CH0302 Process Instrumentation

Lecture 9 – Composition Analysis

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Introduction – Composition Analysis

- Industrial significance
- Spectroscopic analysis
- Gas analysis by thermal conductivity
- Analysis of moisture in gases
- pH ion concentration

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Introduction – Composition Analysis

- Industrial significance
- Why do we need composition analysis in process industries?
- Understand the BIG PICTURE
- 9 Phases in Process industries

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Introduction – Composition Analysis

- Spectroscopic Analysis

What is spectra? and Spectrum?

How it helps us in the analysis of composition of substances?

Classification of Spectroscopic Methods

Introduction – Composition Analysis

- Industrial significance
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Introduction – Composition Analysis

- Gas analysis by thermal conductivity
- Methods used
- Applications

Introduction – Composition Analysis

- Industrial significance
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- pH ion concentration

Introduction – Composition Analysis

- Analysis of moisture in gases (Humidity)
- Definitions
- Methods – Psychrometer, Hygrometer and Dew point
- Moisture measurements in Paper and Lumber

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Why to we need the composition analysis?

Understand the BIG PICTURE

9 Phases in Process industries

Why to we need the composition analysis?

1. Raw Materials
2. Process Control
3. Process trouble shoot
4. Yield improvement
5. Inventory management
6. Product quality
7. Safety
8. Waste disposal
9. Research and Development

Raw material to product

9 Phases

1. Raw Materials

- To check the purchase specification
- Detection of contamination in raw material by trace impurities
- Analysis check on raw material priced on an active – ingredient basis
- Water, fuels and other utilities
- Continuous analysis of raw materials delivered to manufacturing facility

2. Process Control

- Speed up and improve the process based on sample analysis
- Improves process control with more significant composition data

3. Process Trouble Shooting

- Composition data helps to trouble shoot the entire process

4. Yield Improvement

- Continuous analysis of process streams measure the effect of variables influencing yields
- Analysis in overflow or purge streams, re-circulated streams and sumps helps to determine the product loss.
- Detect the material build up of undesirable by-products that affects yield.

5. Inventory Management
   - Analytical monitoring of material flowing between process steps and plant areas to establish an inventory on the basis of active or essential ingredients.
6. Product Quality
   - Determination of product composition
   - Structural dependent attributes such as color, melting or boiling point and refractive index.
   - Assists in the adjustment of product to meet specifications.

7. Safety
   - Detection of leaks (toxic materials) in equipment's especially materials from leaks or spills that are not readily detected by human senses.
   - Detection of flammable or explosive mixtures in process lines.

8. Waste Disposal
   - Monitoring plant stacks for accidental discharge of toxic or nuisance gases, vapors or smoke.
   - Analysis of waste streams for toxic or other objectionable materials.

9. Research and Development

- Continuous analysis to speed up research and optimize results.
- Produce results in more directly usable form.

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Raw material to product

9 Phases

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Introduction – Composition Analysis

- Spectroscopic Analysis

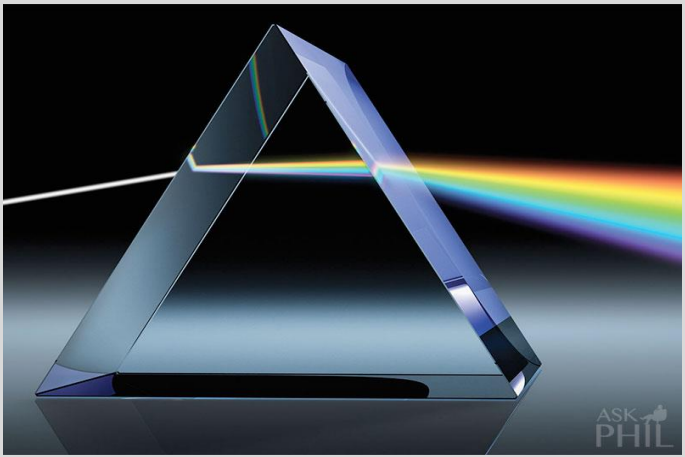
What is spectra and Spectrum as well?

How it helps us in the analysis of composition of substances?

Classification of Spectroscopic Methods

- Spectra

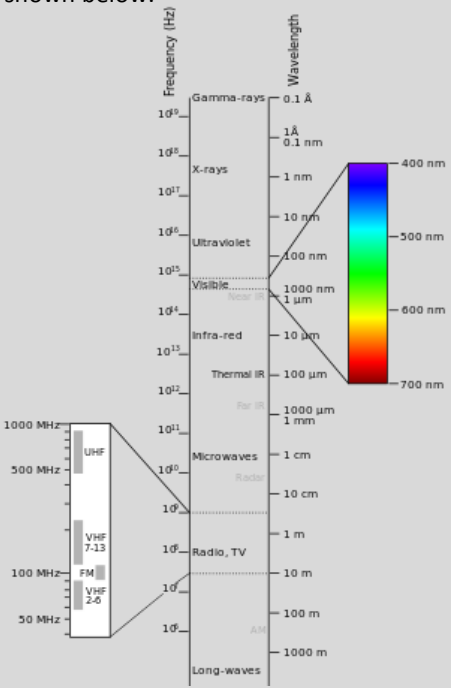
In the 17th Century, the word spectrum was introduced into optics by Sir Issac Newton, referring the range of colors observed when light was dispersed through a prism



Spectrum

The **electromagnetic spectrum** is the range of all possible frequencies of electromagnetic radiation as shown below.

- It is the range of all possible frequencies of electromagnetic radiation.
- It is a measure of light emission as the function of wave length or frequency.
- Hence the atomic and molecular spectra helps to identify the fundamental properties of different atoms of a substance.



