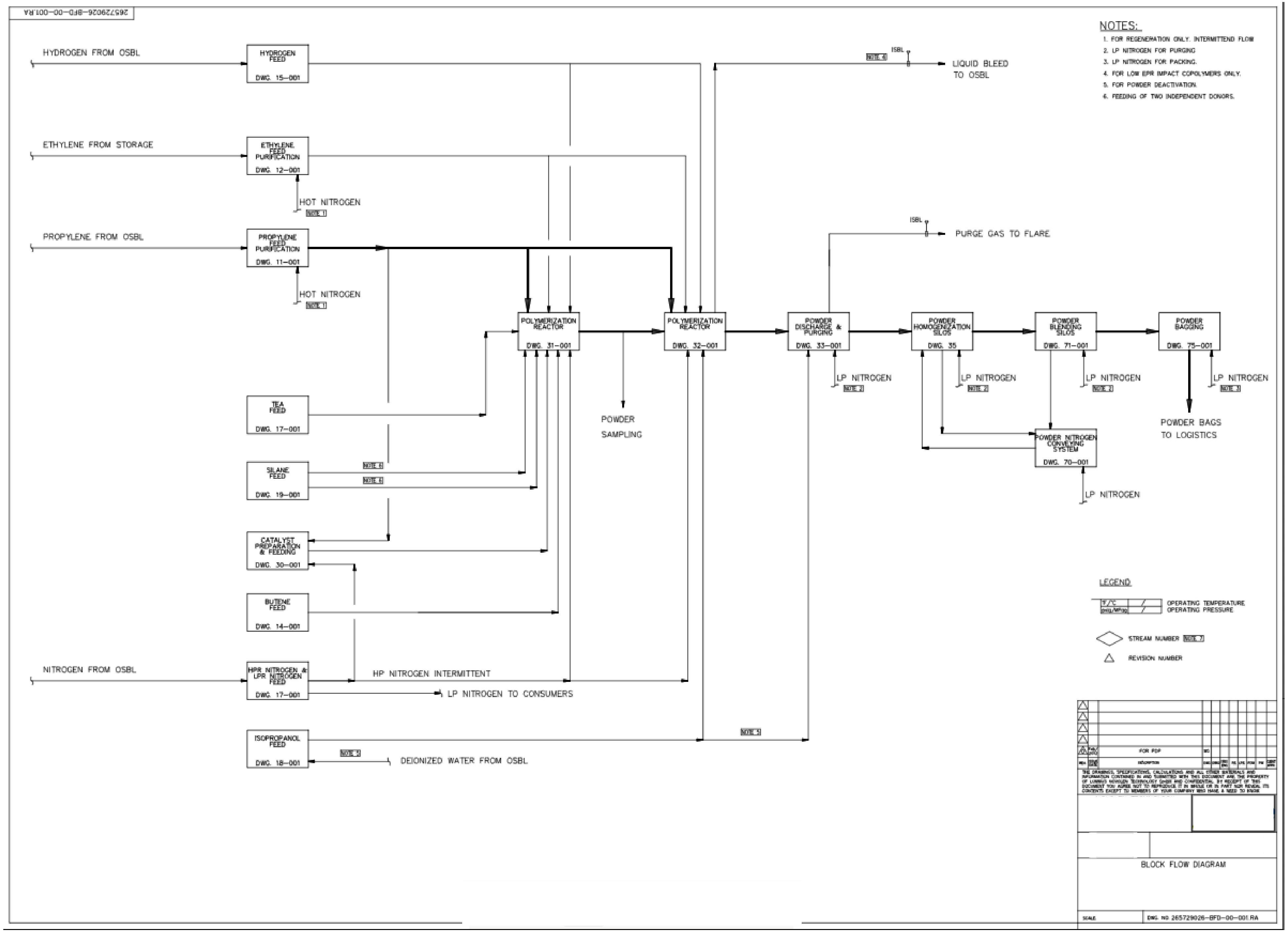
PIPING & INSTRUMENT DIAGRAM

FOR

PROJECT NO.

