GENERAL INTRODUCTION
1. **Historical Review**

One can trace the origin of the method of Spectro-chemical analysis about the middle of the nineteenth Century, to the recognition that the spectrum emitted by an atom of an element is characteristic of that atom and later on of the fact that the intensity of spectral lines is proportional to the number of atoms emitting. W.H. Fox Talbot, who may be credited as the founder of Spectro-chemical analysis, devoted much attention to the study of the light emitted by the salts of sodium, lithium and strontium in the flame of an alcohol lamp, and of copper, silver and gold in a spark discharge. J.F.W. Herschel made extensive study of the flame spectra of various salts. He described the different colours imparted to flames by the salts of various metals and the colours communicated to flames afford a ready and neat way of detecting minute quantities of the metals.

Kirchhoff and Bunsen showed after a study of the spectra of the known alkali elements, that certain spectral lines, not belonging to the spectra of the known alkalies, appeared in the light emitted by some of their preparations. They thus discovered two alkali metals Cesium and Rubidium in the year 1860. Fraunhofer in 1817, observed that the yellow lines in a sodium flame were double and seemed identical in wavelength with the two dark D lines in the Solar spectrum. Kirchhoff and Bunsen applied their knowledge of Spectro-chemical analysis to the study of Fraunhofer lines and the identification of many elements in the Sun's atmosphere.
They identified most of the lines of the elements such as, hydrogen, iron, nickel, calcium, chromium, titanium, sodium and magnesium in the Solar spectrum. Thus qualitative Spectro-chemical analysis was possible not only for substances readily available on the earth but also for many self-radiating distant bodies such as the Sun and the stars. Qualitative Spectro-chemical analysis was thus firmly established by these achievements. It was later on extended in its scope, precision and sensitivity.

For many decades the use of Spectro-chemical analysis was almost entirely qualitative. The quantitative Spectro-chemical analysis is based on the fact that when an element is present in a matrix in successively smaller amounts, its spectral lines grow weaker and disappear in a definite order, which means their intensities at any concentration are simple function of the concentration. Lockyer was one of the first workers to propose the use of the spectrograph for quantitative analysis. His suggestion involved the determination of the length of the spark line at each electrode as a measure of the concentration of the element. The actual determination of line intensity was previously made by a visual comparison of the unknown sample line with a series of photographs of the samples of known composition. These visual estimations are satisfactory where much accuracy is not required. However these visual estimations are approximate and if any considerable wavelength range is involved, the accuracy is further affected by the variation in the sensitivity of the eye with the
wavelength. Much of the improvement in Spectro-chemical quantitative methods has been made in the direction of increased accuracy in measurement of line intensity.

2. Limitations:

(a) An accurate quantitative analysis, utilizing emission spectra, is based on the principle of internal standard first introduced by W. Gerlach. In the case of internal standard method, the ratio of the intensity of the analysis line to that of the line of an internal standard present in constant amount is measured with the help of a microphotometer. The advantage of an internal standard is that, it affords a compensation for various factors which affect the quantitative estimation. Since both the unknown and the internal standard lines are a part of the same sample, the variations in the time of exposure, plate characteristics, developing conditions will not affect the relative density of the two lines which are equal in intensity in the light source. Before selecting the internal standard several factors should be considered.

(1) The rate of volatilization of both the internal standard and the analysis line should be equal.

(2) The excitation potential of the internal standard and the analysis line should be of the same order.

(3) The line of the internal standard should be free from self-absorption.

(4) The analysis and the internal standard line should be near in the spectrum so as to reduce the variation of
photographic sensitivity with wavelength.

(5) The internal standard should be added in a small quantity.

(b) The accuracy attainable in the quantitative Spectro-
chemical analysis is greatly influenced by the choice of
the excitation source. The intensity of a line is affected by the
fluctuations in the source. Sawyer points out that the ideal source
for quantitative estimations would be one, in which all elements
enter the discharge, diffuse through it and are excited to radiation
at a uniform relative rate, regardless of boiling points, atomic
weights, vapour pressure or the variations in the discharge condition
or of the time. It is essential for satisfactory results with any
source to have constant energy input over the time of exposure.

The commonly used excitation sources are flames, arcs and
sparks. At the beginning of the development of Spectro-chemical
analysis only flames were used for excitation of the material by
introducing it into the flame by a platinum wire. Low temperature
excitation is best obtained by a flame method. The flame has got an
advantage in its constancy and the small mutual interaction between
elements introduced in it, but the great disadvantage is that due to
the low temperature, only alkali and lower states of alkaline earth
elements are excited and on account of this, it is not generally
used for the detection of trace elements. On the other hand arcs and
sparks produce high temperatures and many lines of elements which
require high excitation energy are seen in the spectrum of the sample.
Arts are generally used for the detection of trace elements.
In qualitative analysis D.C. arc is chiefly used because of its sensitivity but its use in quantitative analysis is restricted because of the fluctuations taking place in it, which are responsible for the inaccurate and non-reproducible results. Thus the choice of the internal standard in the case of a D.C. arc source is more critical than for other sources. H. Kaiser in the article "On the Physics and technology of spectro-chemical sources" points out that the arc is used mainly for qualitative analysis because of its sensitivity and the spark is recommended for accurate quantitative analysis.

