METAL CHELATES OF QUINALIZARIN AND METHYLTHYMOL BLUE

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by

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SUPERVISOR'S CERTIFICATE

Certified that the research work described in the thesis entitled "Metal Chelates of Quinalizarin and Methylthymol Blue" was carried out by Mr. Kailash Chandra Srivastava, M.Sc., under my guidance and supervision during the period of October, 1965 to June 1969.

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LIST OF PUBLICATIONS

1. K.C. Srivastava and S.K. Banerji: Use of some substituted 8-hydroxy quinolines as colorimetric reagents in the detection of metal ions; Chem. Age India 18(5), 351 (1967).

2. K.C. Srivastava and S.K. Banerji: Substituted benzoic acids as colorimetric reagents for inorganic cations; Chem. Age India 18(4), 295 (1967).

3. K.C. Srivastava and S.K. Banerji: Quinalizarin as a colorimetric reagent in inorganic analysis: Influence of pH on the reagent and colour reactions with metallic ions; Chem. Age India 18(3), 210 (1967).

4. K.C. Srivastava and S.K. Banerji: Chelate formation between lead(II) and 1,2,5,8 tetrahydroxy anthraquinone (quinalizarin) Spectrophotometric studies on the composition and stability; Aus. J. Chem., 20, 1385 (1967).

5. K.C. Srivastava and S.K. Banerji: Spectrophotometric studies on the composition; Stability and analytical applications of lanthanum(III) 1,2,5,8 tetrahydroxy anthraquinone (quinalizarin) chelate in solution; J.Prakt. Chem. 4, 327 (1968).

6. K.C. Srivastava and S.K. Banerji: Iron(III), Quinalizarin chelate - A study of the composition and stability; Proc. Ind. Sci. Congress, Fiftyseven session (communicated).

7. K.C. Srivastava and S.K. Banerji: Zirconium(IV), 1,2,5,8 tetrahydroxy anthraquinone chelate - A study on composition and Stability. Jour. B.I.T.S. Vol. 2 (in press).

8. K.C. Srivastava and S.K. Banerji: Spectrophotometric determination of tungsten with quinalizarin (communicated).

9. K.C. Srivastava and S.K. Banerji: Methylthymol blue as a chromogenic reagent in the inorganic analysis: Influence of pH on the reagent and colour reactions with cations; Chem. Age India 20(7), 607 (1969).

10. K.C. Srivastava and S.K. Banerji: The Spectrophotometric determination of uranium(VI) with methylthymol blue. Micro. Chem. J. 13, 699 (1968).

11. K.C. Srivastava and S.K. Banerji: Uranium(VI) - Methylthymol blue (penta sodium salt) Chelate - A Spectrophotometric study. J. Prakt. Chem. (in press).

12. K.C. Srivastava and S.K. Banerji: Vanadium complexes of methylthymol blue - Composition Stability and analytical applications; Chim. Anal. (in press).

13. K.C. Srivastava and S.K. Banerji: The Spectrophotometric determination of iron(II) with methylthymol blue; Micro. Chem. J. 13, 621 (1968).

14. K.C. Srivastava and S.K. Banerji: Methylthymol blue as a reagent for beryllium; J. I. Chem. Soc. (in press).

15. K.C. Srivastava and S.K. Banerji: A Spectrophotometric study of methylthymol blue as a reagent for lead. Chim. Anal. 51, 28 (1969).

16. K.C. Srivastava and S.K. Banerji: The Spectrophotometric determination of palladium(II) with methylthymol blue. Indian Chemical Society Annual Convention 1969.

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C O N T E N T S

CHAPTER I

I N T R O D U C T I O N

Coordination compounds

Chemistry is concerned with the structures, properties and reactions of substances. The building blocks which make up substances are the atoms of the several elements. The problem of how and why these building blocks - atoms - unite is as old as the chemical science itself and has probably not been completely solved. Two types of valence bonds-ionic and covalent between atoms in a molecule have long been recognised. Modern approaches have shown that these represent the two limiting types and the possibility of molecules with purely covalent or purely ionic bonds does not generally exist.

The theory of valence developed during the nineteenth century provided, for that period, a satisfactory explanation of the formation and properties of most organic and simple inorganic compounds. But this theory of valence offered no adequate explanation of the union of neutral molecules with ions to form these "Complex" compounds. This caused Alfred Werner (28), the founder of coordination chemistry, to introduce his concept of auxiliary valence in 1893 to explain the formation of such complex compounds. A complex compound was regarded as a compound of a higher order, formed by the union in stoichiometric ratio, of two or more saturated molecules which are themselves capable of independent

existence (5) and which do not vapourise without decomposition (10). These compounds retain their indentity in solution (19) and dissociate partly in their constituents.

In his theory Werner postulated that neutral molecules or oppositely charged ions are coordinated around a central atom or ion in the inner sphere of attraction. The number of such groups, which may be arranged around the central atom, is the coordination number of the atom. He suggested that this arrangement of molecules or ions around the central ion produces a symmetrical spatial grouping. The coordination numbers which permit spatial symmetry of some sort are 2, 3, 4, 6 and 8, of which the values of 4 and 6 are most common. During the period of seventy-five years, the coordination theory has been very useful in the understanding of the formation of complex compounds. It has gained support by the impact of the discoveries in the realm of physical sciences. It has strengthened itself with the application of the knowledge derived from the electronic concept of valence, the theory of quantum mechanics and by various refined techniques of instrumentation. These have made it possible to obtain more details regarding the structure of these molecules(1,9,23).

With the availability of physicochemical methods and instruments for investigation, substantial advances have been made in the field of coordination complexes and with their manifold applications in the field of chemistry, biochemistry, biology, agriculture and technology. The formation of a coordinate bond seems to occur on a much wider scale than was earlier suspected and since we are primarily concerned

with complexes which retain their identity in solution it is useful to say that a compound formed between a metal ion and a ligand, through electron pair sharing, using electrons from the ligand, is called a coordination compound. It should be mentioned here that some ligands such as ethylene, armatic hydrocarbon and carbon monoxide do not donate lone pair of electrons and bond through the use of π type orbitals.

Sufficient activity within the domain of the coordination chemistry has been concentrated on the study of complex formation in solution during the last thirty years. There have been two main approaches to this study; thermodynamic and kinetic. The first deals with the composition and the stability of the complexes while the second with the rate and mechanism of reaction.

Metal chelate compounds(17)

A chelate may be defined as a compound possessing a cyclic structure arising from the union of a metal ion with an electron donor (chelating agent) which is a neutral molecule or a charged species, with two or more points of attachment to produce a closed ring. In ordinary complexes the ligand, being monofunctional, the ring formation does not take place. Thus ring formation is a special characteristic of the chelate compounds and the term chelate (chele meaning claw) was introduced in coordination chemistry by Morgan(18) in 1920 to designate such cyclic structures. Usually chelate rings containing five or six members, including the metal

ion, are more stable.

The formation of inner complex compounds also involves a ring structure which was noted by various investigators including Werner (28), Ley (16) and others, who found that these structures are exceptionally stable, very insoluble in water but frequently soluble in nonpolar solvents, and are often intensely coloured. Feigl (6) states that there is a tendency to exaggerate these properties of inner complexes. Thus, he contrasts the relative instability of the inner complexes with the stability of certain ignited metal oxides and of the naturally occuring sulfides and silicates. Further, he states that although colour intensification does occur, colourless components rarely result in coloured inner complexes. Feigl also asserts that the extraordinary solubility of inner complexes in organic solvents is not always to be observed, although chloroform does have exceptionally great solvent capacity for inner complexes. The chemical and physical properties of metal chelates, in general, resemble those of simple complexes and differ only in a qualitative way. Though chelates are now considered as a distinct class of compounds with characteristic behaviour, yet they may be regarded only as a special type of coordination complexes.

For the formation of a chelate, ring formation is an essential condition but the bond involved in a ring in the case of a bidentate chelate may be either by (i) two covalent bonds, (ii) one covalent bond and one coordinate bond or

(iii) even by two coordinate bonds. In fact, in the earlier stages the nature of the linkages has been used as a basis for the classification of chelate compounds. Covalent bonding is produced by the replacement of a proton in an organic group. Functional groups of this type are sometimes called acidic groups because of the fact that hydrogen may be replaced from them. Coordinate linkages, without the replacement of hydrogen, are formed by the donation of an electron pair.

With the discovery of compounds in which the metal atom is linked to the organic molecule through three or more groups, it became necessary to devise another system of classification. Morgan originated for these compounds the name tridentate, quadridentate, quinquidentate and sexadentate. Since polydentate molecules may be attached to the central metal atom through two kinds of functional groups, acidic and coordinating, to form covalent and coordinate linkages, the logical classification should follow the number and kind of attachment involved. Such a classification has been developed by Diehl (4) and is being presented here in its outline. According to the classification, rings may be closed in the case of a tridentate chelate either by (i) three covalent linkages, (ii) two covalent and one coordinate bond, (iii) one covalent and two coordinate bonds or (iv) by three coordinate bonds and so on, for quadridentate, quinquidentate and sexadentate. There is no way of distinguishing a coordinate covalent bond from any other covalent bond present,

once the chelate is formed. In the present work, therefore, the bonds have been indicated by - through out and not by → as suggested by Martell and Calvin (17).

Theories of Chelation

A large number of metal chelates can be isolated in a pure form and these are usually stable compounds. Due to complexation and chelation, the loss of the normal chemical properties of the metal ion in solution occurs and, in general, properties such as conductivity, oxidation potential, absorption spectra, intensity of light absorption, hydrogen ion concentration changes, optical activity, solubility and normal chemical reactions of hydrated ions are drastically altered, which furnish positive proof of complexation or chelation.

Of the more modern theories advanced to explain the bond structures in metal complexes and chelates, the simplest approach is based on valence bond theory. It assumes that the association results from the overlap of an orbital of the ligand containing an unshared pair of electrons with hybridized orbitals of the metal ion. This may be thought of either as a sharing of the electron pair between the metal ion and ligand or as a partial donation of the ligand electron to the metal ion. From the point of view of depicting the bonding in terms of the electron configuration of the metal ion, it is profitable to consider that the ligand

electron pairs enter the metal ion orbitals while still maintaining the electronic configuration originally present in the ligand. The main features of valence bond theory are (i) the formation of directional bonds through the overlap of atomic orbitals (ii) the formation of hybridized bonds by mixing of atomic orbitals, that are capable of forming stable bonds. Covalent σ -bonds can be formed through the overlap of a filled orbital of the central metal, while a π bond through the overlapping of a vacant ligand orbital with a central metal orbital containing available d-electrons.

Usually σ and π bonds occur simultaneously and produce a stronger bond than either would alone. Two types of π bonds are commonly recognized: either a combination of σ (ligand → metal) and π (metal → ligand), or σ (ligand → metal) and π (ligand → metal). The former are generally formed with the metal ion in a low oxidation state (many electrons) and an unsaturated ligand, while the latter type is prevalent with saturated ligands and the metal in a high oxidation state.

The difficulty in explaining some magnetic properties and the inability to explain spectral properties have found the valence bond theory as applied to coordination compounds in a position of diminishing usefulness (15).

In the molecular orbital theory, the formation of molecular orbitals is assumed rather than the simple overlap of the orbitals of the reactants. The configuration of the molecules is then obtained by introducing electrons to the lowest orbital of the molecular frame work. As the lower

energy levels are occupied, the entering electron goes to a higher excited level. These electrons oppose bond formation and are known as antibonding electrons. Electrons occupying a lower energy level are the bonding electrons, while those not participating in the bond formation are known as nonbonding electrons. The energy separation between the nonbonding and the lowest of the antibonding orbitals is the ligand field separation. The introduction of electrons into the antibonding orbitals has the effect of weakening the bonding orbitals.

The crystal field theory revived from the early work of Van Vleck (26) deals with the electrostatic interactions of the ligand ions with the central ion and the consequent effect of the field on the energy of the metal d-orbitals. This theory has now been extended to include neutral polar ligands which are covalently bonded to the central metal ion and consequently it is now called the ligand field theory postulated by Schlapp and Penny (24). This has been worked out mainly by Orgel (20, 21) to interpret certain aspects of the transition metal chemistry. It considers the influence of the electrostatic fields due to the ligand, on the five d-orbitals of a transition metal atom. If a ligand that possesses an electrostatic field approaches a metal ion or atom, the energies of the degenerate d-orbitals (in ligand field free) condition becomes distinguishable, and the orbitals lying in the directions of the ligand acquire a higher energy, relative to those which are present between the line of approach of the ligand. The strength of the

electrostatic field of the ligand is influenced mainly by two factors, viz. the charge density of the central metal ion and the nature of the ligand itself. If the approaching ligand has a weak electrostatic field, then the splitting of the orbital degeneracy is small, and if the field is a strong one then the splitting is large. So when a transition metal is introduced into the field of octahedral symmetry, the electrons preferentially fill up the lower energy level first. The ligand field theory has been found to be more valuable for describing metal-ligand interaction and has been very helpful particularly in explaining the magnetic susceptibility and the visible absorption spectra of the × metal complexes of the transition metals of the first long period.

The importance of Metal Chelates

The application of metal chelates is manifold in various chemical, biological and technological fields. Metals which are essential for plant and animal nutrition are known to form chelates with the materials present in the organism (27). Thus chlorophyll, the green pigment of plants, contains two closely related coloured substances, both of which are magnesium chelates containing four pyrrole neuclei united by methylene groups to form the porphyrin ring. Hemin the red colouring matter of the blood is an iron chelate (22). This compound also contains a porphyrin ring with four pyrrole

nuclei and is structurally quite similar to chlorophyll. It is interesting that among the invertebrates especially in crustaceans and mollusks, the central atom is copper in place of iron.

Many enzymes are active only if trace amounts of metal ions are present. In many cases the active site of the enzyme is at a coordination position of the metal (11). Another important use of chelating agents is in water softening. Ion exchange resins have been developed, based on coordination phenomena, which remove both cations and anions from aqueous solution and the resulting deionized water may approach distilled water in purity. Prevention of precipitate formation of trace metals in a variety of products by the use of chelating agents of the EDTA type is an accomplishment of recent developments.

The formation of metal lakes in mordanting is well known in the textile industry. In leather industry and in smooth electrodeposition of metals coordination and chelation play an important role. Another point of interest is the use of metal ion buffers. The concentration of a free metal ion in a system may be maintained at a fairly constant level in a required range in the presence of a suitable chelating agent.

Chelating agents which form water soluble chelates are called sequestering agents and are used in aqueous solution for the removal of objectionable metal ions. Chelating agents such as ethylene diamine tetra-acetic-acid are used

to speed up the elimination of harmful radio-active metal from the body.

Chelates in Inorganic Analysis:

One of the important applications of chelating agents in inorganic analysis is the detection and determination of inorganic ions. The formation of a coloured precipitate or lake enables the detection of minute quantities of inorganic ions and forms the basis of the so-called spot methods for identification (8). Chelating agents, having specific reactivity with several ions, leading to the formation of sufficiently insoluble inner complex compounds, are used in gravimetric procedures as precipitating agents. The formation of coloured chelates by metals with various chelating agents has received considerable attention in recent years. It forms the basis of colorimetric analysis by the measurements of the intensity of colour of the solution (14). The procedure involving the measurement of intensity of the colour is termed as a photometric method of determination. Almost all metals can be determined colorimetrically with organic reagents and sandell has estimated that for at least three-fourths of the metals, organic reagents are superior to inorganic reagents because of better selectivity or sensitivity.

The advent of excellent and relatively cheap spectrophotometers about thirty years ago has not only given a great impetus to the methodology and technique of

photometric determinations but has also extended the scope of colorimetric analysis by enabling the analyst to work in the nonvisible range of the spectrum and to analyze mixed colours.

Chelating agents which form very stable water soluble metal complexes are suitable as titrants for metals. Either the metal ion is titrated directly with the reagent solution or an excess of the reagent is added and a back titration made with an appropriate metal ion solution. The end points are detected by the use of metal indicators. A metal indicator is an organic reagent that undergoes a pronounced colour change, on reaction with one or more metals to form a complex. It is desirable that both the reagents and complex be water soluble. The metal indicator complex must be sufficiently weaker than the metal chelating agent complex so that a sharp end point is obtained by a shift in equilibrium in favour of the EDTA complex (2, 25).

The formation of metal chelates involves the replacement of hydrogen ions by a metal ion from the acid form of a chelating agent (29). The conventional type of organic acids, particularly those containing the carboxylic group, have limited application in analytical chemistry. Of greater interest are the organic acids or compounds containing groups other than carboxyl and capable of realeasing hydrogen ions in solution on subsequent replacement by metallic ions. Some organic compounds, not ordinarily considered as acids, yield small amounts of hydrogen ions

due to ketoenol isomerism when the equilibria are disturbed by the introduction of certain metallic ions that are capable of forming stable chelates or complexes. The most common acidic group in organic compounds is the hydroxyl (-OH) group. It does not ordinarily split off hydrogen ions, but it does so, frequently, on interaction with a metal ion to yield stable chelates or complexes through the coordination of phenolic oxygen (30). It is interesting to note that generally ligands have considerably lower reactivities when complexed than when in their free state (3). A number of typical nonmetallic elements of group V, VI and VII are nitrogen, phosphorous, sulphur, oxygen and fluorine which also behave as suitable electron donors in chelate or complex formation.

The value of a reagent for its use as a satisfactory colorimetric reagent mainly lies in its specificity and selectivity. Such reagents are difficult to be found and whatever conditionally specific ligands have been discovered, they are mainly as a result of trial and error procedure rather than of a systematic search from theoretical considerations. The value of a reagent may be enhanced enormously by masking and unmasking agents. Masking agents, may greatly increase the selectivity of reagents. The use of organic compounds as masking agents that have seen most development recently are amino carboxylic acids. EDTA and other amino carboxylic acids form stable water soluble complexes with the alkaline earth elements and even to some extent with alkali metals.

Because of high stability and water solubility of their complexes, these reagents are excellent for masking metal ions. Unmasking or demasking (12, 13) also may be used to improve the selectivity of a reaction. Feigl points out (7) that the most obvious example of unmasking is precipitation by pH adjustment. An interesting example to illustrate this phenomena is the demasking of zinc with formaldehyde from the cyanide solution of zinc and nickel.

In general, a reagent may be considered to be useful for spectrophotometric determination of the cations if the following other major requirements are met (i) high sensitivity, (ii) water solubility, (iii) reproducibility, and (iv) availability of other reagents.

It is, therefore, desirable to investigate new chromogenic reactions between metal ions and organic reagents not only from the view point of specificity but also keeping in view the criteria mentioned above.

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R E F E R E N C E S

(1) Bailar, J.C. Jr. and Busch, D. — Chemistry of coordination Compounds, Reinhold, New York (1956).

(2) Barnard, A.J. Jr., Broad, W.C., and Flaschka, H. — The EDTA Titration : Nature and Methods of End Point Detection, J.T. Baker Co., Phillipburg, N.J. (1957)

(3) Busch, D.H., ed., — Reactions of coordinated ligands, Advances in chemistry series, 37, American Chemical Society, Washington, D.C. (1963).

(4) Diehl, H. — Chem. Revs., 21, 39 (1937).

(5) Emeleus, H.J. and Anderson, J.S. — Modern Aspects of Inorganic Chemistry, Routledge and Kegan Paul, London (1960).

(6) Feigl, F. — Anal. Chem., 21, 1298 (1949).

(7) Feigl, F. — Specific, selective, and Sensitive Reactions, Academic Press, New York (1949).

(8) Feigl, F. — Spot Tests in Inorganic Analysis, trans. R.E. Oesper, Elsevier, Amsterdam (1958).

(9) Graddon, D.P. — An Introduction to Coordination Chemistry, Pergamon Press, Oxford (1961).

(10) Grinberg, A.A. — The Chemistry of Complex Compounds, Trans. J.R. Leach, Ed. D.H. Busch and R.F. Trimble, Pergamon Press, London (1962).

(11) Ingraham, L.L. — Biochemical Mechanism, Wiley, New York (1962).

(12) Kinnunen, J. and Merikanto, B. — Chemist Analyst, 41, 76 (1952).

(13) Kolthoff, I.M. and Belcher, R. — Volumetric Analysis III, Interscience, New York - London (1957).

(14) Kortum, G. — Kolorimetric, Photometric Und Spectrophotometric, Springer-Verlag, Berlin (1955).

(15) Larsen, E.M. — Transition Elements, Benjamin, New York (1965).

(16) Ley, H. — Z. Elektro Chem. 10, 954 (1904); Ber. 42, 354 (1909).

(17) Martell, A.E. and Calvin, M. — Chemistry of Metal Chelate Compounds, Prentice Hall, New York (1951).

(18) Morgan, G.T. and Drew, H.D.K. — J. Chem. Soc., 117, 1456 (1920).

(19) Murmann, R.K. — Inorganic Complex Compounds, chapman and Hall, London (1965).

(20) Orgel, L.E. — An Introduction to Transition Metal Chemistry: Ligand Field Theory, Methuen, London (1960).

(21) Orgel, L.E. — Endeavour, 22, 42 (1963).

(22) Pauling, L. and Coryll, C.D. — Proc. Natl, Acad. Sci., (USA) 22, 159, 210 (1936).

(23) Ray, P. — Presidential Address, Symposium on the Chemistry of Coordination Compounds, Agra (1959).

(24) Schlapp, R. and Penny, W.G. — Phys. Rev.,42, 666 (1932).

(25) Schwarzenbach, G. — Die Komplexometrioche Titration, 2nd Ed., Euke, Stuttgart (1956).

(26) Van Vleck, J.H. — Theory of Electric and Magnetic Susceptibilities, Oxford Univ. Press, London (1932).

(27) Wallace, A. — Metal Chelates in Plant Nutrition, National Press, California (1956).

(28) Werner, A. — Neure Auschanungen auf dem Gebiete der anorganischem. chemie 4th ed., F. vieweg Und Sohn, Brunswick (1920).

(29) Yoe, J.H. and Sarver, L.A. — Organic Analytical Reagents, John Willy, New York (1941).

(30) Yoe, J.H. — Fisher Award Address, Analyt, Chem., 29, 1246 (1957).

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CHAPTER II

METHODS OF DISCERNING CHELATE FORMATION IN SOLUTION

METHODS OF DISCERNING CHELATE FORMATION IN SOLUTION

In general, any property of a system which is related to the concentration of one of the species involved in the formation of the complex (hydrogen ion, metal ion, ligand or the chelate) may be used to show the formation of a complex. Some techniques which have been used to study complexation reactions are absorption by Ion exchange (48, 49, 50), pH measurements (10), Polarography (15, 34), Opticochemical methods (31, 46), Solubility (52), reaction kinetics (58) and electrical conductance (33). Among the numerous other methods oxidation reduction potentials, electrophoresis, isotopic metal or ligand exchange, liquid liquid partition, dielectric polarization measurements, magnetic susceptibility, heats of mixing, volume changes, molar refraction, ultrasonic absorption, ultracentrifugation, dialysis and light scattering are useful in specialised situations.

Absorptiometric Measurements

In recent years, investigations on the absorption of light have extensively been employed for the study of the coloured complexes in solution. For the determination of the concentration of a coloured substance in solution, two fundamentally different techniques have been used. The

simplest method involves the duplication of the colour i.e. the colour of a sample solution is matched with that of a standard solution containing a known quantity of the constituent being determined. This technique is known as colorimetry. The second technique is more refined and involves the measurement of absorption of light by a solution and is often termed as absorptiometry. The more common term used for this method is spectrophotometry, since light consisting of a restricted band of wave length is used with advantage.

In the spectrophotometric method, it is possible to employ almost monochromatic light of a narrow band width by the dispersion of light through a prism or a grating. This fact is of great importance for precise measurements of absorbance, since the Beer's Lambert law, holds good only with monochromatic radiations.

$$E = \log(I_o/I) = \epsilon cd \qquad \text{----- (2-1)}$$

Where E is the absorbance of the solution; I_o is intensity of the incident monochromatic beam; I is the intensity of transmitted beam; c is the concentration in moles/liter; d is the depth of solution traversed by light; and ϵ is a constant, extinction coefficient, whose value for specialised units depend upon the solvent, the temperature and the wave length.

In the case of absorption; by a mixture of the substances, not interacting between themselves, the total absorbance is equal to the sum of the absorbance of the constituents in the same thickness of solution, thus

$$E = \log(I_o/I) = \Sigma i\ Ei = \Sigma i\ \epsilon i\ ci\ di$$
$$= (\epsilon_1 c_1 + \epsilon_2 c_2 + \epsilon i\ ci)\ d \quad \text{---- (2-2)}$$

Hence, it is possible to determine the concentration of a coloured species in solution from absorbance studies.

Opticochemical Methods (31, 46)

Formation of complexes can profitably be studied by the application of Beer-Lamberts law by the measurement of absorption of light. A rection between a metal ion M and a chelating agent Ke is given by:

$$mM + n\ Ke \rightleftharpoons M_m\ Ke_n \quad \text{---- (2-3)}$$

and the instability (or the dissociation) constant, kd of the chelate is given by

$$kd = \frac{[M]^m\ [Ke]^n}{[M_m\ Ke_n]} \quad \text{---- (2-4)}$$

and the formation (or the stability) constant is given by

K

$$K = \frac{[M_m\ Ke_n]}{[M]^m\ [Ke]^n} \qquad - (2\text{-}5)$$

If a is the initial concentration of the metal ion, b that of the chelating agent and x the concentration of the chelate formed at equilibrium, then the formation (stability) constant expression becomes

$$K = \frac{x}{(a-mx)^m\ (b-nx)^n} \qquad - (2\text{-}6)$$

By determining x, the value of K can be calculated since the values of a and b are known.

Numerous procedures are known which employ absorption measurements for the calculation of the composition of complexes. A brief account of some of the better known methods is given below:

Methods of Continuous Variations

Job's method of continuous variations of isomolar solutions is often used for study of complexes in solution. Solution properties which are linear functions of the concentrations of the species involved are analyzed in applying the method. Some properties which have been employed are refractive index (56), dielectric constant(59), density (64), and light absorption (21, 61). A solution property adoptable to this method is ion exchange which

has been used by many workers (12, 14, 53) for the study of complexes in solution.

Since the work of Vosburgh and Copper (61), this method has been widely used for the study of complex forming systems in solution (4, 13, 35, 55). It may be mentioned here that the principles of the method of continuous variation were worked out by Ostromisslensky (42) in 1910 and by Denison (16) in 1912. But the credit of invention of the method is generally ascribed to Job (26).

This method has been found very valuable for the study of the stoichiometry of complexes using an additive molecular property as a guide. Mixtures of the solution of M of molar concentration c and ke of molar concentration c' are prepared. The ratio is $c'/c = p$. A volume of the second solution ke is mixed with a volume (1-x) of the first, and there is no contraction in volume. Then the composition of the mixture has to be determined, where the amount of complex formed, i.e. x is maximum. If c_1, c_2, c_3 are the respective molar concentrations of M, Ke and $M_m Ke_n$ after the equilibrium has been attained, the following equations apply for any such mixture.

$$c_1^m \; c_2^n = Kd \; c_3 \qquad \text{-----(2-7)}$$

where Kd is the dissociation constant of the complex

$$c_1 + mc_3 = c\,(1-x) \qquad \text{---- (2-8)}$$

$$c_2 + nc_3 = Pc\,x \qquad \text{---- (2-9)}$$

The concentration c_3 of the complex, then depends only upon the composition x of the given mixture.

On differentiating 2-7, 2-8 and 2-9 we get

$$m\, c_2 \frac{dc_1}{dx} + nc_1 \frac{dc_2}{dx} = 0 \qquad \text{----(2-10)}$$

$$\frac{dc_1}{dx} = -c \qquad \text{----(2-11)}$$

$$\frac{dc_2}{dx} = pc \qquad \text{----(2-12)}$$

Putting the values of dc_1/dx and dc_2/dx in 2-10 we have

$$n\, pc_1 - m\, c_2 = 0 \qquad \text{----(2-13)}$$

Multiplying 2-8 by n and 2-9 by m, and on simplifying

$$c_1 = \frac{mpcx - nc\,(1-x)}{n(p-1)} \qquad \text{----(2-14)}$$

Substituting the value of c_1 in 2-13 and on simplifying equation 2-15 results

$$c_2 = \frac{P}{n(p-1)} \left[mpcx - nc\,(1-x)\right] \qquad \text{----(2-15)}$$

Substitution of the value of c_1 in equation 2-8 gives

$$c_3 = nc(1-x)\,(p-1) - \frac{mpcx - nc\,(1-x)}{mn\,(p-1)} \qquad \text{----(2-16)}$$

Then substituting the value of c_1, c_2 and c_3 in equation 2-7 we have

$$\frac{c^{m+n^{-1}} \; p^{n^{-1}} \; [p^{m+n}) \; X^{-n}]^{m+n}}{m^{n-1} \; n^{m-1}} = Kd \; [n-(m+n) \; X] \; (p-1)^{m+n^{-1}} \quad --(2-17)$$

where p = 1 (i.e. for equimolecular solutions), the right hand side of the equation 2-17 becomes zero and therefore,

$$(m+n) \; x-n = 0$$

$$\text{or} \qquad m/n = (1-x)/x \qquad \text{---- (2-18)}$$

as c, p, m and n are finite constants. Hence from a knowledge of the value of x where c_3 is maximum, the formula of the complex can be determined from the ratio m/n using equation 2-18, taking the simplest values of m and n provided that the two primary solutions used are of equimolecular concentration. After determining the values of m and n, the value of Kd can be determined by equation 2-17, using the value of x for maximum c_3 in the case of two primary solutions which are not equimolecular (i.e. where p is not equal to 1).

The problem then obviously reduces to the determination of the value of x for which the concentration c_3 of the complex $M_m \; Ke_n$ is maximum, using both equimolecular and nonequimolecular primary solutions of M and Ke. This offers no difficulty when $M_m \; Ke_n$ has a property not possessed by M and Ke, then the value of x, where the property is maximum

gives the maximum value of concentration c_3 of the complex. Usually, however, such a property is difficult to be found. In such cases, Job proposed to study as a function of x any molecular property which obeys the mixture law in the following way:

$$p \text{ mixture} = \alpha pA + \beta pB + \gamma pC + \text{------}$$

where α, β, γ ----- are the number of moles of A, B and C ------- present in the solution and pA, pB, pC ------ are the respective molar values of the property p for A, B, C ------.

Job showed that the difference Y, of the observed value of the property p for any mixture of xml of a solution of Ke and (1-x) ml of a solution of M from that calculated for the mixture by the additivity rule with the assumption that no reaction takes place when plotted against the different corresponding values of x, gives a curve, the maximum (or minimum) point of which represents the value of x where c_3 is maximum.

In his studies Job (26, 25) chose molecular extinction coefficient as the property to be studied and he determined it spectrophotometrically for various solutions of pure M and Ke and their mixtures in order to find out the value of Y for different values of x. Job emphasised that the method is applicable to such systems where only one

complex is formed. Vosburgh and Cooper (61) modified Job's method to study the composition in a few cases, where more than one complex is formed in solution by conducting studies at several wave lengths. A more general treatment applicable in such cases is given by Katzin and Gebret (29).

