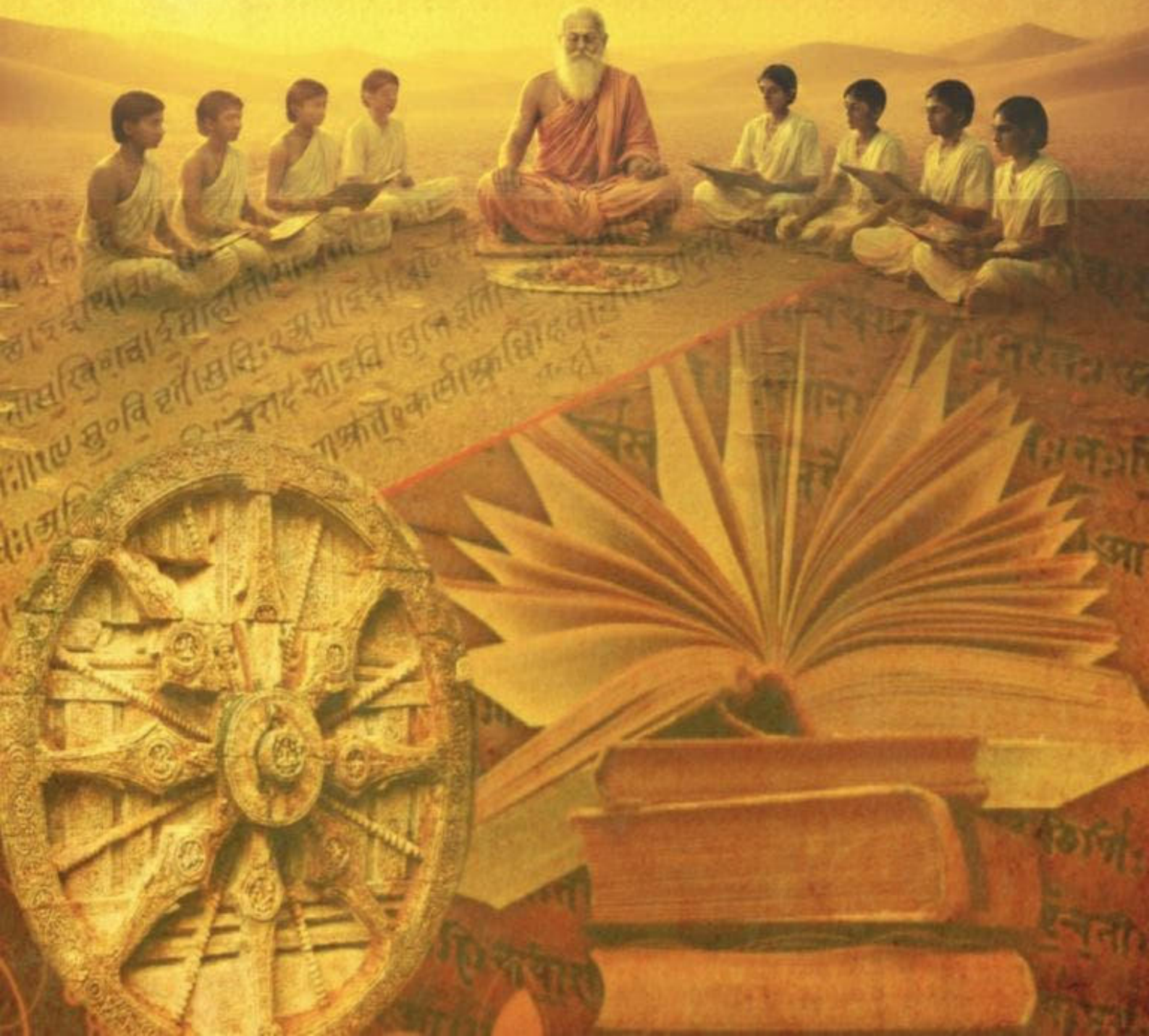
भारतीय ज्ञान प्रणाली
उद्गम और विकास

सम्पादक :
डॉ. दिनेश चन्द्र शर्मा



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19

Atomic Emission Spectroscopy

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INTRODUCTION

Atomic emission spectroscopy pertains to electronic transitions in atoms which use an excitation source like flames, arcs or sparks and are plasma sources. Most of the spectroscopic techniques are related to molecules but emission spectroscopy is related to atoms. It was known since the work of Bunsen and Kirchoff (1860) that many metallic elements under suitable excitation emit radiations of characteristic wavelengths in ultraviolet and of alkali and alkaline earth metals which impart characteristic colours to the visible region. The use of this fact has been made in the qualitative analysis flame. Emission spectroscopy is concerned with the characteristic radiation produced when atoms are excited. They emit radiations in the form are discrete wavelengths of light, called spectral lines while returning to the lower energy states. The wavelength of a spectral line is inversely proportional to the energy difference between the initial and final energy levels. Since to two elements have identical energy levels, no two elements will have the same spectra.

