Atomic Absorption spectrometer :-

Theory :-

If a solution containing metallic salt is aspirated into flame A vapour which contains atoms of the metal is formed some of the gaseous metal atoms may be excited to higher energy levels and permit the emission of radiation is a characteristic of metal This is flame emission.

How ever a large number of gaseous metal atoms remain in ground state. These ground state atoms are capable of absorbing radiant energy of their own resonance wave length (or)

In general, the wave length of radiation, the atoms would emit it excitation from the ground state. Hence it a light resonance wave length is passed through a flame containing the atoms a part of the light is absorbed.

Principle :-

The extent of absorption is proportional to the number of ground state atoms present in the flame. This is the principle of AAS.

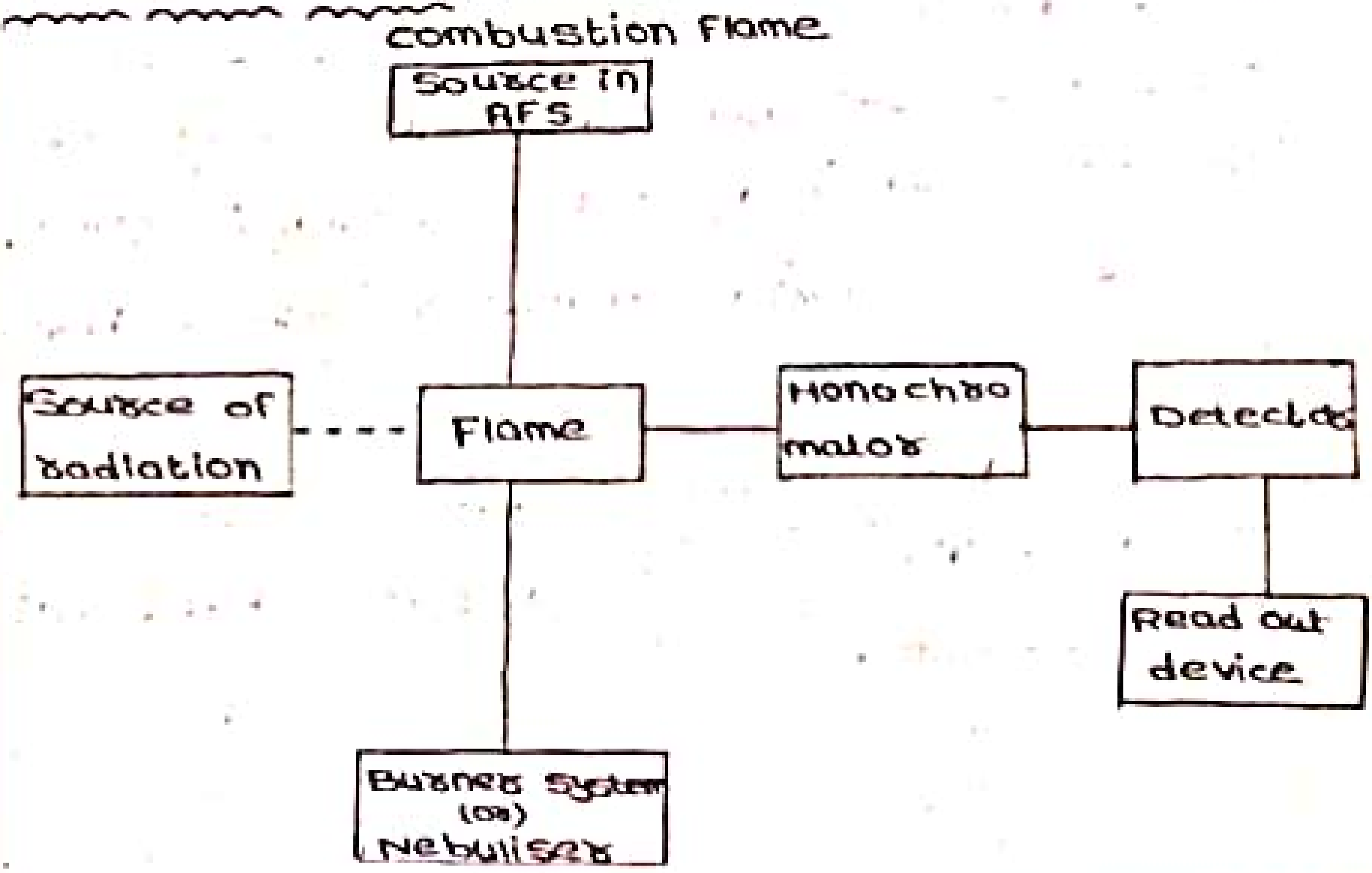
when a sample is introduced into flame, then following steps are