Most of the methods (3, 4, 7, 13, 18, 22, 25, 29, 45, 51, 55, 61) developed for the determination of stability constants of complexes from data obtained from continuous variation studies apply when only one complex is formed. Recently Urszula Stolarczyk (57) has extended the method of continuous variation for the determination of stability constants of several complexes in a metal ion-ligand system.

More recently Klausen (29a) has described a method for the determination of stability constant of complexes in solution based on the method of continuous variation and on computer calculated values of the maximum complex concentration for different total molar concentrations. Thus method can be used to differentiate between monomeric and dimeric complexes $A_m B_m$ with m = n.

The method of continuous variations, has been very popular for the studies of the composition of complexes and in spite of the criticism of the method by a large number of workers (1, 27, 28, 54, 62, 63). it is agreed that the results are reliable when absorbance measurements are carried out.

Mole Ratio Method

Another convenient and popular method for the investigation of coloured complexes in solution is the mole ratio method worked out by Yoe and Jones (66). For this method a series of mixtures is prepared containing a constant amount of the metal ion but with increasing ratios of the concentration of the metal ion to that of the reagent or (vice versa). The curve of absorbance plotted against the concentration ratios rises linearly from the origin when both the reactants are colourless and breaks sharply to a horizontal straight line at molar ratio of the components in the complex. However, a complex that undergoes appreciable dissociation in solution gives a continuous curve, which only becomes approximately parallel to the molar ratio axis when an excess of the variable component is added. It is often seen that such a curve breaks sharply at the correct molar ratio if the ionic strength of the solutions is adjusted to a suitable value by the addition of an indifferent electrolyte. Thus in such cases it is possible to get true composition of the complex. Mayer and Ayres (36) have worked out the mathematical treatment of the mole ratio method for deducing the composition of the several complexes formed in a system under a given set of conditions.

Slope ratio Method

Harvey and Manning (23) proposed the slope ratio method. In this method the stoichiometry is arrived at by comparing

the slopes of the two straight line plots of the absorbance of solutions obtained by varying the concentration of the first one and then the other component in the presence of a large excess of the second component.

If we consider equation 2-3 where the concentration of Ke is constant and in sufficient excess to make dissociation negligible, then the equilibrium constant will be proportional to the analytical concentration of M added in reaction, hence

$$[M_m\ Ke_n] = c\ \ M/m \qquad \text{---- (2-19)}$$

where $[M_m\ Ke_n]$ is equilibrium concentration and c = Analytical or total concentration. From Beer's law, we have the relation,

$$E = e\ [M_m\ Ke_n]\ d \qquad \text{---- (2-20)}$$

where E = measured extinction

e = molar extinction coefficient

d = thickness of the cell in cm.

on substituting the value of $M_m\ Ke_n$ in 2-20, expression 2-21 follows

$$E = e\,d\,cM/m \qquad \text{---- (2-21)}$$

E is plotted against different analytical concentrations of M, keeping the concentration of Ke constant and in excess over the straight line portion of the curve, equation 2-22 is valid and thus straight line will have a slope given by

$$\text{Slope } 1 = \epsilon d/m \qquad \text{---- (2-22)}$$

Similarly if M, the constant component is present in excess and the concentration of Ke is varied,

$$[M_m\ Ke_n] = c\ Ke/n \qquad \text{---- (2-23)}$$

and if E is plotted against c Ke, the slope of the straight line of the curve will be

$$\text{Slope } 2 = \epsilon d/n \qquad \text{---- (2-24)}$$

The ratio of n to m in the complex may be determined by taking the ratio of the two slopes

$$\text{Slope } 1/\text{Slope } 2 = n/m \qquad \text{---- (2-25)}$$

Frank and Oswalt Method

The method described by Frank and Oswalt (20) is effective in identification of 1:1 complex.

In this method an attempt to discover the composition is made with the solution with a given molar concentration of metal at a given pH value, but with varying reagent concentra-

tions. If only a 1:1 complex is formed under certain conditions, and the absorbance of the solution, A, is measured against a reagent blank, the following relationship may be derived:-

$$ab/A = (a+b)\ (\varepsilon c-(\varepsilon o)H) + 1/(k_1')\ H(\varepsilon c-(\varepsilon o)H \quad \text{---} \quad (2\text{-}26)$$

where a and b represent the total molar concentration of metal and the reagent respectively; εc is the molar extinction coefficient of the complex and $(\varepsilon o)H$ is the apparent molar extinction coefficient and $(k_1')H$ is the apparent formation constant of the complex at the given pH value.

On plotting ab/A against (a+b) at a given wave length and at a constant pH, a good linearity of the curves supports the assumptions inherent in Equation 2-26 indicating that only a 1 to 1 complex is formed under the conditions investigated.

Other Methods

Numerous other methods based on absorptiometric measurements have been employed for the study of complexes in solution. Some of them are the logarithmic method (6,17) and the method of isobestic points (47). Molland (38) has worked out a method which is applicable in cases involving more than one central ion in the reaction. Methods applied for the investigation of the formation of step wise

complexes include those of Bjerrum (9), Newman and Hume (41), Janssen (24) and of Yatsimirskii (65), Methods applied in special cases include those of Klotz and Lohming (30) and Lewis and Skoog (32). The method of proportional absorbances developed by Budešinsk'y (11) in recent years, is useful for establishing the existence of binuclear complex formed in solution. The investigation of the nuclearity of complexes is important from a theoretical point of view. It may be mentioned here that in the application of the method of proportional absorbances to the investigation of complexes of relatively high stability, some difficulties are encountered and a full elucidation of the situation is not always possible.

Determination of stability constant

The evaluation of the stability constant is useful for the understanding of the characteristics of a chelate (or a complex). The concept of stability constant is in principle simple but the determination of the thermodynamic constant is beset with many experimental difficulties in obtaining precise, meaningful values. For the study of the stability constant of the chelate two procedures are generally used. The first procedure for evaluation of thermodynamic constant involves the determination of the equilibrium constant at different ionic strengths followed by an extrapolation to zero ionic strength (infinite dilution). The second procedure has been involved by Biedermann and

Sillen (8). It is based on the fact that the activity coefficient can be controlled by keeping the ionic strength constant. In view of the many practical difficulties involved in the determination of true thermodynamic stability constants, Rossotti and Rossotti (43) concluded "It is better to obtain reliable values of the stoichiometric constants than less certain values of the thermodynamic constants, which are useful for practical purposes".

In the present work, the values of stoichiometric constants have been determined at a constant ionic strength wherever possible by swamping the system with an indifferent electrolyte. The values thus obtained have been termed as stability constants in this presentation.

Several methods based on absorptiometric measurements are available for the determination of the stability constants. In the following account, the various methods used in this work for calculating the stability constant are described.

1. Method of Dey and Coworkers

A convenient method has been described by Anderson and Coworkers (19, 60) which is based on the comparison of the composition of the mixtures having identity of colour i.e. the same absorbance values. The method, however, suffers from a limitation that both the interacting solutions forming the complex must be colourless. Dey and

Coworkers (5, 39, 40) modified the method so as to enable it to be applicable to systems where the chelating agent was coloured. The method is discussed below.

The method of continuous variation is adopted and the absorbance of mixtures of varying compositions, at a fixed wavelength is measured. In a graph, the observed absorbance is plotted against $[M]/[M] + [Ke]$ where $[M]$ is the concentration of the metal ion and $[Ke]$ that of the chelating agent. In fig. 2-1 such a graph is shown.

In the system studied during the course of this work, Ke is coloured and M is colourless at the concentrations employed. Hence, with progressive increase of $[M]$, $[Ke]$ decreases and it may reasonably be assumed that in the descending portions of the curves, where M ions are in large excess, most of the chelating agents are bound up in the complex. Therefore, in this portion of the curve the absorbance due to the free chelating agent does not contribute substantially to the absorbance of the system. The observed absorbance, therefore, is due to the colour of the complex. We may, therefore, assume that in curves A, B and C in fig. 2-1 where the optical densities are the same (eg 0.3) the respective amounts of the complex formed in each case are identical.

In a complex forming reaction of the type

$$mM + n\,Ke \rightleftharpoons M_m Ke_n$$

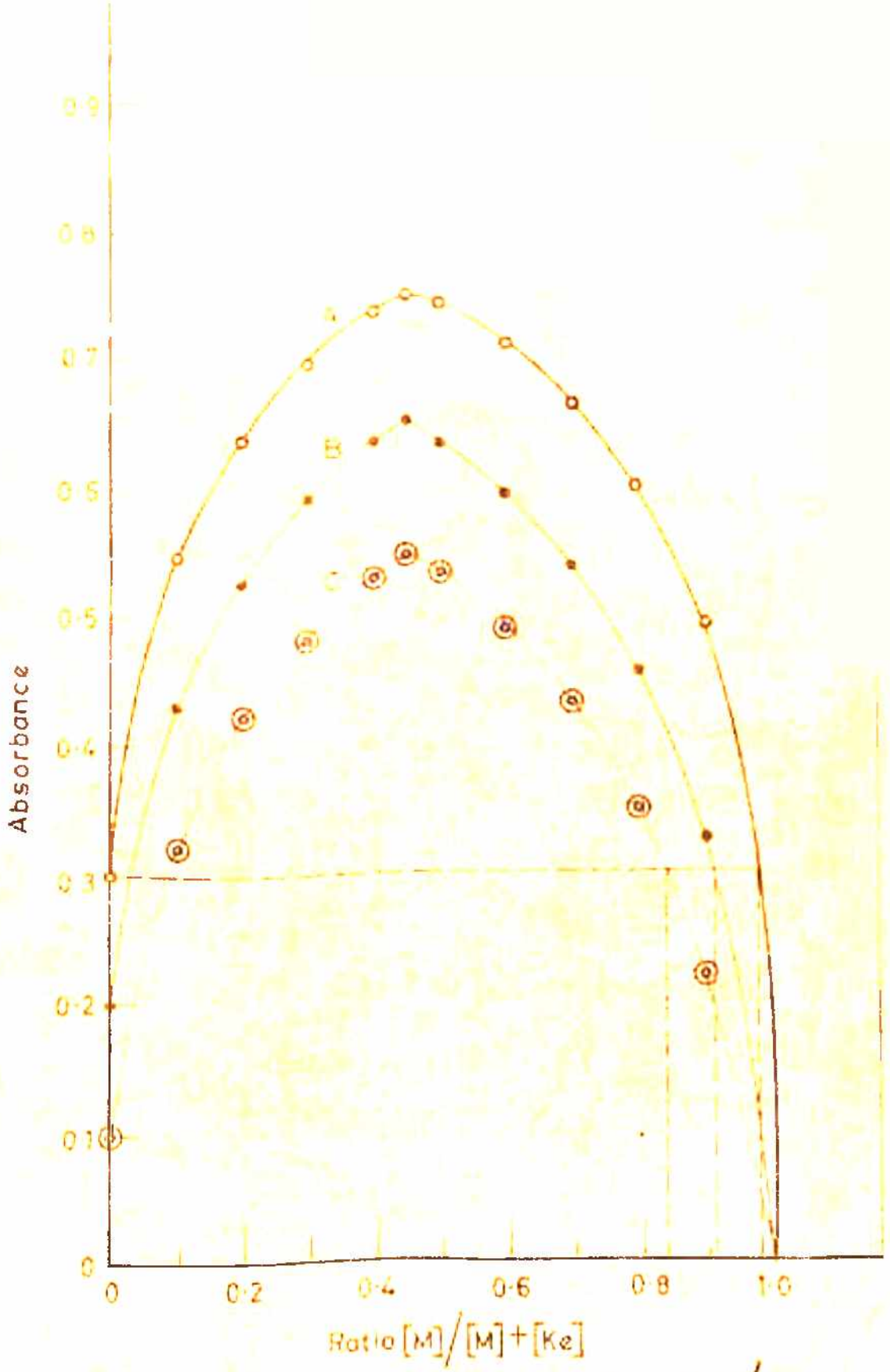

Fig. 2·1 Plot of absorbance against [M]/([M]+[Ke])

. If the reaction is of the type

$$M + 2Ke \rightarrow M Ke_2$$

the formation constant K is given by

$$K = \frac{x}{(a-x)\ (b-2x)^2} \qquad \text{---- (2-29)}$$

and again for two different concentrations of the reactants:

$$K = \frac{x}{(a_1-x)\ (b_1-2x)^2} = \frac{x}{(a_2-x)\ (b_2-2x)^2}$$

$$\text{or} \quad x^2[4\{(a_1+b_1) - (a_2+b_2)\}] + x[(b_2^2 - b_1^2) + 4(a_2b_2 - a_1b_1)] + (a_1b_1^2 - a_2b_2^2) = 0$$

$$\therefore\ x = \frac{-[(b_2^2-b_1^2) + 4(a_2b_2-a_1b_1)] \pm \sqrt{[(b_2^2-b_1^2)+4(a_2b_2-a_1b_2)]^2+4[4\{(a_1+b_1)-(a_2+b_2)\}](a_1b_1^2-a_2b_2^2)}}{8\ [(a_1+b_1) - (a_2+b_2)]} \quad -(2$$

Thus knowing x, K can be evaluated in this case also from equation 2-29 by substitution.

Anderson and Coworkers (19, 60) have concluded as a result of comparative study of the various methods of determination of the formation constants, that the method involving comparison of solutions of equal optical density yields more reproducible results. Many workers (2, 37) have also used the spectrophotometric method for the determination of the composition and stability of the coloured chelates.

2. Method of Continuous Variations

For the calculation of Kd by this method equation 2-17 was used. The symols have their usual significance.

3. Mole Ratio Method

It is also possible to calculate the stability from the mole ratio method also, through a calculation of the degree of dissociation, as proposed by Harvey and Manning. The stability constant K is given by the equation.

$$K = (1-\alpha)/\alpha^2 c \qquad \text{---- (2-31)}$$

where c is the concentration of the complex and α is the degree of dissociation. The degree of dissociation is given by equation.

$$\alpha = (Em-Es)/Em \qquad \text{---- (2-32)}$$

where m = n = 1, the formation constant is given by

$$K = \frac{x}{(a-x)\ (b-x)} \qquad \text{---- (2-27)}$$

where x = the concentration of the complex at equilibrium and a and b are the initial concentrations of the metal ion and the chelating agent respectively.

Taking two concentrations a_1 and a_2 and b_1 and b_2 of the reactants giving the same absorbance of mixture i.e. the same value of x, we have,

$$K = \frac{x}{(a_1-x)\ (b_1-x)} = \frac{x}{(a_2-x)\ (b_2-x)}$$

$$\text{or} \quad x = \frac{a_1 b_1 - a_2 b_2}{(a_1+b_1) - (a_2+b_2)} \qquad \text{---- (2-28)}$$

knowing the value of x from equation 2-28 the value of K can be found out by substitution in equation 2-27.

If the ratio of the reactants in the chelate is 1:2 i.e. if the reaction is of the type:

$$M + 2Ke \rightarrow M Ke_2$$

the formation constant K is given by

$$K = \frac{x}{(a-x)\ (b-2x)^2} \qquad \text{---- (2-29)}$$

and again for two different concentrations of the reactants:

$$K = \frac{x}{(a_1-x)\ (b_1-2x)^2} = \frac{x}{(a_2-x)\ (b_2-2x)^2}$$

$$\text{or} \quad x^2[4\{(a_1+b_1) - (a_2+b_2)\}] + x[(b_2^2 - b_1^2) + 4(a_2b_2 - a_1b_1)] + (a_1b_1^2 - a_2b_2^2) = 0$$

$$\therefore\ x = \frac{-[(b_2^2-b_1^2) + 4(a_2b_2-a_1b_1)] \pm \sqrt{[(b_2^2-b_1^2)+4(a_2b_2-a_1b_2)]^2 + 4[4\{(a_1+b_1)-(a_2+b_2)\}](a_1b_1^2-a_2b_2^2)}}{8\ [(a_1+b_1) - (a_2+b_2)]} \quad -(2$$

Thus knowing x, K can be evaluated in this case also from equation 2-29 by substitution.

Anderson and Coworkers (19, 60) have concluded as a result of comparative study of the various methods of determination of the formation constants, that the method involving comparison of solutions of equal optical density yields more reproducible results. Many workers (2, 37) have also used the spectrophotometric method for the determination of the composition and stability of the coloured chelates.

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where c is the concentration of the complex and α is the degree of dissociation. The degree of dissociation is given by equation.

$$\alpha = (Em-Es)/Em \qquad \text{---- (2-32)}$$

4. By the Measurement of Molecular Extinction Coefficient

Molecular extinction coefficient is defined as specific extinction coefficient for a concentration of one gram mole per liter and a path length of one cm.

$$\epsilon = D/c^t \qquad \text{---- (2-33)}$$

$$= D/c \quad \text{when } t = 1 \text{ cm.}$$

where t = length of absorption cell

c = concentration in gram moles/liter

D = absorbance

The concentration of the complex may be calculated by the equation 2-34

$$c \text{ complex} = D/t.\epsilon = D/\epsilon \qquad \text{---- (2-34)}$$

where c complex = Concentration of complex

t = Absorption cell length

ϵ = Molecular extinction coefficient

Where from K can be calculated from equation 2-27 or 2-29.

5. Frank and Oswalt Method

A convenient method for identification of 1:1 complex is that of Frank and Oswalt. The stability constant $(K_1')H$ is defined as

$$(K_1')H = \frac{x}{(a-x)\ (b-x)} \qquad \text{---- (2-35)}$$

Experimental Details

In order to avoid duplication a brief review will be made here of the experimental details adopted in these investigations which are common to all the system studied.

Instruments

Spectrophotometer

All absorbance measurements were made with a Hilger Uvispek spectrophotometer, using 1 cm matched glass cells.

pH meter

pH values were determined with a Beckman H_2pH meter, with a glass calomel electrode system.

Thermostat

The individual solutions and all the mixtures were kept in a Townson and Mercer precision thermostatic bath maintaining a constant temperature for at least 30 minutes to attain equilibrium

Ion Exchange Absorption Columns

Columns of anionic exchange resin Amberlite IR 45 (oH) and Cationic exchange resin Amberlite IR 120 (H), both BDH AnalaR grade were prepared to find out the nature of the

charge on the chelates.

Materials

All chemicals used through out this work were of reagent grade purity. Double distilled water was used for making the solutions. The working solutions were prepared by appropriate dilution of the stock solution.

Optimum Conditions of Study

All studies were made under optimum conditions so as to get reproducible results eg. measurements were made at a fixed pH in order to avoid any error due to pH variations.

Behaviour of reagents as colloidal electrolyte

The organic dyes used in this thesis were found to behave as colloidal electrolytes; hence extremely dilute solutions of the order of 10^{-4} or 10^{-5} M were employed for the physicochemical measurements. When the solutions are very dilute, it behaves as a true solution and true composition of the complex becomes evident.

Effect of Time on the Colour of the Chelates

The colour formation was found to be instantaneous in most cases and the absorbance attained constancy within a few minutes. However, in same cases it was noted that the colour formation is greatly accelerated by heating; the

maximum colour development is attained within only a few minutes when the mixture is heated in a boiling water bath. It was also found that even upto 24 hours, there was no significant change in absorbance values.

Effect of Temperature

The temperature effect was studied and it was observed that in some cases the colour intensity of the chelate shows marked change within a temperature range of 30 - 90°C.

The Order of the Addition of Reagents

Varying the order in which the reagents were added had no significant effect on the results.

Effect of Reagent Concentration

The effect of reagent concentration was studied with solutions containing a given amount of metal and varying amounts of a solution of ligand. The pH values of the solutions were kept constant and the absorbance measurements were carried out at λ max. It was found that a constant absorbance is obtained when many fold excess of reagent solution is used.

Number of Complex Species Formed

The method of Vosburgh and Cooper (61) was used to ascertain that only one complex is formed in each case

under the specified conditions. Several mixtures containing metal ion and ligand in ratio of 1:0.5, 1:1, 1:2, 1:3 and 1:4 were prepared and then absorbances were measured between a range of wavelength from 400 to 650 nm at 10 and 20 nm intervals as necessary. By the number of shifts in the region of maximum absorbance of mixtures from the λ max of the reagent itself, the number of complexes formed was ascertained.

Composition of the Chelate

The mole ratio of metal to reagent in the complexes was determined by the following methods using absorbance measurements.

(1) Continuous Variations Method;

(2) Mole Ratio Method;

(3) Slope Ratio Method; and

(4) Frank and Oswalt Method (in a few cases).

It was considered desirable to use several independent methods for establishing the composition because often misleading results have been reported by workers who used only one method. It has been found that all different methods reported in this thesis give results which are in good agreement with each other. In case of continuous variation method the results are valid only when equimolecular solution of the interactants are used.

Variation of the stability of the chelate with pH

The organic reagents used in this thesis, change

their colour with the variation in hydrogen ion concentration. The metal chelates of these dyes also show changes in colour with change in pH. Several mixtures containing the metal to ligand in proper ratio were prepared and pH was adjusted to different values. The absorbances were measured from 400 to 650 nm. The pH range within which the λ max of the chelate holds good is taken to be the range of pH in which the chelate is stable.

Evaluation of Stability Constant

The apparent stability constants were determined by the methods already outlined, viz.

(i) Method of Dey et al
(ii) Method of continuous variation
(iii) Mole ratio method and in some cases
(iv) By measurements of molecular extinction coefficient.

In a few cases the method of Frank and Oswalt was used for evaluation of the stability constant.

The values obtained from various methods are in good agreement. The free energy change of formation has also been calculated from the expression.

$\triangle G^{o} = -RT \ln k$ where $\triangle G^{o}$ is the free energy of formation; R the gas constant; T the absolute temperature and K the formation constant.

Beer's law and effective photometric range

The range of concentration for adherence to Beer's law in ppm and also the range for the most effective photometric determination of some metals have been determined.

Sensitivity

The sensitivities of the colour reactions has been determined as defined by Sandell (44) in $\mu g/cm^2$ based on an absorbance of 0.001 Unit.

Molecular Extinction Coefficient

The molecular extinction coefficient was calculated for each of the systems investigated.

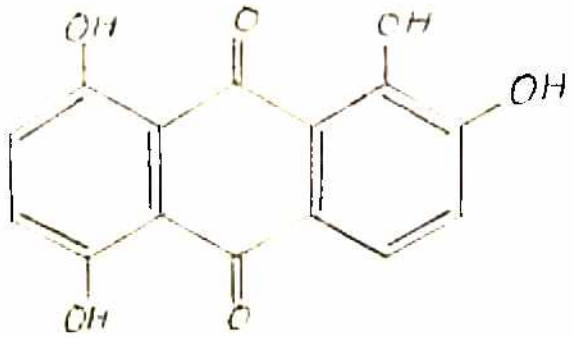
Effect of Diverse Ions

The effect of diverse ions was examined with a solution containing a known amount of metal ion and diverse ion. The pH was adjusted to the required value. The tolerance limit was calculated in each case. The tolerance limit is defined as the concentration of the foreign ion which affects the absorbance of the system by less than $\pm$ 3 percent. Wherever possible an attempt was made to make use of masking agents for elimination of the interference of foreign ions.

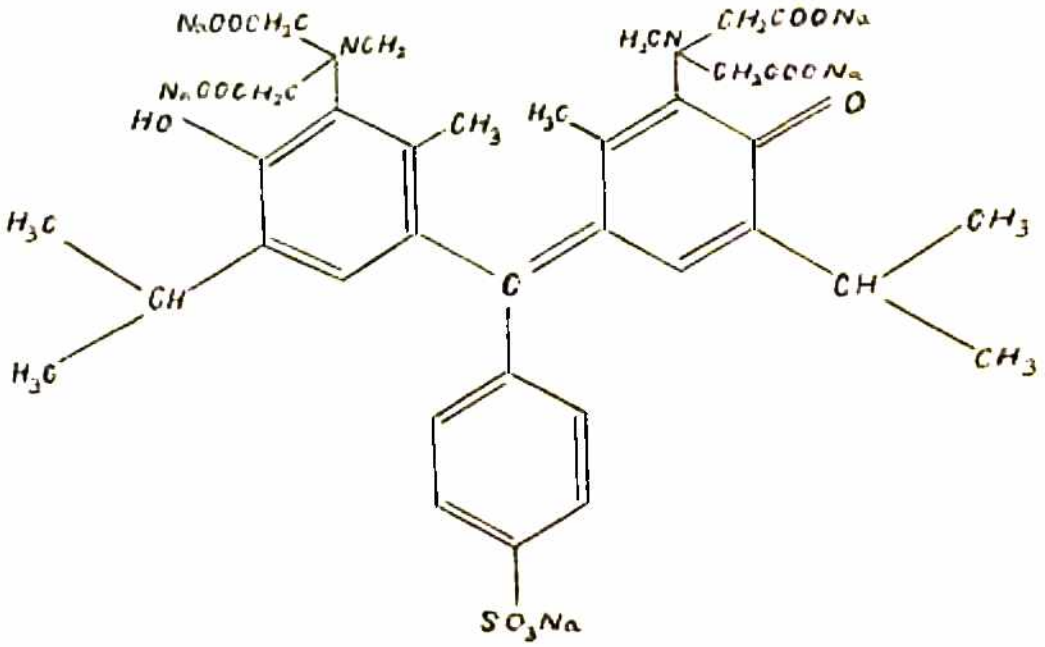
Aim of the present work

In this thesis, five metal chelates involving

quinalizarin (1, 2, 5, 8 Tetrahydroxy anthraquinone) and six involving Methylthymol blue Penta sodium salt (3, 3' - bis [N, N-bi (carboxymethyl) aminomethyl] thymosulphophthalein) as chelating agents have been studied.



QUINALIZARIN



METHYLTHYMOL BLUE PENTA SODIUM SALT

The study has been confined to the coloured chelates only, since these reagents have found application in the colorimetric determination of metals on a micro scale. The reagents investigated are chromogenic reagents and are well known for their applications in colorimetric analysis and have been used successfully for the determination of a few metals. Inspite of the enormous amount of work on record, regarding their use as analytical reagents, not much information is available on the nature, composition and stabilities of the coloured chelates formed as products in these chromogenic reactions. Hence, the aim of the present work has been to investigate systematically the composition, stability and other characteristics of the metal chelates formed in solution, while working with low concentrations. Attempts have also been made to find further applications of the reagents in photometric determination of metals and some observations have been reported in this thesis.

The chelates which have been studied in detail are described in Chapters 3 to 6.

1. Quinalizarin chelates of lead (II), lanthanum(III), iron (III) and zirconium (IV).
2. Quinalizarin chelate of hexavalent tungsten and its photometric determination.
3. Methylthymol Blue - Chelates of hexavalent uranium pentavalent vanadium and bivalent iron.
4. Methylthymol blue - chelate formation with bivalent beryllium, lead, and palladium and their photometric determination.

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R E F E R E N C E S

1. Asmus, E. — Z. analyt. Chem. 183, 321 (1961); 190, 390 (1962).

2. Babko, A.K. — Zavodskaya Lab. 13, 9 (1947).

3. Babko, A.K. — J. Gen. Chem. Russ., 15, 745 (1945).

4. Babko, A.K. — Analiza fizyko-chemiczna Zwiazków kompleksowych Wroztworach, PWN, Warszawa (1959).

5. Baneji, S.K. and Dey, A.K. — Proc. Symp. Chem. Coordination compounds, Agra, 1959 (2) 198 (1960).

6. Bent, H.E. and French, C.L. — J. Amer. Chem. Soc., 63, 568 (1941).

7. Betts, R.H. and Michels, R.K. — J. Chem. Soc., 5286 (1949).

8. Biedermann, G.and Sillen, L.G. — Arkiv Kemi, 5, 425 (1953).

9. Bjerrum, J. — Kgl. danske videns Kab, Sals Kab. Mat. - fys. Sk rifter, 21, 4 (1944); 22, No. 18 (1946).

10. Bjerrum, J. — Metal Ammine formation in Aqueous solution; P. Haase, Copenhagen (1941).

11. Budĕsinský, B. — Z. Analyst. Chem., 209, 379 (1965).

12. Bukata, R.H. and Michels, R.K. — J. Phys. Chem., 68, 258 (1964).

13. Charlot, G.and Gaugin, R. — Les méthodes, d'analyse des réactions en solution, Masson and cie, Paris (1959)

14. Cornec, E.and Urbain, G. — Bull. Soc. Chim.(France) 25, 215 (1914).

15. De Ford , D.D. and Hume, N. — J. Amer. Chem. Soc., 73, 5321 (1951).

16. Denison, R.B. — Trans. Faraday. Soc., 8, 20, 35 (1912).

17. Edmonds, S.M. and Birubaum, N. — J. Amer. Chem. Soc., 63, 1471 (1941).

18. Ernst, Z.L. and Menashi, J. — Trans. Faraday. Soc., 59, 1794 (1963).

19. Foley, R.T. and Anderson, R.C. — J. Amer. Chem. Soc., 70, 1195 (1948); 71, 909 (1949).

20. Frank, H.S. and Oswalt, R.L. — J. Amer. Chem. Soc., 69, 1321 (1947).

21. Gould, R.K. and Vosburgh, W.C. — J. Amer. Chem. Soc., 64, 1630 (1942).

22. Hagenmuller, P. — Compt. rend, 230, 2190 (1950).

23. Harvey, A.E. and Manning, D.L. — J. Amer. Chem. Soc., 72, 4488 (1950); 74, 4744 (1952).

24. Janssen, M.J. — Rec. Trav. Chim., 75, 1397 (1956).

25. Jbb, P. — Compt. rend, 180, 928 (1925).

26. Job, P. — Ann. Chim. (France) (x), 9, 113 (1928).

27. Jones, M.M. and Innes, K.K. — J. Phys. Chem., 62, 1005 (1958)

28. Jones, M.M. — J. Amer. Chem. Soc., 81, 4485 (1959).

29. Katzin, L.I. and Gebret, E.	J. Amer. Chem. Soc., 72, 5455 (1950).
29a. Klausen, K.S.	Anal. Chim. Acta 44, 377 (1969).
30. Klotz, I.M. and Lohming, W.C.	J. Amer. Chem. Soc., 75, 4159 (1953).
31. Kortum, G.	Kolorimetric, Photometric Und Spectrophotometric, Springer Verlag, Berlin (1955).
32. Lewis, C. and Skoog, D.A.	J. Amer. Chem. Soc., 84, 1101 (1962).
33. Ley, H.	Z. electrochem., 10, 954 (1904); Ber. 42, 354 (1909).
34. Lingane, J.J.	Chem. Rev. 29, 1 (1941).
35. Martell, A.E. and Calvin, M.	Chemistry of metal chelate compounds, Prentice Hall, Inc; New York 1952.
36. Mayer, A.S. and Aryes, G.H.	J. Amer. Chem. Soc., 49, 79 (1957).
37. Meeks, H.V. and Banks, C.V.	J. Amer. Chem. Soc., 73, 4108 (1951).
38. Molland, J.	J. Amer. Chem. Soc., 62, 54 (1940).
39. Mukherji, A.K. and Dey, A.K.	J. Inorg. Nucl. Chem., 6, 314 (1958).
40. Mukherji, A.K. and Dey, A.K.	Analyt. Chim. Acta, 18, 324 (1958).
41. Newman, L. and Hume, D.N.	J. Amer. Chem. Soc.,79, 4571 (1957).