DWG NO.

REV. 2



NOTES:

1. FOR REGENERATION ONLY. INTERMITTEND FLOW
2. LP NITROGEN FOR PURGING
3. LP NITROGEN FOR PACKING.
4. FOR LOW EPR IMPACT COPOLYMERS ONLY.
5. FOR POWDER DEACTIVATION.
6. FEEDING OF TWO INDEPENDENT DONORS.

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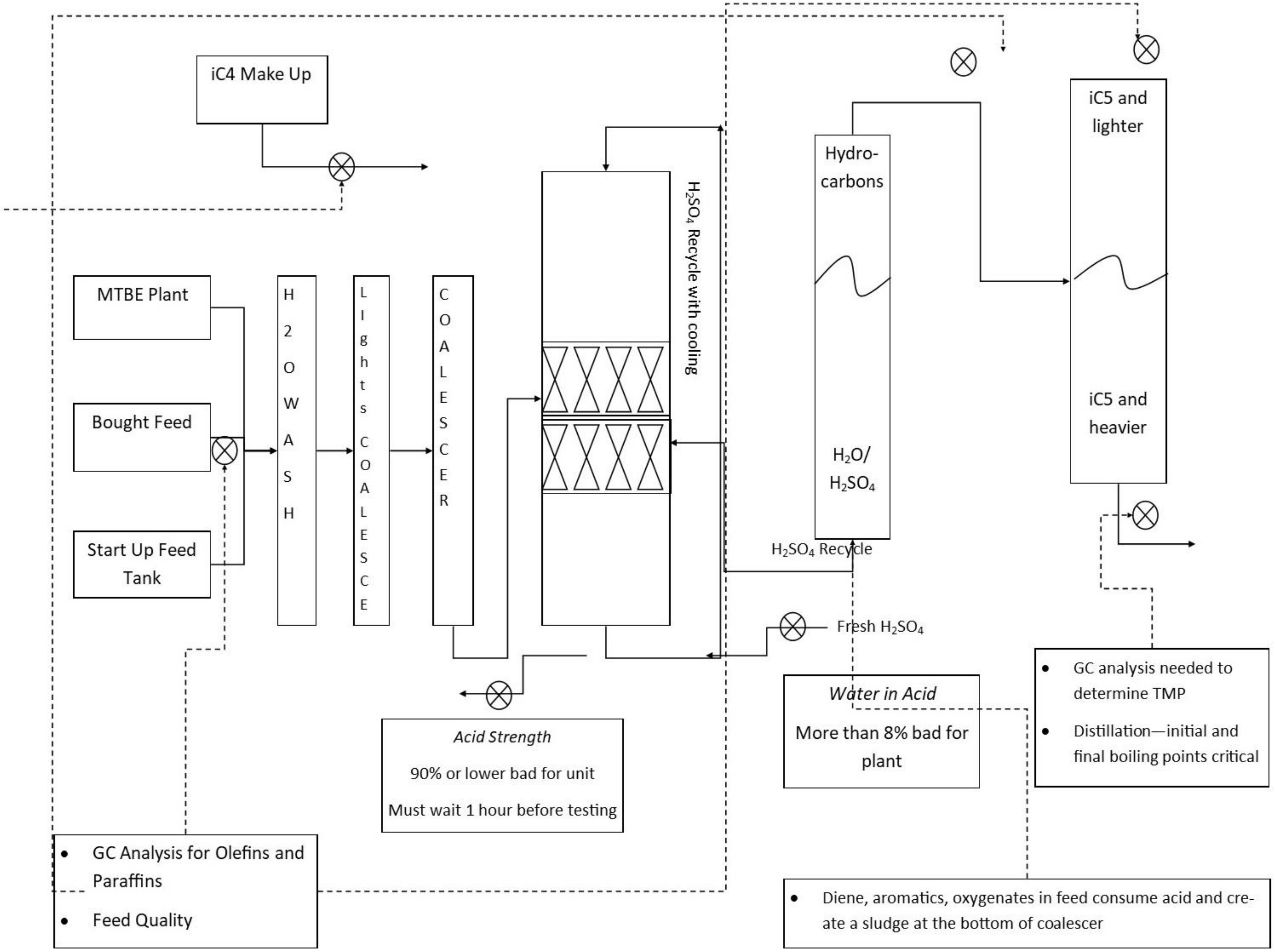
Flow Diagram