ADVANTAGES OF EMISSION SPECTROSCOPY

1. The technique is highly specific, the unique character of the wavelength pattern produced by each element is the reason for its specificity.

2. The method is extremely sensitive. With this technique all metallic elements can be detected even if they are present in very low concentration (0-0001%).

3. Even metalloids (arsenic, silicon and selenium) have been identified by this technique.

4. The analysis can be performed either in solid or liquid state with almost equal convenience. Gas samples are rarely analysed.

5. The technique requires minimum sample preparation, as the sample can be directly introduced into the arc or spark.

6. The sample requires no preliminary treatment and can be analysed as received.

7. Spectra can be taken simultaneously for more than two elements. No separation is required. A very small amount of sample (1-10 mg) is sufficient for analysis.

8. The technique provides results very rapidly. If automated, time required is just from 30 seconds to a minute.

9. The analysis is based on the relation between the power of the emitted radiation of some particular wavelength and the quantity of the corresponding element in the sample. This method has been used for a wide variety of samples like metals, alloys, paints, geological specimen, forensic material, environmental and biological samples.

10. The technique permits non-destructive analysis.

DISADVANTAGES OF EMISSION SPECTROSCOPY

1. The equipment is costly and wide experience is required for its successful handling and interpretation of spectra.

2. Recording is done on a photographic plate which takes sometime to develop, print and interpret the results.

3. The spectrograph is essentially a comparator. For quantitative analysis, standards of similar composition are required. For quantitative results, therefore, a problem is often posed for unknown samples.

4. Radiation intensities are not always reproducible.

5. The method is limited to the analysis of elements.

6. The accuracy and precision are not as high as gravimetric, titrimetric and some spectrophotometric methods for elements present in quantities greater than 2 to 5% of the total.

ORIGIN OF SPECTRA

When light emitted by an incandescent (heated to a very high temperature) solid is seen through spectroscope, we observe a seven coloured emission spectra. An examination of emission reveals that there are three kinds of emission spectra i.e., continuous, band and line spectra.

Continuous spectra are emitted by incandescent solids and sharply defined lines are absent. Band spectra consist of groups of

lines that come closer and closer together as they approach a limit, the head of the band. These are caused by excited molecules. Line spectra consist of definite, usually widely and irregularly spaced lines. These are characteristic of atoms which have been excited and emit their energy in the form of light of definite wavelengths. The wavelength of these lines varies for each element and depends on the energy of excitation source. Sodium for example, emits two characteristic lines which appear due to the splitting of p-orbitals into two levels of al?nost same energy difference as a consequence of the interaction between spin-magnetic moment (due to p-electrons) and the magnetic field resulting from the orbital motions of all the electrons. The spin magnetic moment either opposes or reinforces with orbital field and leads to two energy states.

All the single electron systems (Na, Mg, Al, K, Rb, Cs) emit characteristic doublets. The wavelength decreases with increasing atomic number of atom because larger the nuclear charge greater will be the energy differences between the quantum levels of the atom or ion. The emission spectra of Mg atom is different and one gets a singlet and a triplet series of lines. This behaviour is characteristic of all the alkaline earth metals. The origin of this pattern can be traced into the interaction between spin-magnetic moment and magnetic field due to orbital motion. The energy difference owing to d-and f-orbital splitting is too small to be observed. For a three electron system, a doublet and a series of four lines is produced. Transition metals produce complex spectra. Spectrographs with greater dispersion and resolution are required to separate adequately the lines in complex spectra. The intensity of a spectral line depends largely on the probability of the required energy transition taking place. The intensity of some of the stronger lines may be decreased by self-absorption caused by reabsorption of energy by the cool gaseous atoms in the outer region of the source.