42. Ostromisslensky, I. — J. Russ. Phys. Chem. Soc., 42, 1332, 1500 (1910), Ber 44, 268, 1189 (1911).

43. Rossotti, F.J.C. and Rossotti, H. — The Determination of Stability Constants, Mc. Graw-Hill, New York (1961).

44. Sandell, E.B. — Colorimetric determination of traces of metals, 2nd Ed. Inter Science, New York (1950).

45. Schaeppi, Y. and Treadwell, W.D. — Helv. Chim. Acta, 31, 581 (1948).

46. Schläfer, H.L. — Komplex bildung in Losung, Springer verlag, Berlin (1961).

47. Schläfer, H.L. and Kling, O. — Angew. Chem., 68, 667 (1956).

48. Schubert, J. — J. Phys. Colloid. Chem., 52, 340 (1948).

49. Schubert, J. and Richter, J.W. — J. Phys. Colloid. Chem., 52, 350 (1948).

50. Schubert, J. and Richter, J.W. — J. Amer. Chem. Soc., 70, 4259 (1948).

51. Schwarzenbach, G. — Helv. Chim. Acta, 32, 839 (1949).

52. Seth, R.L. and Dey, A.K. — J. Inorg. Nucl. Chem., 17, 312 (1961).

53. Shibata, Y. and Nakatsuka, N. — Japan J. Chem., 1, 1 (1922).

54. Sommer, L. and Hnilička, M. — Bull. Soc. Chim. (France), 36 (1959).

55. Sommer, L. and Lin. Tsin Jao. — Chem. Listy, 55, 574 (1951).

56. Spacu, G. and Popper, E. — Bull. Soc. Chim. (France) 15, 395 (1948).

57. Stolarczyk, U. — Chemia Analityczna 11, 853 (1966).

58. Taube, H . — J. Amer. Chem. Soc., 70, 1215 (1948).

59. Trinh, N.Q. — Compt. rend., 226, 403 (1948).

60. Turner, S.E. and Anderson, R.C. — J. Amer. Chem. Soc., 71, 912 (1949).

61. Vosburgh, W.C. and Cooper, G.R. — J. Amer. Chem. Soc., 63, 437 (1941); 64, 1630 (1942).

62. Watkins, K.O. and Jones, M.M. — J. Inorg. Nucl. Chem., 24, 1235 (1962).

63. Woldbye, F. — Acta. Chem. Scand., 9, 299 (1955).

64. Wormiser, Y. — Bull.Soc. Chim.(France), 15, 395 (1948).

65. Yatsimirskii, K.B. — Zhur. neorg. Khim, (i), 10, 2306 (1956).

66. Yoe, J.H. and Jones, A.L. — Ind. Eng. Chem. Analyt. Ed., 16, 111 (1944).

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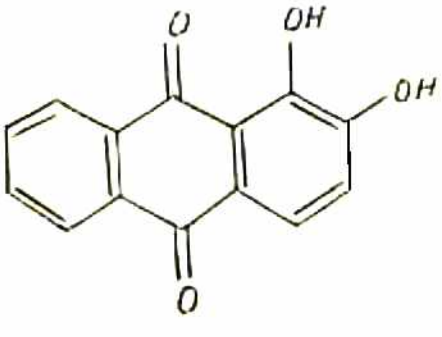
C H A P T E R III

CHELATES OF SOME METAL IONS WITH QUINALIZARIN

Dyes of the hydroxy anthraquinone group are well known for their interesting property of forming coloured products with inorganic ions, and this property has been profitably used in the field of inorganic analysis. The chromogenic reaction between a metal ion and the dye is essentially due to the formation of coloured metal chelate or lake which may be soluble or insoluble, depending upon the concentrations, as well as on the nature of the metal ion. The colour reaction is often sensitive enough to permit micro detection and determination of ions.

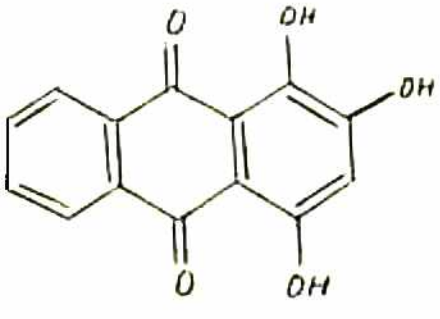
Considerable work has been done on the use of the hydroxy anthraquinone group of dyes and their use as spot reagents and as colorimetric reagents for the detection and determination of various inorganic ions at micro level concentrations.

The chief among the hydroxy anthraquinone dyes are alizarin, purpurin and quinalizarin. They are represented by the following structures.



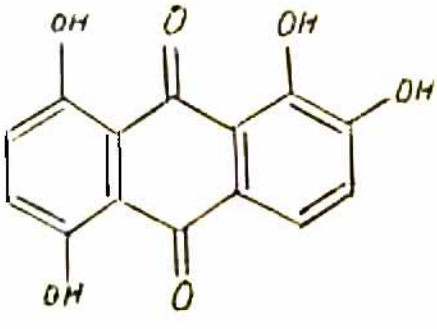
Alizarin

1-2-Dihydroxy anthraquinone



Purpurin

1-2-4-Trihydroxy anthraquinone



Quinalizarin

1-2-5-8 Tetrahydroxy anthraquinone

Quinalizarin (colour index Mordant Violet 26; 58500) is two or three times more sensitive than alizarin as a chromophoric reagent, although it shows large deviations from Beer's law. The deviation may be attributed to the scattering of light by the dye particles, which are relatively large in this case.

Quinalizarin (QZR) may be expected to be more suited for chelation due to the presence of a hydroxyl group to the presence of a hydroxyl group in each of the 1, 2, 5 and 8 positions. Hahn, Wolf and Jäger (32) suggested the use of quinalizarin for the detection of magnesium and since that time it has been used for the detection and determination of many other substances.

An alkaline solution of quinalizarin changes in colour from reddish violet to a cornflower blue in the presence of as little as 0.001 mg of magnesium ion in one ml of solution. Large quantities of magnesium quantitatively yield a blue precipitate. The behaviour of the dye in the presence of magnesium has been made the basis of methods for the detection and determination of small quantities of magnesium (32, 31, 41, 22, 42). Cervinka (19) detected magnesium by adding 2 ml of alcoholic solution of quinalizarin to 2 ml of the solution to be tested and then by adding dropwise 1 ml of 2N sodium hydroxide. In the presence of magnesium the violet red solution turns blue. Hahn (33) detected 0.001 µg of magnesium in a micro drop by a refined technique.

Flood and Smedsaas (28) and Venturello (81) have used

quinalizarin as a developer for the chromatographic detection of magnesium. For the developer, Venturello recommends the use of a 0.5 per cent solution of quinalizarin in 0.2 N sodium hydroxide. After washing out the column with distilled water, and doing a preliminary treatment with 0.2N sodium hydroxide, the developing solution is added to the adsorption tube.

Cauer and Cauer (18) have used quinalizarin for the detection of magnesium in fog particles. The reagent has also been used for the microchemical detection of magnesium as an impurity in ammonium molybdate (57). Hahn and Meyer(34) have used quinalizarin for determination of either phosphate or magnesium. Thiel and Von Hengel (80) have proposed the use of quinalizarin magnesium colour reaction as the basis for a colorimetric method for determining magnesium. Quinalizarin has also been used for the determination of magnesium in aluminium alloys (33), copper zinc alloy (69) and in plant materials (14).

Pavelka and Setta (58) have used quinalizarin for the microchemical detection of calcium as an impurity in ammonium molybdate. Fischer (24) developed a method for detecting beryllium using quinalizarin and suggested that quinalizarin reaction may be used as a spot test for beryllium. It has been reported that quinalizarin also gives sensitive reactions with neodymium, praseodymium, cerium, lanthanum, zirconium and thorium (22). Consequently the test for beryllium can not be successfully employed in the presence of these metals. The quinalizarin test is very satisfactory when applied to

solutions of a beryllium salt that has been purified either by extraction with ethyl ether or by sublimation (10).

A microchemical method which will detect 0.14 μg of beryllium is described by Dubsky and Krametz (21). Quinalizarin has also been used in the qualitative analysis of the arsenic and iron groups (30, 11). Rienäcker (64) has used Fischer's method to detect beryllium in minerals. A number of methods (25, 43) have been devised for determining beryllium by means of the colour which it yields with quinalizarin.

In a weakly acid solution, quinalizarin reacts with aluminium to give a violet purple lake which flocculates on long standing. Magnesium and beryllium may also give coloured lakes with quinalizarin, but in the presence of sodium hydroxide, a lake is obtained only with magnesium, while the beryllium and aluminium remain in solution. Beryllium may, however, give a precipitate in the presence of considerable ammonium salts. Aluminium, on the other hand, is determined in a faintly acid solution, without interference from either beryllium or magnesium. The aluminium quinalizarin reaction has been used for the detection and determination of aluminium (44, 35). Thanheiser (79) has developed a test for aluminium in steel by using a drop of the solution obtained when 1-2 drops of a mineral acid is applied to the freshly cleaned surface of a piece of steel. Schams (68) has used quinalizarin for the determination of aluminium in plants. Burriel and Bolle Tacheo (16) studied aluminium quinalizarin complex by

the method of continuous variation and reported that the complex has got the composition $Al_2(QZR)_3$.

Quinalizarin reacts with solutions of gallium salts to give a pink to amethyst colour depending on the pH of the solution and its gallium content. Gallium may be determined colorimetrically by means of the colour reaction with quinalizarin (88). The best concentration for colour comparison in nessler tubes lie between 0.02 and 0.2 mg gallium per litre. Tin, antimony, indium, platinum and germanium also form lakes with the reagent. Vanadium and molybdenum must be absent and not more than 10 mg of aluminium may be present while determining gallium. Because of many common interferences various procedures must be used for detecting gallium in the presence of different ions. Morin gives the most sensitive test for gallium but quinalizarin is almost equally good for the detection of this metal (86). Akhmedli and Glushchenko (1) studied the suitability of sixteen organic reagents for the spectrophotometric determination of gallium in aqueous and nonaqueous media and found that diphenyl carbazone, magneson and morin are more suitable than quinalizarin.

Pietsch and Roman (60) reported that quinalizarin forms a violet lake with indium and this reaction is useful for the detection and determination of the latter. Von Stein (82) proposed a method for the detection of indium in flue dust. Babko and Kish (3) made a comparative study of photometric reagents for indium and found that pyrocatechol violet and

4-(2-pyridyl azo) resorcinol are more sensitive than quinalizarin. In a further communication (4) they examined the spectrophotometric characteristics of xylenol orange, methylthymol blue, eriochrome cyanine, quinalizarin and 12 other reagents that form coloured compounds with indium and reported that xylenol orange, methylthymol blue and eriochrome cyanine were the most satisfactory ones.

Bevillard (12) reported that the salts of gallium and indium combine with O-diphenols to give complex acids in which the metal is hexacoordinated. The combination of indium with dyes such as alizarin and quinalizarin results in colour changes from yellow to red and yellow to violet. He further reported that O-diphenols of the anthraquinone series can be used to determine the solubility coefficient of the complex formed.

Thallium yields a lake with quinalizarin, but the test is not sufficiently sensitive (60).

The blue coloration or precipitate which Scandium gives with quinalizarin may be used for the detection of the metal. This reaction is analogous to that with magnesium and beryllium (9). Shu-Wei Pang and Coworkers (71) studied chromatographic separation, detection and determination of scandium. Lanthanum gives a reaction similar to that of magnesium and may be detected in the same way as magnesium.

Quinalizarin yields a violet colour when dissolved in concentrated sulphuric acid and this colour changes to blue

when a little boric acid is added (23). Smith (72) suggests the use of a solution of quinalizarin in 93 per cent sulphuric acid. About 0.002 µg of boron can be detected by this reaction. The colour of the boric ester is also used for determining boron. This method may be used for the determination of as small an amount as 0.005 - 0. 0250 mg of boric acid. The colour can be satisfactorily measured by Lovibond tintometer.

Rudolph and Flickinger (66, 67) and other (87, 54a,27) have proposed the use of quinalizarin for the colorimetric estimation of boron in steel. Dickinson (20) has proposed a method for determining boron colorimetrically by comparing the colour formed with alizarin - sulfonic acid with a series of standards prepared with methyl orange. Kelly (40), Shrafan (70) used quinalizarin for the colorimetric determination of boron. Lubomir and Kurzova (51) determined boron in steels.

Germanic acid gives with quinalizarin a reaction similar to that of boric acid. This reagent is more satisfactory than p-nitrobenzene azo chromotropic acid (61) which is commonly used for the detection of germanium. Korenman and Coworkers (46) studied the suitability of a number of hydroxy anthraquinoues for the detection of germanium. Nair and Das Gupta (55) used quinalizarin acetate for the colorimetric estimation of germanium.

Babko and Nazarchuk (5) studied the reaction between tin and quinalizarin and reported that the complex has a composition 1:3.

Wakamastu (84) used quinalizarin for the spectrophotometric determination of tin in iron and steel. Babko and Karnaukhova (6) made a comparative study of the reagents for the photometric determination of tin (IV) and found that hematoxylene, phenyl fluorone, p-nitro phenyl fluorone, quercetin and pyrocatechol violet were the most satisfactory ones.

Nemirovskaya (56) used quinalizarin for the detection and determination fo lead. Leibhafsky and Winslow (49) have reported that by means of a photoelectric recording spectrometer, it is possible to determine zirconium and hafnium by means of the coloured lake which they form with quinalizarin. Other cations may be present in small quantities, but it is impossible to differentiate between hafnium and zirconium. Some attempts are on record to elucidate the composition of the coloured lakes and among them may be mentioned the detailed work on zirconium and hafnium lakes by Leibhafsky and Winslow (50).

The combining ratio of metal to alizarin was found to be non stoichiometric by many workers including Leibhafsky and Coworkers (50, 26). Larsen and Hirozawa (48) suggested that the apparent deviation from stoichiometry was due to hydrolysis of the metal ion which masked the true composition of the complex formed. The determination of zirconium in steel using quinalizarin has been studied by Wakamatsu(85).

Purushottam (62) has used quinalizarin for the estimation of thorium. Burkhard and Teresa (15) have suggested

the use of butyl cellulose or any other glycol monoether as stabilising solvent in the photometric determination of thorium quinalizarin lake.

Kallistratos and Coworkers (39) studied the colour reactions and paper chromatographic separation of yttrium and zirconium.

Babko and Shtokalo (7) made a comparative study of sixteen reagents for the colorimetric determination of tantalum and reported that pyrocatechol violet and hemato-xylene are more suitable than quinalizarin and other reagnets.

Kasey and Maddock (17) observed that protoactinium gives colour reaction with pyrogallol, catechol, gallic acid, tannic acid and quinalizarin.

Ishidat and Yamane (37) reported that uranium (VI) forms coloured chelates with β diketones which have a structural similarity with quinalizarin and suggested the use of uranyl ion for the detection of β diketones.

Ramirezde Verger and Pino Perez (63) used quinalizarin for colorimetric determination of uranium. Pavlorskya (59) made a spectrophotometric study of the reaction of uranyl ion with quinalizarin and determined the composition and the stability constants of the complex formed. The reaction between quinalizarin and plutonium has been investigated by Wolter (89).

Quinalizarin gives a sensitive test with neodynium,

praesodymium and cerium (45). Korenmann and Coworkers (47) used quinalizarin for the determination of rare earths. Recently the reaction between quinalizarin and praesodymium (78) has been investigated and the use of quinalizarin has been recommended for the photometric determination of this element. The formation of a 2:1 complex with an absorbance maximum at 658 nm at pH 8 to 10 has been reported. Akhmedli and Coworkers (2) have reported that quinalizarin forms coloured compounds with some rare elements such as gadolinium, neodymium and ytterbium in a slightly acid medium.

Bodov (13) reported that quinalizarin was polarographically reducible at pH values above 5 and its half wave potential was - 0.6 V in 0.1 M NH_4OH NH_4Cl and - 0.9 V in 0.1 M NaOH. He further states that in strongly alkaline solution Al^{+3} ions did not interfere, but Ca^{+2} and Zn^{+2} ion decreased the diffusion current in proportion of the concentration of the metal ion.

Smith and Ducher (73) state that quinalizarin appears to have certain advantages over alizarin when used for the determination of fluorine. It is more sensitive to small changes in fluoride concentration and the change of colour is easier to distinguish. Freis and Lauckner (29) have used quinalizarin as an indicator in the titration of fluoride by means of thorium nitrate.

Mukherji and Dey (53) have reported that quinalizarin is very sensitive to uranium (VI), iron (III) and calcium(II) as well. These authors recommend that quinalizarin could

possibly be used as a colorimetric reagent for these metals.

In recent communications from this laboratory the results of a detailed search for new colorimetric reagents in inorganic analysis have been reported. Srivastava and Banerji tried some substituted benzoic acids (74), some substituted 8-hydroxy quinolines (75), methylthymol blue(76) and quinalizarin (77) and suggested further applications of these reagents in colorimetric analysis. It is interesting to note from the enormous literature published on the use of quinalizarin in colorimetric analysis, that no systematic work has been done on the composition and stability of the coloured chelates. In this chapter chelates of bivalent lead, trivalent lanthanum, trivalent iron and of tetravalent zirconium have been reported.

Quinalizarin changes its colour with the variation in hydrogen ion concentration and the study of the absorption spectra shows that the region of maximum absorption λ_{max} of the dye shifts with the change in pH of the media. In this chapter we have also reported the influence of the variation of the hydrogen ion concentration on the colour of the dye and also qualitative observations on the colour formation of a number of metallic ions with quinalizarin. We have found that certain ions respond sensitively to the reagent. Ouy observation further suggests the use of this reagent in the colorimetric estimation of these ions under proper conditions.

EXPERIMENTAL

Variation of the colour of quinalizarin with hydrogen ion concentration of the medium.

Standard solution of quinalizarin (BDH organic reagent) was prepared in redistilled ethyl alcohol. To measured amounts of the solution acid or alkali was added and the total volume raised to 25 ml. The pH of the solutions were measured by the Beckman H2 pH meter. The absorption spectra were studied with a Hilger Uvispek spectrophotometer using glass cells of 1 cm thickness supplied with the instrument. The experiments were conducted at 20°C. The results obtained have been represented in fig. 3.1 and summarised in table 3.1.

Table 3.1

Shift of λ_{max} with change in pH of quinalizarin

pH	Region of maximum absorption, nm
2.0 - 6.5	450
6.6 - 6.8	500
7.0 - 7.8	500
8.0 - 10.0	520
11.0 - 12.0	540

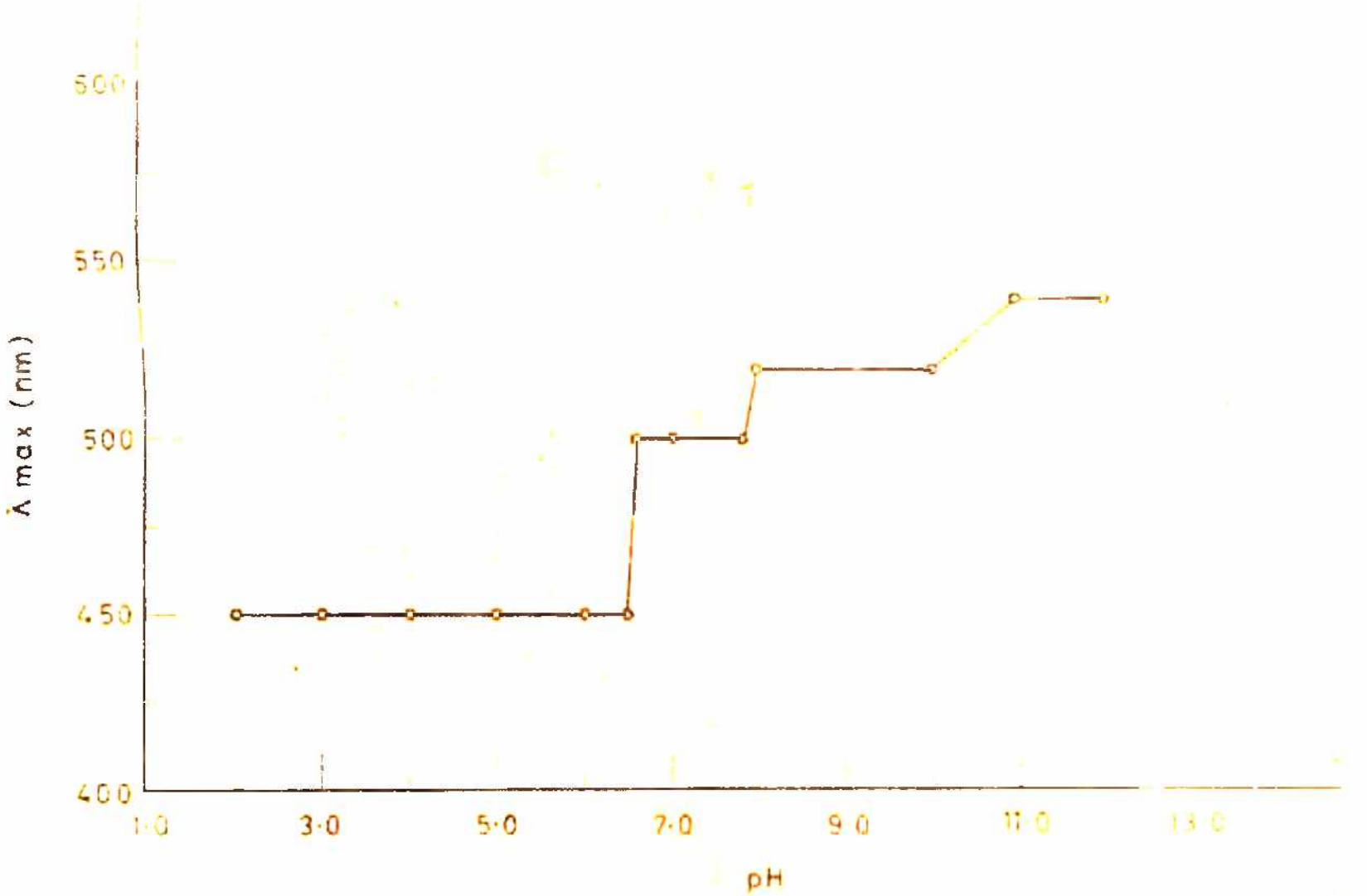


Fig._3·1 Variation of λ max with pH of Quinalizarin $c' = 2 \cdot 0 \times 10^{-4}$ M

Colour formation with inorganic cations

For studying colour reactions with metal ions a 0.001 M solution of quinalizarin was prepared in redistilled ethyl alcohol. Solutions of metal salts of concentration 0.01M were prepared in double distilled water and acid was added in some cases to prevent hydrolysis.

In several test tubes, 1 ml of the solutions were taken and 1 ml of the reagent solution was added to each and the colour was compared with an equal amount of the reagent diluted to the same extent. Table 3.2 records the colour reactions produced with various metallic salts.

Table 3.2

Colour reactions of metal ions with quinalizarin

Sl. No.	Salt solution	Colour	Remarks
1.	Reagent	Orange red	- - -
2.	$AgNO_3$	Yellow	- - -
3.	$Pb(CH_3COO)_2$	Violet blue	Most sensitive with dilute solutions.
4.	$HgCl_2$	Light yellow	- - -
5.	$CdCl_2$	Pinkish	- - -
6.	$BiCl_3$	Yellow	- - -
7.	$CuSO_4$	Pinkish violet	Sensitive with dilute solutions.

contd.

Table 3.2 contd.

Sl. No.	Salt solution	Colour	Remarks
8.	H_3ASO_3	Violet	Sensitive
9.	$SbCl_3^*$	Yellow	---
10.	$S_nCl_2^*$	Yellow	---
11.	$AlCl_3$	Violet	Sensitive with dilute solutions.
12.	$FeCl_3$	Greenish Yellow	Sensitive with dilute Solutions.
13.	$FeSO_4(NH_4)_2SO_4$	Light blue	Sensitive with dilute solutions.
14.	$ZnSO_4$	Violet	No change
15.	$MnSO_4$	Pinkish violet	No change
16.	$NiSO_4$	Light violet	Not sensitive enough to be used for colorimetric analysis
17.	$CoSO_4$	Yellowish pink	
18.	$BaCl_2$	Violet	Not sensitive
19.	$SrCl_2$	Violet	Not sensitive
20.	$CaCl_2$	Violet	Sensitive with dilute solutions.
21.	$MgSO_4$	Violet	Sensitive with dilute solutions
22.	NH_4VO_3	Light pink	Sensitive with dilute solutions.
23.	$(NH_4)_2MOO_4$	Pinkish violet	Sensitive with dilute solutions.
24.	$TeNO_3$	Pinkish violet	No change
25.	$UO_2(NO_3)_2$	Blue	Most sensitive with dilute solutions.
26.	$BeSO_4$	Violet	Sensitive with dilute solutions.

contd.

Table 3.2 contd.

Sl. No.	Salt solution	Colour	Remarks
27.	$Zr(NO_3)_4$	Violet	Most sensitive with dilute solutions.
28.	K_2TeO_3	Violet	Most sensitive
29.	Na_2WO_4	Pink	Most sensitive
30.	$K_2TiO(C_2O_4)_2$	Light pink	Sensitive
31.	$La(CH_3COO)_3$	Violet	Most sensitive

*Acid added to prevent hydrolysis.

The reagent has been found to be sensitive to vanadium, molybdenum, titanium, tellurium, tungsten, lanthanum, iron(II), and copper besides thorium, gallium, magnesium, zirconium, beryllium, aluminium, boron, lead, iron(III), calcium, uranium and rare earths already reported.

Behaviour of the reagent as colloidal electrolyte

The study of the nature of the 50 per cent aqueous ethanolic solution of quinalizarin is useful, before establishing the composition and stability of quinalizarin metal complexes. This was considered essential, because deviations in the composition of the chelate from true stoichiometry were observed to occur in some cases. Electrical conductance studies were, therefore, performed with 50 per cent aqueous ethanolic solutions of quinalizarin. The results

established the behaviour of the reagent as a colloidal electrolyte. The curve between square root of concentration and equivalent conductance is not linear and resembles that of a colloidal electrolyte (52). The temperature of zero conductance lies at $-28.5^{\circ}C$ and the temperature coefficient per degree centigrade per 100 of conductance at $35^{\circ}C$ has been found to be below 2.0. This confirms the colloidal nature of the reagent and hence extremely dilute solutions of the order of $10^{-4}M$ and $10^{-5}M$ have been employed.

LEAD-QUINALIZARIN SYSTEM

1, 2, 5, 8 tetra hydroxy anthraquinone (trivial name quinalizarin abbreviated as QZR) forms coloured complexes with many metal ions and has been widely used as a reagent in analytical chemistry for the detection and photometric determination of various metals.

The main work done with this reagent has hither to been confined to making a detailed study of the applications of this reagent in colorimetric analysis. No systematic work seems to have been done on the metal chelates of quinalizarin with regard to composition and stability. The reagent possesses pronounced chelating tendencies due to the presence of quinoid oxygen atoms, together with a hydroxyl group in each of the 1, 2, 5 and 8 positions. In this work detailed studies have been made on the composition and stability of lead quinalizarin chelate. The beautiful blue-

violet complex of lead(II) with quinalizarin has been studied in 50 per cent ethanolic medium.

EXPERIMENTAL

Standard solutions were prepared by dissolving lead acetate (BDH AnalaR) in double distilled water. A purified sample of quinalizarin (BDH reagent grade) was used for the preparation of a 0.001 M stock solution in redistilled ethyl alcohol. Suitable standard solutions were prepared from this solution by dilution with ethanol. In all cases freshly prepared solutions were used.

Conditions of study

All experiments were performed at $30^{\circ} \pm 01^{\circ}C$. The total volume in all the mixtures prepared for measurements was kept at 25 ml. The individual solutions and the mixtures were kept in a Townson and Mercer precision thermostat maintained at $30^{\circ} \pm 0.01^{\circ}C$. The mixtures were allowed to stand for 30 minutes in the thermostat to attain equilibrium. The pH of all the mixtures was adjusted to 6.3 ± 0.1 by the addition of suitable amounts of sodium hydroxide or hydrochloric acid.

Quinalizarin, like most of the chromophoric dyes, was found to behave as a colloidal electrolyte; hence extremely dilute solutions of the order of 10^{-4} or 10^{-5}M were employed for the physicochemical measurements.

Effect of time on the colour of the chelate

Colour formation was found to be instantaneous and even upto 48 hours there was no change in the absorbance values at room temperature. The order of addition of the reagents was not found to be of any significance.

Nature of the complexes formed

The method of Vosburgh and Copper (83) was employed to determine the nature of the complexes formed in solution. Mixtures containing varying proportions of lead acetate: quinalizarin (0:1, 2:1, 1:1, 1:2 etc.) were prepared, keeping the volume of ethanol 12.5 ml in each case, and the optical densities of the solutions at different wave lengths in each case were measured.

Table 3.3

Mixture	Ratio Lead acetate : Quinalizarin
A	0 : 1
B	2 : 1
C	1 : 1
D	1 : 2

Table 3.4

Initial concentration of lead acetate = 2.0×10^{-4}M

Initial concentration of quinalizarin = 2.0×10^{-4}M

Total volume = 25 ml

Wavelength nm	Optical density A	B	C	D
400	0.405	0.310	0.325	0.375
410	0.450	0.318	0.330	0.392
420	0.492	0.330	0.342	0.425
430	0.540	0.340	0.360	0.450
440	0.572	0.350	0.385	0.470
450	0.580	0.368	0.405	0.484
460	0.575	0.395	0.438	0.496
470	0.565	0.445	0.472	0.500
480	0.552	0.485	0.500	0.496
490	0.545	0.530	0.545	0.492
500	0.535	0.545	0.570	0.498
510	0.504	0.555	0.590	0.505
520	0.476	0.575	0.605	0.510
530	0.455	0.572	0.602	0.480
540	0.425	0.568	0.592	0.455
550	0.395	0.545	0.568	0.435
560	0.356	0.518	0.536	0.400
570	0.318	0.490	0.495	0.360
580	0.280	0.460	0.464	0.320
590	0.244	0.420	0.425	0.285
600	0.200	0.395	0.398	0.245

The observations have been plotted in figure 3.2. It is evident from curve A that the region of maximum absorbance of the reagent lies at 450 nm. In curves B, C and D the wavelength of maximum absorbance shifts to 520 nm. This shows that only one complex is formed in solution.

