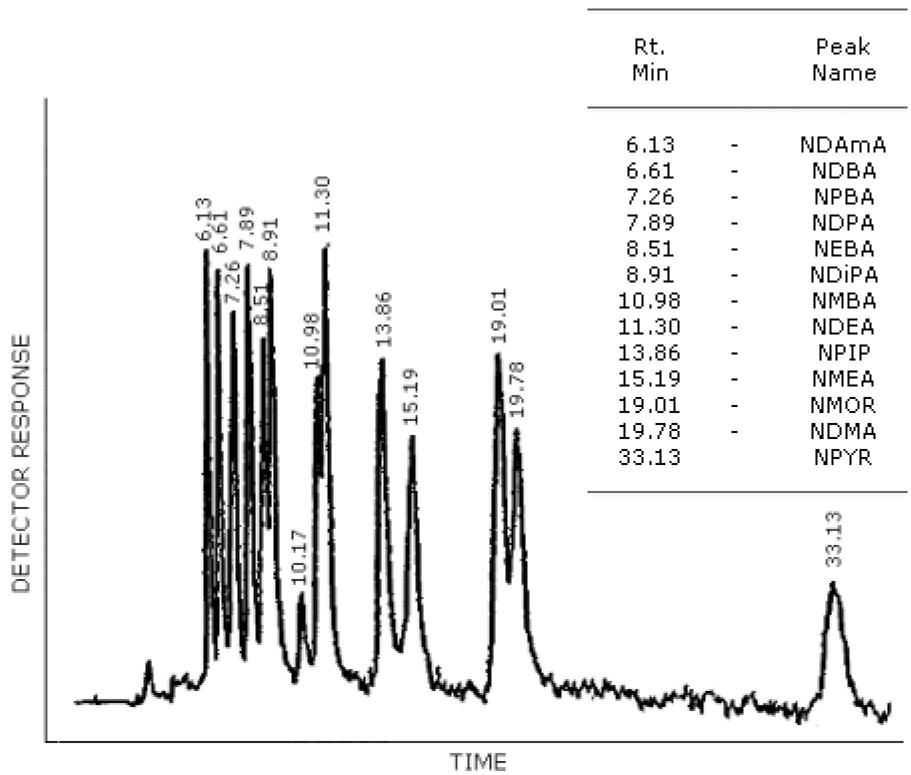
Analytical Instrumentation Lecture Notes

Introduction to Chromatography

Chromatography, ohh the editor showing me this as a error !! But i am sure u must be known to aleast to this word that u can say such a word exist. This is a common and simple instrument in analytical instrumentation.

The technique is used for analysis of available chemical components in a fluid(gas or liquid) mixture. The technique adopt several methods to separate the components and then detecting the concentration of each component.



A Sample Chromatogram

The output is graph with time in x-axis and concentarion of different components on the Y-axis

What is the Principle and the method ?

when a fluid is allowed to pass through some another fluid or solid tunnel, the rate of flow for the components of mixture will be different. So at the other end of the tunnel the components will reach at different time.(the medium or the column called separator).

OK now our job turned easy becoz we know which component will come out at which time(its called retention time). we have to detect the gas coming out at different time.

Why different retention time?

Now the questions is why these components(our analyte is a mixture of different molecules and ions). The prime cause is the average speed. Acording to kinetic theory the average speed of gas molecules will depend upon its molecular mass.

except this there are different processes invloved in side the chromatography column/channel. The molecules may be adsorbed on the columns inner surface temporarily and then released. this stick and release may happen many times before it comes out of the column.

Scintillation, luminescence, Fluorescence & Phosphorescence

All these three are used in instrumentation engineering. But is this all are the same, what is the relation, similarity or difference between these processes.

florescence means absorbing energy in some higher energy or higher frequency band end emit in lower band.

luminescence is the type radiation from a cold body. here the excitation of the molecules must be by some other method than heating.