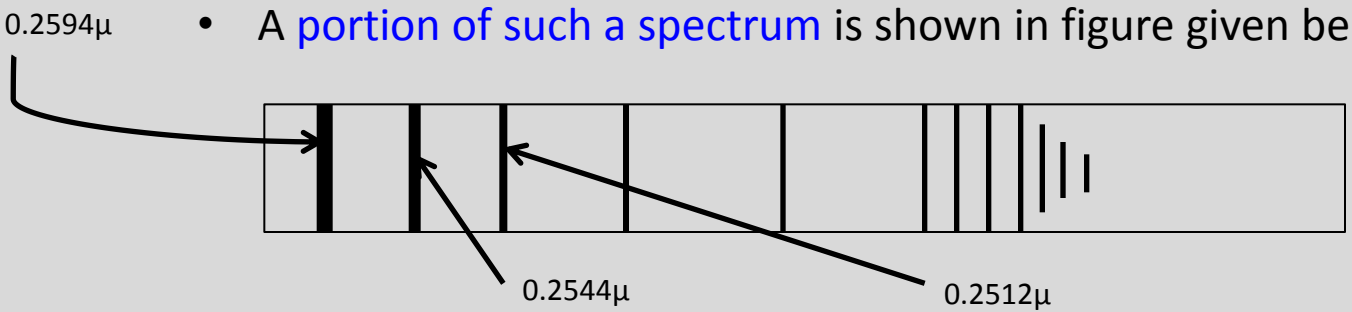
- Spectroscopic Analysis

- Composition analysis through atomic or molecular or crystalline characteristics constitute the spectroscopic methods, because atoms or molecules arranged in a given configuration uniquely identify the substance.

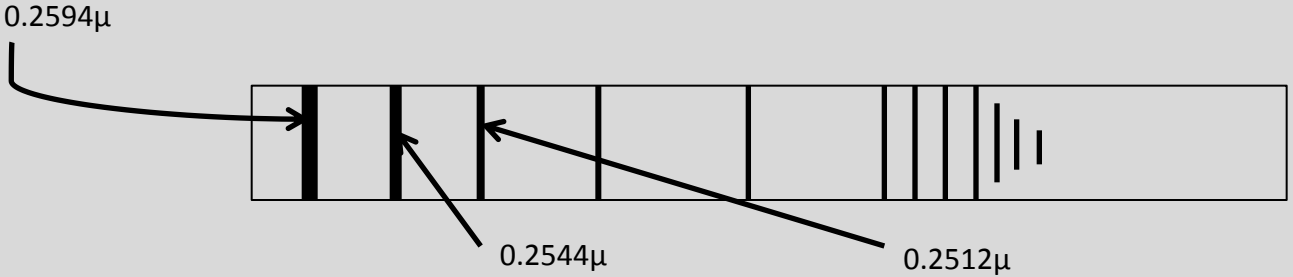
Thus it is possible to analyze substances where the quantity, number and identity of components are known.

Spectroscopic Analysis – Example

- Suppose that a light beam containing all frequencies is passed through a film of sodium and then through a refracting prism.
- The prism breaks the light beam into a spectrum which can be recorded on a photographic prism.
- A portion of such a spectrum is shown in figure given below

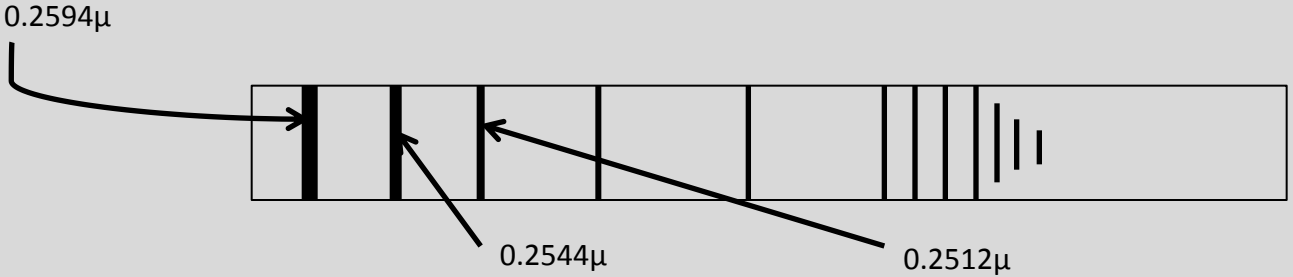


Spectroscopic Analysis – Example

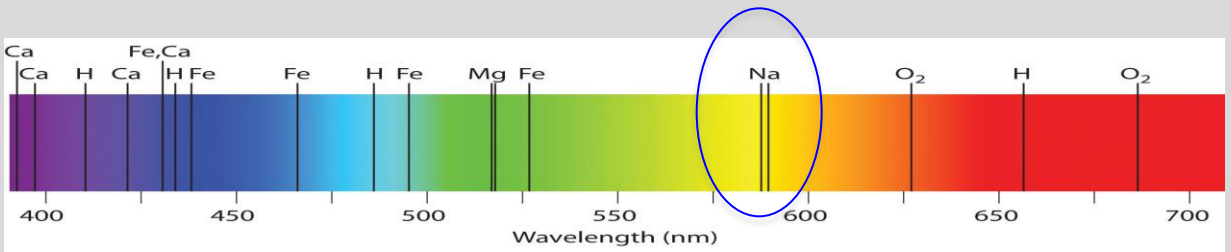


- Notice that several line indicates the frequencies absorbed by sodium.
- Each of the frequencies corresponds to particular change of energy levels of the atom