Stoichiometry of the components

Job's method of continuous variation (38) was adopted for the determination of the composition of the coloured complex. The total volume in each case kept at 25 ml. The

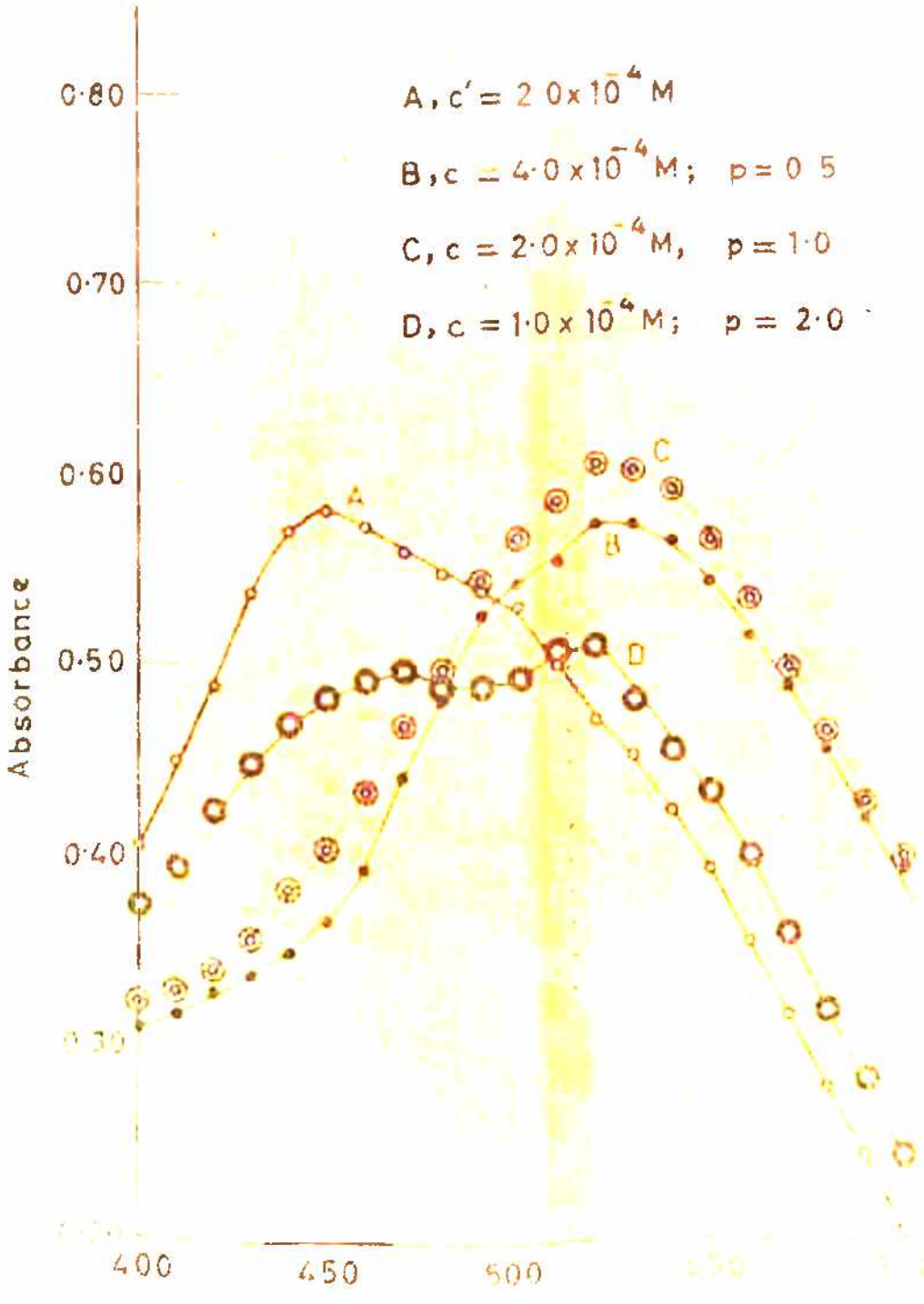


Fig. 3.2 Absorption [illegible]

and Quench[illegible]

pH of the solutions was kept at 6.3 ± 0.1. The absorption spectra of lead chelating agent and mixtures were measured in 50 per cent ethanolic medium at 600 nm. The results are given in tables 3.5 to 3.9 and represented graphically in figures 3.3 to 3.4.

Table 3.5

Concentration of lead acetate (c) = 5.0×10^{-4}M

Concentration of quinalizarin (c') (QZR) = 5.0×10^{-4}M

pH = 6.3 ± 0.1

λ = 600 nm, p = c'/c = 1

peak at 1:1 (Fig. 3.3 curve A)

Volume of lead acetate ml	Volume of quinalizarin ml	Optical density of mixture (a)	Optical density of QZR (b)	Difference in optical density (a-b)
0.0	25.0	0.575	0.575	0.000
2.5	22.5	0.610	0.550	0.060
5.0	20.0	0.635	0.520	0.115
7.5	17.5	0.655	0.460	0.195
10.0	15.0	0.675	0.410	0.265
12.5	12.5	0.680	0.340	0.340
15.0	10.0	0.540	0.260	0.280
17.5	7.5	0.412	0.202	0.210
20.0	5.0	0.305	0.140	0.165
22.5	2.5	0.165	0.080	0.085

Table 3.6

Concentration of lead acetate (c) = 2.5×10^{-4} M

Concentration of quinalizarin(QZR) (c')= 2.5×10^{-4} M

pH = 6.3 ± 0.1, λ = 600 nm, p = c'/c = 1

peak at 1:1 (fig. 3.3, curve B)

Volume of lead acetate ml	Volume of quinalizarin ml	Optical density of mixture (a)	Optical density of QZR (b)	Difference (a-b)
0.0	25.0	0.392	0.392	0.000
2.5	22.5	0.410	0.375	0.035
5.0	20.0	0.425	0.360	0.065
7.5	17.5	0.440	0.345	0.095
10.0	15.0	0.455	0.320	0.135
12.5	12.5	0.465	0.300	0.165
15.0	10.0	0.360	0.220	0.140
17.5	7.5	0.256	0.156	0.100
20.0	5.0	0.160	0.100	0.060
22.5	2.5	0.085	0.050	0.035

Table 3.7

Concentration of lead acetate (c) = 2.0×10^{-4} M

Concentration of quinalizarin (c') = 2.0×10^{-4} M

pH = 6.3 ± 0.1, λ = 600 nm, p = c'/c = 1

peak at 1:1 (Fig. 3.3 curve C)

0.0	25.0	0.300	0.300	0.000
2.5	22.5	0.310	0.280	0.030
5.0	20.0	0.320	0.260	0.060
7.5	17.5	0.325	0.240	0.085
10.0	15.0	0.340	0.220	0.120
12.5	12.5	0.350	0.210	0.140
15.0	10.0	0.300	0.180	0.120
17.5	7.5	0.190	0.115	0.075
20.0	5.0	0.120	0.070	0.050
22.5	2.5	0.060	0.035	0.025

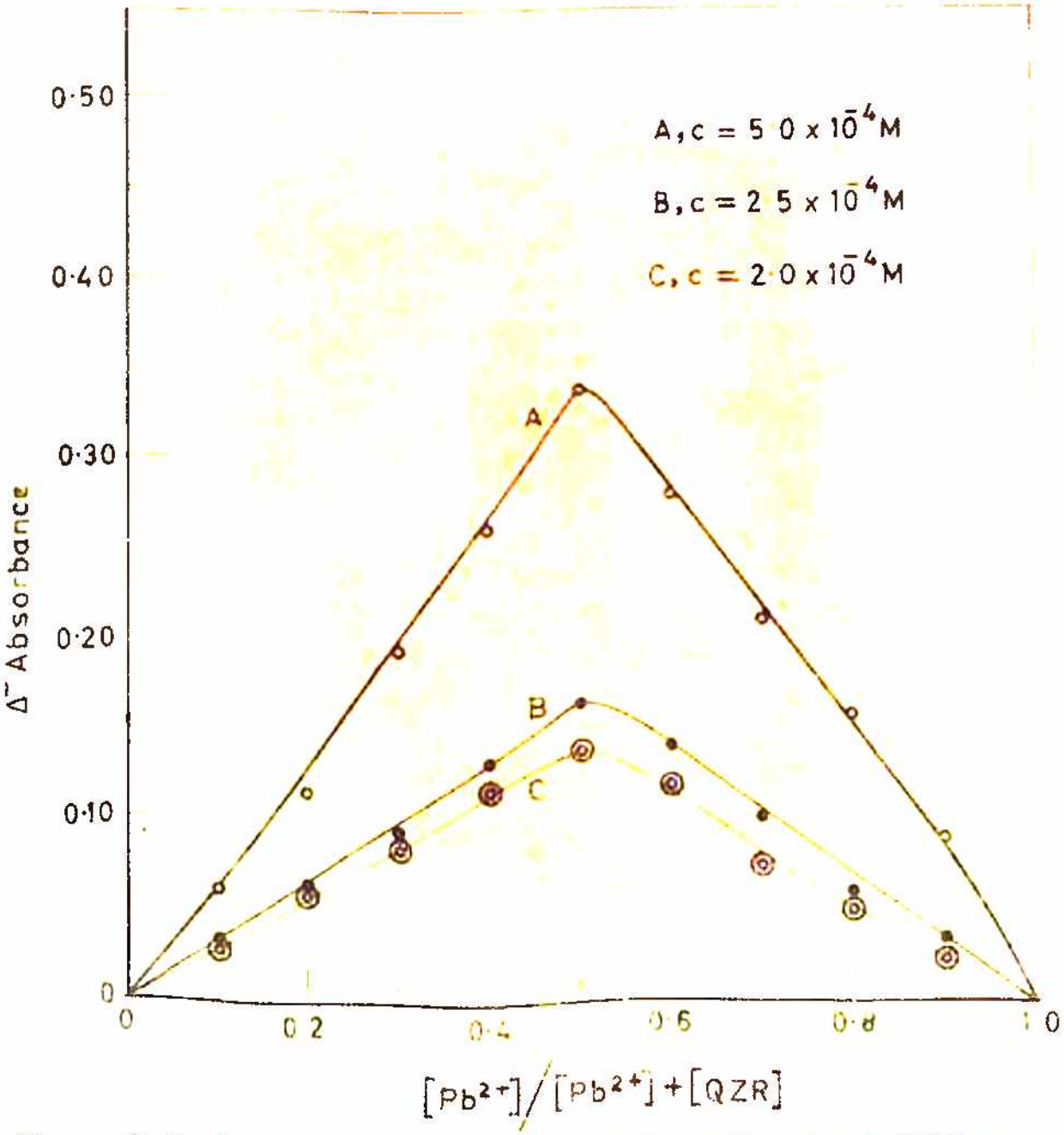


Fig – 3·3 Continuous variation method at 600 nm;

p=1, pH:6·3 ± 0·1

Table 3.8

Concentration of lead acetate (c) = 5.0×10^{-4}M

Concentration of quinalizarin(QZR)(c') = 2.5×10^{-4}M

pH = 6.3 ± 0.1, λ = 600 nm, p = c'/c = 0.5

peak at 1:1 (Fig. 3.4 curve A)

Volume of lead acetate ml	Volume of quinalizarin ml	Optical density of mixture (a)	Optical density of QZR (b)	Difference (a-b)
0.0	25.0	0.392	0.392	0.000
2.5	22.5	0.470	0.375	0.095
5.0	20.0	0.560	0.360	0.200
7.5	17.5	0.525	0.345	0.180
10.0	15.0	0.485	0.320	0.165
12.5	12.5	0.445	0.300	0.145
15.0	10.0	0.340	0.220	0.120
17.5	7.5	0.256	0.156	0.100
20.0	5.0	0.185	0.100	0.085
22.5	2.5	0.095	0.050	0.045

Table 3.9

Concentration of lead acetate (c) = 4.0×10^{-4}M

Concentration of quinalizarin(QZR)(c') = 2.0×10^{-4}M

pH = 6.3 ± 0.1, λ = 600 nm, p = c'/c = 0.5

peak at 1:1 (Fig. 3.4 curve B)

0.0	25.0	0.300	0.300	0.000
2.5	22.5	0.365	0.280	0.085
5.0	20.0	0.430	0.260	0.170
7.5	17.5	0.395	0.240	0.155
10.0	15.0	0.360	0.220	0.140
12.5	12.5	0.330	0.210	0.120
15.0	10.0	0.275	0.180	0.095
17.5	7.5	0.190	0.115	0.075
20.0	5.0	0.125	0.070	0.055
22.5	2.5	0.070	0.035	0.035

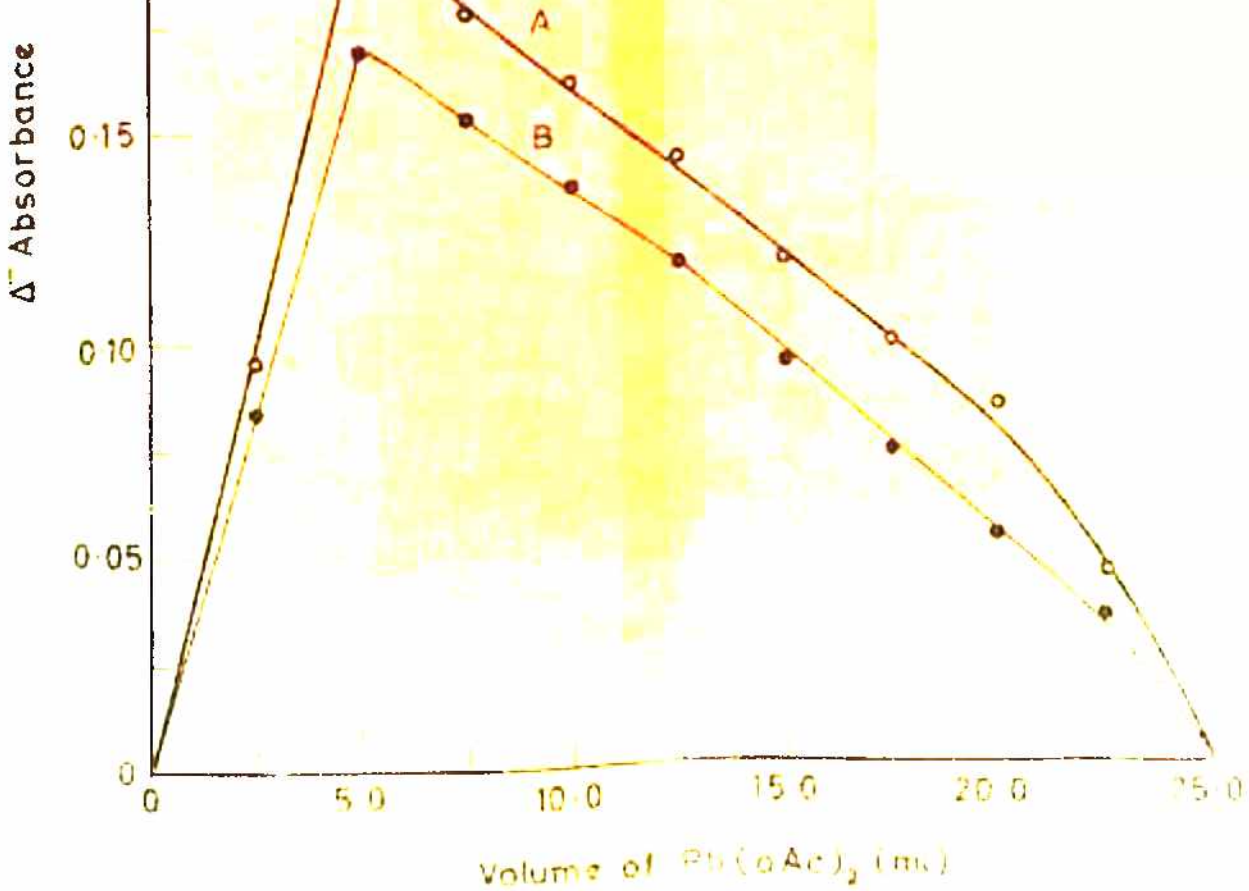
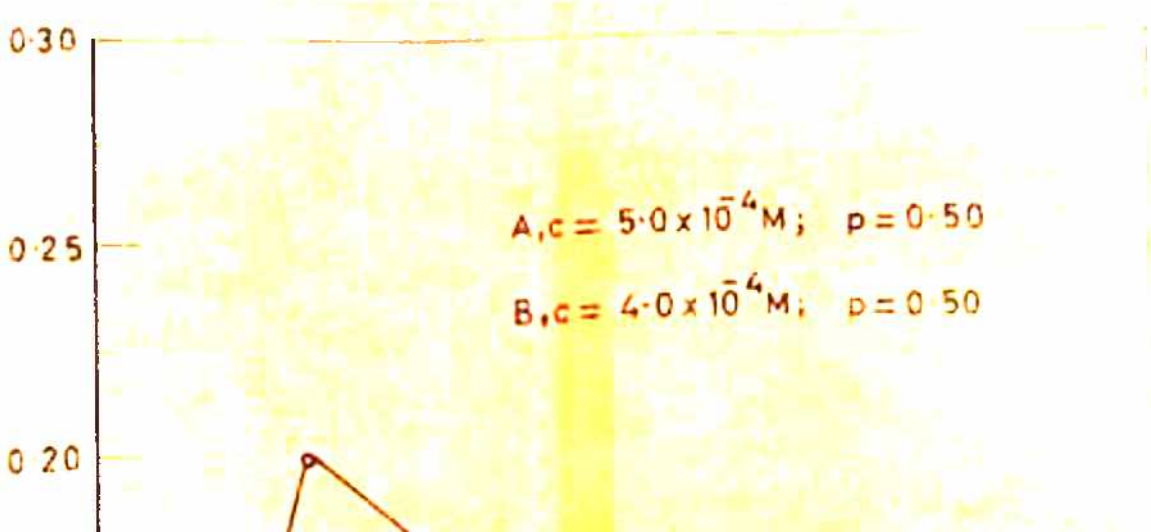


Fig._3·4 Continuous variation method at 600 nm

pH: 6·3±0·1


0·30
0·25
0·20
A, c = 5·0 x 10⁻⁴ M; p = 0·50
B, c = 4·0 x 10⁻⁴ M; p = 0·50

Mole ratio method (90)

A series of solutions was prepared from 5.0×10^{-4}M and 4.0×10^{-4}M of lead acetate and quinalizarin at pH 6.3, maintaining a 50 per cent ethanolic medium and varying the amount of equimolecular solutions of lead acetate which were added so that the mole ratio of quinalizarin to lead varied from 1:0.25 to 1:8. Some of the typical results are recorded in table 3.10 and 3.11 and represented in figure 3.5.

Table 3.10

Concentration of lead acetate = 5.0×10^{-4}M

Concentration of quinalizarin (QZR) = 5.0×10^{-4}M

pH = 6.3 ± 0.1, Total volume made up = 25 ml

Break at 1:1 (Fig. 3.5 curve A)

Ratio QZR:lead	1:0.25	1:0.50	1:0.75	1:1	1:2	1:3	1:4	1:5
Optical density at 600 nm	0.082	0.155	0.250	0.340	0.400	0.460	0.496	0.520

Table 3.11

Concentration of lead acetate = 4.0×10^{-4}M

Concentration of quinalizarin (QZR) = 4.0×10^{-4}M

pH = 6.3 ± 0.1, Total volume made up = 25 ml

Break at 1:1 (Fig. 3.5 curve B)

Ratio QZR:Lead	1:025	1:050	1:0.75	1:1	1:2	1:3	1:4	1:5
Optical density at 600 nm	0.068	0.140	0.210	0.270	0.320	0.370	0.400	0.420

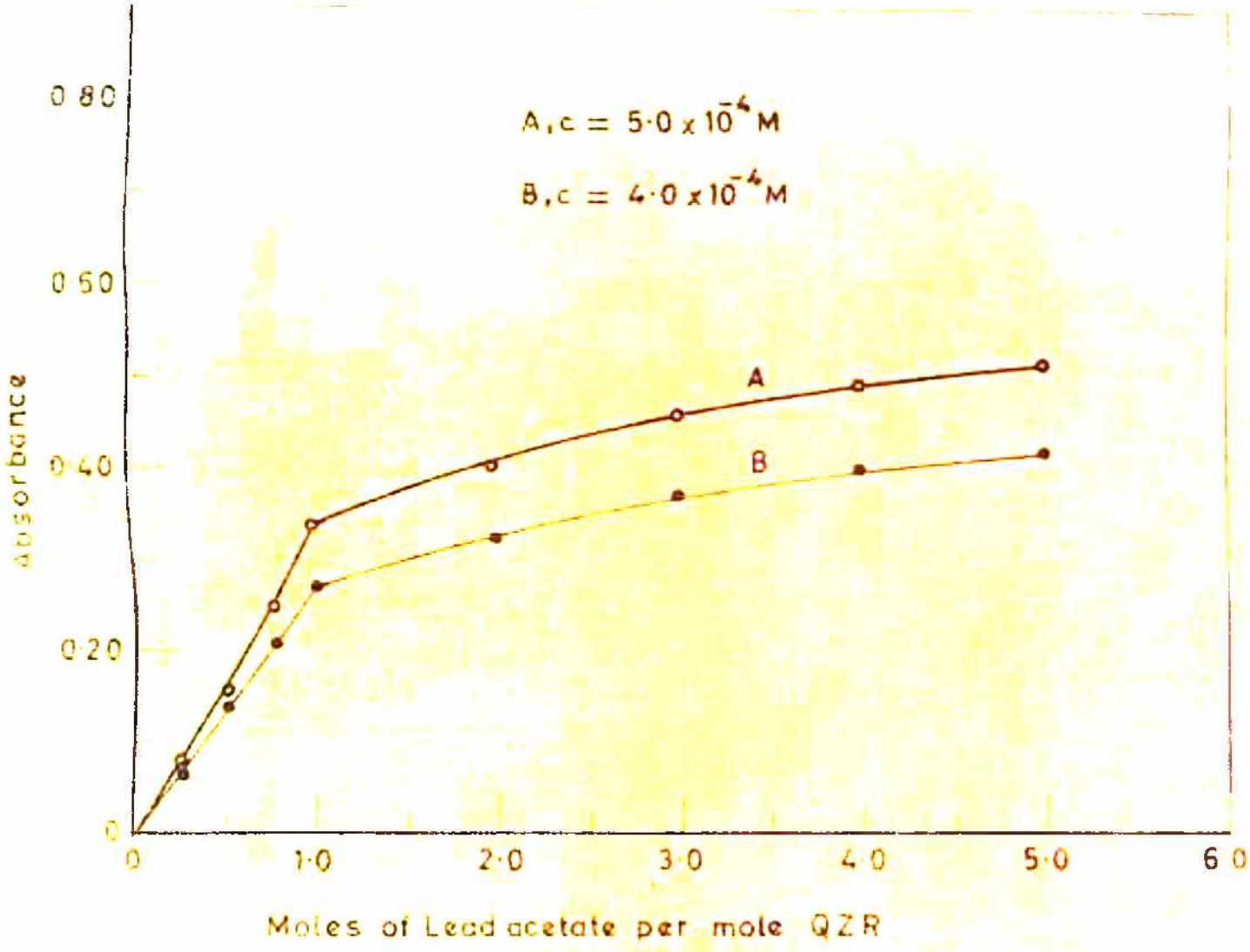


Fig — 3·5 Mole ratio method at 600 nm; pH : 6·3 ± 0·1

Slope ratio method (36)

The concentration of the variable component was 2.0×10^{-4}M. The volume of the variable component was varied from 1 to 12.5 ml in the presence of 12.5 ml of excess concentration of 5.0×10^{-4}M of the constant component. The total volume in each case was kept at 25 ml and volume of ethanol at 12.5 ml. The pH of the solution was maintained at 6.3. The absorbance was noted at 600 and 610 nm. Figure 3.6 shows the measured absorbance at 600 and 610 nm plotted against the volume of the variable component. The slopes of the two straight lines in each case gave the lead:quinalizarin ratio as 1:1. Some of the typical results are given in table 3.12 and 3.13.

Table 3.12

Concentration of constant component (lead acetate)= 5.0×10^{-4}M

Volume of constant component (lead acetate) = 12.5 ml

Concentration of variable component (quinalizarin)= 2.0×10^{-4}M

pH of mixtures = 6.3 ± 0.1, Total volume = 25 ml

Volume of variable component QZR (ml)	Optical density at	
	600 nm	610 nm
1.0	0.028	0.025
2.0	0.040	0.035
3.0	0.051	0.042
4.0	0.065	0.050
5.0	0.071	0.056
6.0	0.082	0.064
7.0	0.095	0.074
8.0	0.105	0.086
9.0	0.115	0.090
10.0	0.125	0.098
11.0	0.136	0.111
12.0	0.150	0.120
12.5	0.155	0.125

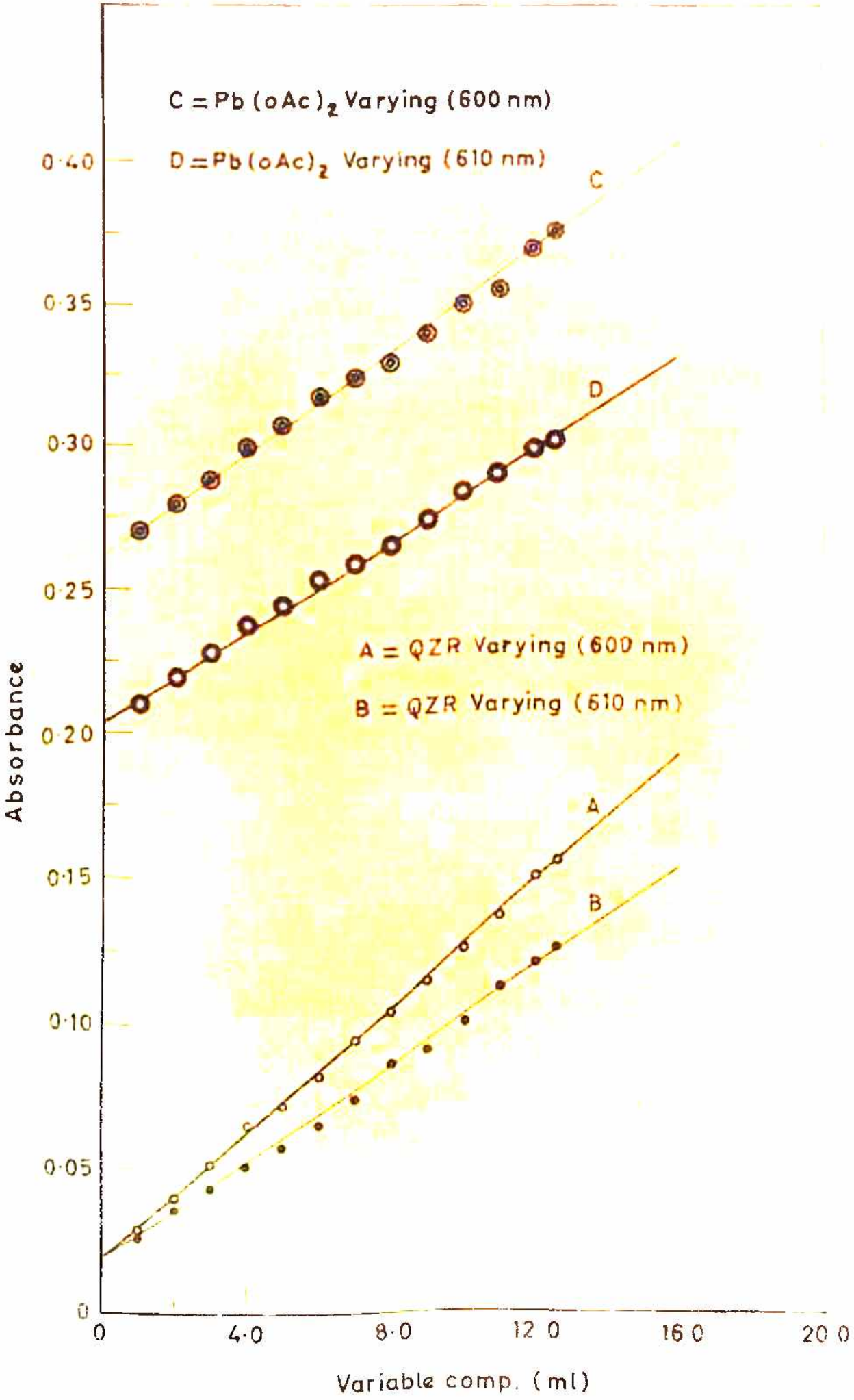


Fig._ 3·6 Slope ratio method at pH: 6·3 ± 0·1; $5{\cdot}0 \times 10^{-4}$ M excess comp. (12·5 ml) + $2{\cdot}0 \times 10^{-4}$ M variable comp. (x ml) + water [12·5 − x ml]

Table 3.13

Concentration of constant component (QZR) = 5.0×10^{-4}M

Volume of constant component (QZR) = 12.5 ml

Concentration of variable component (lead acetate) = 2.0×10^{-4}M

pH of midtures = 6.3 ± 0.1, Total volume = 25 ml.

Volume of variable component lead acetate (ml)	Optical density at	
	600 nm	610 nm
1.0	0.270	0.210
2.0	0.280	0.220
3.0	0.288	0.228
4.0	0.300	0.238
5.0	0.308	0.245
6.0	0.318	0.255
7.0	0.325	0.260
8.0	0.330	0.265
9.0	0.340	0.275
10.0	0.350	0.284
11.0	0.356	0.290
12.0	0.370	0.298
12.5	0.375	0.300

The influence of pH on the stability of the chelate

Figure 3.7 represents the variation in the region of maximum absorption of the complex solution containing lead acetate and quinalizarin in the stoichiometric ratio i.e. 1:1 (each 2.0×10^{-4}M) at different pH values. It was thought that it would be of interest to compare the influence of pH on the λ_{max} of the complex with that of the dye. The change of λ_{max} of quinalizarin with pH is represented in table 3.1, fig. 3.1. It is found that the chelate is stable between 5.5 and 6.5.