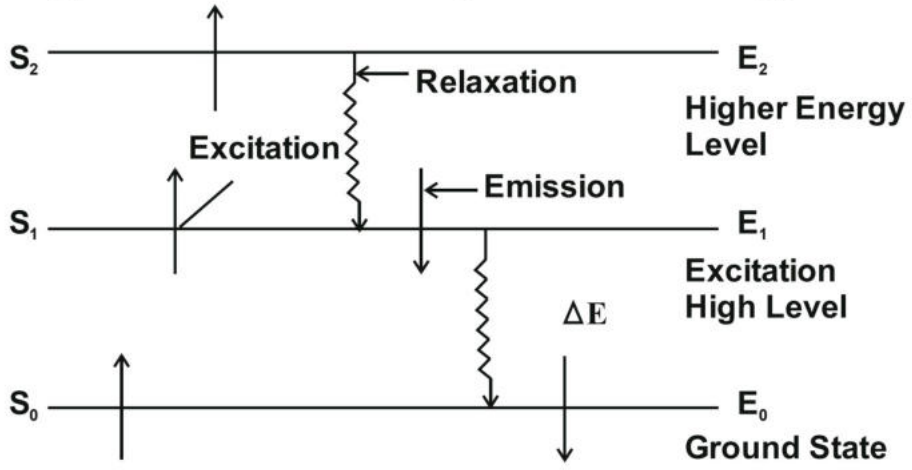
PRINCIPLES OF EMISSION SPECTROSCOPY

The source vapourise the sample and causes electronic excitation of elementary particles in the gas. Though we can get band and line spectra, the latter are useful for emission analysis. Excited molecules in the gas phase emit band spectra. Thus, a E_{1} molecule in an excited state of energy, E_{2} undergoes a transition

to a state of lower energy and a photon of energy, hv is emitted where

$hv = E_2 - E_1$

In each electronic state a molecule in a number of vibrational and rotational substates of different energies, so radiation from excited molecules comprises a number of frequencies which are grouped into bands. Finally, excited atoms or monoatomic ions in the gaseous state emit line spectra. As vibrational and rotational fine structure is absent from the spectra of monoatomic species, so emission spectrum is composed of a series of individual frequencies matching transitions between various electronic energy levels. The emission, absorption or fluorescence spectra of atomic particles consist of well defined narrow lines due to electronic transitions of the outermost electrons. Measurements in emission spectroscopy are feasible because each atom has a definite quantum of energy in which electrons reside. Ordinarily they are in the ground state. These can be excited by absorption of energy. The excited electrons return to the ground state and in this process extra energy in the form of a photon of radiant energy is emitted. This results in definite transitions. If the excitation energy is large then the emitted energy is large, which results in several lines for measurements. The use of a high energy source is not always helpful as it ionises the gas with the loss of one or electrons. The spectrum of an ionised ion is radically different from that of a neutral atom. A spectrum of singly ionised ion, e.g., Mg+ ($3s^1$) will be similar to a neutral atom like Na ($3s^1$). The types of emission are depicted in the energy level diagram.



Na – $1s^2 2s^2 sp^6 3s^1$ (Sodium Metal)

Mg^+ – $1s^2 2s^2 sp^6 3s^1$ (Isolated ion of Magnesium)

Atomic Emssion Phenomenon

INSTRUMENTATION

The essential part of an emission spectrograph are a source, sample holder, optical system, monochromators, slits, detectors or a camera for recording the spectrum.

ATOMIC EMISSION SPECTROSCOPY

The sample is into the discharge, where it is vapourized and excited. The excited sample emits radiation which is detected and measured by the detector (Fig. 2).

Excitation Sources.

The source of emission analysis differs from that used in absorption analysis mainly in that the test sample itself must provide the photons. The sourcent accomplish the following processes

(i) The source should provide both sufficient and constant intensity

(ii) The source must emit radiation of sufficient intensity to provide, in conjunction with the detector and other portions of the apparatus, measurements of desired accuracy and precision.

In addition, the emitted radiation must be constant over a series of measurements, including measurements on samples and on solvent to permit a comparison of one measured value with another for desired accuracy.

(iii) The sample must vapourise in the source. The sample should dissociate into atoms.

(iv) The electrons in the atoms must be excited to higher energy levels from the ground state.

(v) The source should provide reproducible excitation conditions from sample to sample.