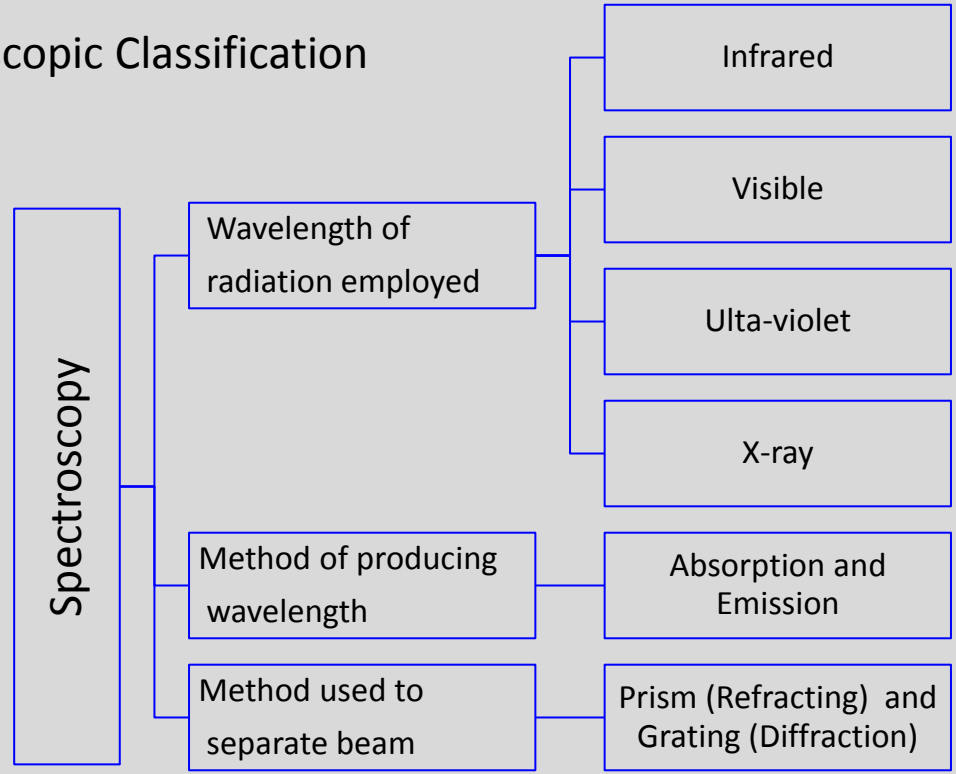
Spectroscopic Analysis – Example



- Thus, any compound containing sodium will produce these particular lines absorption spectrum.



Spectroscopic Classification



- Spectroscopic Analysis – Absorption Spectroscopy

•When Infrared , Ultra-Voilet or X- Ray radiation is passed through the sample of unknown material, certain frequencies of radiations are absorbed.

•This is determined by separating the radiation into a spectrum and measuring the intensity of radiation at each frequency.

•Absorption lines are dark lines on a light background on a photographic spectrum.

- Spectroscopic Analysis – Emission Spectroscopy

•It is accomplished by placing the sample of known substance in a flame or in an arc. This causes an emission of radiation based on the characteristics of substance

•By collecting the emitted radiation and separating it by refraction or diffraction, the intensity of radiation at each frequency are measured.

- Spectroscopic Analysis – Emission Spectroscopy

•An emission spectrum for an element is very similar to that of absorption spectrum, except of course, that each line indicates an absorbed frequency

•Emission lines are bright lines on a dark background on a photographic spectrum.

- Spectroscopic Analysis – Mass Spectrophotometer

•Yet another means of identifying substances in an unknown sample.

•A sample of unknown substance, usually a vapor or gas, is bombarded by an electron beam in an evacuated chamber.

•The bombardment produces ions by "knocking off" an electron from each of the various kinds of atoms present in sample.

- Spectroscopic Analysis – Mass Spectrophotometer

•The ions are then accelerated into a circular path, the radius of which varies with mass of the ions. Thereby the ions are sorted into beams.

•By measuring the strength of the each beam, all the various kind of the atoms present in the sample can be counted and identified, thereby enabling the composition of substance to be found.

- Applications - Absorption Spectroscopy

- UV Spectroscopy

  - Determination of vitamin components.
  - Benzene and Toluene in petroleum industries.
  - Butadiene in saturated hydrocarbons
  - Ethylene and carbonyl compounds.
  - Poly unsaturates in fatty acids

- Applications - Absorption Spectroscopy

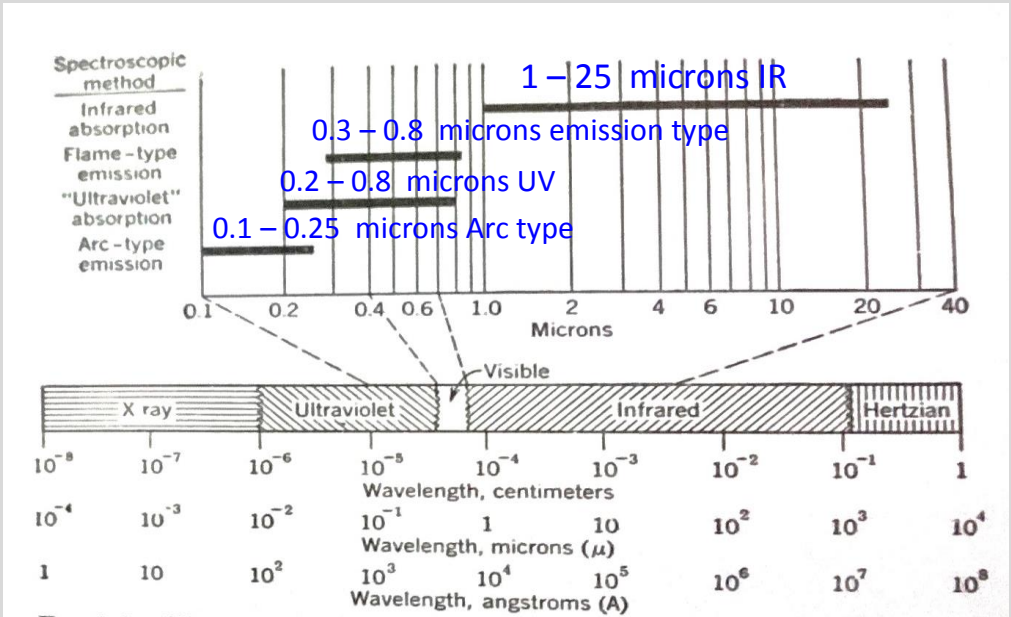
IR Spectroscopy

- In petroleum refining and synthetic rubber production for analysis of liquid hydrocarbons and gases.
- In pharmaceutical industries, such as penicillin production, they are used for determining the structure of compound.
- In chemical plants, they can be used for analyzing both organic and inorganic compounds.