iC4 Make Up

MTBE Plant

Bought Feed

Start Up Feed Tank

H2O WASH

Lights COALESCE

COALESCER

H_2SO_4 Recycle with cooling

Hydro-carbons

H_2O/ H_2SO_4

iC5 and lighter

iC5 and heavier

H_2SO_4 Recycle

Fresh H_2SO_4

Acid Strength

90% or lower bad for unit

Must wait 1 hour before testing

Water in Acid

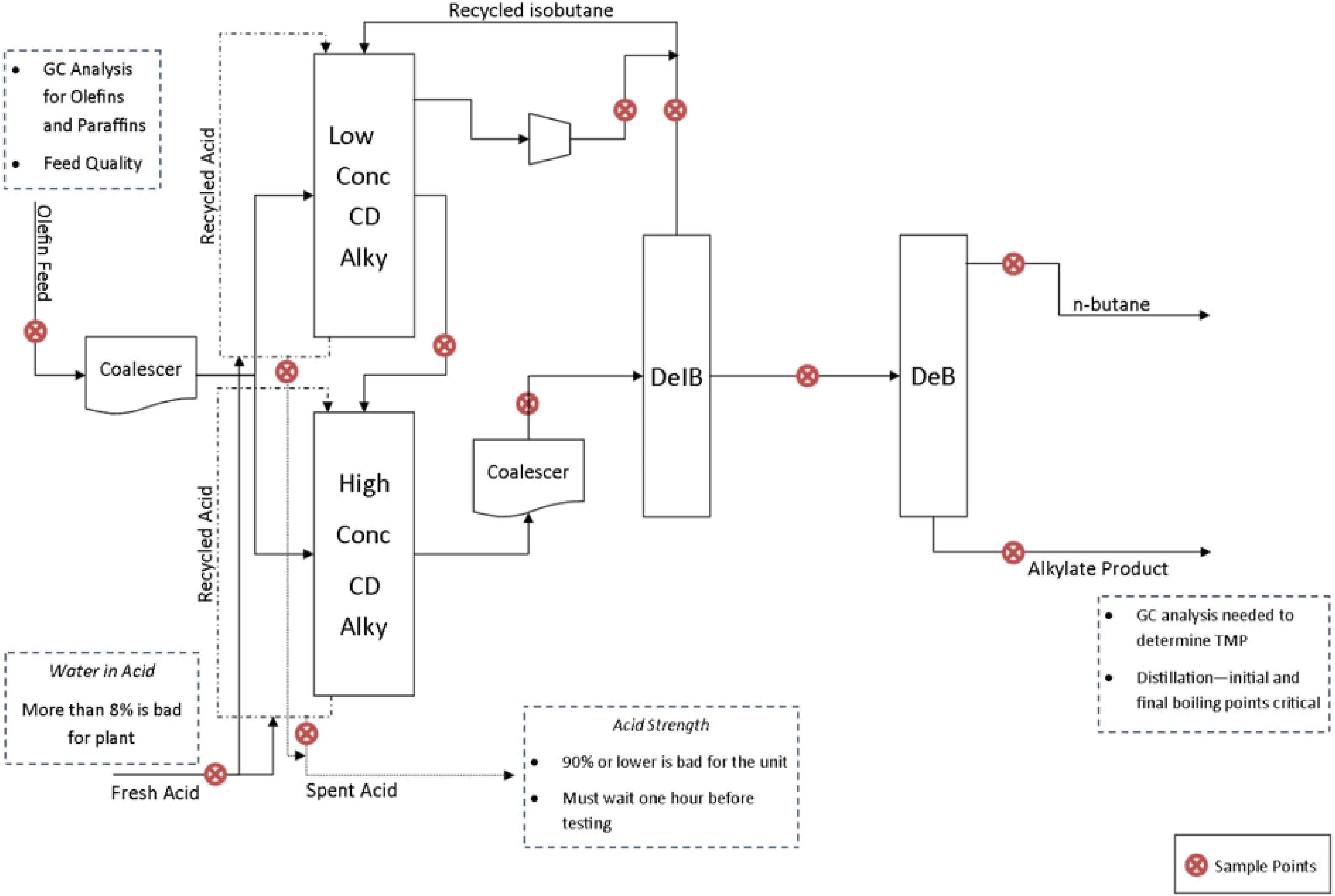
More than 8% bad for plant

- GC analysis needed to determine TMP
- Distillation—initial and final boiling points critical

- GC Analysis for Olefins and Paraffins
- Feed Quality

- Diene, aromatics, oxygenates in feed consume acid and create a sludge at the bottom of coalescer