In emission methods, electronic excitations are rather frequently encountered than are rotational or vibrational excitations. Therefore X-ray, ultraviolet and visible regions of Electromagnetic spectra are most useful.

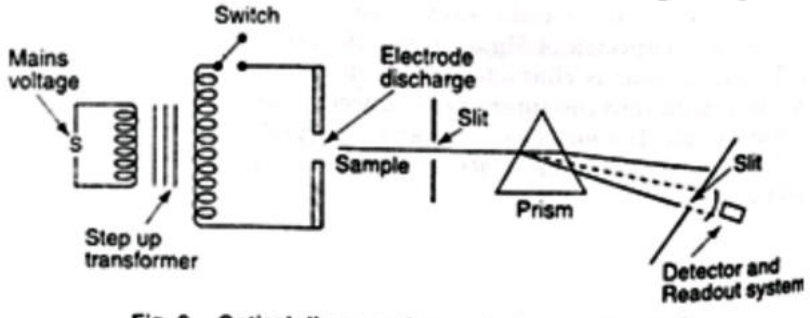


Fig. 2. Optical diagram of an emission spectrograph.

Visible and Ultraviolet Sources. Flame, alternating current arc (AC are), direct current arc (DC arc), alternating current spark (AC spark), gas discharge tube and laser beam are the sources that are used in emission method.

Flame. Flame is used for those molecules which do not require very high temperatures for excitation into atoms during quantitative analysis. The sample is prepared in the form of a solution and sprayed into the flame of a burner. There are several combinations of fuel and oxygen sources. The flame temperatures for different fuels are as follows:

(a) Gas and air = 1973 K

(b) Hydrogen and air = 2373 K

(c) Acetylene and air = 2473 K

(d) Acetylene and oxygen = 3323 K.

The lack of sufficient constant emission intensity, the difficulty encountered in introducing the sample into flame steadily, reproducibility and longer time taken i measurements make this source less favourable to be used in quantitative work.

High Voltage AC Spark. It is perhaps the simplest excitation source for many qualitative measurements, though its intensity is relatively low but is more effective and stable than AC arc. High voltage transfer 10-50 KV across two electrodes gives a spark. The use of a condenser increases the current (Fig. 3). A brilliant spark is obtained at 0-005 microfarad capacity to the capacitor.

The spark is preferred to an arc when high precision rather than high sensitivi required. A spark usually excites ionic spectra. It is reproducible, less material is gene consumed, high concentration of solution can be employed, the heating effect is less which is

useful for analysis of low melting materials and there is no interference from onalika indication of the concentration of the substance. Although spark excitation provides better cyanogen band. The drawback of the method is that it may give a non-representatins precision than arc yet the total amount of sample volatilized during a pulse is smaller, spark spectrum is thus less sensitive than the one produced by an arc.

AC are employs a potential difference of 1000 volts or more. The arc is drawn at a distance of 0-5-3 mm. For reproducible results

the separation distance between the two electrodes, the potential and the current must be properly controlled. The AC arc is steadier than the DC arc. AC arc source is one of the best sources for qualitative analysis becaus it is very stable and reproducible. It is not fit for qualitative analysis because the excitation of the sample is mainly electrical. AC arc is not a sensitive source since only minute amounts of sample are volatilised.

DC Arc. The DC arc is generated with a potential gradient of 50-300 volts, the current used is about 1 to 300 amps and emission is due to neutral atoms. The temperature in the are stream ranges from 2273-5273 KA DC arc is struck between carbon and graphite electrodes, sometimes flickering of the arc is observed. When an arc is operated between carbon electrodes in air, some cyanogen molecules are formed. These may emit molecular band spectra in the region 320-420 nm.

The DC arc is a sensitive source but its reproducibility is not of the highest order. It is generally used for the identification and determination of elements present in very small concentrations. The sample to be analysed is passed through an arc and an average value of the concentration is known. This is achieved by placing a small amount of the substance on a graphite electrode with a recess drilled to a depth of 4-5 mm and continuing the excitation until the sample is completely volatilised.

Important advantages of DC arc are:

(i) DC arc is self sustaining and provides a good continuous light output.

(ii) It is widely used in qualitative and quantitative determination of trace elementa. Inert atmosphere excitation and gas shearing techniques are also used.

Difficulties arising with DC arc are:

(i) Failure of the arc column to cover the entire surface of the electrode, instead contact is made only at spots. Thus only a part of the electrode surface is sampled.