- Applications – Emission Spectroscopy

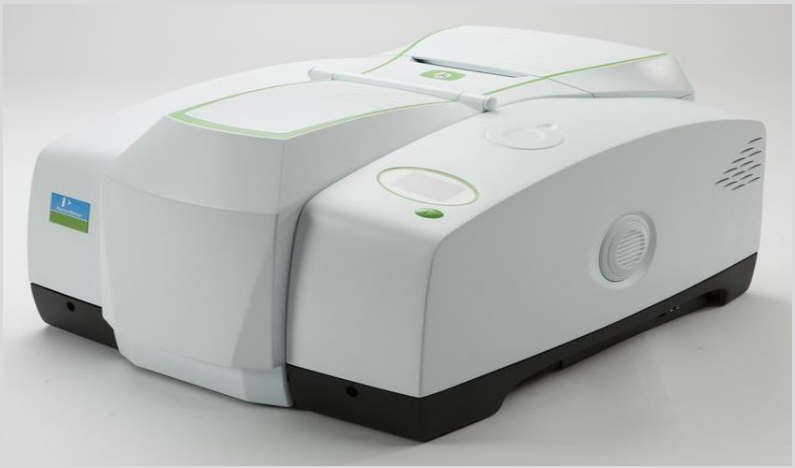
  - Can be employed for analysis of metallic compounds.
  - Used for magnesium, aluminum and steel analysis.
  - Used for analysis of inorganic compounds containing sodium and potassium and other elements such as boron, calcium, cobalt, copper, iron, lithium, magnesium, manganese and nickel.

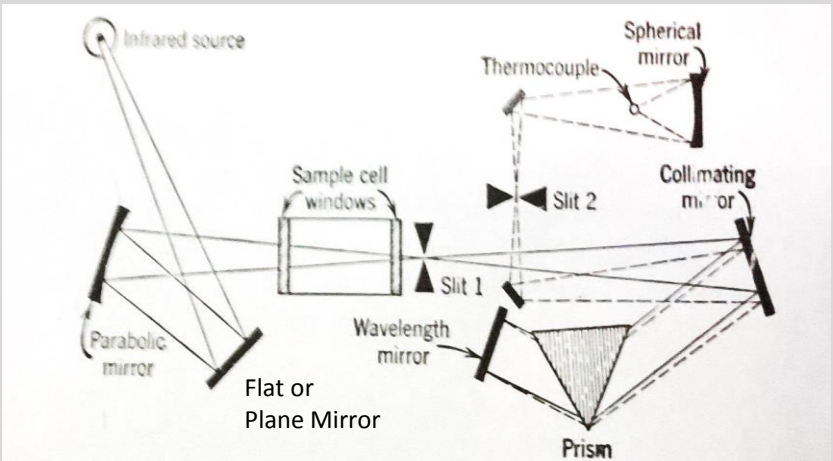
- Spectroscopy



Composition Analysis- Absorption Spectrophotometer

IR Spectrophotometer



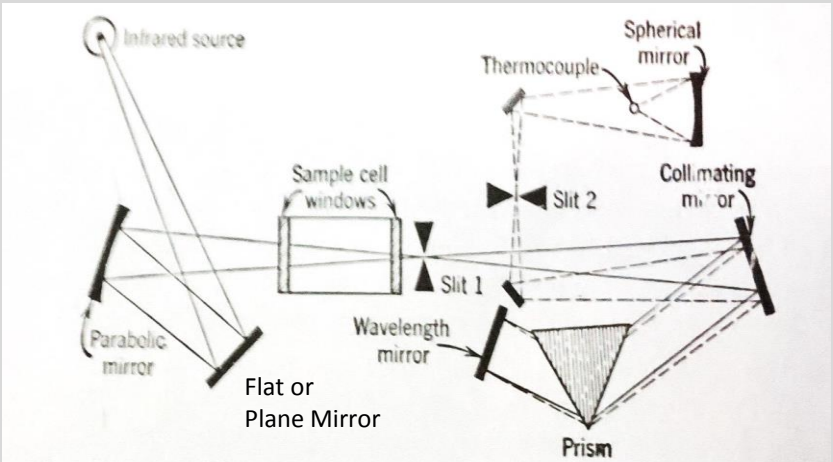


M/s. Perkin – Elmer Corporation

IR Spectrophotometer – Working Principle

When Infrared is passed through the sample of unknown material, certain frequencies of radiations are absorbed.

Separating the radiation into a spectrum and measuring the intensity of radiation at each frequency



M/s. Perkin – Elmer Corporation

IR Spectrophotometer – Working Principle

Beer's Law

$$C = \frac{1}{ax} \log_{10} \frac{I_o}{I_x}$$

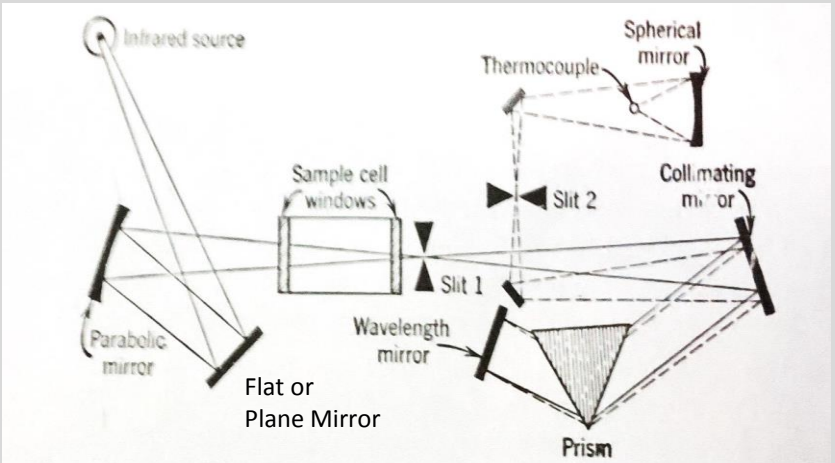
Where C = Concentration of substance

α = absorption factor of substance

x = thickness of sample (along the optical length)