(c) Another factor, which should be taken into account in the quantitative spectro-chemical analysis, is the extraneous element effect. It has been shown by many workers that the line intensity is usually very sensitive to the composition of the matrix and that both anion and cation changes produce a marked effect on the line intensity. For this reason standard samples are usually prepared from a base mixture whose chemical composition and physical properties resemble as closely as possible with those of the specimens to be analysed. Some people have studied this extraneous element effect while estimating the quantity of a particular element in a sample. T. Negresco states that in a given alloy the introduction of a third metal totally changes the sensitivity of the spectrum lines of the other two elements. Duffendack and Smith in comparing the intensity of barium lines in nickel and nickel-copper alloys, noted that copper had an appreciable effect on the relative intensities of the barium lines. These examples
thus show that due consideration must be given to this effect in quantitative spectro-chemical analysis.

(d) The accuracy of the quantitative analysis depends also upon the choice of the spectral region used for estimation. The efficiency of any photographic plate depends on its behaviour towards spectral lines of different wavelengths and intensity. The defects associated with the nature of the photographic emulsion are responsible for the low accuracy. Van Tongeren using a glass spectrograph and the cathode layer of a D.C. arc excited the powdered sample mixed with graphite and sodium carbonate and reported 0.30 percent of tin in SiO$_2$ as the least detectable concentration. His results would have been greatly improved if the much more sensitive ultra-violet tin line (3175.01 Å) of excitation potential 4.31 volts, could have been used rather than the lines in the visible region chosen by him.

The gamma factor of a plate is a measure of the contrast of the emulsion and it is the value of gamma which determines the utility of the plate for use in wide concentration ranges. The gamma of a plate is not constant but shows an increase towards the visible and infra-red region. For most plates used in Spectro-chemical analysis gamma value lies within the range 1 to 2. (12) Ahrens has pointed out that nearly all emulsions have the gamma factor constant between the range 2500 - 3100 Å. Before actually starting with the quantitative spectro-chemical analysis the above mentioned important factors which limit the use of this method, should be taken into account.
3. **Sensitivity:**

The spectrograph is used now-a-days to a great extent for the determination of the composition of a wide variety of materials and to find out the concentration of the constituents, by measuring the intensity of the lines. Standard chemical methods have provided analytical data about the major constituents of alloys, minerals, rocks, soils and plants, but considerable attention has recently been given to the distribution and abundance of numerous trace elements and to development of methods more sensitive than the chemical methods. The spectro-chemical method is used for trace elements because it possesses the advantage of speed and is also effective even if minute quantity of the material under test is available. For such a small quantity one would require the elaborate, tedious and slow micro-chemical method. Further the spectrum is a permanent record of the analysis of the element. With good equipment and proper conditions, the presence of an element as low as one part in a million is readily detectable. Owen's used solutions, dried on the tips of graphite electrodes, and reported in the analysis of caustic liquor an absolute sensitivity as low as \(1 \times 10^{-6}\) mg of the test element and a relative sensitivity for manganese of \(2 \times 10^{-6}\) per cent.

4. **Applications:**

(a) **Geology:** The use of Spectro-chemical analysis is done in the determination of trace elements in soils and many workers in the field of Geology have correlated their results with the formation of soils from rocks. Koshini and Tsuge have
dealt with the determination of trace elements in Japanese soils. The trace elements present in any soil, are not present in completely random amounts, but particularly where the soil is derived from an igneous rocks, it is possible from a knowledge of Geological material, to anticipate which trace constituents are likely to be present in high and in low contents. This knowledge has been derived from the analysis of rocks and minerals.

(b) Pathology: This method has been used quite successfully for the criminal investigation of certain cases where other methods did not prove plausible for that purpose. W. Gerlach was the first to apply his high frequency spark source for the criminal investigations. He excited the samples in their original form with the help of the high frequency spark source and was able to locate the cause of the case. C.W. Rankin used spectrograph in the criminal investigation and determined the elements present on cloth through which a bullet had been fired and from the variation of intensity of lines in the spectrum, the distance from where the bullet was fired was determined.

(c) Botany and Agriculture: The application of Spectrochemical methods, to the determination of the total content of trace elements in soils, and materials from which they are derived should lead to a clear understanding of the factors which are involved in causing disorders in plants and animals. The importance of certain elements present in minute quantity, for the healthy growth of plants, has been studied by many workers in the field of Botany and Agriculture. These are
usually called micro-nutrients or trace elements. In recent years a lot of work has been done on soil fertility and the factors which influence the plant growth. The experiments performed along these lines tend to show that some of the elements needed only in small quantities, namely manganese, titanium, boron and zinc exercise a marked influence on plant growth. If the quantities of the trace elements exceed the amount required for good growth, then the plant either will suffer from some disease or have diminished growth thus affecting the yield in general.