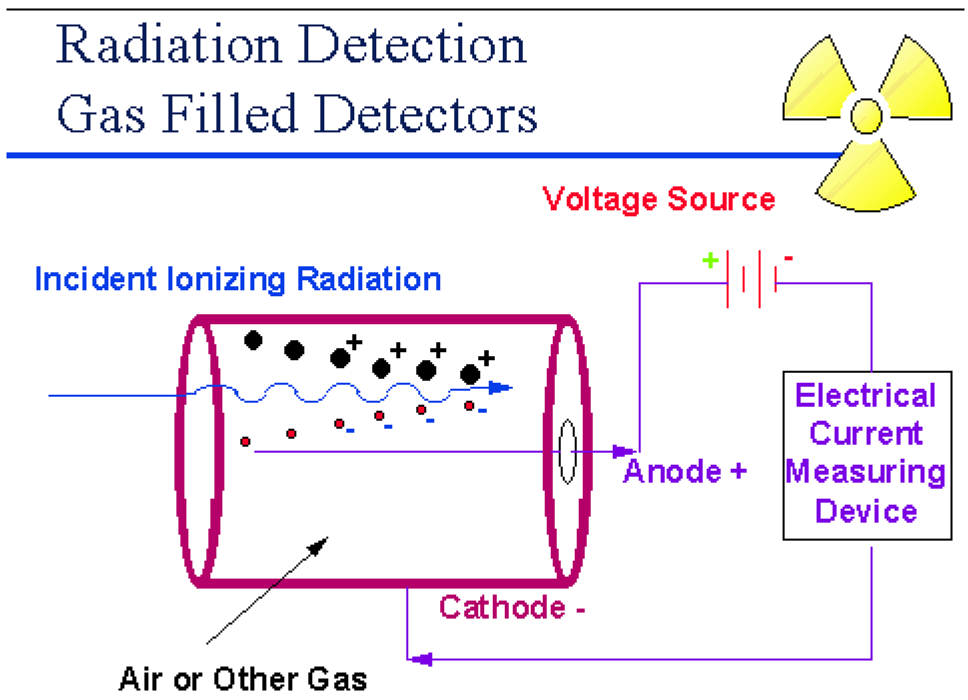
Scintillation is when the material is excited by some radiation and give out some emission in lower band(visible range)

X-Ray Detectors

X-Ray Detectors are same as the radiation detectors used for detection of neutral (chargeless particle) radiation detectors.

These are two types

Gas Ionization Chamber
Solid State detectors
Gas ionisation chambers are generally a tubular structure in which a gas placed between two electrons allowed to be exposed to the radiation. which in turn ejects out an electron from the gas atoms shells giving a charge particle (ionised gas atom). This ion can now be drifted by the electric field. The ion is collected at the anode(+ve) so producing a pulse of current in circuit.



X-Ray Methods in Analytical instruments

What is X-Ray ?

X-Ray is an electromagnetic wave with frequency 3x10E16Hz to 3x10E19 Hz or in wavelength scale 0.01 to 10 nano meters i.e. shorter than UV and longer than gamma radiation. In energy scale 120eV to 120 KeV. these are em waves with High penetrating Power.

What are the Properties useful for Us?

Penetration power: this ray can penetrate deep into metals atteneuting throughout. So can used probe into solid blocks.

optical Resolution: as per raleigh criterion the resloution of an optical microscope increases with decrease in wavelength and these are em waves with lowest wavelength.

Diffraction:Wavelength suitable for crystalography. The planes of crystals produce a diffraction pattern when radiation of suitable wavelength target on it. the xray wavelength suitable for this.
as pern barggs equation
2dsin(theta)=n x Lambada

Spectroscopic Analysis: T**he emission / absorption is not just a single line or just a single band.** It is a set of quantized bands. Now you can say then sodium(Na) has only two lines 589.0 and 589.6 nm , yes it is true if you are looking only at the visible spectra.
there are more spectras which belongs to transition other than 3p1/2->3s1/2(589nm) and 3p3/2->3s1/2(589.6nm).

We have more no of spectra for most of the elements in X-ray region.
What are the classes ?

These rays are categorised according to penetrability through matter. Hard Xrays (12ev to 120Kev)/0.1 to 0.01nm wavelength. and soft xrays (0.12 to 12KeV)/(10->0.1nm). These are sometimes also classified as per the method of generation or its spectrum.

Continuous / white X-ray
Discrete / Characteristic X-ray

Generation Methods:
There are two methods two generate x-ray based on two physics processes.