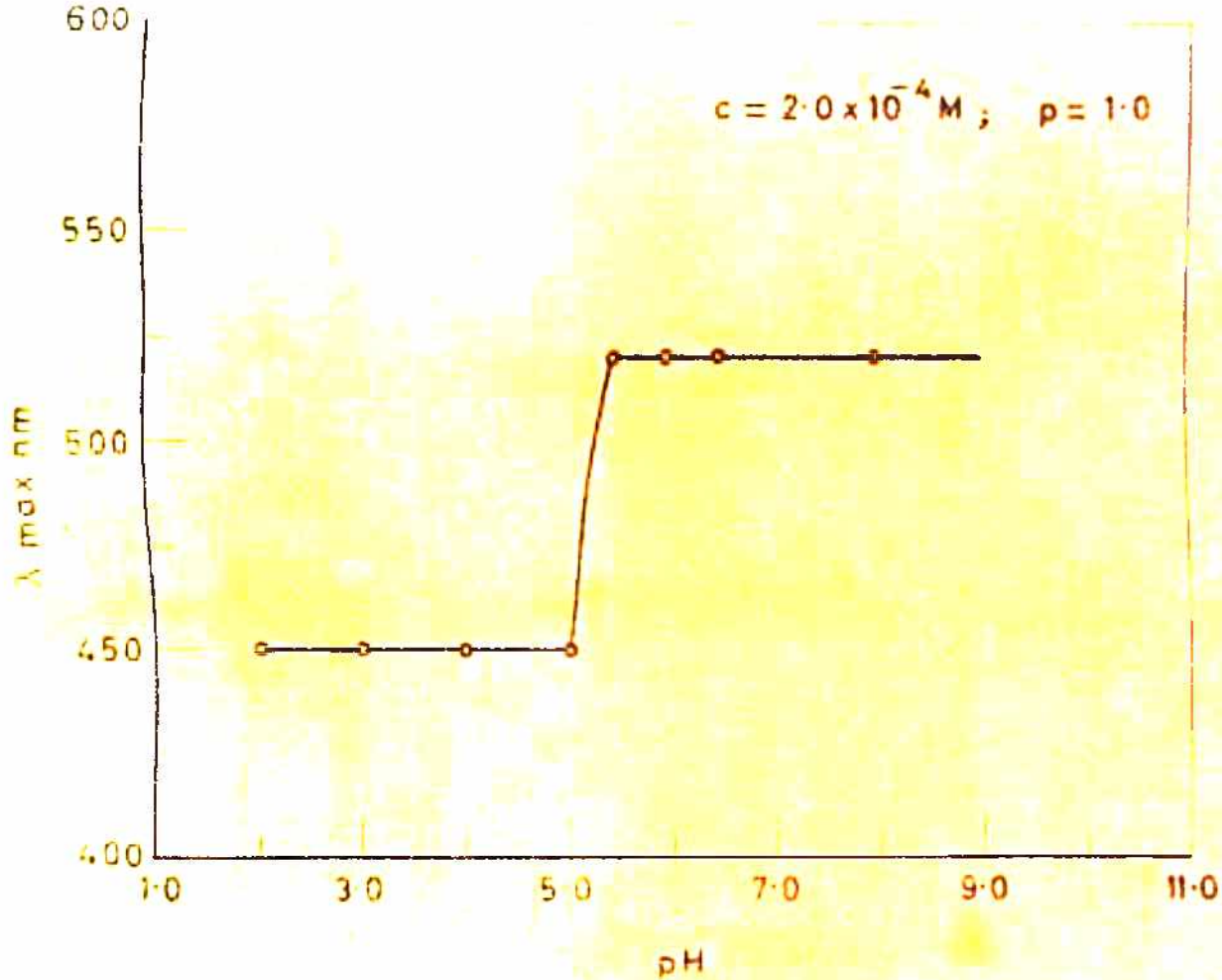


Fig._ 3·7 Variation of λ max with pH of Quinalizarin – lead complex

Calculation of the stability constant

The stability constants were calculated by three different methods, namely, (a) the method of Dey and Coworkers (54, 8) (b) the method of continuous variation using non equimolecular solutions and (c) the method of mole ratio. The values of change in free energy of formation were also calculated.

For the calculation of K by method (a) concentrations of metal ions used are shown in fig. 3.8. For method (b) the concentrations and the volume of the metal ion used at the peak are shown in fig. 3.4. For calculation of K by method (c), the concentrations Em, Es and α are shown in table 3.14 (figure 3.5).

Table 3.14

Fig.	curve	10^4C(M)	Em	Es	α
3.5	A	5.0	0.52	0.34	0.346
	B	4.0	0.42	0.27	0.357

Suggestions on the structure of the chelate

From the experimental results it is not possible to obtain definite information regarding the position of the chelate ring, but tentative suggestions about the structure of the chelate can be made. There are two alternative positions

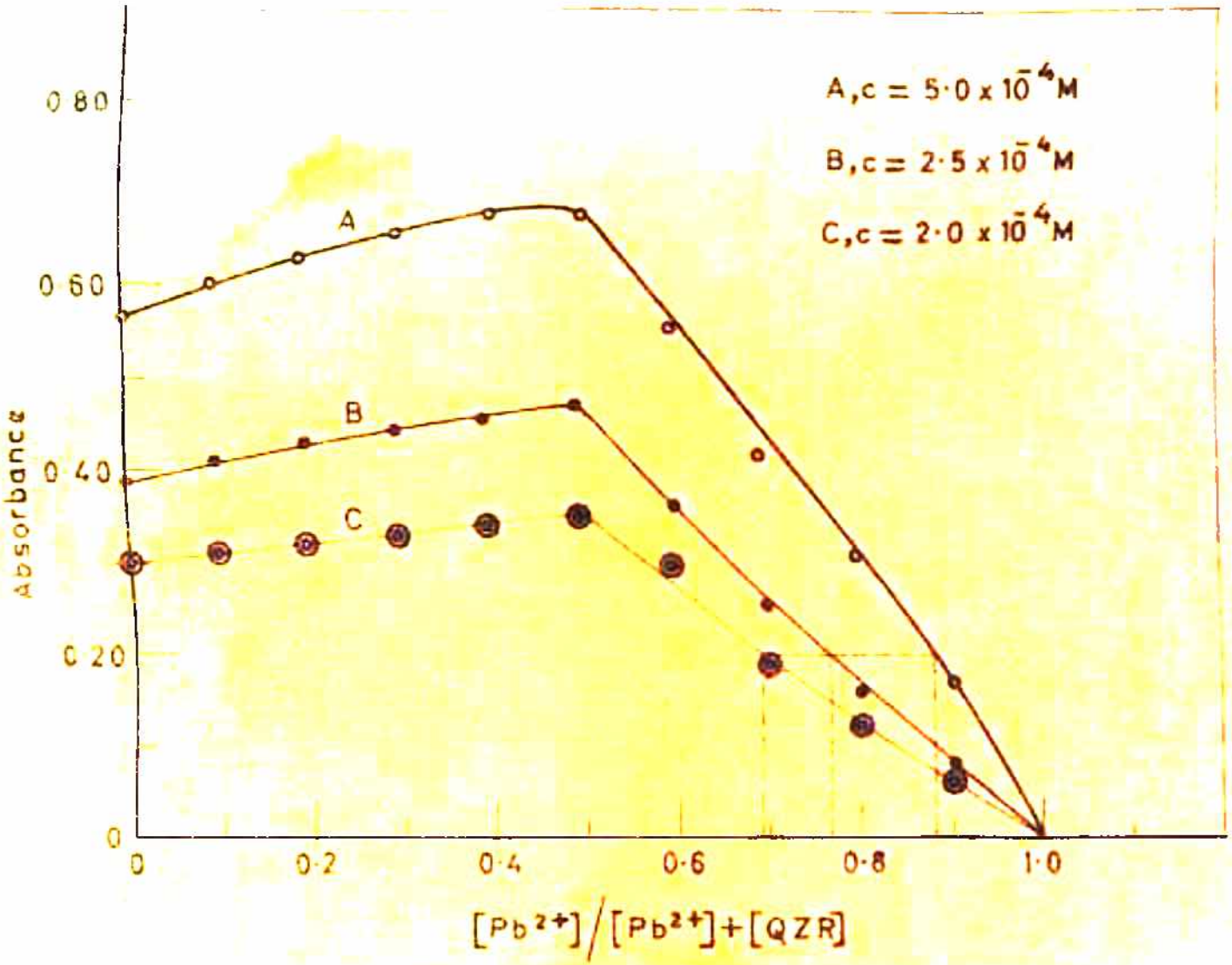


Fig. 3·8 Determination of the stability constant at 600 nm; pH: 6·3 ± 0·1

where the chelation might occur. Either the chelation takes place between the phenolic oxygens or between quinoid oxygen and adjacent phenolic oxygen, yielding an anionic complex. In the present case, adsorption studies by ion exchange resin Amberlite IR 45 (OH) (B.D.H. AnalaR) have indicated that the complex is anionic.

Discussion

The variation of λ_{max} with the change in pH of the reagent in solution has been shown in table 3.1 and the results graphically represented in fig. 3.1. It has been deserved there from that with the change in hydrogen ion concentration λ_{max} shifts. These changes are due to the exitence of the reagent in different forms.

A study of the variation of equivalent conductivity with concentration revealed that the curve between square root of concentration and equivalent conductance is not linear and resembles that of a colloidal electrolyte. It may further be noted that the temperature of zero conductance lies at $-28.5^{\circ}C$ and the temperature coefficient per degree centigrade per 100 of conductance at $35^{\circ}C$ has been found to be below 2.0. This confirms the colloidal nature of the reagent. Hence dilute solutions of the order of $10^{-4}M$ or $10^{-5}M$ were employed during these studies.

The composition of lead quinalizarin chelate as determined by the method of (1) continuous variation (table 3.5 to 3.9, figure 3.3 to 3.4) (2) mole ratio method (table 3.10 and 3.11, figure 3.5) and (3) slope ratio method (table 3.12 to 3.13, figure 3.6) indicate that only one lead quinalizarin chelate is formed and that the mole ratio of quinalizarin to lead in this chelate is 1:1.

The values of log K at pH 6.3 ± 0.1 and at 30° have been calculated using the method of (a) Dey and Coworkers (b) continuous variation method and (c) Mole ratio method. The results have been shown in table 3.15. The free energy change of formation has also been calculated with the help of the expression $\triangle G^{\circ} = -RT\ell nk$

Table 3.15

Method	pH	log K	$\triangle G^{\circ}$ at 30° (K cals)
(a) Dey and Coworkers	6.3 ± 0.1	4.3 ± 0.1	- 5.9 ± 0.1
(b) Continuous variation	6.3 ± 0.1	4.2 ± 0.1	- 5.8 ± 0.1
(c) Mole ratio	6.3 ± 0.1	4.1 ± 0.1	- 5.7 ± 0.1

Table 3.16 records the regions of maximum absorption of quinalizarin and the complex at various pH values.

Table 3.16

pH	Region of maximum absorption, nm	
	QZR	Complex
2. 0 - 5.0	450	450
5.5	450	520
6.0	450	520

contd.

Table 3.16 contd.

pH	Region of maximum absorption, nm	
	QZR	Complex
6.5	450	520
8.0	520	520

From the above table it may be seen that between pH range 5.5 - 6.5 the region of maximum absorption of the complex is 520 nm which is different from that of quinalizarin at the same pH ranges. At the other pH values the regions of maximum absorption are more or less identical in two solutions. This is because the complex is stable only in the pH range 5.5 to 6.5.

LANTHANUM - QUINALIZARIN SYSTEM

Quinalizarin forms coloured complexes in solution with many metal ions and has widely been used in analytical chemistry. It has been observed that quinalizarin also forms coloured chelate with lanthanum.

In the present work the formation of lanthanum quinalizarin chelate is reported for the first time along with the composition, nature and stability of the chelate. The beautiful violet coloured chelate of lanthanum (III) with quinalizarin has been studied in 50 per cent ethanolic medium by the spectrophotometric method. Suitable conditions for the micro determination have been worked out, and described.

EXPERIMENTAL

Johnson and Matthey sample of lanthanum acetate was used for making the solutions. Quinalizarin (B.D.H. reagent grade) was the same as used previously. Other chemicals employed were of the reagent grade.

Absorbance studies were made on a Hilger Uvispeck

spectrophotometer and pH measurements were taken on a Beckman H_2 model pH meter.

Conditions of Study

All experiments were performed at 30 ± 0.1°C. The total volume of all the mixtures prepared for the measurements was 25 ml, and the pH adjusted to 6.8 by the addition of 2.5 ml of 1 M ammonium acetate. The ionic strength of the system was maintained at 0.1 M with sodium perchlorate.

As quinalizarin behaves as a colloidal electrolyte, very dilute solutions of the order of 10^{-4}M were used during these studies.

Effect of pH on chelate

The chelate is stable between pH 6.6 and 7.8, as shown by the constancy of λ_{max} within this range. However, as the absorbance is constant only between pH 6.7 and 7.5, studies have been made in this pH range.

Effect of reagent concentration

The absorbance values of different mixtures of lanthanum acetate solutions with varying ratios of the excess of quinalizarin at pH 6.8 and at 530 nm shows that the maximum colour formation is attained when mixtures contained five fold excess of the reagent with respect to the metal

solutions.

Stability of the colour intensity at room temperature: The absorbance of the solutions does not change on standing for at least three hours at room temperature which is sufficient for the purpose of absorbance measurements.

The order of the addition of the reagents: Varying the order in which the reagents were added had no significant effect on the results. In all cases the colour was fully developed within two minutes.

Beer's law and optimum range

Beer's law is obeyed over the concentration range from 1.26 to 6.32 ppm of lanthanum. The optimum concentration range for the determination of lanthanum was determined by the method described by Ringbom (65) and was found to be 1.4 to 3.5 ppm.

Nature of the complexes formed

For the determination of the nature of complexes formed in solution, the method of Vosburgh and Cooper (83) was followed. Mixtures containing varying proportions of lanthanum acetate: quinalizarin (0:1, 2:1, 1:1, 1:2, 1:3 and 1:4) were prepared keeping the volume of ethanol at 12.5 ml and total volume 25 ml at pH 6.8 ± 0.1. The absorbance of

the solutions were measured at suitable wave length interval.

Table 3.17

Mixture	Ratio Lanthanum acetate : Quinalizarin
A	0 : 1
B	1 : 0.5
C	1 : 1
D	1 : 2
E	1 : 3
F	1 : 4

Table 3.18

Initial concentration of lanthanum acetate = 2.0×10^{-4}M

Initial concentration of quinalizarin = 2.0×10^{-4}M

Total volume = 25 ml

Wavelength nm	Optical density					
	A	B	C	D	E	F
400	0.355	0.135	0.290	0.550	0.745	1.500
410	0.392	0.138	0.294	0.555	0.750	1.550
420	0.428	0.142	0.300	0.560	0.775	1.750
430	0.460	0.148	0.305	0.585	0.825	1.800
440	0.490	0.162	0.320	0.610	0.920	1.820
450	0.505	0.185	0.350	0.665	1.040	1.840
460	0.510	0.206	0.400	0.755	1.220	1.860
470	0.528	0.236	0.455	0.850	1.400	1.880

contd.

Table 3.18 contd.

Wavelength nm	Optical density					
	A	B	C	D	E	F
480	0.536	0.268	0.515	0.970	1.640	1.960
490	0.545	0.304	0.575	1.260	1.830	2.100
500	0.560	0.352	0.640	1.375	2.020	2.210
510	0.555	0.355	0.695	1.490	2.120	2.330
520	0.550	0.370	0.735	1.565	2.250	2.370
530	0.526	0.375	0.765	1.590	2.260	2.380
540	0.500	0.368	0.760	1.565	2.220	2.310
550	0.480	0.358	0.755	1.555	2.160	2.250
560	0.440	0.335	0.740	1.535	2.050	2.120
570	0.365	0.305	0.700	1.380	1.920	2.010
580	0.305	0.272	0.650	1.285	1.740	1.830
590	0.252	0.235	0.625	1.205	1.560	1.580
600	0.210	0.206	0.530	1.050	1.310	1.320
610	0.150	0.165	0.485	0.955	1.100	1.205
620	0.126	0.135	0.410	0.815	0.910	0.920
630	0.085	0.095	0.340	0.680	0.720	0.730
640	0.055	0.070	0.285	0.535	0.555	0.570
650	0.030	0.050	0.205	0.405	0.430	0.460
660	0.000	0.000	0.190	0.330	0.350	0.360
670			0.155	0.260	0.280	0.290
680			0.145	0.230	0.250	0.255
690			0.110	0.220	0.240	0.250
700			0.100	0.200	0.215	0.225

Fig. 3.9 shows that the reagent has its λ_{max} at 500 nm, whereas in all the mixtures the region of maximum absorption shifts to 530 nm, indicating the formation of only one chelate having λ_{max} at 530 nm under the conditions of study.

Stoichiometry of the components

In order to determine the composition of the coloured complex Job's method of continuous variation (38) was adopted. The absorbance of the mixture and chelating agent were measured at 530 nm using both equimolecular and nonequimolecular

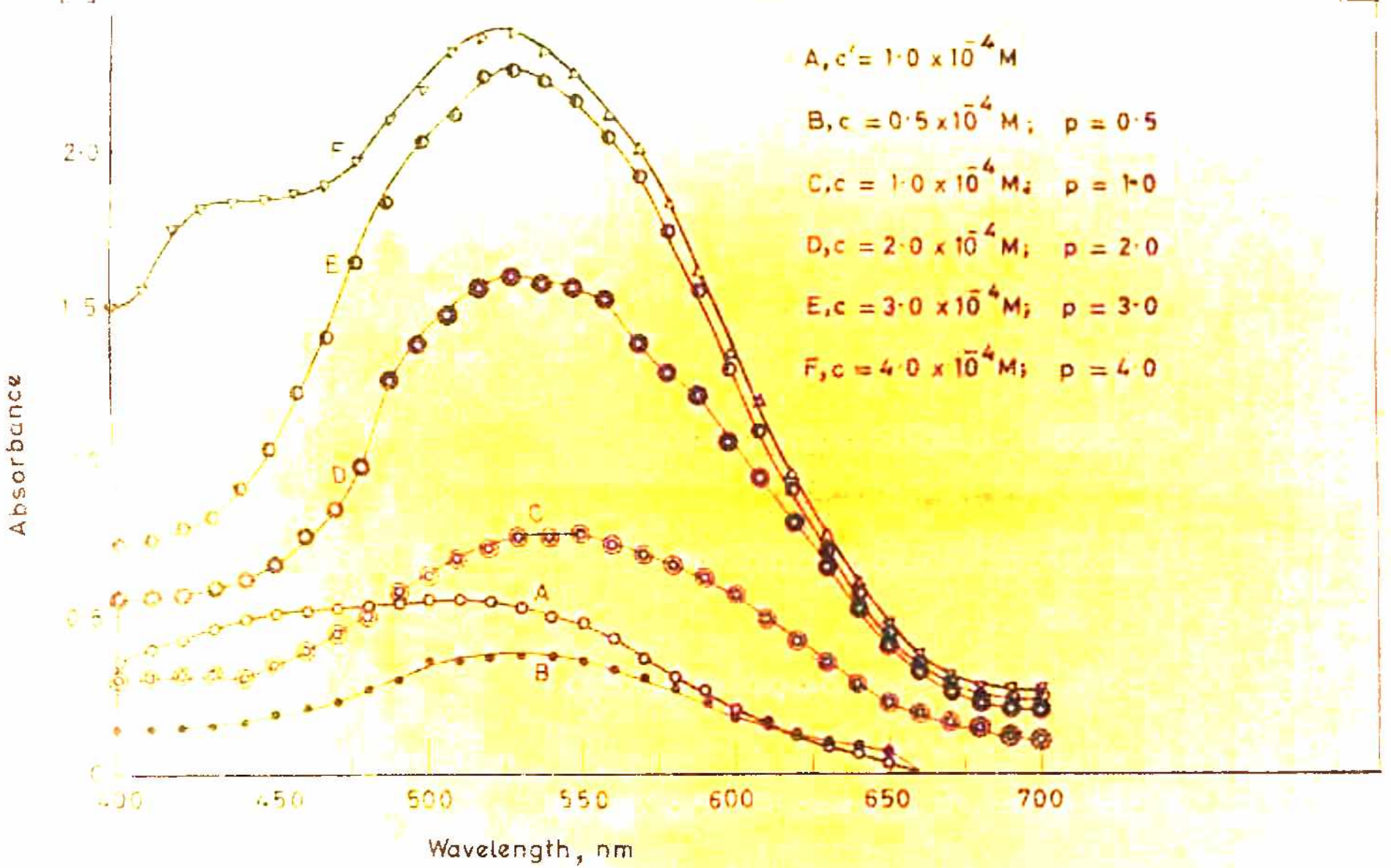


Fig. Absorption spectra of mixtures of Lanthanum acetate and Quinalizarin at pH 6·8±0·1; μ: 0·1 $NaClO_4$

solutions, adjusting the pH at 6.8; ionic strength 0.1 M in 50 per cent ethanolic medium, keeping the volume constant at 25 ml. The results are given in tables 3.19 to 3.23 and represented graphically in figures 3.10 and 3.11.

Table 3.19

Concentration of lanthanum acetate (c) = 2.0×10^{-4} M

Concentration of quinalizarin(QZR) (c') = 2.0×10^{-4} M

pH = 6.8 ± 0.1, p = c'/c = 1, λ = 530 nm, μ = 0.1 $NaClO_4$

peak at 1:2 (Fig. 3.10 curve A)

Volume of lanthanum acetate ml	Volume of QZR ml	Optical density of		Difference (a-b)
		mixture (a)	QZR (b)	
0.0	25.0	0.968	0.968	0.000
2.5	22.5	0.980	0.910	0.070
5.0	20.0	1.000	0.850	0.150
7.5	17.5	1.010	0.780	0.230
10.0	15.0	0.900	0.660	0.240
12.5	12.5	0.725	0.520	0.205
15.0	10.0	0.615	0.440	0.175
17.5	7.5	0.422	0.280	0.142
20.0	5.0	0.300	0.200	0.100
22.5	2.5	0.210	0.150	0.060

Table 3.20

Concentration of lanthanum acetate (c) = 1.25×10^{-4}M

Concentration of quinalizarin (c') = 1.25×10^{-4}M

pH = 6.8 ± 0.1, p = c'/c = 1, λ = 530 nm, μ = 0.1 $NaClO_4$

peak at 1:2 (Fig. 3.10 Curve B)

Volume of lanthanum acetate ml	Volume of QZR ml	Optical density of		Difference (a-b)
		mixture (a)	QZR (b)	
0.0	25.0	0.590	0.590	0.000
2.5	22.5	0.615	0.570	0.045
5.0	20.0	0.625	0.520	0.095
7.5	17.5	0.635	0.495	0.140
10.0	15.0	0.545	0.410	0.135
12.5	12.5	0.442	0.325	0.117
15.0	10.0	0.370	0.270	0.100
17.5	7.5	0.248	0.170	0.078
20.0	5.0	0.175	0.115	0.060
22.5	2.5	0.115	0.080	0.035

Table 3.21

Concentration of lanthanum acetate (c) = 1.0×10^{-4}M

Concentration of quinalizarin (c') = 1.0×10^{-4}M

pH = 6.8 ± 0.1, p = c'/c = 1, λ = 530 nm, μ = 0.1 $NaClO_4$

peak at 1:2 (Fig. 3.10 curve C)

0.0	25.0	0.490	0.490	0.000
2.5	22.5	0.500	0.460	0.040
5.0	20.0	0.505	0.425	0.080
7.5	17.5	0.510	0.395	0.115
10.0	15.0	0.450	0.330	0.120
12.5	12.5	0.360	0.260	0.100
15.0	10.0	0.300	0.215	0.085
17.5	7.5	0.200	0.135	0.065
20.0	5.0	0.140	0.095	0.045
22.5	2.5	0.095	0.065	0.030

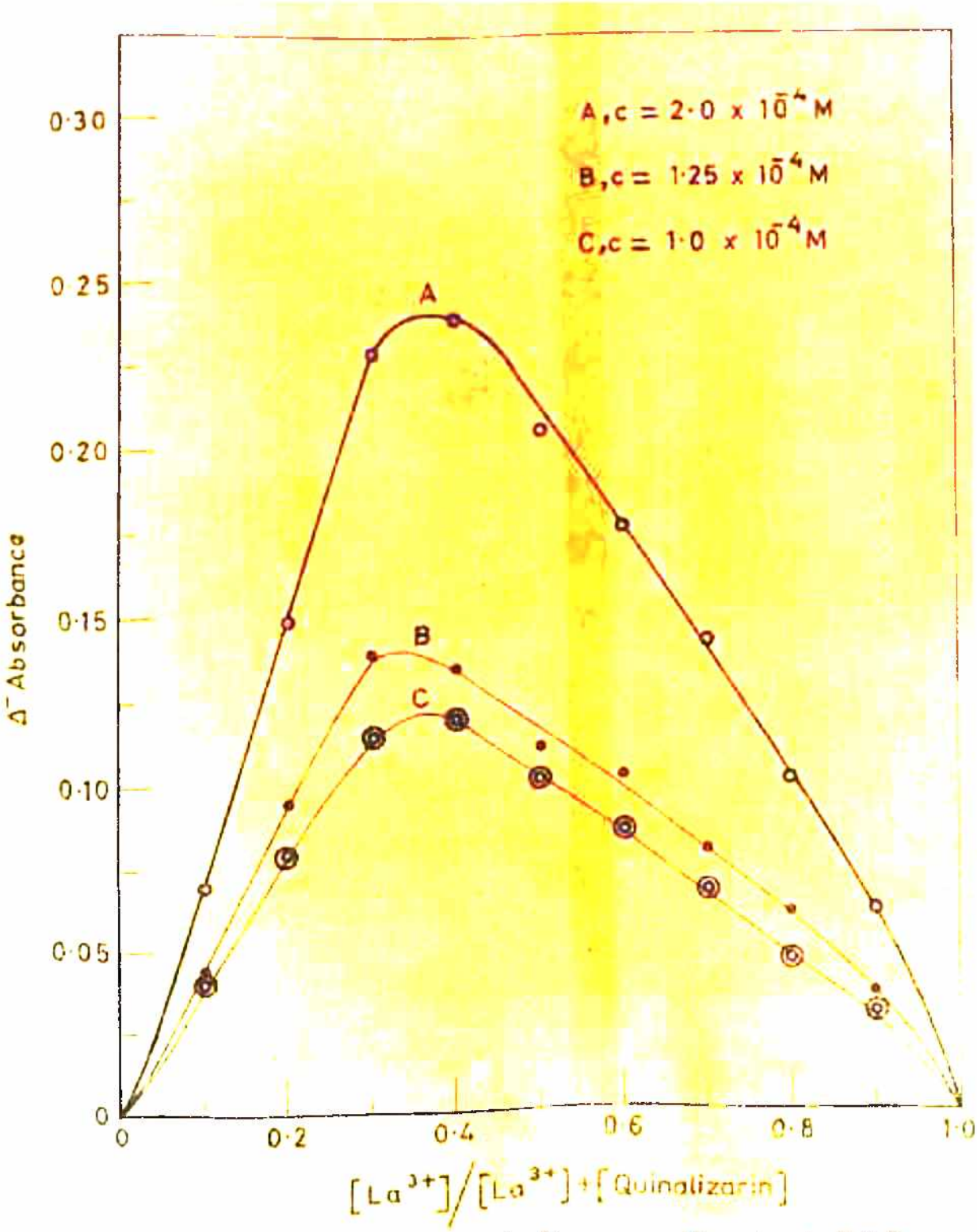


Fig._ 3·10 Continuous variation method at 530 nm;

p = 1; pH: 6·8 ± 0·1; μ: 0·1 $NaClO_4$

Table 3.22

Concentration of lanthanum acetate (c) = 2.0×10^{-4}M

Concentration of quinalizarin (c') = 3.3×10^{-4}M

pH = 6.8 ± 0.1, p = 1.5, λ = 530 nm, μ = 0.1 $NaClO_4$

peak at 1:2 (Fig. 3.11 curve A)

Volume of lanthanum acetate ml	Volume of QZR ml	Optical density of mixture (a)	Optical density of QZR (b)	Difference (a-b)
0.0	25.0	1.445	1.445	0.000
2.5	22.5	1.450	1.365	0.085
5.0	20.0	1.455	1.275	0.180
7.5	17.5	1.460	1.220	0.240
10.4	14.6	1.245	0.980	0.265
12.5	12.5	1.025	0.780	0.245
15.0	10.0	0.870	0.660	0.210
17.5	7.5	0.585	0.420	0.165
20.0	5.0	0.430	0.300	0.130
22.5	2.5	0.300	0.220	0.080

Table 3.23

Concentration of lanthanum acetate (c) = 1.0×10^{-4}M

Concentration of quinalizarin (c') = 2.0×10^{-4}M

pH = 6.8 ± 0.1, p = 2.0, λ = 530 nm, μ = 0.1 $NaClO_4$

peak at 1:2 (Fig. 3.11 curve B)

0.0	25.0	0.968	0.968	0.000
2.5	22.5	0.970	0.910	0.060
5.0	20.0	0.975	0.850	0.125
7.5	17.5	0.930	0.780	0.150
10.0	15.0	0.830	0.660	0.170
11.75	13.25	0.755	0.575	0.180
12.5	12.5	0.690	0.520	0.170
15.0	10.0	0.585	0.440	0.145
17.5	7.5	0.375	0.280	0.095
20.0	5.0	0.265	0.200	0.065
22.5	2.5	0.180	0.150	0.030

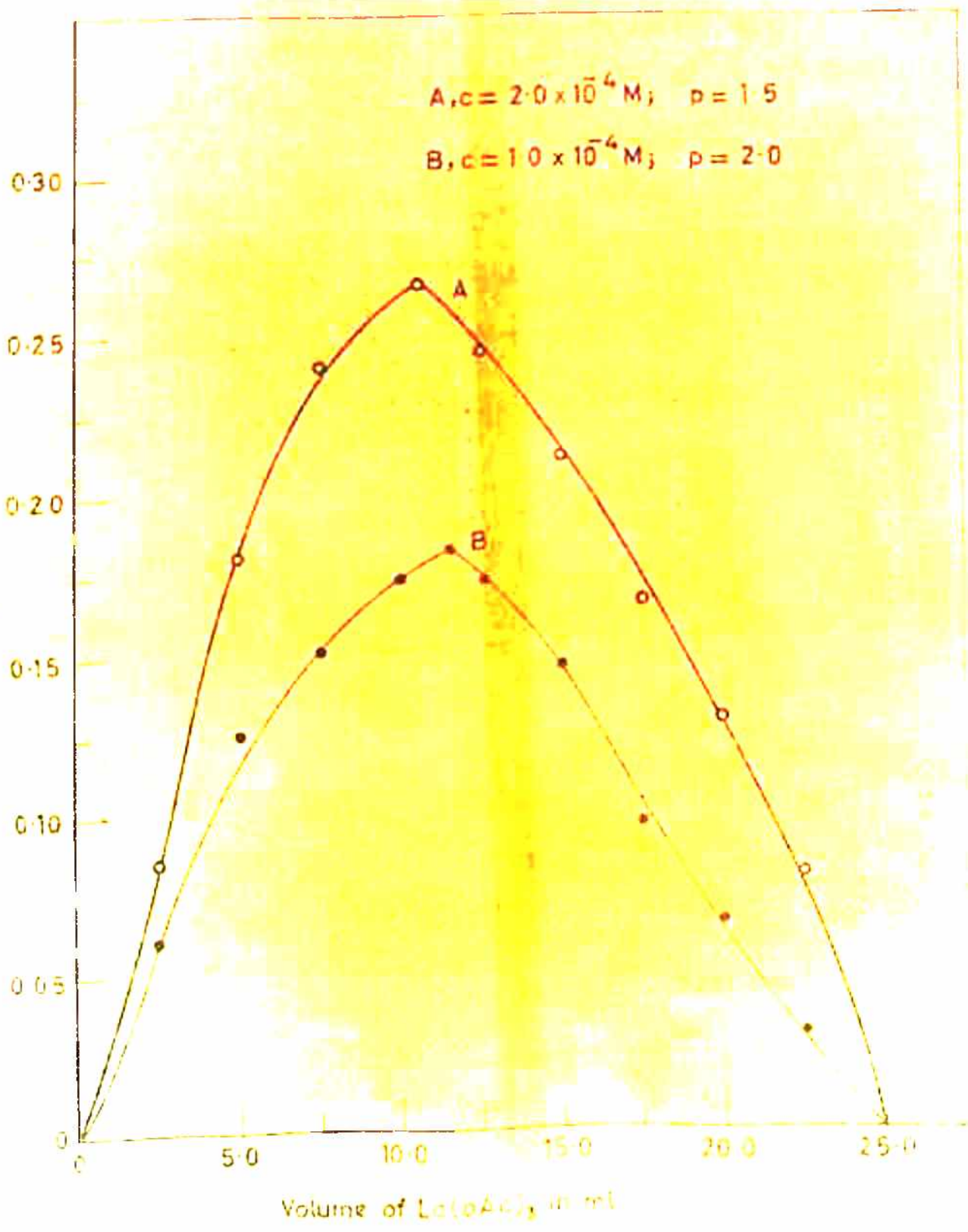


Fig. 3·11 Continuous variation method at 530 nm;
pH: 6·8±0·1; μ: 0·1 $NaClO_4$

Mole ratio method

A series of solutions were prepared from 2.0×10^{-4}M of the lanthanum acetate and quinalizarin at pH 6.8 and ionic strength 0.1, maintaining a 50 per cent ethanolic medium and varying amounts of equimolecular solutions of the metal were added such that the mole ratio of the reagent to metal was from 1:0.2 to 1:3. The results recorded in table 3.24 and plotted in fig. 3.12, show a break at a ratio of one mole of the reagent to 0.5 mole of the metal indicating that a 1:2 (Metal : Chelating agent) complex is formed.