(ii) Erratic behaviour,

(iii) Poor reproducibility.

(iv) Selective vapourisation of the sample.

(vi) Tendency to flicker which can be reduced by introducing

a reactor in the circuit.

LASER BEAM

Laser beam has been used for exciting the atoms or ions of a sample, particularly when the beam is focussed to irradiate only a small area of the specimen. Solid specimens with area as small as 50 microns may be readily ionised. The method of excitation by laser is non-destructive since a very small portion of the sample is vapourised. The use of laser beam is advantageous as it helps in studying variations in composition from one small region of the sample to another. Also the sample need not be electrically conducting.

Gas Discharge Tube. It is used in emission analysis, if the sample is gas or it can be conveniently vapourized. The limited use of this source is on account of handling problems of gases and also difficulties in maintaining the necessary pressure conditions.

Controlled Spark Sources. These sources are based on the use of an auxillary spari gap having uniform characteristics, which are used to control the discharge.

Multisource of excitation is a highly versatile unit (discharges similar to arcs and sparks. The unit consists of charges a variable capacitance placed in parallel with analytical gap.

A variable inductance and resistance are also placed in series with analytical gap in the power circuit. The discharge is initiated by 25000 V ignitor circuit connected across the analytical gap and controlled by a synchronous interupter. Variation in the resistance can produce short duration spark like discharges as well as long duration are like discharges. X-Ray Sources. X-ray photons of even greater energy are used for bombarding the sample in qualitative and quantitative applications of X-ray emission spectra since the energy required for excitation of atoms or ions of the test sample is generally quite high.

Sample Holder.

The function of the sample holder is to introduce the sample into the electrical discharge. There are two types of sample holders, those for solid samples and those for liquid samples. Whether the sample is solid or liquid, it must be regularly distributed upon the surface of at least one of the electrodes that serves as the source.

If the sample is metal or an alloy, one or both electrodescan be formed from the sample by melting or by casting the molten metal in a mould. It is rather convenient to use a polished flat surface of a large piece of metal as one electrode and a graphite or metal rod as the other for some samples. The ideal shape for the electrode is cylindrical, 1/4 or 1/8 inches in diameter and tapered at one end (Fig. 5). If the solid sample is not a good conductor and cannot withstand high temperature, it is first reduced to powder and then mixed with powdered graphite (called a buffer) to increase reproducibility. The sample is loaded in a carbon sample holder. The sample holder is then placed at one of the electrodes while electric discharge takes place from the top surface of the electrode. The sample is vapourised into plasma of the discharge and spectrographic emission takes place. Organic compounds e.g., animal tissue, body fluids, plant materials and solid extracts are analysed for their metal contents. Copper and silver rods are also used as sample holders when theseelements are not to be detected. The surface of these electrodes can be cleaned and reshape after each analysis. For liquid samples two types of holders are frequently used (Fig. 61 The porous base of the container permits the sample to percolate through it at a steady rate into the electrical discharge. The sample slowly runs into the discharge which would be sustained till the burning away of the base. The rotating disc rotates through the sampla which wets the surface of the dise. This wet disc carries the sample into discharge at a steady rate. Both the devices are equally useful. Organic solutions tend to ignite in the discharge and produce erratic emission.

MEASUREMENT OF LIGHT INTENSITY

The intensity of an emission line, if self absorption is excluded, is directly proportional to the number of atoms or ions of the emitting species that exist in the gaseous plasma of the arc or spark gap. The line intensity is linearly related to elemental concentration under ideal conditions. Due to various variables affecting volatilization and excitation of the constituents of the sample, continuous and random fluctuations in line intensities are characteristic of arc and spark sources. The intensity of line does not help measuring concentration, therefore, it is necessary to integrate the line intensity over a period that is long with respect to the frequency of random fluctuations.

Hence averaging gives a quantity related to concentration. A signal from photomultiplier is used for integration .

APPLICATIONS OF EMISSION SPECTROSCOPY

1. Qualitative Analysis. The emission spectrum obtained on a photographic plate is identified by comparing it with previously recorded spectra of known elements. For trace quantities raies ultima or RU lines must be identified.