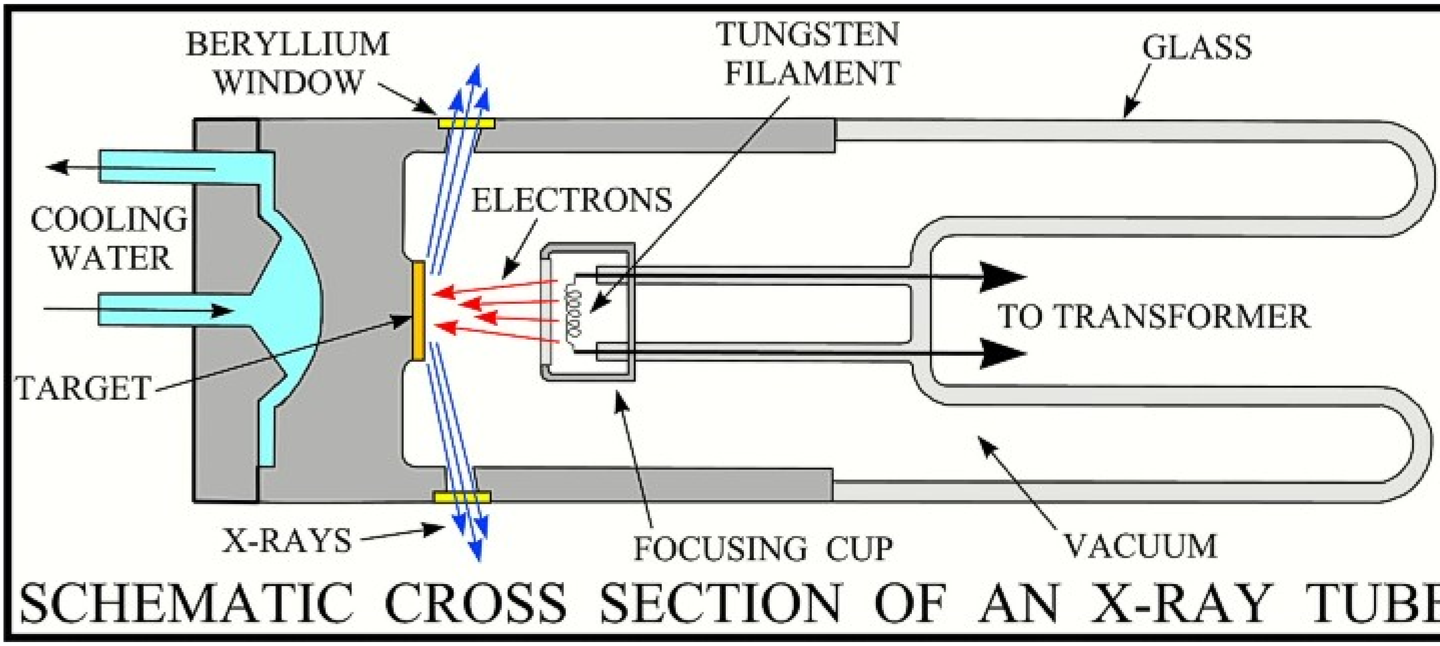
Flouroscence: when a high energy photon stikes a electron it ejects out the electron from the shell leaving a blank space. That blank space filled by a electron from upper shell which means dexcitation of the electron so there is a emission of a photon.

Bremhallstrahlung: This is radiation given off by the electrons as they are scattered by the strong electric field near the high-Z (proton number) nuclei. These X-rays have a continuous spectrum. The intensity of the X-rays increases linearly with decreasing frequency, from zero at the energy of the incident electrons, the voltage on the X-ray tube.

So the resulting output of a tube consists of a continuous bremsstrahlung spectrum falling off to zero at the tube voltage, plus several spikes at the characteristic lines.

X-ray Generation Techniques:

X-ray is generated by X-ray tubes. I have diagram of the two oldest tubes and the commercial tube. The basic design is same as we have to achieve the process "bombardment of high eneergy electron beam over some metal surface". The enhancements in this tube is
1) Enhancement of the cathode (use of filaments, use of isolated filament)
2) Use of cooling systems for anode.
3) Replaceable anode as the anode is continuously corroded.
4) Rotating anode tube



The output of the X-Ray tube is dependent on the enrgy of the electron beam, which in turn dependent on the electric field provided by the applied potential.
So the applied potential will be one key parameter for the output energy.