Table 3.24

Concentration of lanthanum acetate = 2.0×10^{-4}M

Concentration of quinalizarin (QZR) = 2.0×10^{-4}M

pH = 6.8 ± 0.1, Total volume made up = 25 ml

Break at 1:0.5 (Fig. 3.12 curve A,B)

Ratio Quinalizarin: Lanthanum	Optical density at 530 nm	Optical density at 550 nm
1 : 0.1	0.635	0.615
1 : 0.2	0.660	0.635
1 : 0.3	0.675	0.655
1 : 0.4	0.700	0.675
1 : 0.5	0.715	0.690
1 : 0.6	0.720	0.695
1 : 1.0	0.720	0.695
1 : 2.0	0.720	0.700
1 : 3.0	0.725	0.695

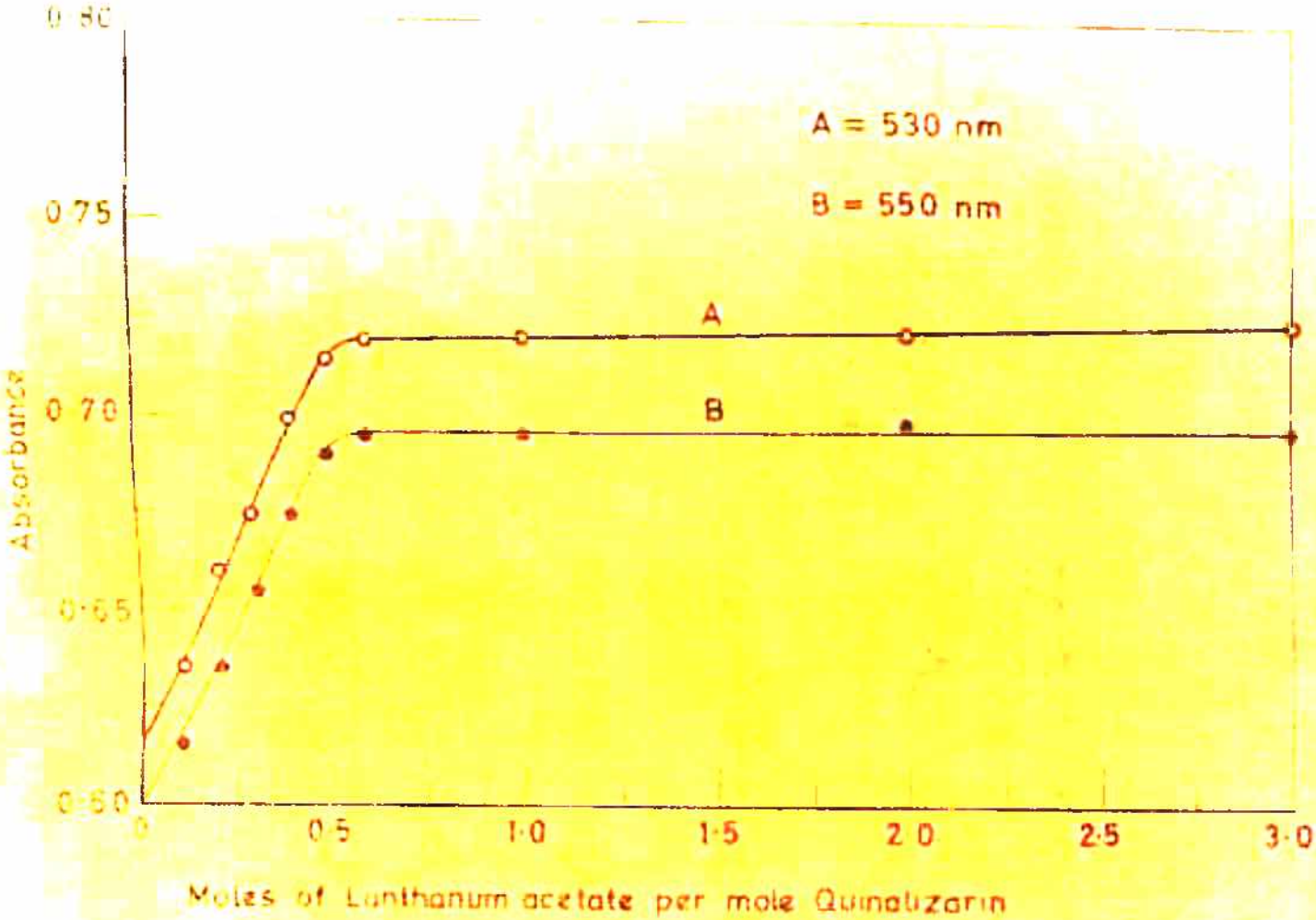


Fig _ 3.12 Mole ratio method at pH 6·8±0·1; μ: 0·1 $NaClO_4$; conc: $2{\cdot}0 \times 10^{-4}$ M

Slope ratio method

The concentration of the variable component was 1.0×10^{-4}M. The volume of the variable component was varied from 1 to 12.5 ml in the presence of 12.5 ml of excess concentration of 2.5×10^{-4}M of the constant component. The total volume was 25 ml and the volume of ethanol in each case was 12.5 ml. The pH of the solution was maintained at 6.8 and ionic strength at 0.1. Fig. 3.13 shows the absorbance at 530, 550 and 580 nm plotted against the volume of the variable component. The slopes of the two straight line in each case gave lanthanum quinalizarin ratio as 1:2. Some of the typical results are given in table 3.25 and 3.26.

Table 3.25

Concentration of constant component (QZR) = 2.5×10^{-4}M

Volume of the constant component (QZR) = 12.5 ml

Concentration of the variable component (lanthanum acetate) = 1.0×10^{-4}M

pH of mixtures = 6.8

Total volume = 25 ml

Volume of the variable component lanthanum acetate (ml)	Optical density at		
	530 nm	550 nm	580 nm
1.0	0.505	0.450	0.325
2.0	0.540	0.480	0.360
4.0	0.610	0.550	0.420
5.0	0.640	0.585	0.460
6.0	0.670	0.620	0.495
7.0	0.705	0.650	0.530
8.0	0.740	0.690	0.560
10.0	0.800	0.750	0.625
12.0	0.870	0.820	0.685
12.5	0.875	0.840	0.710

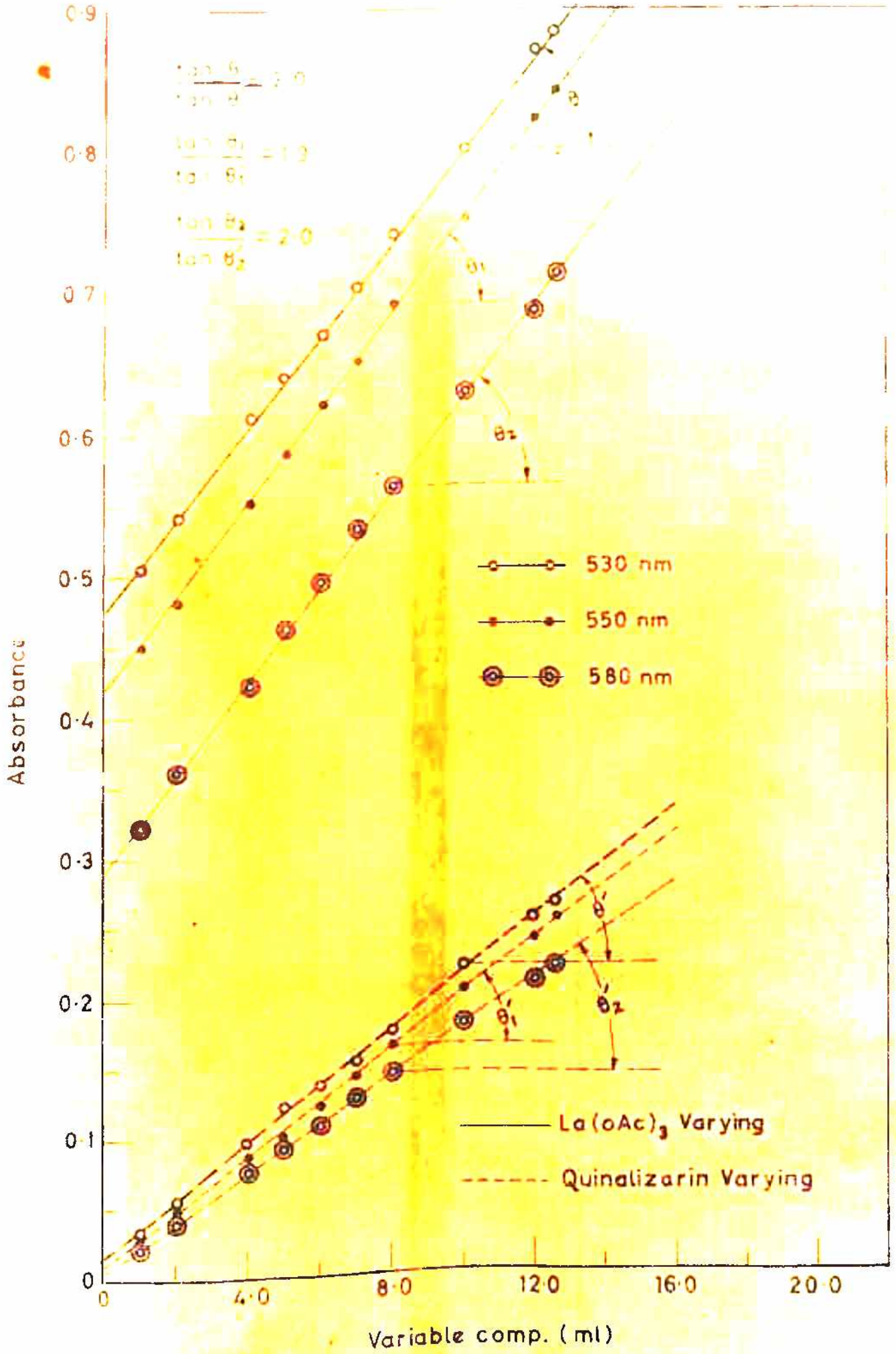


Fig._3·13 Slope ratio method; pH: 6·8±0·1; μ: 0·1 $NaClO_4$
$2{\cdot}5 \times 10^{-4}$M excess comp. (12·5 ml) + $1{\cdot}0 \times 10^{-4}$M
variable comp. (x ml) + water or ethanol (12·5-x ml)

Table 3.26

Concentration of constant component (lanthanum acetate) = 2.5×10^{-4} M

Volume of constant component (lanthanum acetate) = 12.5 ml

Concentration of variable component (QZR) = 1.0×10^{-4} M

pH of mixtures = 6.8 ± 0.1

Total volume = 25 ml

Volume of variable component QZR (ml)	Optical density at		
	530 nm	550 nm	580 nm
1.0	0.035	0.030	0.025
2.0	0.055	0.050	0.040
4.0	0.095	0.085	0.075
5.0	0.120	0.100	0.090
6.0	0.135	0.120	0.105
7.0	0.150	0.140	0.125
8.0	0.170	0.160	0.140
10.0	0.215	0.200	0.175
12.0	0.250	0.235	0.205
12.5	0.260	0.250	0.215

Calculation of the stability constant

The stability constants were calculated from absorbance data by the three methods, viz,

(a) method of Dey and Coworkers (fig. 3.14)

(b) method of continuous variation using non equimolecular solutions.

(c) mole ratio method.

The values of change in free energy of formation

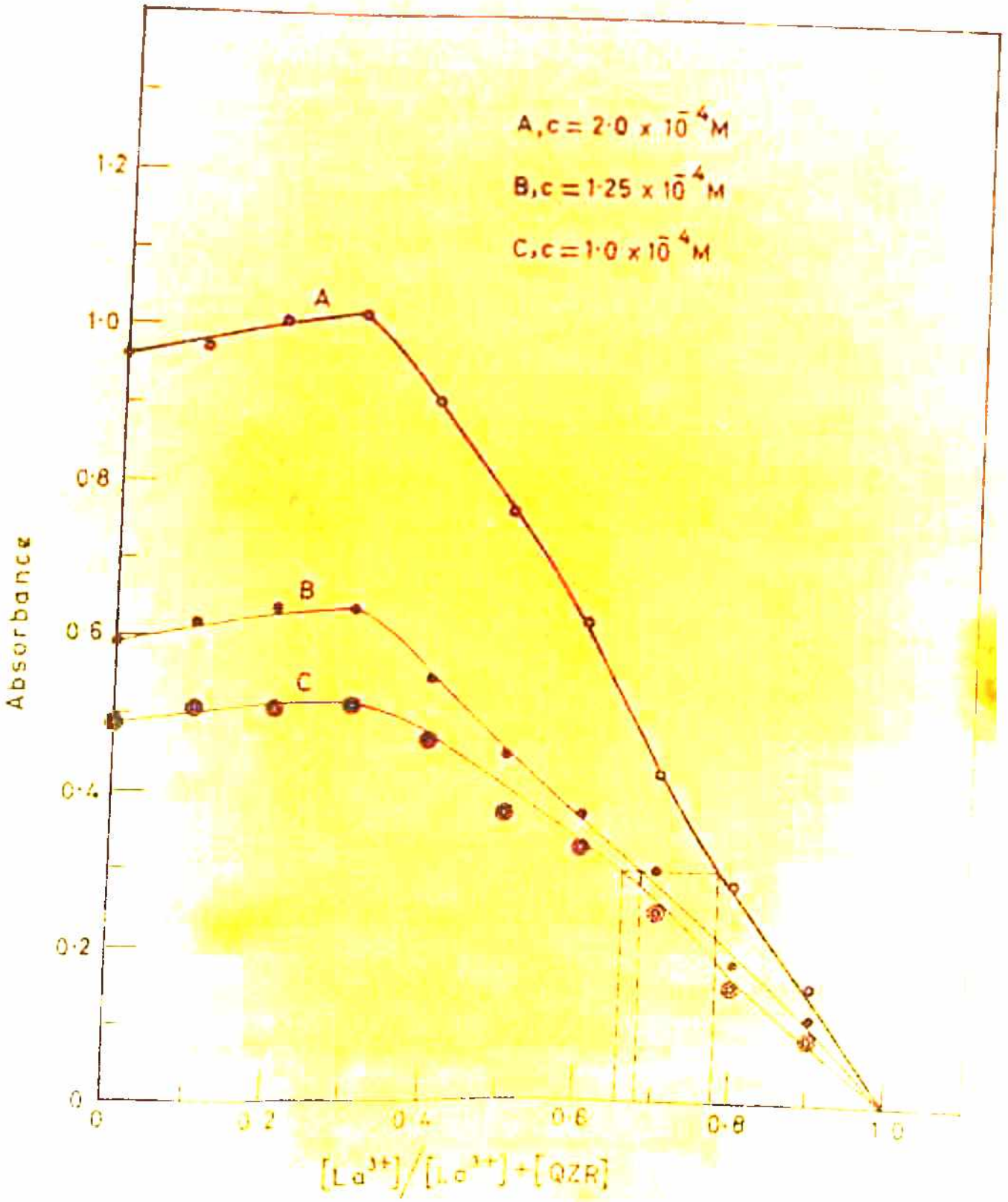


Fig._ 3·14 Determination of the stability constant from absorbance data at 530 nm, p=1; pH: 6·8±0 1 μ: 0·1 $NaClO_4$

were also calculated (table 3.27).

Nature of charge on the chelate

Ion exchange studies have been made and it has been found that the chelate formed is anionic.

Procedure for the determination of lanthanum

Into a 25 ml volumetric flask an aliquot of the solution containing upto 85 µg of lanthanum was pipitted after which 5 ml of ammonium acetate buffer solution of pH 6.8 and 5 ml of 1 x 10^{-3}M quinalizarin solution were added. The volume of ethanol was kept at 12.5 ml, total volume 25 ml. After mixing, the solution was allowed to stand for 30 minutes. The absorbance of the solution was measured at 530 nm against a reagent blank treated in a similar manner.

Discussion

The formation of a violet colour produced by the interaction of quinalizarin and lanthanum has been studied to determine the composition, stability and other characteristics of the chelate formed. The absorbance curves of the complex show maxima aat 530 nm indicates that only one complex is formed. The composition of the chelate has been determined by the method of

(1) continuous variation (tables 3.19 to 3.23, figures 3.10 to 3.11).

(2) mole ratio method (table 3.14, figure 3.12) and (3) slope ratio method (table 3.25 and 3.26, figure 3.13).

The results indicate that the molar ratio of the metal to chelating agent is 1:2. The chelate is soluble in aqueous ethanol and is stable between pH 6.5 - 7.8.

The maximum colour formation is attained at pH 6.8, when the mixture contains greater than five fold excess of the reagent with respect to the metal solution and the colour intensity remains unaltered even after keeping the mixture for three hours at room temperature.

The values of log K at pH 6.8 ± 0.1 and at 30° calculated using the three different methods, referred to earlier, are shown in table 3.27.

The free energy change of formation has also been calculated and is tabulated in the same table.

Table 3.27

Method	pH	log K	ΔG° at 30° (KCal)
(a) Dey and Coworkers	6.8 ± 0.1	10.1 ± 0.1	- 14.0 ± 0.1
(b) Continuous variation	6.8 ± 0.1	10.1 ± 0.1	- 14.0 ± 0.1
(c) Mole ratio	6.8 ± 0.1	10.2 ± 0.1	- 14.1 ± 0.1

The close adherence of these values indicate the excellent agreement of the results obtained.

The range of concentration for adherence to Beer's law and value of optimum concentration range are 1.26 to 6.32 ppm and 1.4 to 3.5 ppm. Studies have also been made to establish optimum conditions for the spectrophotometric determination of lanthanum.

IRON (III) QUINALIZARIN SYSTEM

In analytical chemistry quinalizarin has been used as a reagent for the detection and photometric determination of various metals. However, very few metal complexes with quinalizarin have been studied with regard to composition and stability. The present work describes the studies on the composition and stability of the iron (III) quinalizarin chelate in 50 per cent ethanolic medium.

EXPERIMENTAL

Spectrographically standardized iron sponge (Johnson, Metthey and Co., Ltd.) was used for the preparation

of iron solution. The sample was standardized by usual methods. Quinalizarin was the same as used previously. Potassium chloride employed was of reagent grade.

Conditions of study

All experiments were performed at 20 ± 0.1°C. The total volume of all the mixtures prepared for measurement was kept at 25 ml. The individual solutions and mixtures were kept in a thermostat maintaining a temperature of 20° ± 0.01°C for about 30 minutes to attain equilibrium. The pH of solutions and mixtures was adjusted to 3.0 ± 0.1 by addition of suitable amounts of hydrochloric acid or sodium hydroxide. Ionic strength of the system was kept constant by maintaining a concentration of 0.1M potassium chloride. Quinalizarin behaves as a colloidal electrolyte, hence dilute solutions of the order of 10^{-4} or 10^{-5}M were employed for the physico chemical measurements.

Effect of pH on the chelate

Solutions containing the same concentration of ferric chloride and the reagent were prepared at different pH and the absorbance at various wavelengths were noted. The complex showed λ_{max} at 560 nm in the pH range 2 - 4.5 and it gave a constant optical density in pH range 2.8 - 3.8 hence a pH 3.0 was selected for subsequent studies.

of 2.5 ml of 1.0 M potassium chloride. The pH was adjusted by usual methods.

The composition of the solutions prepared is given in table 3.28. The absorbance of the solutions was measured at suitable wavelength interval (table 3.29).

Table 3.28

A survey of solutions prepared for measurement of absorption curves

Ml added of 1.0M KCl Solution	10^{-3}M iron(III) solution	10^{-3}M QZR solution	Mole ratio of iron (III)to QZR	Absorption curves reproduced in fig.3.15
2.5	5	5	1 : 1	A
2.5	2.5	10	1 : 4	B
2.5	10	2.5	4 : 1	C

Table 3.29

Wavelength nm	Optical density		
	A	B	C
480	0.154	-	0.226
490	0.275	-	0.290
500	0.370	0.048	0.370
510	0.450	0.134	0.450
520	0.725	0.266	0.515
530	0.820	0.512	0.560
540	0.850	0.612	0.615
550	0.920	0.642	0.625
560	0.950	0.652	0.635

contd.

Table 3.29 contd.

Wavelength nm	Optical density		
	A	B	C
570	0.870	0.648	0.610
580	0.855	0.640	0.570
590	0.815	0.625	0.540
600	0.780	0.605	0.505
610	0.725	0.580	0.460
620	0.690	0.565	0.400
630	0.640	0.520	0.365
640	0.600	0.505	0.330
650	0.560	0.470	0.280
660	0.520	0.445	0.240
670	0.490	0.410	0.215
680	0.455	0.400	0.200
690	0.400	0.360	0.180
700	0.320	0.340	0.160
710	0.240	0.300	0.120
720	0.185	0.280	0.080

Fig. 3.15 shows that the complex has an absorption maximum at 560 nm against a reagent blank.

Stoichiometry of the components

The composition of the complex was determined at 560 nm by Job's method of continuous variation using both equimolecular and nonequimolecular solutions. The results are given in tables 3.30 to 3.25 and represented graphically in figures 3.16 to 3.17.

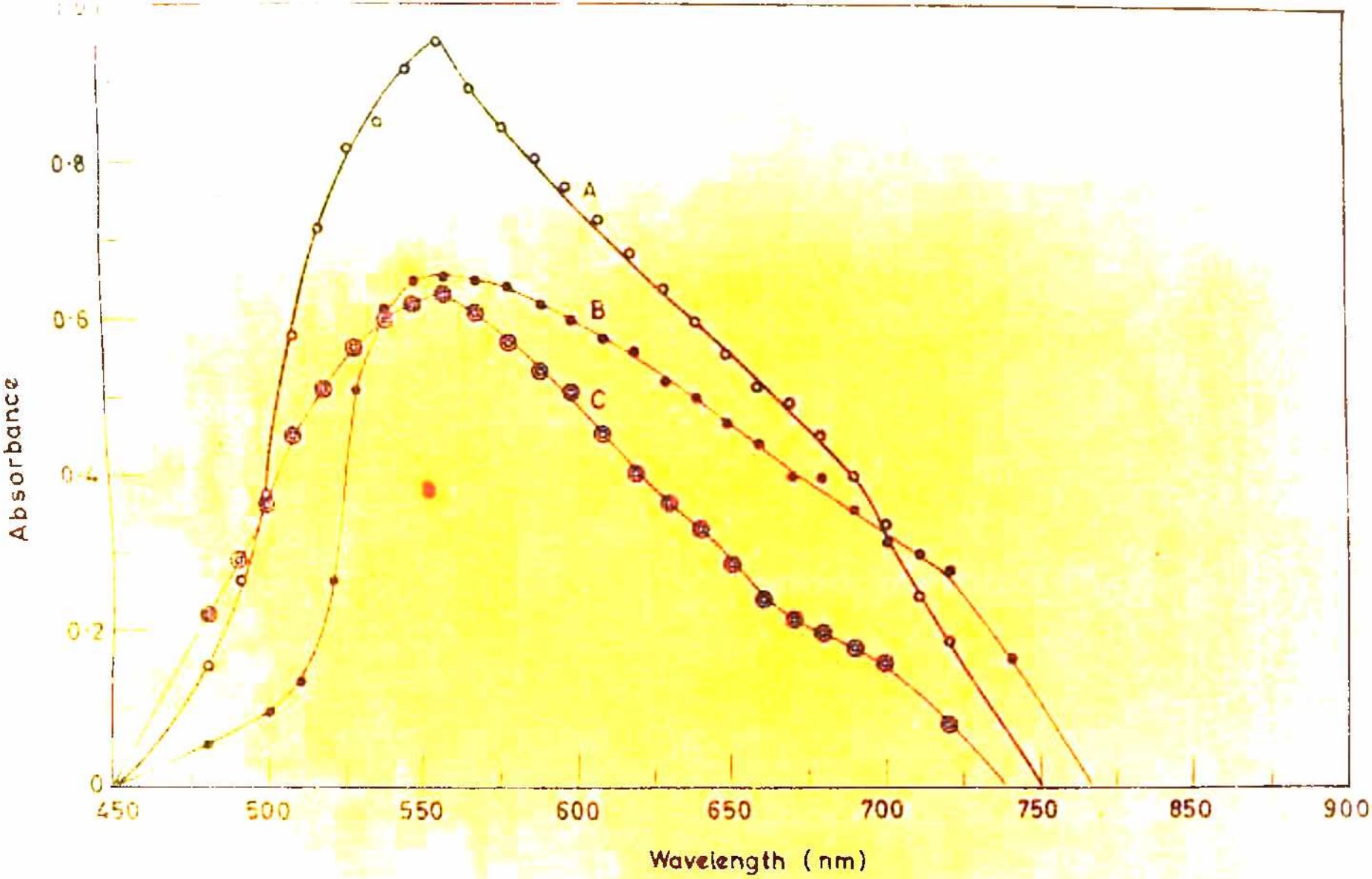


Fig._ 3·15 Absorption curves of Ferric chloride and Quinalizarin Vs a reagent blank at pH 3·0±0·1. (For details see table 3·28)

Table 3.30

Concentration of ferric chloride (c) = 4.0×10^{-4}M

Concentration of quinalizarin (c') = 4.0×10^{-4}M

pH = 3.0 ± 0.1, p = c'/c = 1, λ = 560 nm, μ = 0.1 KCl

peak at 1:1 (Fig. 3.16 curve A)

Volume of ferric chloride ml	Volume of QZR ml	Optical density of		Difference (a-b)
		mixture (a)	QZR (b)	
0.0	25.0	0.095	0.095	0.000
2.5	22.5	0.320	0.080	0.240
5.0	20.0	0.550	0.065	0.485
8.33	16.67	0.855	0.055	0.800
10.0	15.0	0.930	0.050	0.880
12.5	12.5	0.970	0.045	0.925
15.0	10.0	0.940	0.040	0.900
16.67	8.33	0.805	0.035	0.770
20.0	5.0	0.445	0.030	0.415
22.5	2.5	0.235	0.020	0.215

Table 3.31

Concentration of ferric chloride (c) = 2.5×10^{-4}M

Concentration of quinalizarin (c') = 2.5×10^{-4}M

pH = 3.0 ± 0.1, p = c'/c = 1, λ = 560 nm, μ = 0.1 KCl

peak at 1:1 (Fig. 3.16, curve B)

0.0	25.0	0.060	0.060	0.000
2.5	22.5	0.190	0.050	0.140
5.0	20.0	0.325	0.045	0.280
8.33	16.67	0.480	0.040	0.440
10.0	15.0	0.530	0.035	0.495
12.5	12.5	0.597	0.032	0.565
15.0	10.0	0.510	0.030	0.480
16.67	8.33	0.445	0.025	0.420
20.0	5.0	0.255	0.020	0.235
22.5	2.5	0.130	0.015	0.115

Table 3.32

Concentration of ferric chloride (c) = 2.0×10^{-4}M

Concentration of quinalizarin (c') = 2.0×10^{-4}M

pH = 3.0 ± 0.1, p = c'/c = 1. , λ = 560 nm, μ = 0.1 KCl

peak at 1:1 (Fig. 3.16 curve C)

Volume of ferric chloride ml	Volume of QZR ml	Optical density of mixture (a)	Optical density of QZR (b)	Difference (a-b)
0.0	25.0	0.050	0.050	0.000
2.5	22.5	0.140	0.045	0.095
5.0	20.0	0.237	0.042	0.195
8.33	16.67	0.360	0.040	0.320
10.0	15.0	0.400	0.035	0.365
12.5	12.5	0.435	0.030	0.405
15.0	10.0	0.368	0.028	0.340
16.67	8.33	0.340	0.022	0.318
20.0	5.0	0.220	0.020	0.200
22.5	2.5	0.105	0.015	0.090

Table 3.33

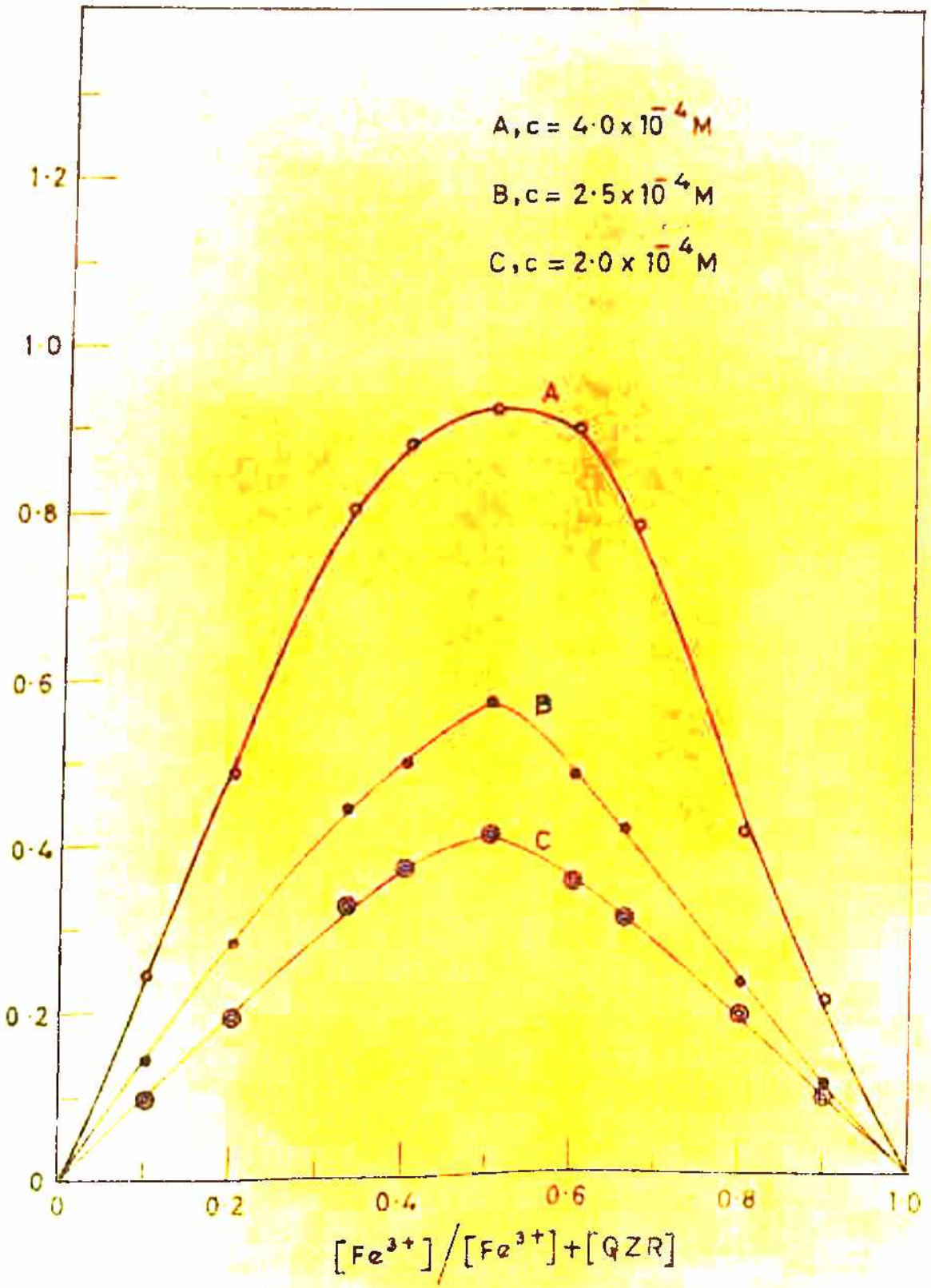
Concentration of ferric chloride (c) = 4.0×10^{-4}M