(1) Evaporation of solvent leaving a solid residue.

(2) vaporisation of solid and dissociation into constituent atoms

(3) some atoms exit by thermal energy of flame to higher energy levels.

* Instrumentation :-



The basic design of the AAS and the subsystems are shown in follows. The important component in AAS are

(1) source of radiation

(2) combustion flame

(3) Nebuliser burner system

(4) Monochromator

(5) Detector

(6) Read out device

(1). Source of radiation :-

This is 2 types They are

(a) continum source

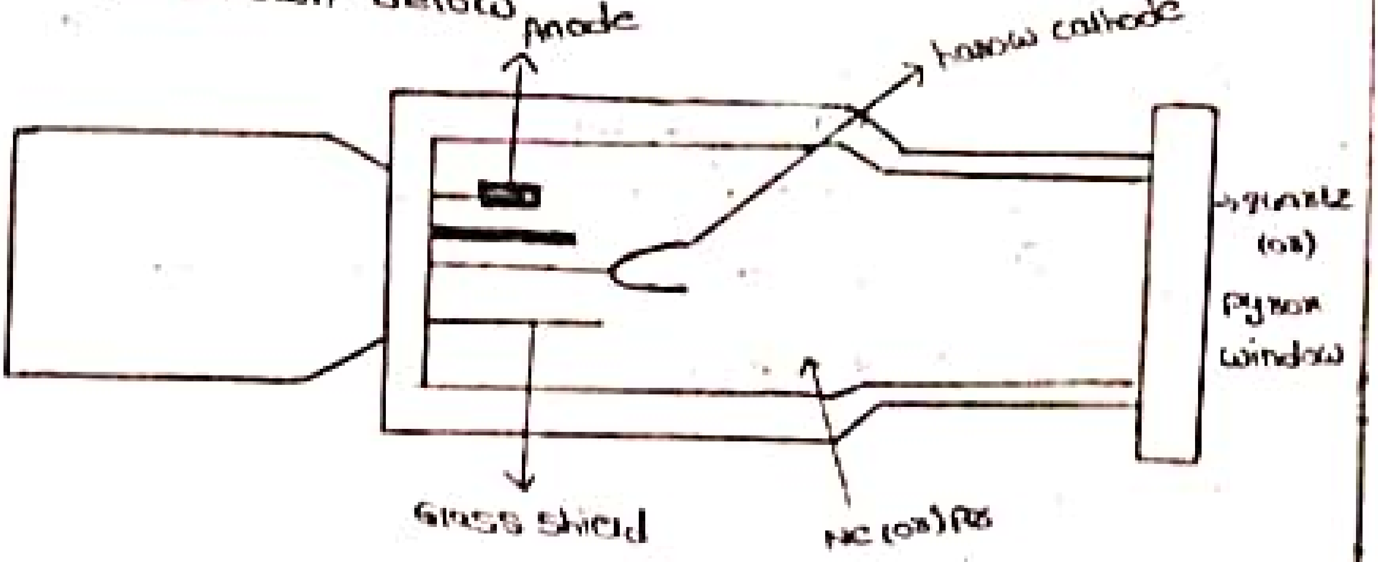
(b) line source

(a). continum source :-

Xe (or) D_2 lamp containing Xe (or) H_2 lamp at high pressure are used as best continum source. These lamps emit band of radiation when excited electrically out of desired wavelength is selected.