(a) Raies Ultima. When a metal is excited it emits a complex spectra consisting of several lines, some strong and other weak. If the concentration of the metal is decreased, the weaker lines disappear. On further diluting the sample, some of the less strong lines disappear. The lines with the lowest concentration of the metal are known as RU lines. By comparing RU lines of the unknown sample with the RU lines of the known sample, the metal can be identified. The RU lines are particularly useful in detecting small concentrations of impurities. Table 1 records position of RU lines for some elements.

(b) Metals. Generally the photograph of the emission spectrum of an unknown sample taken together with the spectrum of iron. By comparison with the iron spectra th wavelength of the lines from the sample can be determined and by comparison with th spectra of other elements the elements in the sample can be identified. With a grating spectrograph, linear interpolation between lines of known wavelengths suffices to calcules the wavelength of unknown lines. If the dispersion is prismatic, the interpolation may la and in a region where the An alternative method to calculate wavelength is given by Hartmann formula.

2. Quantitative Analysis. For quantitative analysis, the intensity of one line of each element is to be determined. The choice of the line depends upon the concentration of the concentration a weaker line would be measured. The measurement of intensity is carried ou element. If only a small quantity is present, most intense line must be chosen. For larger by using photomultipliers as detectors. With automatic analysers such as the Quantometer-twelve elements can be simultaneously determined. With special equipments upon the concentration of the metal. For higher concentration 1% error is obtained whils as many as 60 elements can be determined

at a time. The precision of the method depends error for low concentration is as high as 5%. Procedures employed in quantitative analysis involve the following methods. (a) Comparison Sample Method. The spectrum of an unknown sample is compared with the spectra of a range of samples of known composition with respect to a particular component. The spectra of the unknown sample and various standards are photographed on the same plate under same conditions. Comparison of the blackening of lines of the constituents under study with the same lines on the standards would be helpful in evaluating the concentration of the desired constituents.

(b) Internal Standard Method. This method is generally employed to compensate various variables affecting the blackness of the image of a spectral line on photographic plate A known amount of the standard is added to the sample. The standard should itself be absent in the sample. The intensity of one of its lines is measured. The intensity is directly dependent on the quantity of the sample present.

3. Semi-quantitative Analysis. Concentration data reliable within 30 to 100% of the trace amount of an element present in the sample have been semi-quantitatively obtained. This method is adopted if the choice of good standard is not economical. Analysis involves total volatilization of 1 to 10 mg of sample in the arc. The knowledge of the minimum amount of an element necessary to cause the appearance of each of a series of lines is the basis for the estimation of concentration.

In some of the methods, the optical densities of the elemental lines and that of the line of an added matrix material are compared. Concentration is then calculated on the basis of the assumption that the line intensity is independent of the elemental state. Mixing of large amount of a suitable matrix element, called spectroscopic buffer, with the sample minimizes the effects of other elements on the line intensity.

4. Specific Applications.

(a) Metals and Alloys. Emission spectroscopy has been employed in determining the impurities of Ni, Mn, Cr, Si, Cu, Al, Mn, As, Sn, Co, V, Pb, Bi, P and Mo in iron and steel in metallurgical processes. The percentage determined is 0-001% in iron to 30 in

steel. Alloys of Zn, Cu, Pb, Al, Mg and Sn have been analysed.

(b) In Oil Industry. Lubricating oils have been analysed for Ni, Fe, Cr, Mn, Si, Al and excessive wear and the need for engine overhaul. Some of these metals can poison the so on. If the concentration of metal in lubricating oil has increased during use, it indicates catalyst used in the cracking process. In petroleum industry oil feed stocks are analysed for V, Ni, Fe, the presence of which makes fuel poor.

(c) Men and Animals. Solid samples and animal tissues have been analysed for several elements including K, Na, Ca, Zn, Ni, Fe and Mg etc. Changes in the concentration of trace elements have been correlated to the ageing process.

(d) Plants and Soils. Emission spectroscopy has been used to detect 40 elements in plants and soils. Thus metal deficiency in plants and soils can be diagnosed. Hence one can make up the deficiency through soil applications or through sprays on to the leaves.

(e) The following list will give a sampling of the great variety of materials being analysed by emission spectroscopy.

(i) Ceramics, for both trace and major constituents.

(ii) Aluminium, for traces of cobait.

(iii) Graphite, for traces of Co, Ni, Mo and V.

(iv) Analytical reagents, for trace metal impurities.

(v) Spent nuclear fuels, for rare earths.

(vi) Blood, for traces of Ca, Cu, Zn and

(vii) Pancreatic tissue for zinc.

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