Concentration of quinalizarin (c') = 2.0×10^{-4}M

pH = 3.0 ± 0.1, p = c'/c = 0.5, λ = 560 nm, μ = 0.1 KCl

peak at 1:1 (Fig. 3.17 curve A)

0.0	25.0	0.050	0.050	0.000
2.5	22.5	0.285	0.045	0.240
5.0	20.0	0.467	0.042	0.425
7.5	17.5	0.635	0.040	0.595
10.0	15.0	0.615	0.035	0.580
12.5	12.5	0.560	0.030	0.530
15.0	10.0	0.493	0.028	0.465
17.5	7.5	0.402	0.022	0.380
20.0	5.0	0.260	0.020	0.240
22.5	2.5	0.125	0.015	0.110



ig._ 3·16 Continuous variation method at 560 nm;

pH: 3·0 ± 0·1; μ: 0·1 KCl

Table 3.34

Concentration of ferric chloride (c) = 5.0×10^{-4}M

Concentration of quinalizarin (c') = 2.5×10^{-4}M

pH = 3.0 ± 0.1, p = c'/c = 0.5, λ = 560 nm, μ = 0.1 KCl

peak at 1:1 (Fig. 3.17 curve B)

Volume of ferric chloride ml	Volume of QZR ml	Optical density		Difference a-b
		mixture (a)	QZR (b)	
0.0	25.0	0.060	0.060	0.000
2.5	22.5	0.355	0.050	0.305
5.0	20.0	0.545	0.045	0.500
7.5	17.5	0.758	0.038	0.720
10.0	15.0	0.715	0.035	0.680
12.5	12.5	0.622	0.032	0.590
15.0	10.0	0.510	0.030	0.480
17.5	7.5	0.425	0.025	0.400
20.0	5.0	0.280	0.020	0.260
22.5	2.5	0.140	0.015	0.125

Table 3.35

Concentration of ferric chloride (c) = 2.5×10^{-4}M

Concentration of quinalizarin (c') = 5.0×10^{-4}M

pH = 3.0 ± 0.1, p = c'/c = 2.0, λ = 560 nm, μ = 0.1 KCl

peak at 1:1 (Fig. 3.17 curve C)

0.0	25.0	0.110	0.110	0.000
2.5	22.5	0.275	0.095	0.180
5.0	20.0	0.450	0.080	0.370
7.5	17.5	0.575	0.070	0.505
10.0	15.0	0.675	0.065	0.610
12.5	12.5	0.755	0.060	0.695
15.0	10.0	0.817	0.052	0.765
16.0	9.0	0.850	0.050	0.800
17.0	8.0	0.805	0.045	0.760
20.0	5.0	0.515	0.035	0.480
22.5	2.5	0.290	0.020	0.270

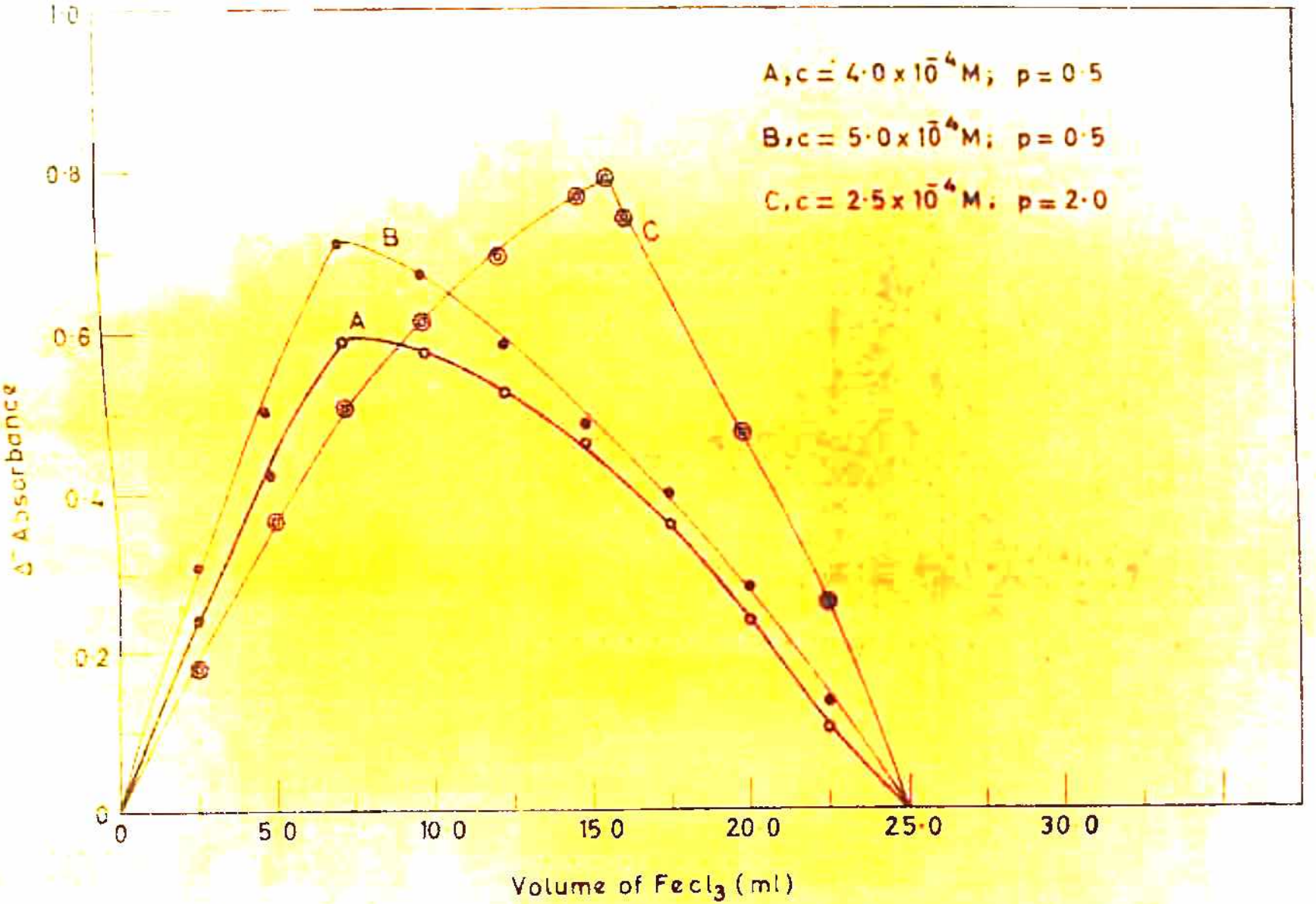


Fig _ 3·17 Continuous variation method at 560 nm; pH: 3·0±0·1; μ: 0·1 KCl

Mole ratio method

A series of solutions was prepared from 2.5×10^{-4}M and 2.0×10^{-4}M of ferric chloride and quinalizarin at pH 3.0 and ionic strength 0.1, maintaining a 50 per cent ethanolic medium and varying amounts of equimolecular solutions of the metal were added such that the mole ratio of the reagent to metal was from 1:0.2 to 1:6. The results are recorded in table 3.36 - 3.37 and plotted in fig. 3.18, show a break at a ratio of 1 mole of quinalizarin to 1 mole of iron.

Table 3.36

Concentration of ferric chloride = 2.5×10^{-4}M

Concentration of quinalizarin = 2.5×10^{-4}M

pH = 3.0 ± 0.1, μ = 0.1 KCl

Total volume made up = 25 ml

Breat at 1:1 (Fig. 3.18 curve A)

Ratio QZR : Iron	Optical density at 560 nm
1 : 0.2	0.160
1 : 0.4	0.280
1 : 0.6	0.400
1 : 0.8	0.495
1 : 1.0	0.590
1 : 1.5	0.640
1 : 2.0	0.670
1 : 2.5	0.700
1 : 3.0	0.720
1 : 3.5	0.730
1 : 4.0	0.740
1 : 5.0	0.760
1 : 6.0	0.760

Table 3.37

Concentration of ferric chloride = 2.0×10^{-4}M

Concentration of quinalizarin = 2.0×10^{-4}M

pH = 3.0 ± 0.1, μ = 0.1 KCl

Total volume made up = 25 ml

Break at 1:1 (Fig. 3.18 curve B)

Ratio QZR : Iron	Optical density at 560 nm
1 : 0.2	0.122
1 : 0.4	0.213
1 : 0.6	0.300
1 : 0.8	0.375
1 : 1.0	0.450
1 : 1.5	0.495
1 : 2.0	0.520
1 : 2.5	0.545
1 : 3.0	0.570
1 : 3.5	0.575
1 : 4.0	0.580
1 : 5.0	0.590
1 : 6.0	0.590

Slope ratio method

The concentration of the variable component was 1.0×10^{-4}M. The volume of the variable component was varied from 1 to 12.5 ml in the presence of 12.5 ml of excess Concentration of 4.0×10^{-4}M of the constant component. The total volume in each case was kept at 25 ml and volume of ethanol at 12.5 ml. The pH of the solution was maintained at 3.0 and ionic strength at 0.1. Figure 3.19 shows the measured absorbance at 560 nm plotted against the volume of the variable component. The slopes of the two straight lines in each case gave iron: quinalizarin ratio as 1:1. Some of the typical results are given in tables 3.38 and 3.39.

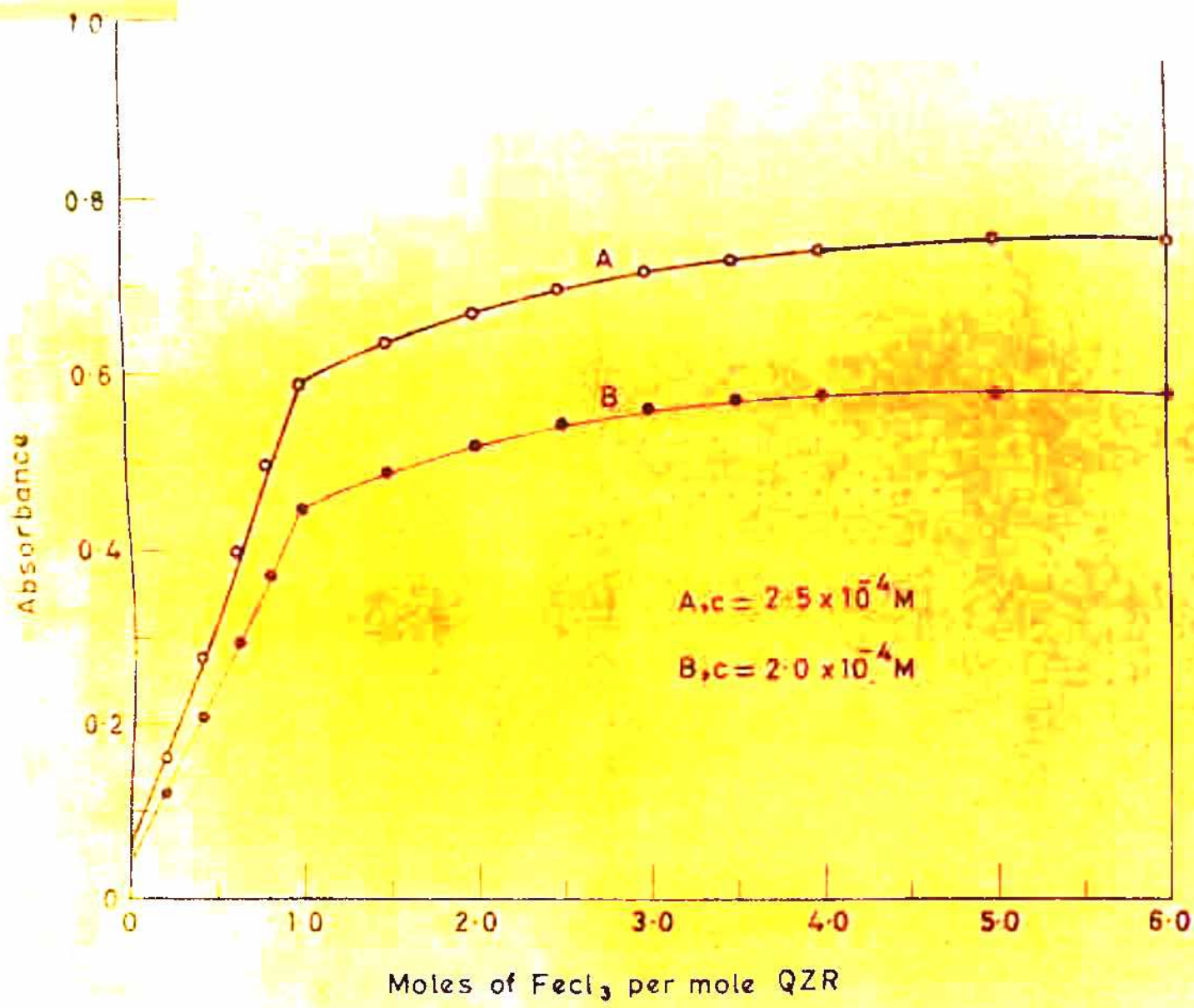


Fig._3·18 Mole ratio method at 560 nm; pH: 3·0±0·1; μ: 0·1 KCl

Table 3.38

Concentration of constant component (QZR) = 4.0×10^{-4}M

Volume of the constant component (QZR) = 12.5 ml

Concentration of the variable component (ferric chloride) = 1.0×10^{-4}M

pH = 3.0, Total volume = 25 ml

Volume of variable component ferric chloride (ml)	Optical density at 560 nm
1.0	0.058
2.0	0.075
3.0	0.100
4.0	0.120
5.0	0.140
6.0	0.165
7.0	0.186
8.0	0.205
9.0	0.230
10.0	0.252
11.0	0.276
12.0	0.295
12.5	0.310

Table 3.39

Concentration of constant component (ferric chloride) = 4.0×10^{-4} M

Volume of constant component (ferric chloride) = 12.5 ml

Concentration of variable component (QZR) = 1.0×10^{-4}M

pH = 3.0, Total volume = 25 ml

Volume of variable component QZR (ml)	Optical density at 560 nm
1.0	0.048
2.0	0.065
3.0	0.085
4.0	0.102
5.0	0.122

contd.

Table 3.39 contd.

Volume of variable component QZR (ml)	Optical density at 560 nm
6.0	0.140
7.0	0.160
8.0	0.180
9.0	0.200
10.0	0.220
11.0	0.240
12.0	0.255
12.5	0.265

Evaluation of the stability constant

The stability constants were calculated from absorbance data by four methods, viz,

(a) method of Dey and Coworkers (fig.3.20)

(b) method of continuous variation using non equimolecular solutions.

(c) mole ratio method and

(d) by the measurements of molecular extinction coefficients.

The values of change in free energy of formation were also calculated.

Suggestions on the structure of the chelate

It is not possible to derive a definite information, on the basis of the experimental results mentioned in the present work regarding the structure of the chelate excepting that the iron exchange adsorption studies show that the chelate of iron is anionic.

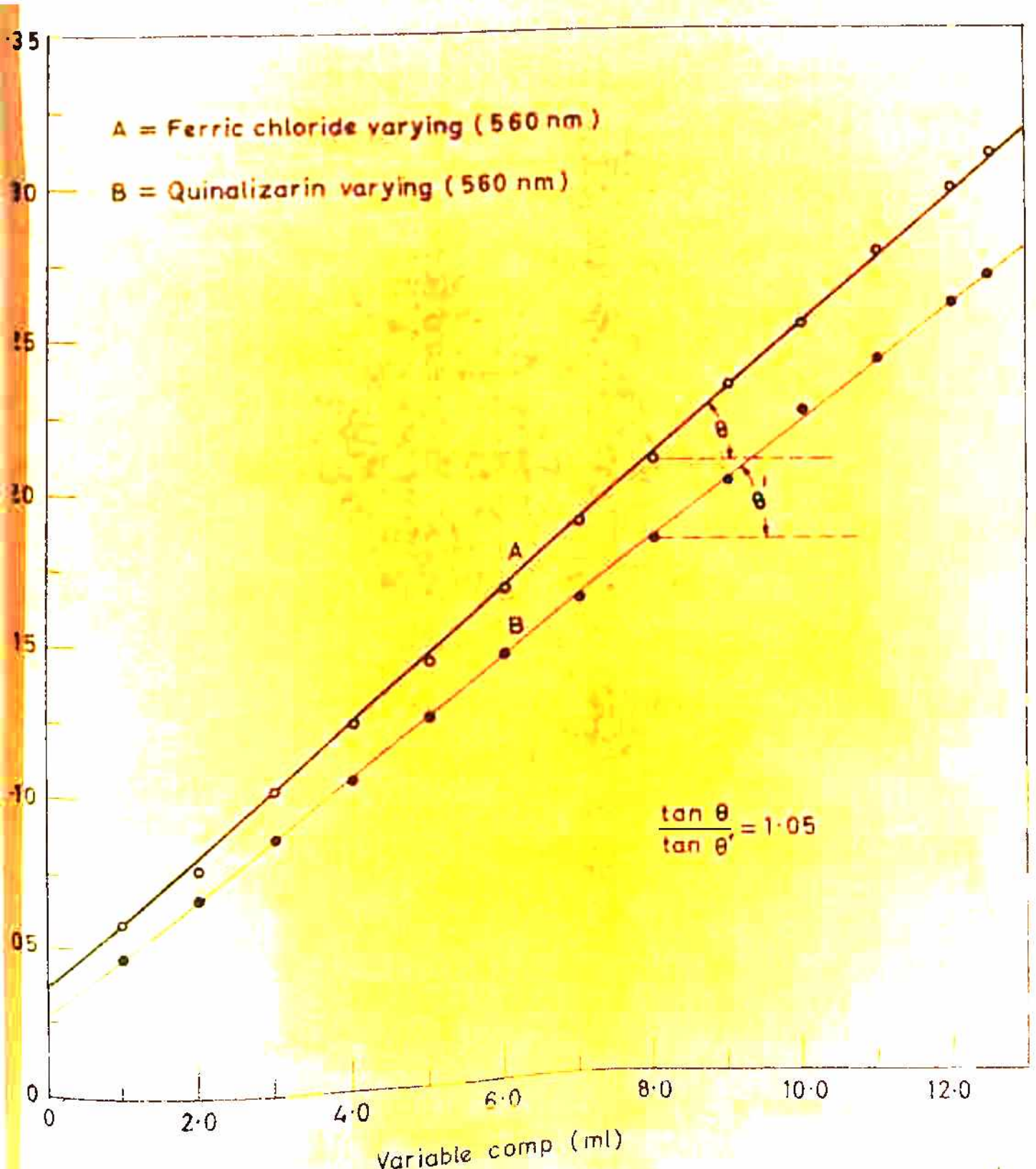


Fig. 3·19 Slope ratio method; pH: 3·0±0·1; μ: 0·1 KCl; $4·0 \times 10^{-4}$ M excess comp. (12·5 ml) + $1·0 \times 10^{-4}$ M variable comp. (x ml) + ethanol or water (12·5 − x ml)

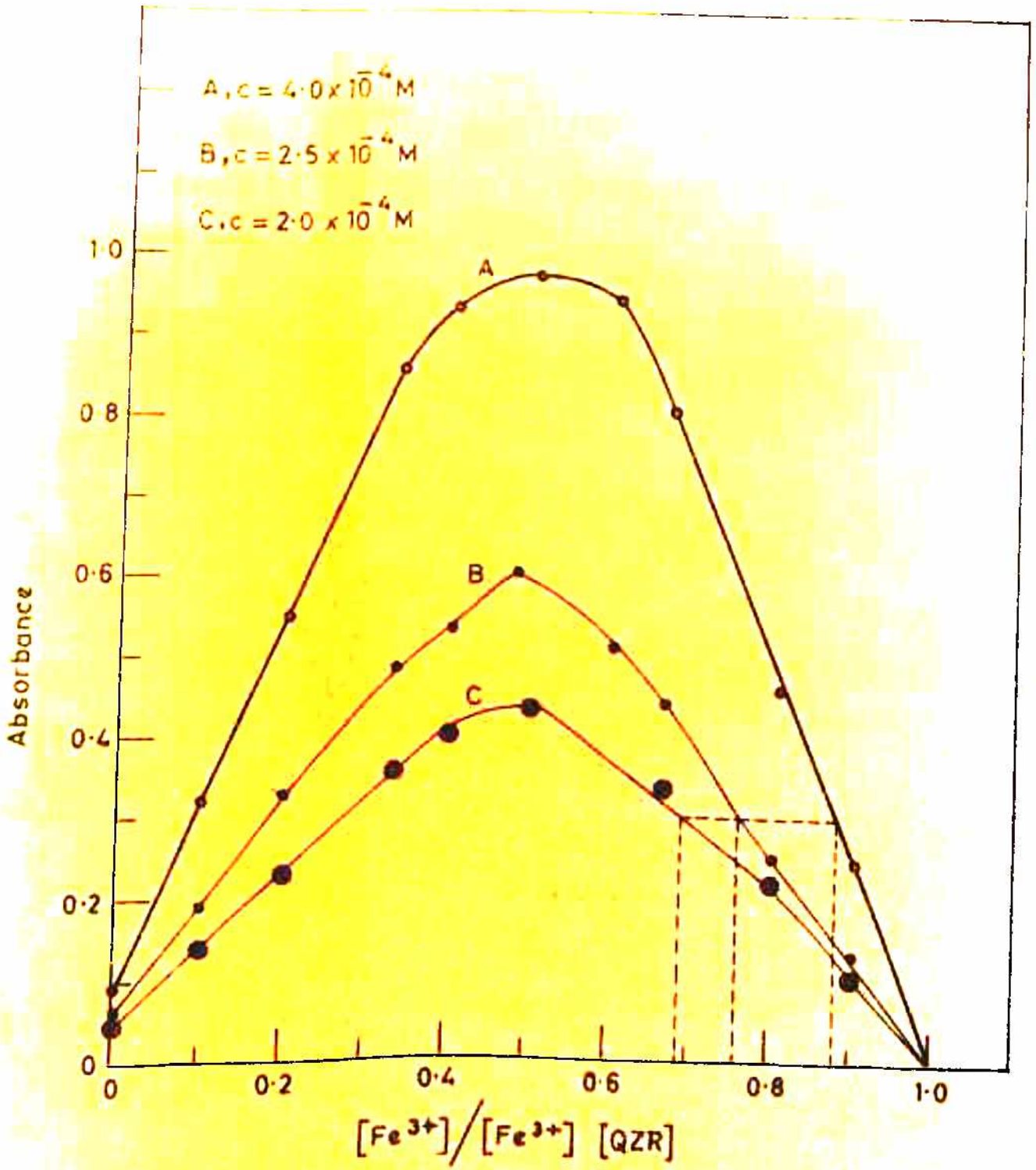


Fig._ 3·20 Determination of the stability constant from absorbance data at 560 nm; p=1; pH: 3·0±0·1; μ: 0·1 KCl

Discussion

A spectrophotometric study of the complex formed between iron (III) and quinalizarin has been made. The composition of the complex as established by three different methods is 1:1.

The chelate is soluble in aqueous ethanol, stable in pH range 2.0 - 4.0 and has an absorption maximum at 560 nm against a reagent blank.

The values of log K along with the value of $\triangle G^{o}$ as determined by various methods are given in table 3.40.

(pH = 3.0 ± 0.1; μ = 0.1 M KCl)

Table 3.40

Method	log K	$\triangle G^{o}$ at 20° (KCal)
1. Dey and Coworkers	5.0 ± 0.1	- 6.7 ± 0.1
2. Continuous variation	5.2 ± 0.1	- 7.0 ± 0.1
3. Mole ratio	5.3 ± 0.15	- 7.1 ± 0.2
4. Molecular extinction coefficient	5.0 ± 0.0	- 6.7 ± 0.0

The optimum pH range between which the complex is stable, range of concentration for adherence to Beer's law, the value of molecular extinction coefficient and sensitivity

have been given in table 3.41.

Table 3.41

Optimum conditions for the photometric determination of iron (III) with quinalizarin*

Wavelength nm	Optimum pH range	Range of adherence to Beer's law (ppm)	Molecular extinction coefficient	Sensitivity (Sandell) µg/sq. cm.
560	2.8 - 3.8	0.45 - 4.5	6350	0.011

* pH = 3.0; temperature 20^{o}

The results as discussed above indicate that the logK values show a close correlation. The values of ΔG^{o} obtained for the four different methods have also been found to be of the same order.

The optimum conditions of photometric determination indicate good potentialities for estimation of iron by this method.

ZIRCONIUM (IV) QUINALIZARIN SYSTEM

Inspite of the large amount of work done on the chromogenic properties of this reagent, the composition and stability of metal chelates involving quinalizarin, have not received sufficient attention and no work has been done on zirconium (IV) chelate. It was therefore thought fit that this system may be investigated.

EXPERIMENTAL

Zirconium Nitrate (B.D.H.) was dissolved in double distilled water and standardised. Quinalizarin (B.D.H. reagent grade) was the same as used previously. All other chemicals employed were of reagent grade.

Conditions of study

All experiments were performed at 20 ± 0.1°C. The volume of ethanol was kept at 12.5 ml. and total volume 25 ml. The pH was adjusted to 6.0 with ammonium acetate buffer solution.

Quinalizarin, like most of the chromophoric dyes, behaves as a colloidal electrolyte, hence dilute solutions of the order of 10^{-4} or 10^{-5}M were used in these investigations.

Effect of time on the absorbance of the chelate - The colour

formation was observed to be immediate and the absorbance values remained constant at least upto 72 hours.

The order of the addition of reagents

Studies were made of the addition of the chelating agent to the metal solution and vice versa. It was found that there was no change, whether the metal was added to the reagent or vice versa. To maintain uniformity, however, the chelating agent was added to the metal solution.

Nature of the complex formed

The method of Vosburgh and Cooper (83) was followed. Mixtures containing zirconium nitrate and quinalizarin in different stoichiometric ratios (0:1, 1:0.5, 1:1, 1:2, 1:3, 1:4) were prepared keeping the volume of ethanol at 12.5 and total volume at 25 ml. in each case and absorbances were measured.

Table 3.42

Mixture	Ratio Zirconium nitrate : Quinalizarin
A	0 : 1
B	1 : 0.5
C	1 : 1
D	1 : 2
E	1 : 3
F	1 : 4

Table 3.43

Initial concentration of zirconium nitrate = 2.0×10^{-4}M

Initial concentration of quinalizarin = 2.0×10^{-4}M

Total volume = 25 ml.

Wavelength nm	A	B	C	D	E	F
400	0.400	0.165	0.275	0.680	0.990	1.400
410	0.440	0.175	0.302	0.750	1.100	1.530
420	0.490	0.190	0.330	0.815	1.160	1.675
430	0.530	0.205	0.360	0.875	1.260	1.785
440	0.570	0.225	0.385	0.915	1.330	1.865
450	0.580	0.240	0.415	0.935	1.370	1.890
460	0.565	0.260	0.445	0.955	1.410	1.915
470	0.535	0.280	0.470	0.965	1.455	1.940
480	0.490	0.295	0.495	0.970	1.485	1.950
490	0.440	0.310	0.515	0.975	1.520	1.955
500	0.410	0.320	0.530	0.990	1.580	1.998
510	0.375	0.315	0.522	0.975	1.560	1.985
520	0.325	0.310	0.506	0.915	1.495	1.885
530	0.295	0.295	0.478	0.865	1.430	1.780
540	0.270	0.280	0.445	0.812	1.345	1.705
550	0.240	0.260	0.395	0.735	1.190	1.555
560	0.200	0.235	0.345	0.615	0.980	1.280
570	0.165	0.200	0.295	0.510	0.800	1.050
580	0.140	0.168	0.240	0.410	0.650	0.830
590	0.110	0.140	0.190	0.340	0.500	0.635
600	0.088	0.110	0.140	0.255	0.375	0.475
610	0.070	0.085	0.105	0.195	0.275	0.330
620	0.056	0.065	0.075	0.140	0.195	0.235
630	0.046	0.050	0.060	0.110	0.145	0.175
640	0.035	0.045	0.050	0.075	0.110	0.120
650	0.030	0.030	0.045	0.050	0.090	0.095

The observations have been plotted in fig. 3.21. It is evident from curve A that the region of maximum absorbance of quinalizarin lies at 450 nm at pH 6.0. In curves B, C, D, E and F the wavelength of maximum absorbance shifts to 500 nm. This shows that only one chelate having λ_{max} at 500 nm is formed under the conditions of study.