* (b) line source (or) Resonance line source hollow cathode lamp :-

Hallow cathode lamps are widely used in AAS as a line source. The diagram of hollow cathode lamp is shown below



Hallow cathode lamp is a glow discharge tube consists of hollow cylindrical cathode made of the element of interest. It consists of an anode enclosed in a glass enevelop filled with Ar (or) Ne gas at reduced pressure having a window made of si (or) Borosilic [illegible] the wa

length of the spectrum emitted.

when a voltage is applied between the ele trodes of hallow cathode lamp, a glow discharge of gass and electron passes from cathode to anode The filled gas is ionisation takes place due to no elastic collisions of gas atoms. These gas ions are accelerated by the applied potential and colloid cathode releasing a cloud of metallic atoms from it surface. This process is called spettering.

.. A Photon of sputtered metal atoms are Excited to higher energy levels states by collision These excited metalic ions returns to the ground state by emitting wave length of radiation. The emit light is transmitted through a glass medium and it Servers as a line source.

The cathode and anode are designed to Produce a stable dischanged of radiation, narrow of width 0.01nm.

The efficiency of hallow cathode lamp is d pend upon its Geometry and oprating potential high Potential high currents lead to greater intensities advantage is increase in Doppler. Broadaning of emiss lineas from the lamp further the greater curren produce on increased number of an emited atoms the cloud.

(2). combustion flames:-

* For flame spectroscopy flame produce temperature of order about 2000°c.

* In AAS a combustion of fuel gas and oxident gas are used.

* The temperatures given by some mixture of gases are below.

S.NO	fuel gas	oxident gas air.	oxident gase(N_2O)
1	Acetylene	2.200K	3,200K
2	Propane	2300K	3,000K
3	Hydrogen	23.20K	2,900K

we observe the different flames are used for the analysis of different elements.

(3). Nebulizer - burner system:-

The purpose of Nebulizer burner system is to convert sample solution to gaseous atoms. The function of Nebulizer - burner system (NBS) produce aero solution of the test solution.

The NBS is classified into two types They are

(1) Flame technique.

(2) Non - flame technique.

* Flame technique:-

In flame technique is two types of burner systems are their.

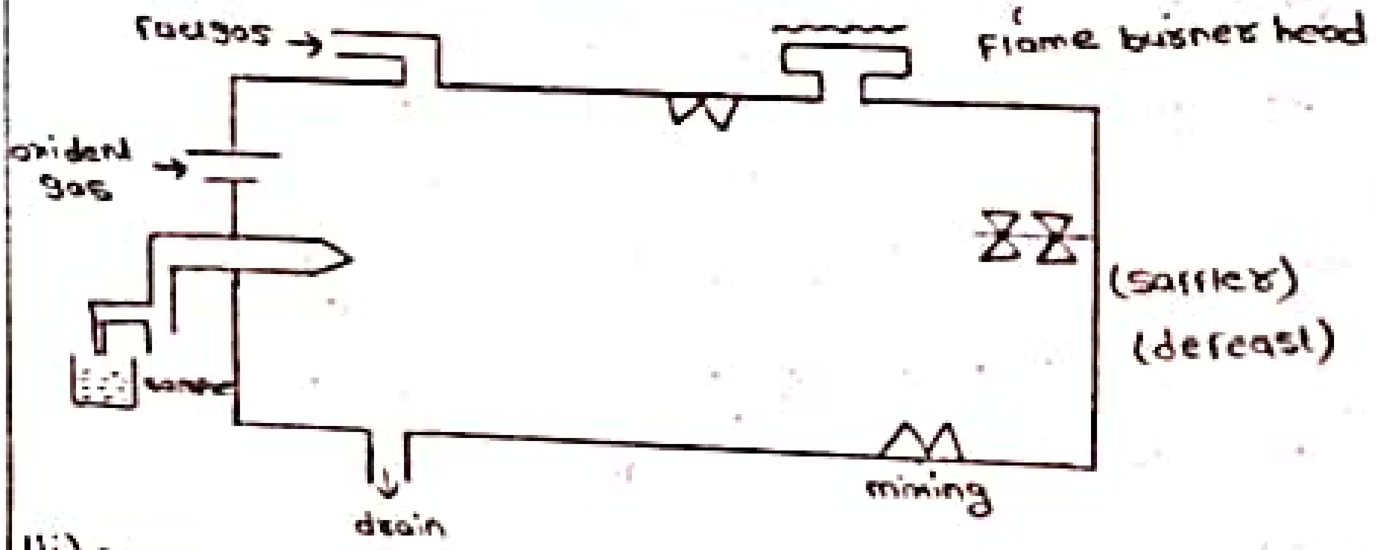
(i) Pre - mix (or) laminor flow burner.