I_o = Intensity of beam before the sample

I_x = Intensity of beam after the sample



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Spectrophotometer – Prism

Lithium fluoride	1 to 5.5 microns	Sodium fluoride	3 to 15 microns
Calcium fluoride	2.0 to 8.5 microns	Potassium bromide	15 to 25 microns

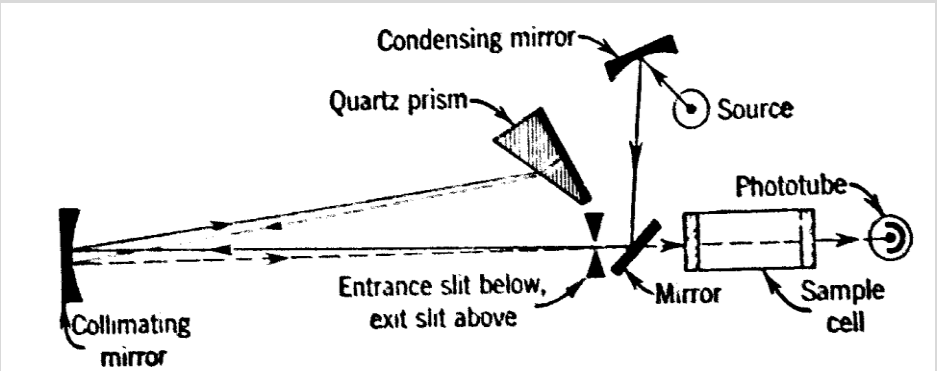
IR Spectrophotometer – Constructional features

Part	Function
IR source	Electrically heated thermal resistor is the source that provides IR radiation in the form of light beam
Plane or flat Mirror	Receives the radiation from source and reflects it to a parabolic mirror. The angle of reflection is equal to the angle of incidence in the plane or flat mirror
Parabolic Mirror	It collects the rays from the plane mirror and brings in a common focal point and project it to the sample window
Sample Window	Transparent glass window where the sample is placed and it allows the light waves to pass through it
Slit 1 and 2	It forms the beam of narrow width coming. That is the light waves (beam) passing through the sample window is made into narrow width
Collimating mirror	The light rays are brought into parallel and spread slowly as it propagates.

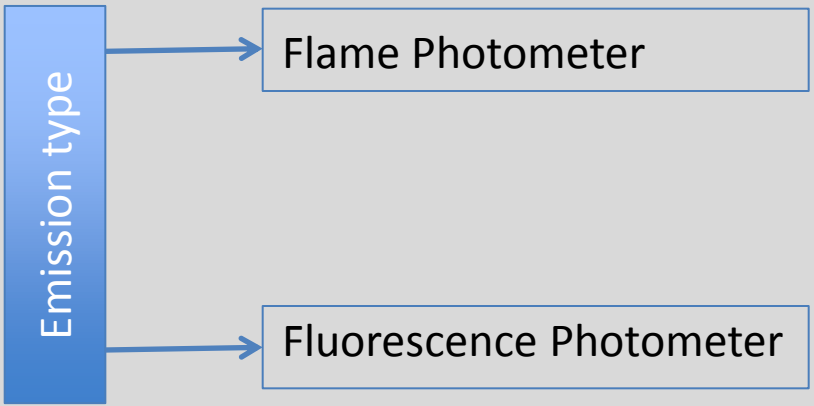
IR Spectrophotometer – Constructional features

Part	Function
Prism	It receives the parallel beams produced by the collimating mirror and refracts it.
Wavelength mirror	Reflect back to the prism in order to filter the spectrum
Spherical Mirror	It has a convex or concave type reflecting surface to collect the light beam from the slit and reflect it to the thermocouple
Thermocouple	To measure the beam intensity . That is the wave length passed to the thermocouple is measured by the angle of setting of wave length mirror

UV Spectrophotometer – Constructional features



Composition Analysis- Emission Spectrophotometer



Flame Photometer

A flame photometer is an instrument that is used mostly in inorganic chemistry to identify metal ions present in a sample.

The unknown sample is introduced to the flame at a constant rate, and then the photometer uses color to identify the metal ions present.

http://www.chemheritage.org/discover/collections/collection-items/scientific-instruments/perkin-elmer-model-52a-flame-photometer.aspx

Composition Analysis- Emission Spectrophotometer

Fluorescence Spectrophotometer

These are used in the analysis of some pharmaceuticals and vitamin compounds

The sample of substance placed in the spectrophotometer is irradiated with light of desired wavelength and the absorbed energy causes the substance to emit radiation.

By measuring the intensity of radiation the concentration of the sample substance can be found