Another Key factor is the anode temperature, how much heat the anode can sustain, only 0.05% of the electron beam is converted to x-Ray then what happen to rest part is converted to heat. So this amount of heat should be dissipiated in anyway otherwise our anode will melt down.

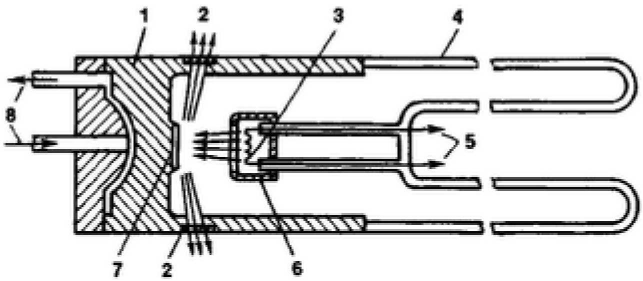


Figure 1. Schematic of an X-ray tube for X-ray diffraction analysis: (1) metallic anode block (usually grounded); (2) beryllium window for exit of X-radiation; (3) hot cathode; (4) glass envelope insulating the anode part of the tube from the cathode part; (5) cathode leads, to which the filament voltage and high (with respect to the anode) voltage are supplied; (6) electrostatic electron-focusing system; (7) anode (anticathode); (8) inlet and outlet pipes for the flowing water that cools the anode block

Do We Use Thorium The Radioactive Carcinogen

Here in berhampur we have a Plant of DAE extracting rare earth materials from sea beach mud. The prime element is Thorium a radioactive element can be used as a nuclear fuel.

But the intresting fact is we are using it in home also. Yes that is **inside the picture tube, in gas lamp mantels.** In lab its with the Photo MultiPlier Tube (PMT), PMT is are inside almost every analytical instruments.

Why is it used in picture tube ?

Filaments in electronic tubes and television picture tubes have be coated in thorium oxides to produce electrons more easily

Radioactivity:

Thorium oxide coated gas lamp mantles used in ornamental gas lanterns and gas burning camping lamps are radioactive. The thorium oxide is chosen because it can be raised to white heat without decomposing. However, the mantle does become extremely fragile and will powder into a fine ash which can potentially be inhaled or ingested. Thorium is a natural alpha emitter with the potential for increasing lung tumors. Thorium disintegrates to produce radon-220, an alpha particle emitting radioactive gas.

A number of substances have been used as positive contrast agents: silver, bismuth, caesium, thorium, tin, zirconium, tantalum, tungsten and lanthanide compounds have been used as contrast agents. The use of thoria (thorium dioxide) as an agent was rapidly stopped as **thorium causes liver cancer.**

For conventional dynode materials, such as BeO and MgO, a multiplication factor of 10 can normally be achieved by each dynode stage.
Microchannel plate detector