(ii) Total combustion burner.

(i). Pre - mix burner (or) laminor flow burner :-

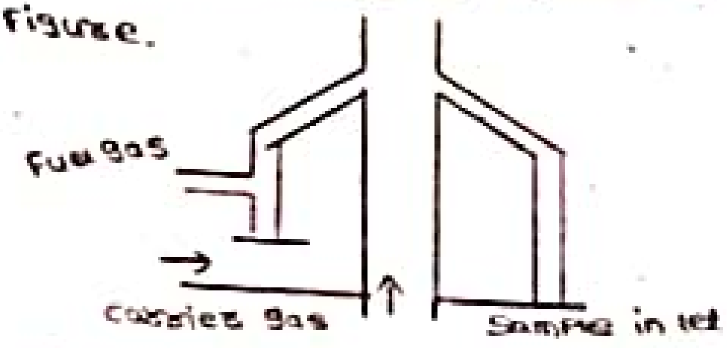
In Pre - mix burner aerosol is Produced in vapourised chamber where large droplet of the solution are discharge to be waste. The resulting fine must be mixed with fuel gas and oxident gas. These reaches the burner lead.

In AAS the burner is a long horizontal tube with a narrow slit. This narrow slit produces a thin flame of path length 10 - 12cm with air + Propane air + acetylene, air + H_2 mixtures. But with $C_2H_2 + N_2O$ mixture it produce a path length in 5cm due to high burning velocity of gas mixture.



(ii) Total combustion burner :-

It consists of three concentric tubes as shown in figure.



The sample solution is carried (Passed) by a fine capillary tube 'A' directly into the flame.

The fuel gas & oxident gas are carried along separate tubes, so, they mix at tip of burner. since all the liquid is aspirated by capillary tube reaches flame. It would be appear their burner is more efficient than pre-mix burner.

Non-flame technique :-

Instead of employing the high temperature of flame production at atoms from the sample. The modern techniques are developed such as.