(17) M.K. Ghosh and K.C. Mazumdar using Spectro-chemical method determined molybdenum content in green peas. Brackpot determined certain trace elements in sugar beet. He noted that the earth adhering to the beets was rich in titanium and contained manganese, nickel and iron in general. Dix and Magoon have studied the content of magnesium, manganese, calcium, aluminium, copper, iron, potassium and phosphorus in young grape leaves of different varieties grown on the same soil.

Not only the plants suffer from the deficiency or excess of the micro-nutrients but the animals who feed on them suffer from serious diseases. A disease of cattle known as 'teart' occurring in Somerset is due to the higher content of molybdenum in herbage. In such cases the spectrograph is of tremendous help in tracking down the causes of diseases of plants and animals. W. Gerlach used his high frequency spark source for the determination of trace elements in human and animal organs. With the help of this method he was able to examine the distribution of a particular element in
the different parts of an organ. Comparing the spectra of the
diseased and healthy organs he found out the cause of the disease
to be either due to deficiency or excess of certain important
trace elements required for healthy growth.

5. **Aim and Scope of present work:**

The present work originated in the first instance in the
study of wheat samples of different varieties and of different
stages of growth grown on the same plot in order to find out as to
which particular trace element was responsible for these variations.
The wheat samples were kindly supplied by the Director of the Govt:
Wheat Research Station near Powarkheda (M.P.). The samples
consisted of some varieties susceptible to rust and others rust
resistant. Other samples were obtained from the Govt: Wheat Station
near Saugor (M.P.). They supplied different varieties of the
samples, consisting of three gradations, best growth, moderate
growth and small growth.

The qualitative analysis is done by using a high frequency
spark as the excitation source. The technique of the high frequency
spark is given in detail in the first chapter. The advantage of the
high frequency spark method lies in the fact that the samples to be
analysed are used in their original form. This not only saves the
lengthy and laborious work of preparation of ashes but eliminates
the danger of introduction of extraneous impurities. From the
intensity of manganese lines it is found that the quantity of
manganese is varying from sample to sample.
Chapter second deals with the basic theory of quantitative spectro-chemical analysis. Before doing the quantitative estimation of manganese content in the various samples available and drawing conclusions therefrom, it was thought that a critical study of the method of quantitative estimation of manganese would be highly profitable. As it was already remarked earlier the quantitative estimation is highly susceptible to various factors and experimental conditions. For example, one of the many available methods of excitation may prove to be more accurate and reproducible than others. The presence of other elements in the sample will affect the intensity of the lines of the particular element under consideration, and may vitiate the correctness of the estimated quantity. Hence the following problems were undertaken for consideration. Firstly to find out the best method of excitation as regards accuracy and reproducibility. Secondly to find out the influence of different extraneous elements on the intensity of manganese lines. On going through the literature it is noted that no such complete study has been done from all angles in the case of a particular element. No doubt people have studied the erratic behaviour of sources at random and also the influence of extraneous elements in general.

Hence it is thought that this critical study about the estimation of manganese from all aspects will be of great use to this particular problem as well as in others in helping the workers to draw correct conclusions.
The critical study of the excitation sources namely D.C. arc, condensed spark and high frequency spark, as regards the accuracy and reproducibility in quantitative estimation of manganese, is described in the third chapter of this work. This study is done by preparing standard samples containing varying amount of manganese. The spectra of the samples are taken by using three types of excitation sources. From the intensity and percentage of manganese curve, the amount of manganese in a test sample is calculated for each source, and the average deviation is found out in each case. The reproducibility is shown by taking a number of lines from each plate and considering the same lines for four plates taken for each source. This provides in all twelve analysis for each source.

The fourth chapter deals with the extraneous element effect. The effect of calcium, magnesium, potassium and phosphorus is studied individually on the intensity of manganese lines in detail. The contamination effect also is studied by using different salts of magnesium like MgSO₄, MgCO₃ etc. It has been studied by preparing samples in which the percentage of the test element namely manganese is kept constant and that of the extraneous element is varied. Curves are drawn from the readings for each extraneous element, showing the effect of changing concentration of the element on the test element. This effect is studied both in D.C. arc and condensed spark. An attempt has been done to explain quantitatively the influence of extraneous elements in terms of the thermal ionization theory of Saha. Though the extraneous element effect has been explained qualitatively by some workers, no attempt has so far been made to explain it quantitatively.
The fifth chapter deals with the quantitative estimation of manganese in the wheat samples and the results are discussed in the light of the findings of the critical study given in chapters three and four. This study reveals how the concentration of manganese above as well as below a certain percentage is harmful to wheat plant growth. The observations fit in with the findings of the other workers on other plants. Thus in addition to the particular application to manganese estimation in wheat, main stress of this work is on the study of the Physics of the method. It is hoped that this study would be of help to other workers in the biological and agricultural fields by giving an insight into the method from the point of view of Physics and showing them the limitations as well as the strong points.
REFERENCES

   Phil. Mag. 20, 89, 1860 and 22, 329, 1861.
5. Lockyer, J.N. Phil. Trans. Roy. Soc. 163, 253,1873
   Chapt. V Adam Hilger 1929.
   Spectro-chemical analysis.
   Addison-Wesley Press. Inc. 1950.