This analysis is useful to avoid photochemical deterioration of vitamins

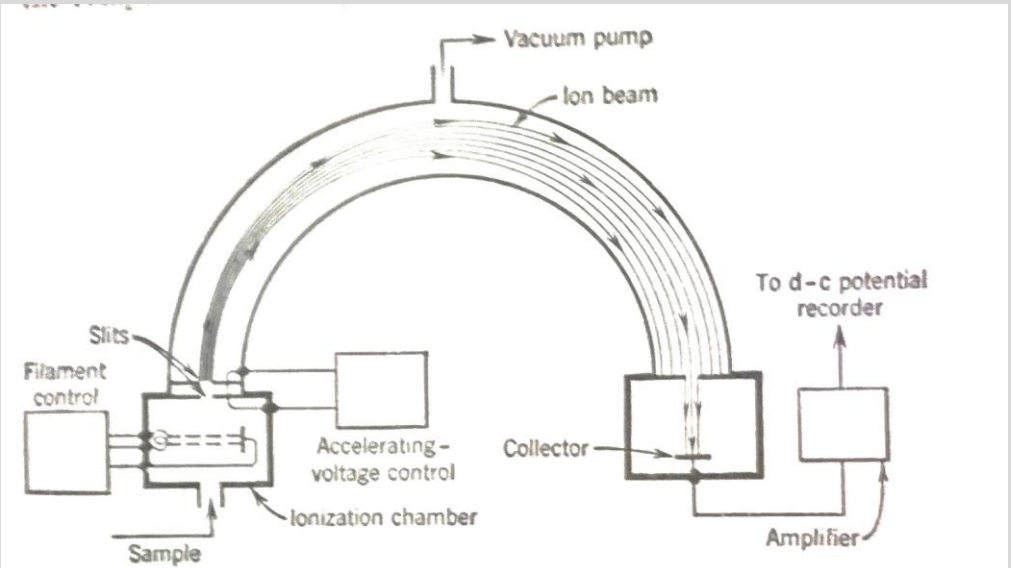
Mass Spectrophotometer

Stage 1: Ionization

Stage 2: Acceleration

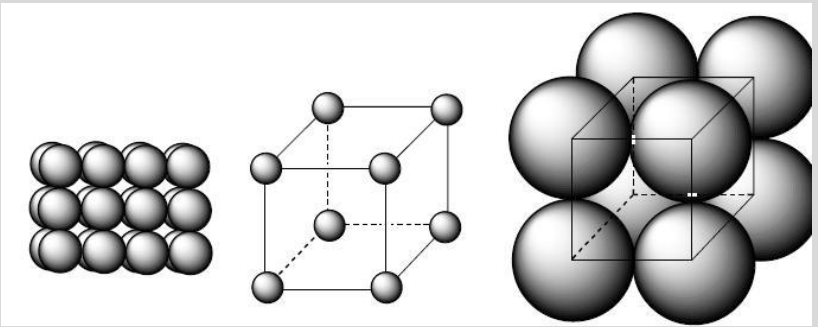
Stage 3: Deflection

Stage 4: Detection/Collection



X-ray diffraction

- In most of the crystalline and amorphous solids the atoms of each element of the substance lie in regular spacing and form so called space lattice.



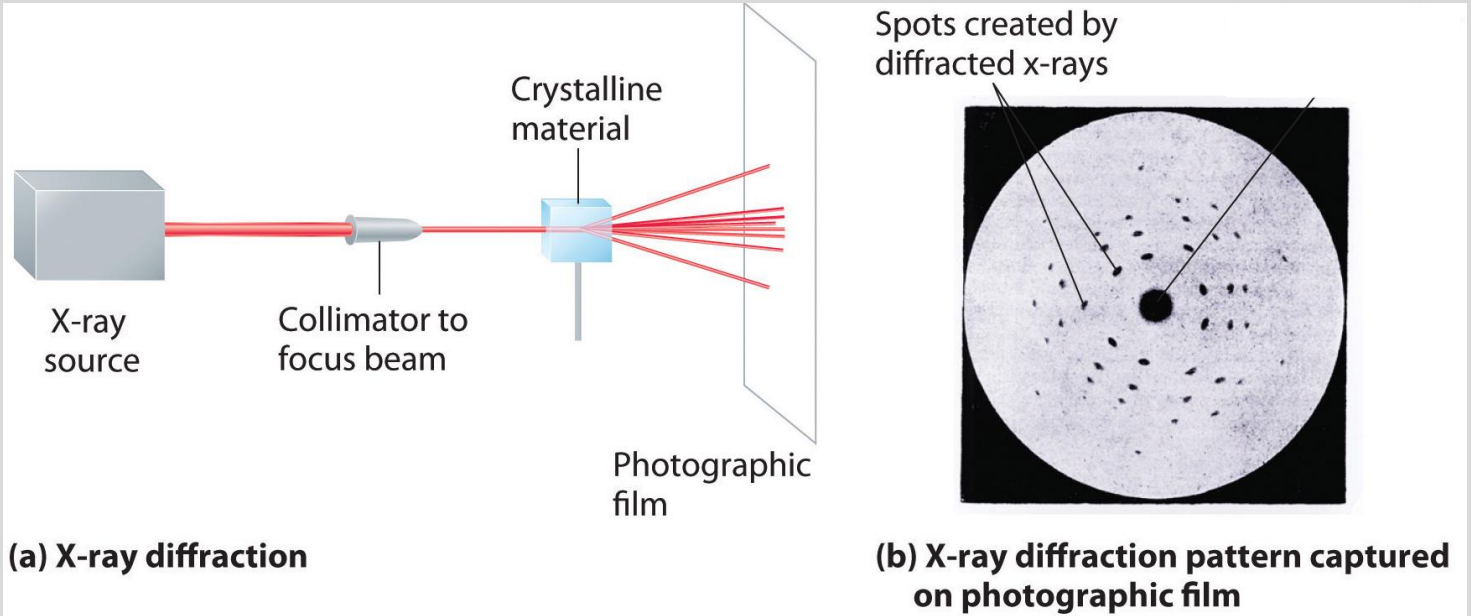
http://www.chem.fsu.edu/chemlab/chm1046course/solids.html

X-ray diffraction

- If X-Ray radiation of one frequency (monochromatic) if passed into a small sample of solid at specified angle, the radiation emerges from the solid in several beams, because some radiation is reflected in the given direction by certain rows of atoms and some is reflected in other directions.