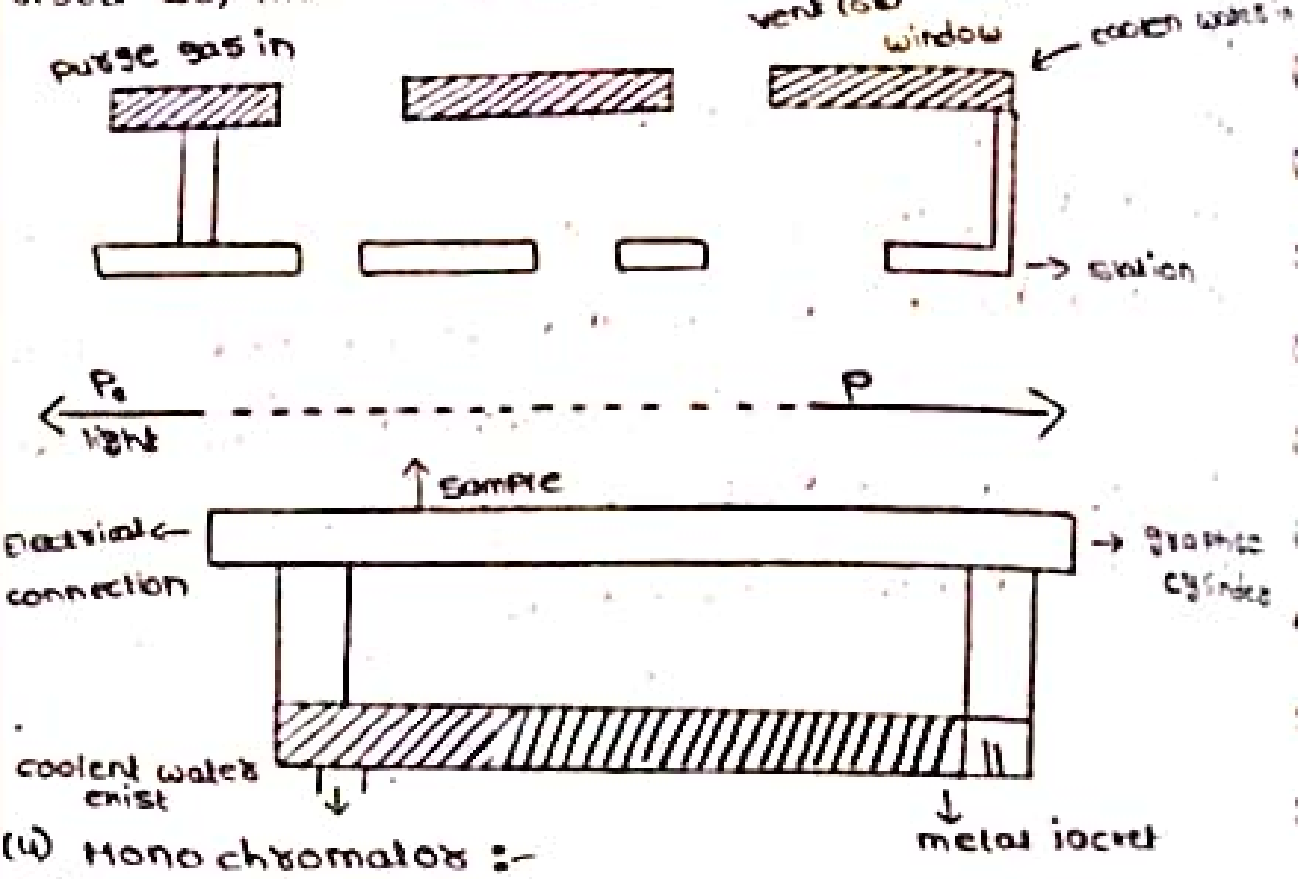
(1) Graphite tube (or) Rod furnace (or) electro thermal atomiser.

(2) cold vapour technique.

Graphite tube (or) Rod furnace :-

It consists of a hallow graphite cylinder about 50mm in length 9mm internal diameter. It is placed in such a way that, the radiation beam passes along the area of tube. This graphite tube is surrounded by a metal jacket, water is circulated and separated from the graphite tube by gas space (Ar)

The sample is introduced by increasing the tip of the micropipette through a port in the outer jacket and into the gas inlet in the centre of graphite tube. The graphite tube is heated by passing electric current to a temperature at solvent is evaporated from the solution. The current is measured so, that sample is ashed and then estimate by it is vola rised so, that metal atoms are produced.