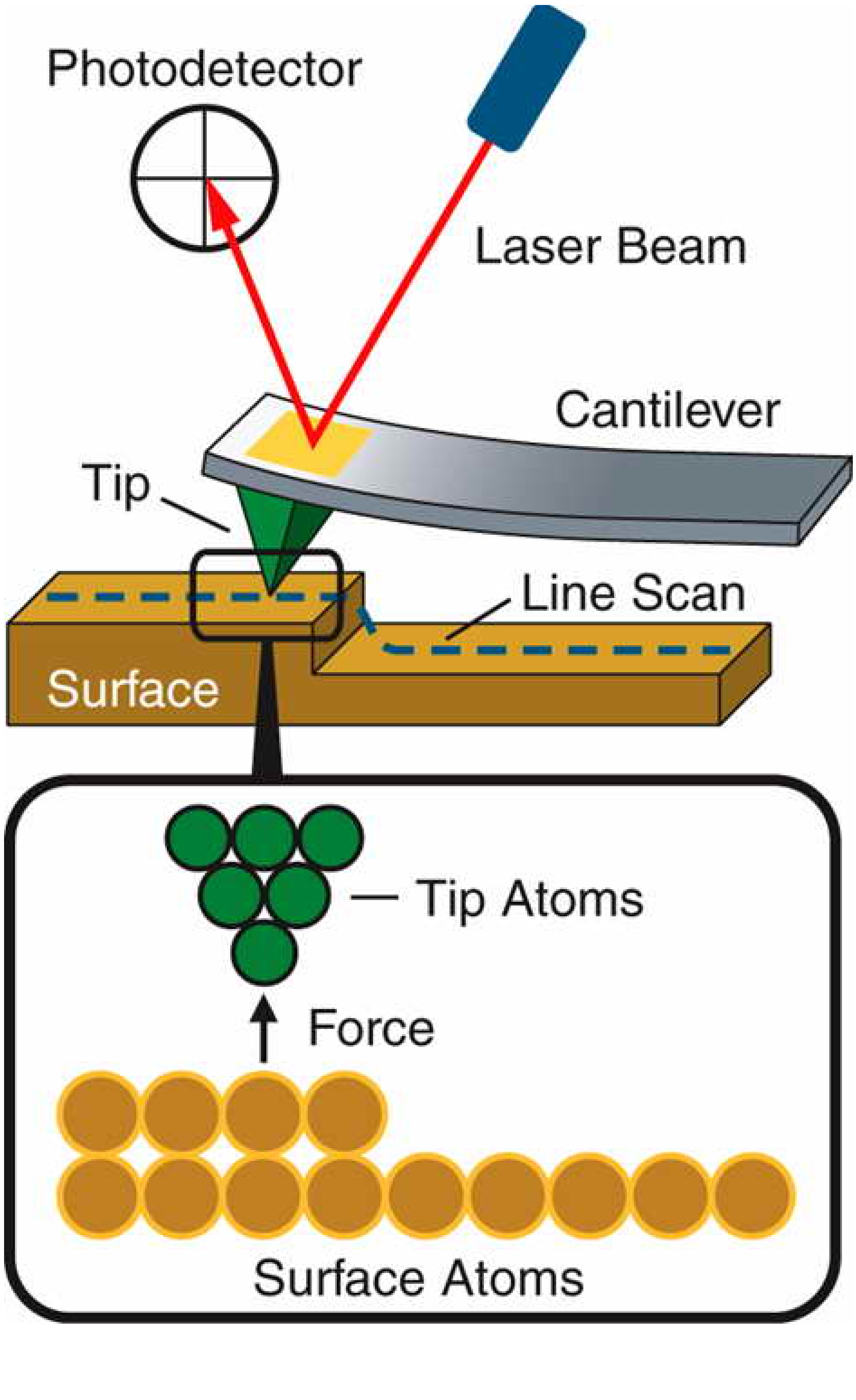
Scanning Tunneling Microscope(STM) & Atomic Force Microscope (AFM)

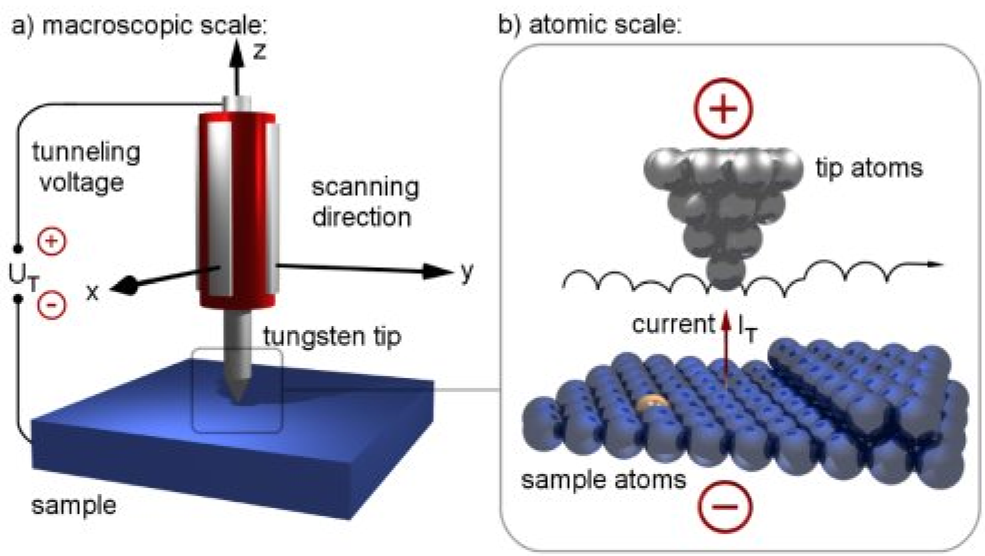
STM & AFM

Scanning Tunneling Microscope (STM)