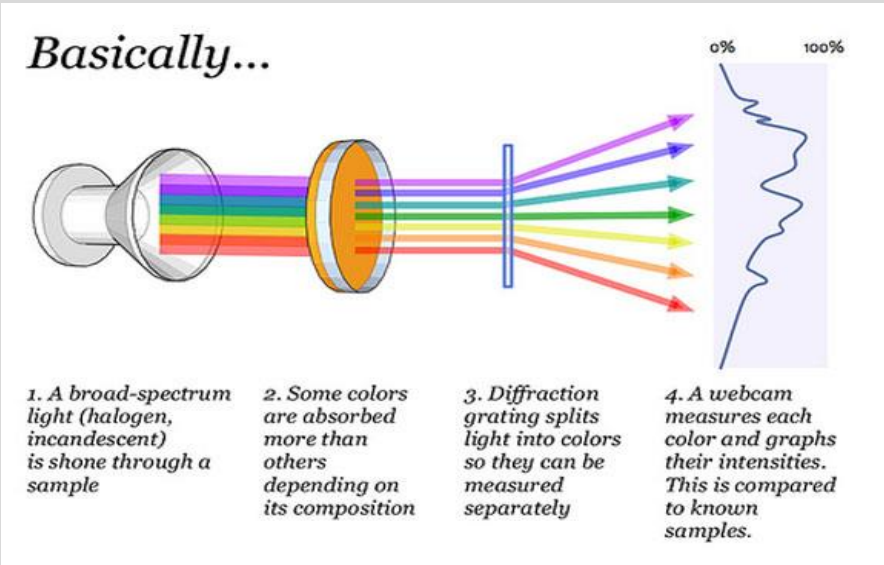
- Therefore a photograph of the diffracted beam will indicate certain arrangement and spacing of the atom of the substance

X-ray diffraction



http://www.xtal.iqfr.csic.es/Cristalografia/parte_02-en.html

Color Measurements by spectrophotometer



http://www.peachridgeglass.com/2013/05/color-measurement-latest-from-michael-seeliger/

Thermal Conductivity of gases

- Methods for determining quantitatively the composition of gas in a mixture is important for all kinds of industrial operations.

- Thermal conductivity is commonly employed to meet the above mentioned

Thermal Conductivity of gases

Used in the determination of the amount

- hydrogen, oxygen and nitrogen in air.
- ammonia, sulfur dioxide, carbon monoxide, hydrogen sulfide and hydrocarbons.
- combustion efficiency of fuel.

Thermal Conductivity

- Thermal conductivity is a property of particular substance.
- Higher the thermal conductivity, more the heat conduction through the substance.
- Apparently the thermal conductivity of a substance depends on the chemical composition, phase (solid, liquid, and gases), crystalline structure (if solid), temperature, pressure and its homogeneity.

http://nptel.ac.in/courses/103103032/module/lec2/1.html

Thermal Conductivity

$$Q \; a \; A\frac{DT}{Dx}$$

$$Q = - kA\frac{DT}{Dx}$$

Heat transfer per unit area, W/m^2

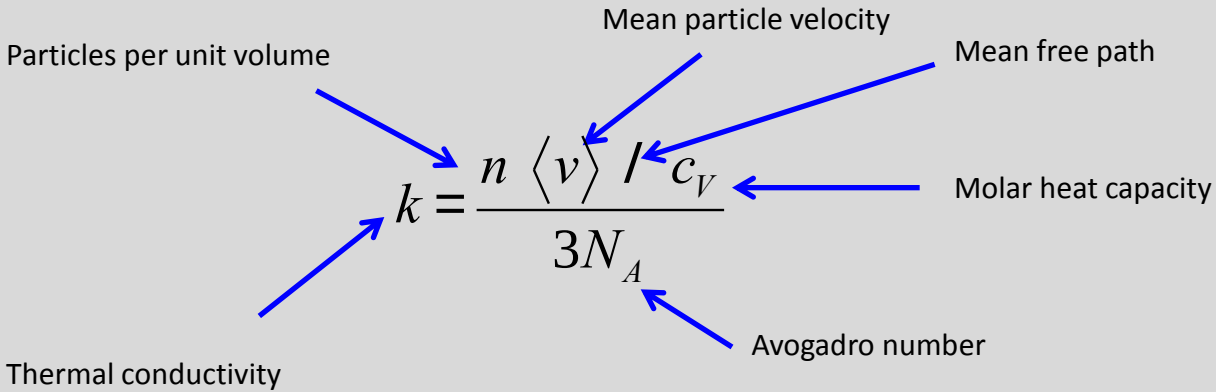
Change in temperature, K

$$\frac{Q}{A} = - k\frac{DT}{Dx}$$

Change in the thickness, m

Thermal conductivity, W/m K

Thermal Conductivity for gases



For an ideal gas heat transfer rate is proportional to average molecular velocity, the mean free path, and molar heat capacity of the gas.

www.hyperphysicsphy-astr.gsu.edu/hbase/thermo/thercond.html#c3

Composition Analysis- Thermal Conductivity of Gases

Gas analysis by thermal conductivity

- Thermal conductivity depends on the chemical composition of the substance.
- Thermal conductivity of liquid is more than the gases and the metals have the highest.
- Thermal conductivity of gases and liquids increases with increase in temperature.

Substance	Thermal Conductivity (W/m·°C)	
Gases (at 1 atm. pressure)	At 0°C	At 100°C
Carbon dioxide (CO_2)	0.0146	0.02224
Nitrogen (N_2)	0.02404	0.03086
Air	0.02408	0.03127
Oxygen (O_2)	0.02449	0.03226
Liquid	At 0°C	At 50°C
Lubricating oil (SAE 50)	0.147	0.142
Glycerine ($C_3H_5(OH)_3$)	0.282	0.287
Water	0.5619	0.6405
Solid		
Metal	At 0°C	At 100°C
Steel	73	67
Copper	386	379
Silver	417	415
Non-metal		
Asbestos	0.151 (at 0°C)	0.192 (at 100°C)
Brick	0.69 (at 0°C)	0.185 (at 600°C)
Marble	2.77 (at 20°C)	-

Composition Analysis- Thermal Conductivity of Gases

Gas analysis by thermal conductivity

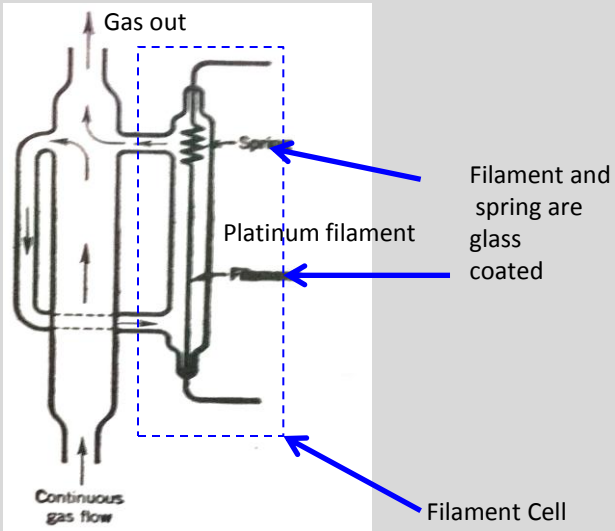
- A mixture of hydrogen and dry air produces a relative thermal conductivity from 1.0 to 6.98. i.e. 1 for 0% hydrogen and 6.98 for 100% hydrogen

- The thermal conductivity of these two gases can be related to concentration of each component.