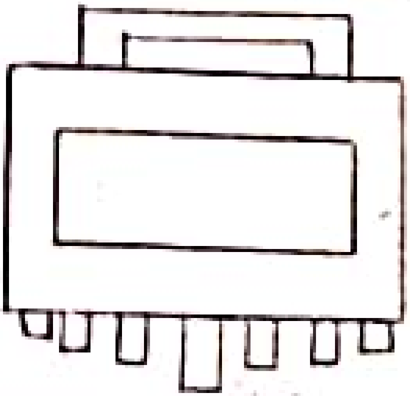


(4) Mono chromator :-

It is isolate the resonance linear for non-absorbed linear emiting by radiation sources It consistes of an entrance slit, a mirrors produces Pos ued beam of radiation. Then it enters into grating system The grating system is used for the dispersion of radiation and produce uniform radiation to pass into detect system.

(5) Detectors :-

The function of detector AAS is to convert incident radiation into electrical signal. Here Photo multiplier tubes are widely used as detectors A Photo multiplier tube is a tube with photo sensitive electrode and several diameter The high voltage is applied between the diameter by a resister. The voltage drop between successive diameter is 50-90V. A Photo electrons are released by photo cathode, it attracted by the first diameter and gains c.c. Due to their fact secondary $e^{\ominus}$s are produced. These 2° $e^{\ominus}$s. attached by the dianode and release more number of $e^{\ominus}$s. This process continuous untill the last dianode receives $e^{\ominus}$s. The multiplied photo current is measured b/w last diamode and cathode.



photomultiplier tube (PMT)

4) Read out device :-

chart Recorders (or) digital Read out devises are used in AAS. A chart recorder is a potentiometer using a servomotor to move the recording pen. The pen displacement is directly proportional to the input voltage.

Interferences :-

These are several factors which influence the emission at flame to given element, cause interference.

The Interferences are classified into two types. They are

(1) chemical interference

(2) spectral interference.

* (1). chemical interference :-

on the basis of flame spectroscopy the gaseous atoms produce ground state. This is inhibited by two forms of chemical interferences.

(i) stable compound formation

(ii) Ionization of ground state of gaseous atoms

Stable compound formation :-

The substance placed in flame incomplete dissociation takes place. These type of interfere may be eliminate different methods.

⇒ By increasing the temperature of flame dissoc of stable compound takes place.

Eg:- 'Al' forms stable oxides, it does not under go any dissociation in C_2H_6 + air flame.

⇒ In $C_2H_5 + N_2O$ flame complete dissociation of 'Al' oxide takes place. So, 'Al' is available in metalic form.

⇒ By use of $C_2H_5 + N_2O$ mixture the formation of calcium Aluminate may be over by increasing the temperature of flame.

Ionization of ground state gaseous atom :-

Due to ionization of ground state gaseous atoms with in flame will reduce the intensity of emision of spectral lines.

The high temperature of C_2H_2+ air (or) $C_2H_2-N_2O$ flames may result of these elements can be reduced by adding Ionization supressants.

The ionization supressants is a solution containing a cation having low Ionization Potential than the analyte.

* 2. Spectral interference :-

In AAS spectral interference arises from the overcapping of frequency of selected resonance lines with the linear emited by some (or) other element. It will appear in AES compared to AAS. Such type of interferences may be eliminated by improving the resolution power of the instrument by using a prism rather than a filter.

In some cases it is separated element to be determining from interfering elements by ion exchange and solvent extraction.

In some cases these type of spectral interferencies can be eleminated by selecting non-interference line for the determination. These type of interferences also called Back ground corrections.

In order to decreasing the spectral interfe

rences Zeeman [illegible] ing mag
etic field. This is caled Zeeman method. In this method splitting of spectral lines takes place in presence of magnetic field.

Zeeman method is two types They are

(1) Direct Zeeman method

(2) Inverse Zeeman method

In direct Zeeman method, the magnetic fie is placed around the source of radiation and emission lines are split into two different components.

=) If the magnetic field is parallel to the light source is called σ - components.

=) If the magnetic field is perpendicular to the light so rce it is called π - components.

The π - component is used to measure the total absorbance due to analyte and back ground.