Simplified Flow Diagram



- GC Analysis for Olefins and Paraffins
- Feed Quality

Water in Acid

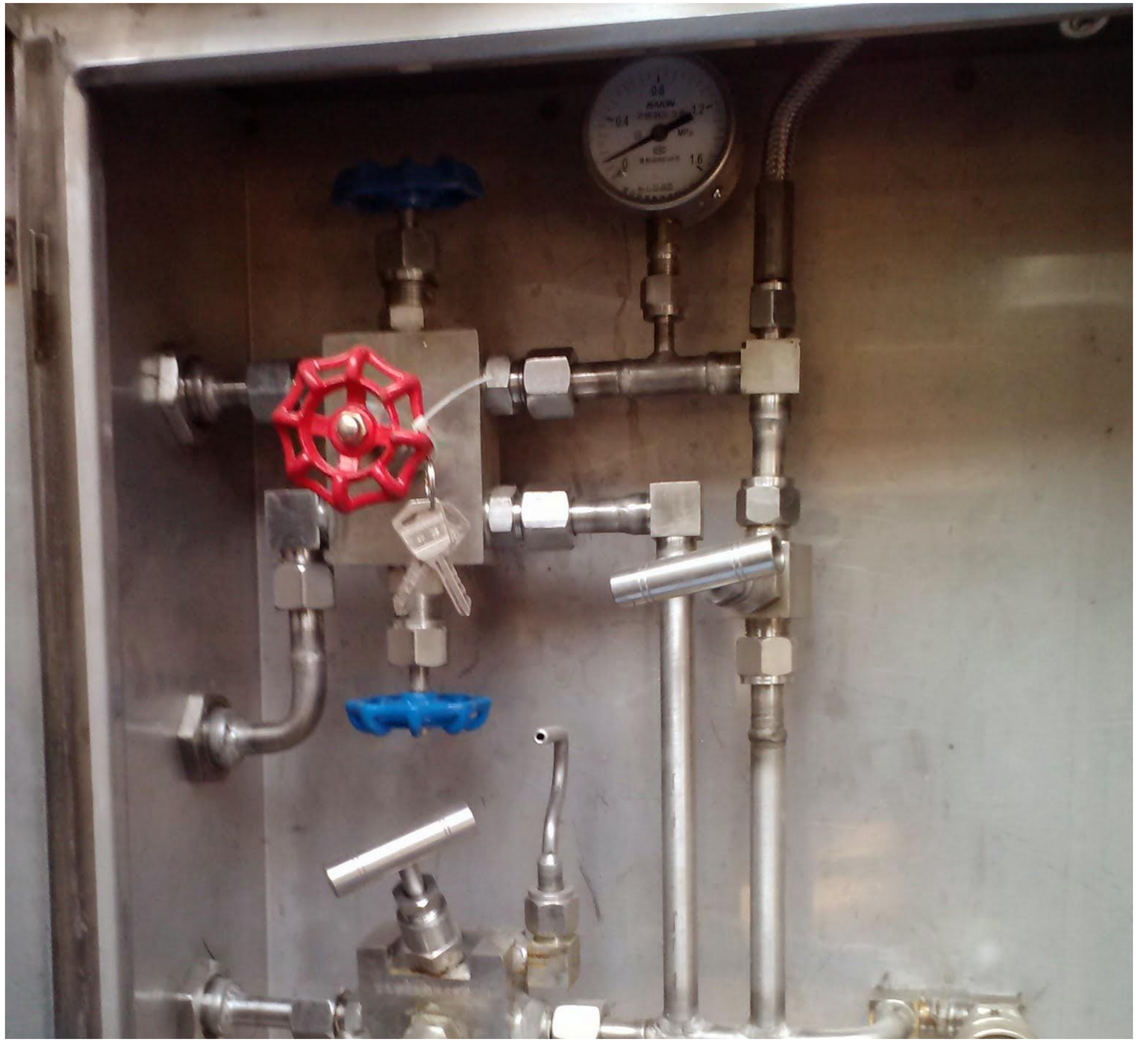
More than 8% is bad for plant

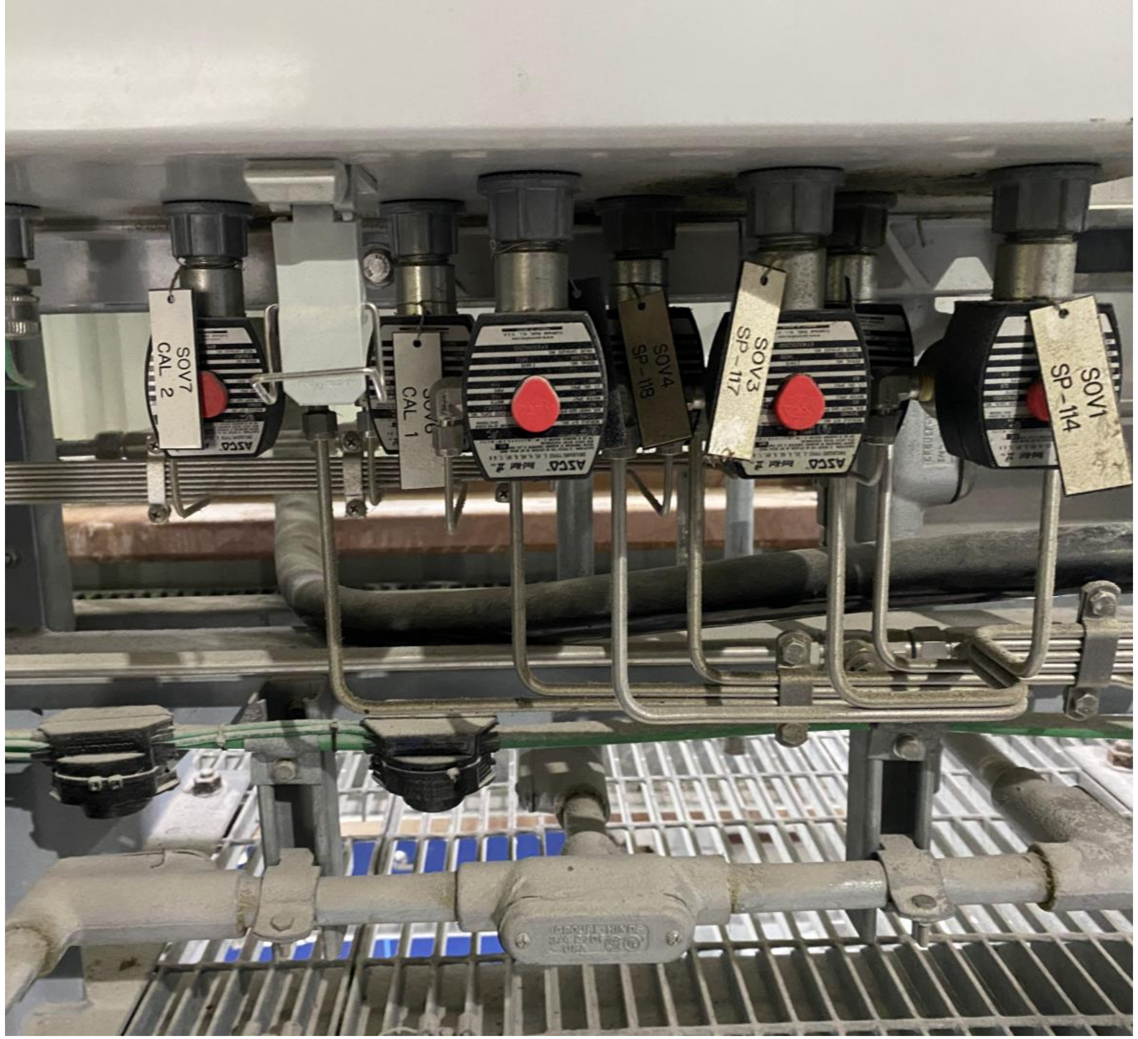
Acid Strength

- 90% or lower is bad for the unit
- Must wait one hour before testing

- GC analysis needed to determine TMP