- It is apparent that, in a mixture more than two gases, thermal conductivity is a measure of concentration of two components only if all the components of gas mixture present in constant amount.

Gas Analysis by thermal conductivity

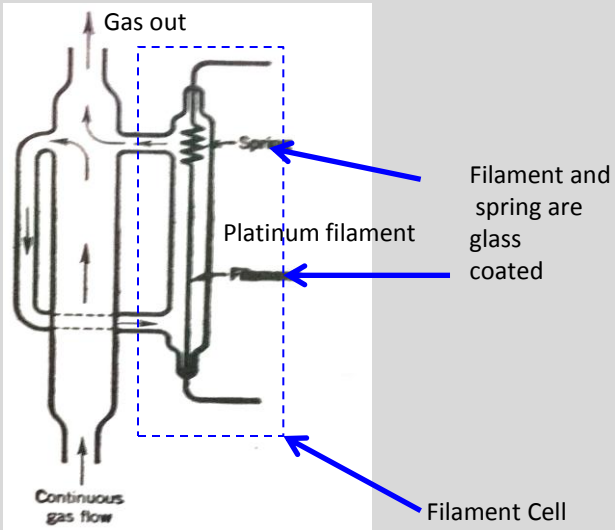
Thermal conductivity cell



- The cell is constructed with glass.
- The right hand side tube contains a platinum held under constant tension by a spring.
- The filament and spring are glass coted
- The gas flow occurs at constant rate by natural convection through filament cell.

Gas Analysis by thermal conductivity

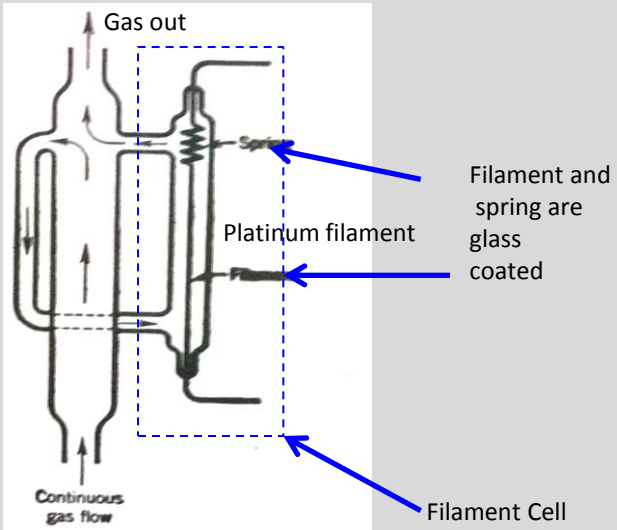
Thermal conductivity cell



- When gas flows through the filament, the heating of filament and consequent temperature rise of the filament depends on the rate at which heat is conducted away from the filament
- That is depending on the thermal conductivity of the gas inside the tube the filament attains steady sate thermal conditions.

Gas Analysis by thermal conductivity

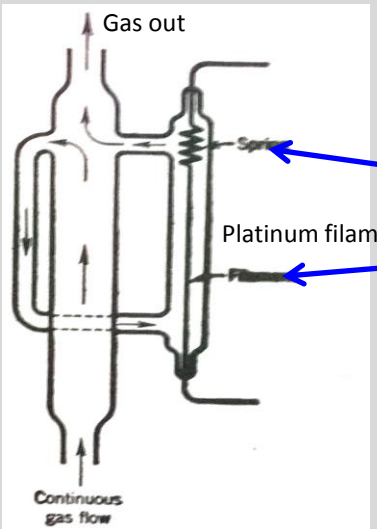
Thermal conductivity cell



- The resistance of the filament towards its thermal conductivity by gas serves as the reference for the identification of various components present in the gas mix.
- The change in resistance of the filament is converted into an equivalent output voltage through a wheat stone bridge circuit.

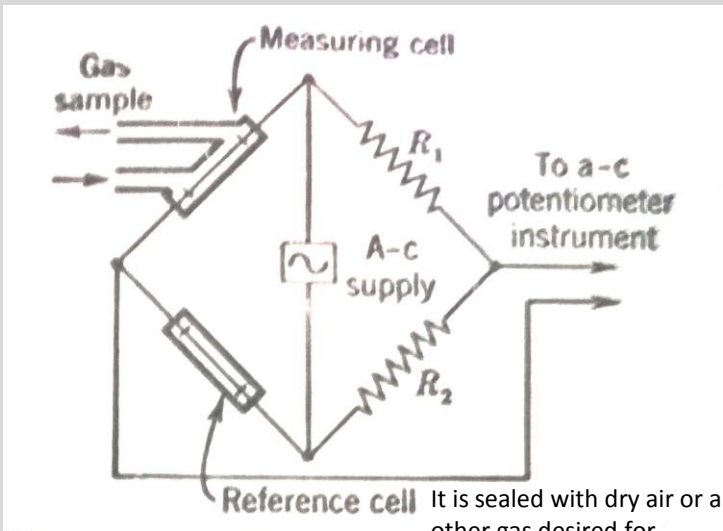
Gas Analysis by thermal conductivity

Thermal conductivity cell



Filament and spring are glass coated

Resistance bridge circuit



It is sealed with dry air or any other gas desired for reference.

References

1. Donald P. Eckman, (2004) *Industrial Instrumentation*, CBS Publishers, Pp. 1- 27.

Thank You