While σ - component is used to measure only bac ground. The difference b/w these two gives true abso nce of the analyte. So, loss in intensity of radiation fr the source is less.

Applications with special references to analysis of trace metals in oils, alloys and toxic metals in dr king water and effluents :-

(1) Determination of 'Cr' in 'Ni' Alloy:-

Dissolve 1 gm of alloy in a mix of 1:1 H

HNO_3. Heat the solution untill no fumes are evolved. Transfer the solution to a beaker add 5 ml of HF drop wise, cool the solution at a temperature 30°c, transfer the solution in 100ml V.F and make up distilled water their solution containes 50% Cr.

Preparation of Standard Solution :-

Dissolve 1 gm of pure 'Cr' powder in HCl, make up distilled water. Appropriate dilution of the stock 'Cr' solution will give a series of standard containes 0, 1000, 1500, 2000 of 'Cr'.

Now set a single beam AAS & select a hollow cathode lamp, made of 'Cr'. Select the resonance line at 520.8 nm.

Now aspirate the standard solution and sample solution into $C_2H_2 + N_2O$ flame. Note the absorbance of standard and test solution. S. calculate the % of 'Cr' in alloy.

2. Analysis of Toxic metals in drinking water :-

As :- As^{+5} reduced to As^{+3} state and converted to AsH_3 directly aspirated to Ar - H_2 flame

A = 193.7nm

Ce :- Reduced to ±2 state, converted CeH_2 Aspirated into Ar - H_2 flame

A = 196 nm

Hn :- Direct aspirated of water sample into C_2H_5 +

air flame.

$\lambda = 277.5nm$

Hg:- Reduction of Hg → Hg° by $SnCl_2$ followed Hg0 by air into an absorption cell.

$\lambda = 253.7nm$.

Ag:- Direct aspirated into air C_2H_2 flame.

$\lambda = 328 nm$

Cr:- Direct aspirated into air C_2H_2 flame.

$\lambda = 358nm$

Cu:- $\lambda = 325 nm$

Fe:- $\lambda = 248.3nm$

3. Analysis of trace metals in oils :-

Analysis of vanadium by lubrication oils :-

The oil is discoved in white spirit and the absorption of their solution is compared with standards made from vanadium napthanate dissolved in white spirit.

Preparation of standard solution :-

0.6 gms of vanadium napthanate is dissolve in white spirit make up to 100ml V.F. Their solution contain 130 mg/ml of 'V'. This solution is known as stock solution. Dilute their stock solution to give '4' solution containing 10,20, 30,40 mg/ml of 'V'.

Procedure :-

5 gms of oil sample dissolved in white spirit transfer to 50ml VF. By using double beam AAS. set up a 'V' hallow cathode lamp selecting the resonance

(c) Inductively coupled Plasma Spectrometer (ICP- AES, ICP- ms)

* Principles :-

Plasma technique is available in 1970 off rs several advantages over atomic spectroscopy Pa ma atomisation has been used for atomic emision

An atom can be raised to higher energy states by supplying external energy At low temper ture each particle is present possess minimum poten energy and all atoms present in ground state.

If energy is supplied by heating, the K E of the atoms increases through collisions. Some of partic will excite to higher energy states and convert K E PE since particles in higher energy state are not sta They will return to ground state. In duing to so they emit the extra energy in the form of radiation (or) spectral linear of characteristic wave length This phenomenon of spontaneous emision is the basis of emis ion spectroscopy. Here we excite the sample by mea of 'Arc, spark flame and plasma. Among these made pla technique find numurous advantage. By using their te nique we can analyse the sample in precipitate level

At high temperature need for excitation proc like varous isation and dissociation takes place produ free atoms. The total number of atoms (N) in source is proportional to concentration of the element in sample line of $\lambda = 38\ 5$ nm adjust the gas control to give fuel rich $C_2H_5-N_2O$ flame aspirate into flame, absorb recording, Plot calibration curve and determination of 'V' in oil.