These are devices 2D & 3D Surface analysis of Materials at micrometer resolution. Scanning Tunneling Microscopic is based upon the tunneling theory i.e. an electron may tunnel (or jump) through a barrier when the barrier is thin enough. So produces

an elctric current at the surface. If we can use a microtip probe. we can monitor the tunneling current profile in a 2D surface. Which will give a 2D picture of the atomic structure. But the necessary condition for the probe to get image at atomic scale is that the probe shou
ld be moved at such resolution.
Here comes the role of Piezo transducers, we have used steppers Servos for precison positioning but when the precison we need is of micrometer level we have the only option Piezo Transducers.


Photodetector
Laser Beam
Cantilever
Tip
Line Scan
Surface
Tip Atoms
Force
Surface Atoms

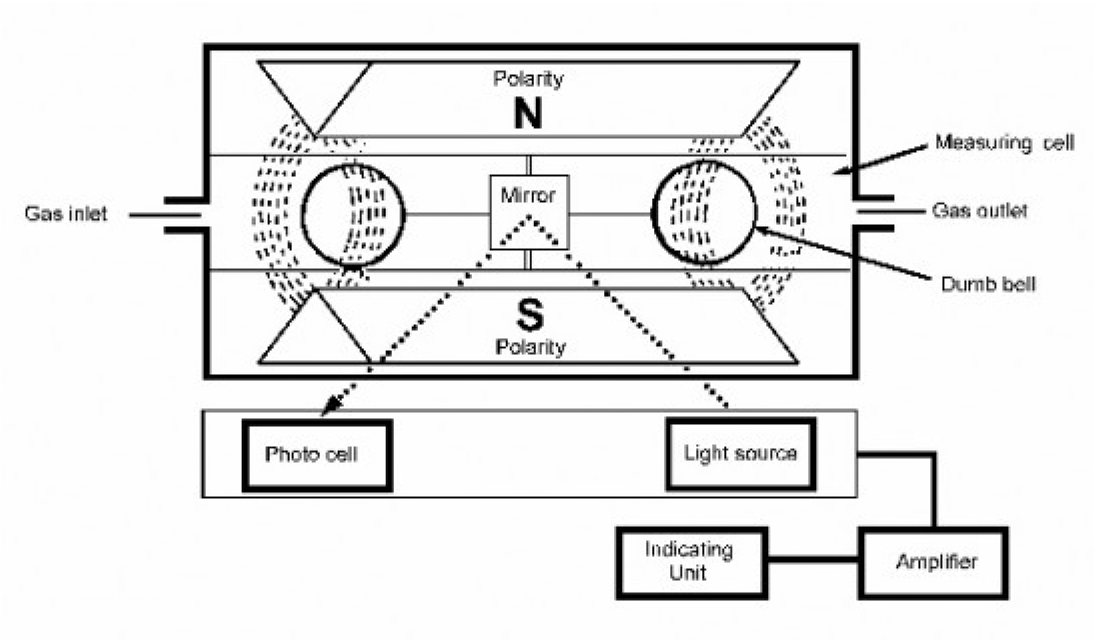


As we know Piezo materials produce Structurals change (expand or compress) in the axis of applied field. So for an X Y scan we can use two piezo plates or a single block and the probe at a corner. Commonly we use two piezo plates at two sides.

Some more PIC of AFM

ParaMagnetic Gas Analyser GA-2

This method is primarily for oxygen content analysis. As the method described is suitable for paramagnetic gases its usable for few industrial gases.



Block Diagram Paramagnetic Gas Analyzer

This method is primarily for oxygen content analysis. As the method described is suitable for paramagnetic gases its usable for few industrial gases.

Relative volume magnetic Susceptibilty at 20deg celcius(Zero ref:Nitrogen, 100 ref O2)
Oxygen 100.00
Nitric Oxide 43.00
Air 23.50
Hydrogen 0.24
Carbon monoxide 0.01
Nitrogen 00.00
Nitrogen Oxide -0.20