- Distillation—initial and final boiling points critical

Process Basics





Sampling System Fundamental

What do we need to know

- Why Measure?
- Inputs to Design

What are our Requirements

- Representative
- Timeliness
- Compatibility

Sample Extraction

- Sample Tap
- Probe Consideration

Time Delay

- Fundamentals
- Liquids vs Gases
- Complicating Factors

Phase Fundamentals

- Phase Behavior & Diagrams
- Phase Calculation
- Condensation
- Vaporization

Sample Conditioning

- 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

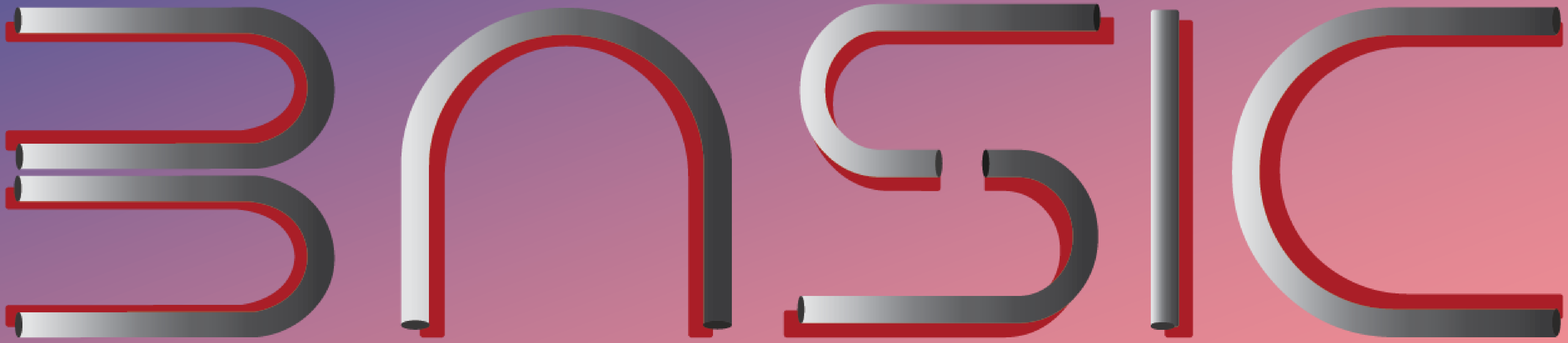
Speed of Response

- 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

jfab@jfabasic.com



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