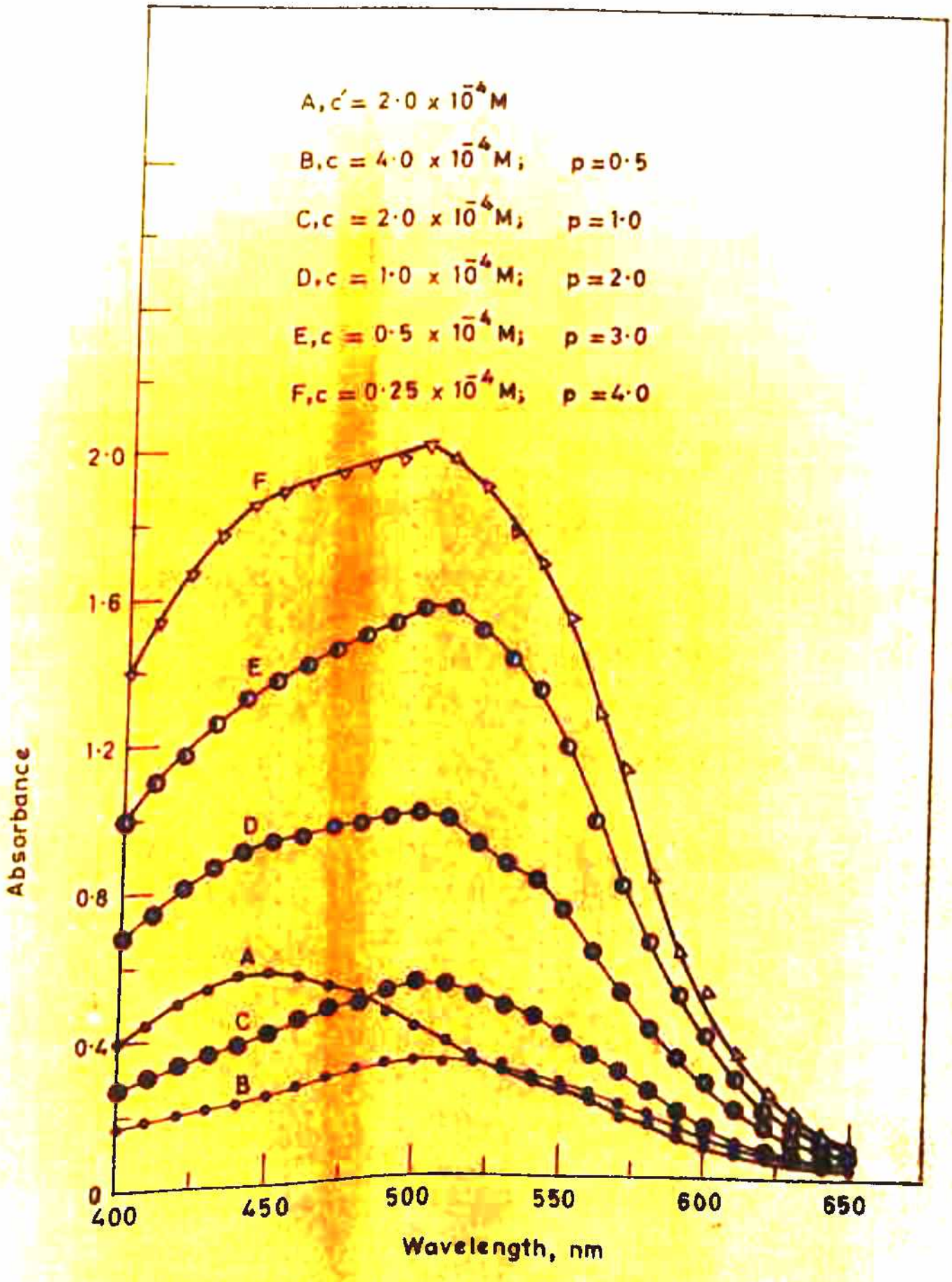


Fig._ 3·21 Absorption spectra of mixtures of Zirconium. nitrate and Quinalizarin at pH 6·0±0·1

STOICHIOMETRY OF THE COMPONENTS

Two different methods, viz, Job's method (38) of continuous variation and the mole ratio method were adopted for determining the stoichiometry of the components. In the Job's method of continuous variation the total volume in each case was kept at 25 ml. The pH of the solutions was kept at 6.0 ± 0.1. The absorption spectra of zirconium chelating agent and mixtures were measured in 50 per cent ethanolic medium at 540 nm. The results have been given in tables 3.44 to 3.48 and represented graphically in figures 3.22 to 3.23.

Table 3.44

Concentration of Zirconium Nitrate (c) = 2.5×10^{-4}M

Concentration of Quinalizarin (c') = 2.5×10^{-4}M

pH = 6.0 ± 0.1, λ = 540 nm, p = (c'/c) = 1

peak at 1:1 (Fig. 3.22 curve A)

Volume of zirconium nitrate (ml)	Volume of QZR (ml)	Optical density of		Difference (a-b)
		mixture (a)	QZR (b)	
0.0	25.0	0.560	0.560	0.000
2.5	22.5	0.575	0.535	0.040
5.0	20.0	0.590	0.505	0.085
7.5	17.5	0.610	0.470	0.140
10.0	15.0	0.620	0.430	0.190
12.5	12.5	0.570	0.340	0.230
15.0	10.0	0.480	0.280	0.200
17.5	7.5	0.380	0.220	0.160
20.0	5.0	0.285	0.160	0.125
22.5	2.5	0.160	0.100	0.060

Table 3.45

Concentration of Zirconium Nitrate (c) = 2.0×10^{-4}M

Concentration of Quinalizarin (c') = 2.0×10^{-4}M

pH = 6.0 ± 0.1, λ = 540 nm, p = c'/c = 1

peak at 1:1 (Fig. 3.22 curve B)

Volume of Zirconium Nitrate (ml)	Volume of QZR (ml)	Optical density of mixture (a)	Optical density of QZR (b)	Difference (a-b)
0.0	25.0	0.470	0.470	0.000
2.5	22.5	0.480	0.450	0.030
5.0	20.0	0.490	0.425	0.065
7.5	17.5	0.500	0.390	0.110
10.0	15.0	0.505	0.355	0.150
12.5	12.5	0.450	0.270	0.180
15.0	10.0	0.380	0.220	0.160
17.5	7.5	0.285	0.160	0.125
20.0	5.0	0.195	0.100	0.095
22.5	2.5	0.110	0.070	0.040

Table 3.46

Concentration of Zirconium Nitrate (c) = 1.0×10^{-4}M

Concentration of Quinalizarin (c') = 1.0×10^{-4}M

pH = 6.0 ± 0.1, λ = 540 nm, p = c'/c = 1

peak at 1:1 (Fig. 3.22 curve C)

0.0	25.0	0.250	0.250	0.000
2.5	22.5	0.250	0.230	0.020
5.0	20.0	0.258	0.220	0.038
7.5	17.5	0.260	0.200	0.060
10.0	15.0	0.265	0.185	0.080
12.5	12.5	0.240	0.150	0.090
15.0	10.0	0.190	0.115	0.075
17.5	7.5	0.145	0.085	0.060
20.0	5.0	0.110	0.060	0.050
22.5	2.5	0.060	0.040	0.020

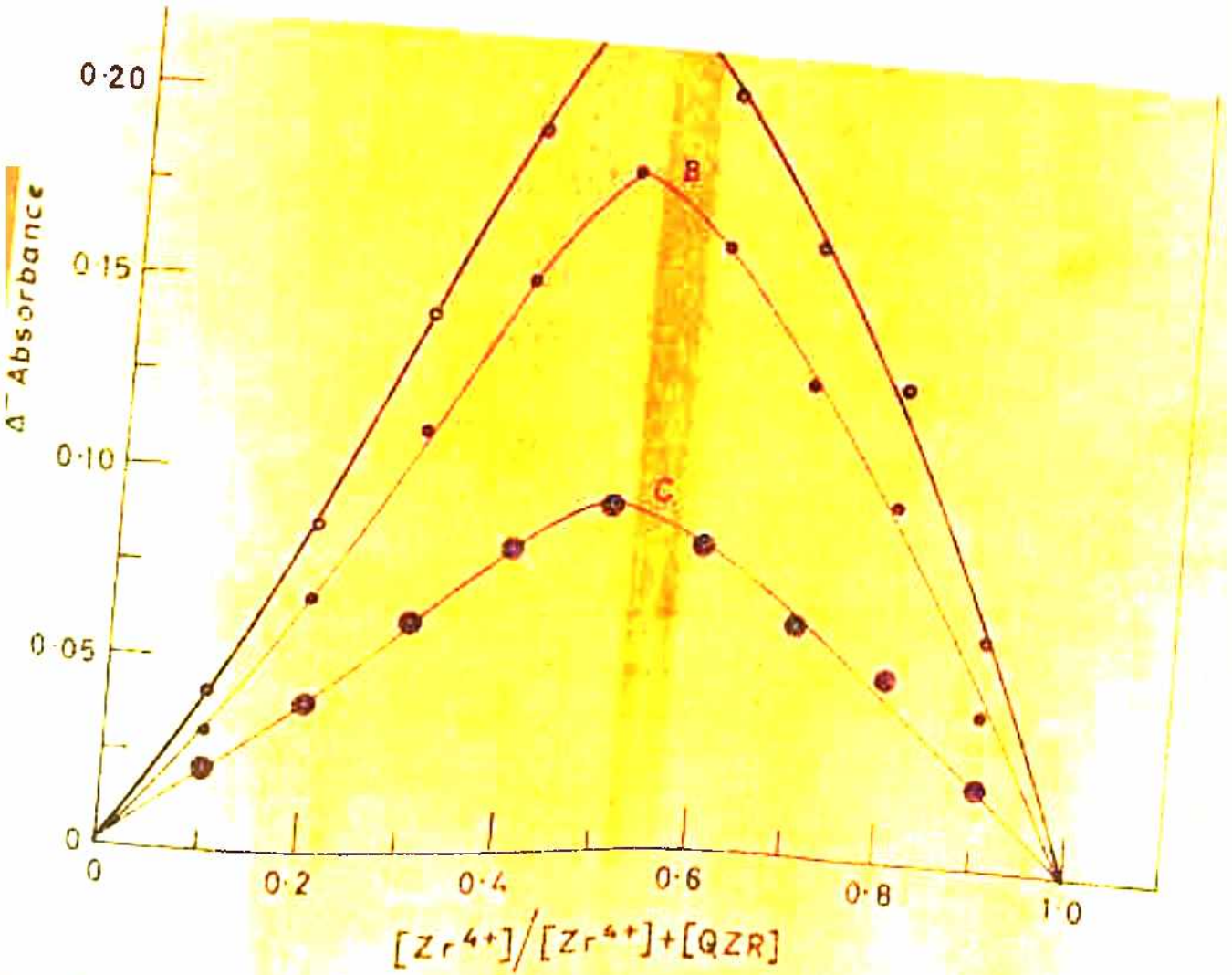


Fig.– 3·22 Continuous variation method at 540 nm; p=1

pH: 6·0±0·1

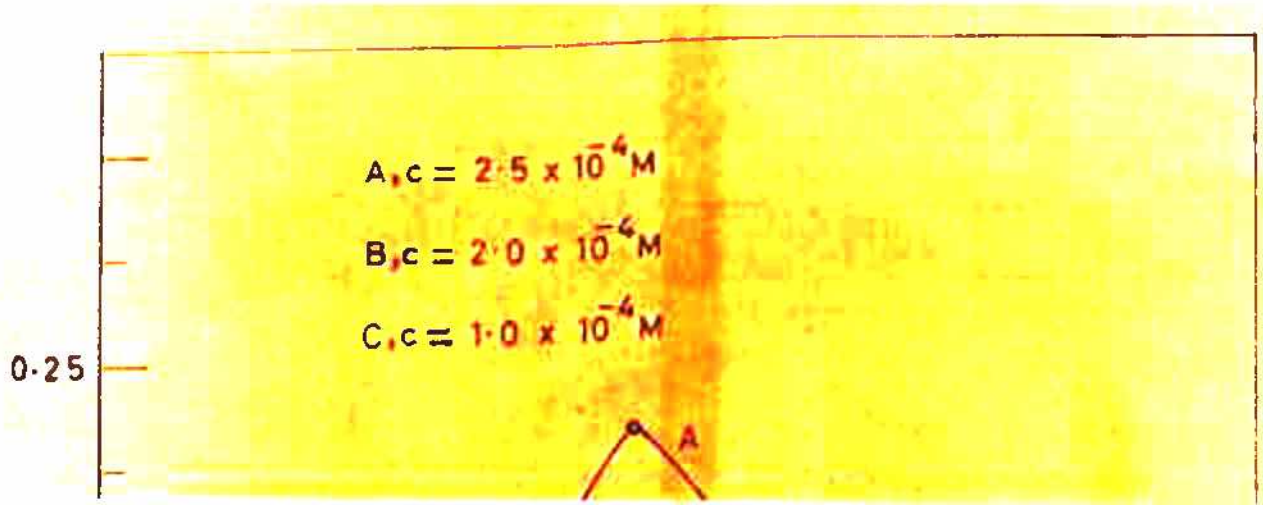

A, c = 2·5 x 10⁻⁴ M
B, c = 2·0 x 10⁻⁴ M
C, c = 1·0 x 10⁻⁴ M
0·25
A

Table 3.47

Concentration of Zirconium Nitrate (c) = 4.0×10^{-4}M

Concentration of Quinalizarin (c') = 2.0×10^{-4}M

pH = 6.0 ± 0.2, p = c'/c = 0.5, λ = 540 nm

peak at 1:1 (Fig. 3.23 Curve A)

Volume of Zirconium Nitrate (ml)	Volume of QZR (ml)	Optical density of mixture (a)	Optical density of QZR (b)	Difference (a-b)
0.0	25.0	0.470	0.470	0.000
2.5	22.5	0.505	0.450	0.055
5.0	20.0	0.545	0.425	0.120
6.0	19.0	0.550	0.410	0.140
7.5	17.5	0.525	0.390	0.135
10.0	15.0	0.490	0.355	0.135
12.5	12.5	0.390	0.270	0.120
15.0	10.0	0.325	0.220	0.105
17.5	7.5	0.245	0.160	0.085
20.0	5.0	0.165	0.100	0.065
22.5	2.5	0.110	0.070	0.040

Table 3.48

Concentration of Zirconium Nitrate (c) = 2.0×10^{-4}M

Concentration of Quinalizarin (c') = 1.0×10^{-4}M

pH = 6.0 ± 0.1, p = c'/c = 0.5, λ = 540 nm

peak at 1:1 (Fig. 3.23 curve B)

0.0	25.0	0.250	0.250	0.000
2.5	22.5	0.260	0.230	0.030
5.0	20.0	0.282	0.220	0.062
6.0	19.0	0.285	0.210	0.075
7.5	17.5	0.273	0.200	0.073
10.0	15.0	0.253	0.185	0.068
12.5	12.5	0.212	0.150	0.062
15.0	10.0	0.170	0.115	0.055
17.5	7.5	0.130	0.085	0.045
20.0	5.0	0.090	0.060	0.030
22.5	2.5	0.060	0.040	0.020

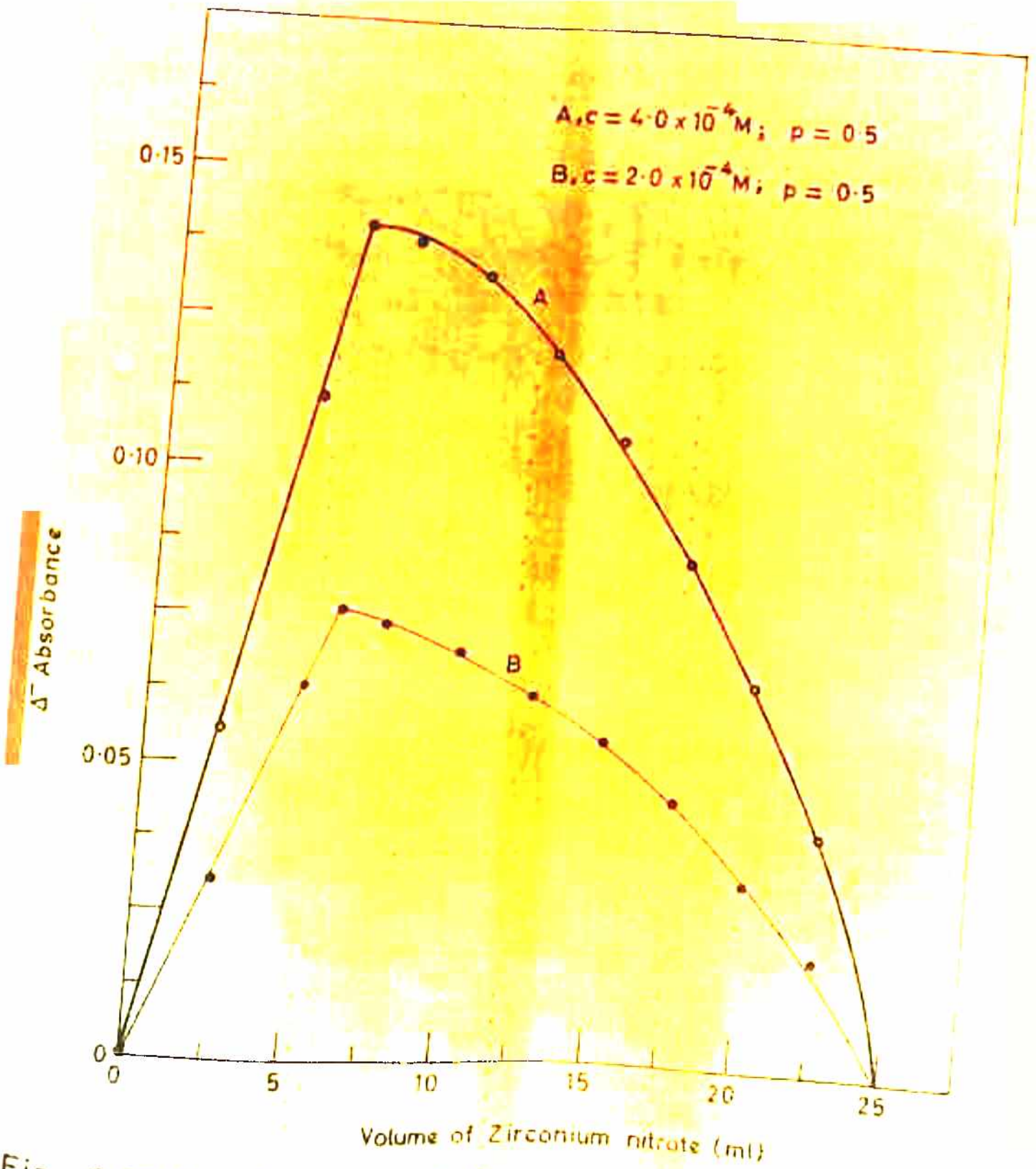


Fig.– 3·23 Continuous variation method at 540 nm;
pH: 6·0±0·1

Mole ratio method

A series of solutions were prepared from 2.0×10^{-4}M of zirconium nitrate and quinalizarin at pH 6.0 maintaining a 50 per cent ethanolic medium and varying amounts of equimolecular solutions of the metal were added such that the mole ratio of the reagent to metal was varied from 1:0.2 to 1:3.5. The results are recorded in table 3.49 and plotted in fig. 3.24 show a break at a ratio of one mole of the reagent to one mole of the metal.

Table 3.49

Concentration of Zirconium Nitrate = 2.0×10^{-4}M.

Concentration of Quinalizarin = 2.0×10^{-4}M

pH = 6.0 ± 0.1, Total volume made up = 25 ml

Break at 1:1 (Fig. 3.24 curve A,B)

Ratio QZR : Zirconium	Optical density against blank	
	500 nm	540 nm
1 : 0.2	0.030	0.040
1 : 0.4	0.055	0.075
1 : 0.6	0.080	0.110
1 : 0.8	0.110	0.140
1 : 1.0	0.130	0.175
1 : 1.5	0.155	0.200
1 : 2.0	0.165	0.210
1 : 2.5	0.165	0220
1 : 3.0	0.165	0.220
1 : 3.5	0.165	0.220

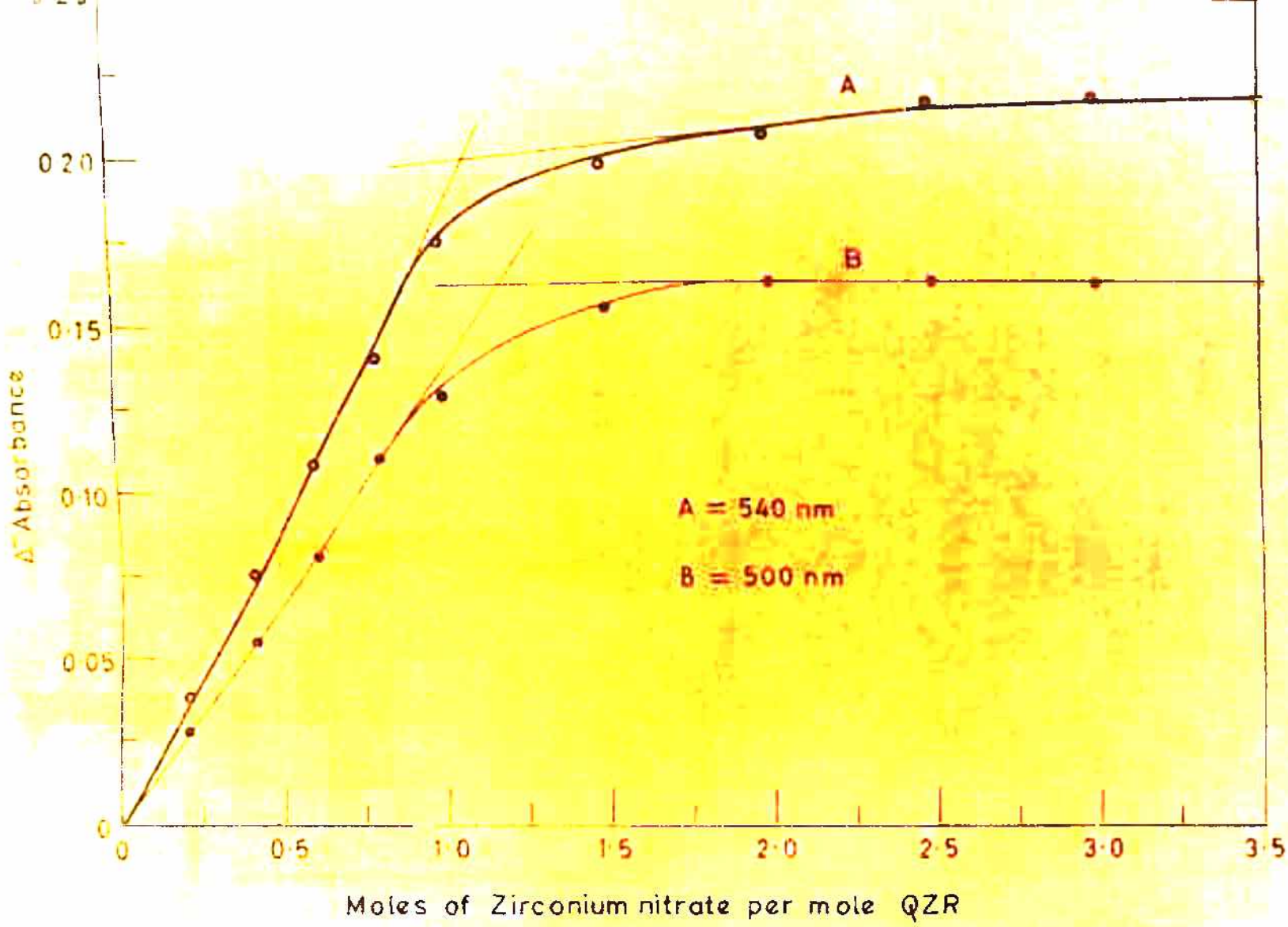


Fig. 3·24 Mole ratio method at pH 6·0±0·2; concentration of QZR = $2{\cdot}0 \times 10^{-4}$ M

Effect of hydrogen ion concentration on the stability of the chelate

The absorbance of various mixtures containing zirconium nitrate and quinalizarin in the ratio of 1:1 at different pH were measured at various wavelengths and it was found that the λ_{max} of the chelate is 500 nm in the pH range 5.0 - 6.5 indicating that the chelate is stable in this pH range. The maximum colour intansity of the chelate at its λ_{max} remains constant between pH 5.5 and 6.5. Studies were therefore made at pH 6.0 ± 0.1.

Calculation of the stability constant

The stability constants were calculated from absorbance data by the method of Dey and Coworkers (figure 3.25), continuous variation method and further corroborated by the mole ratio method.

Discussion

The composition and stability of the violet chelate formed between Zirconium(IV) and quinalizarin have been investigated using spectrophotometric method. The chelate is soluble in aqueous ethanol and has λ_{max} at 500 nm. The composition as determined by different methods is 1:1. The chelate is stable between pH 5.0 and 6.5.

The values of log K at pH 6.0 ± 0.1 and at 20°C calculated using different methods are given in table 3.50.

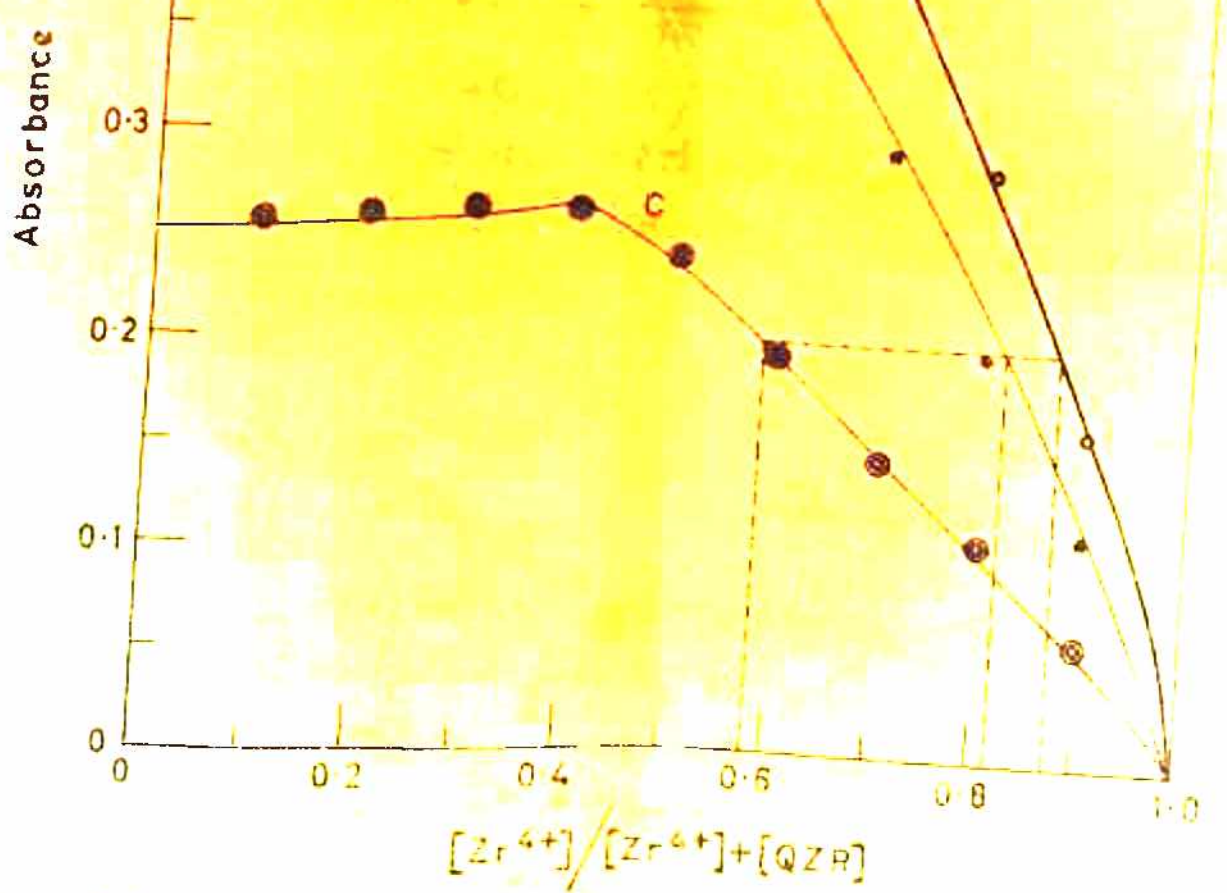
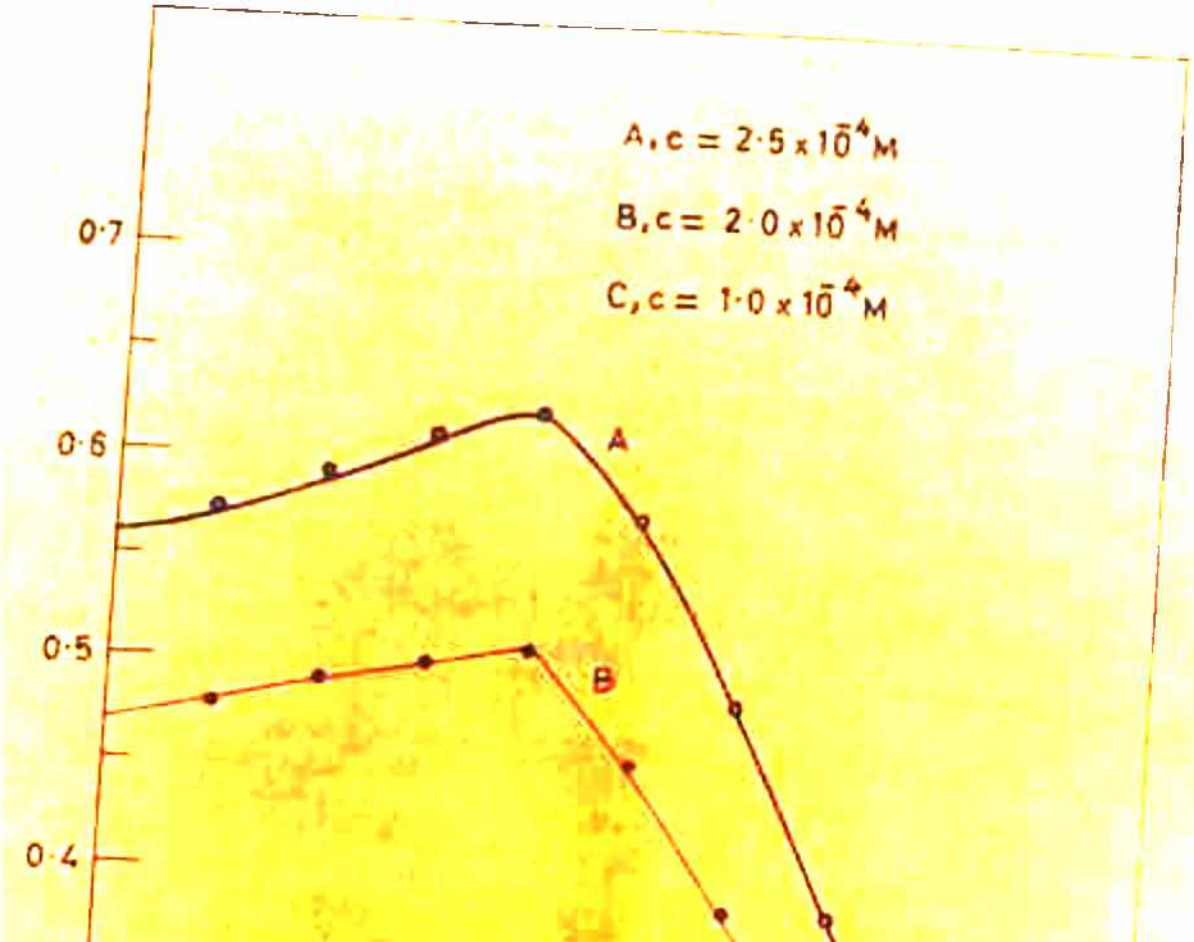


Fig._ 3·25 Determination of stability constant from absorbance data at 540 nm; p=1; pH: 6·0±0·1


A, c = 2·5 x 10⁻⁴ M
B, c = 2·0 x 10⁻⁴ M
C, c = 1·0 x 10⁻⁴ M
0·7
0·6
0·5
0·4
A
B

The free energy change of formation has also been calculated.

Table 3.50

Method	pH	log K	ΔG^{o} at 20^{o} (KCal)
(a) Dey and Coworkers	6.0 ± 0.1	4.8 ± 0.2	- 6.5 ± 0.2
(b) Continuous variation	6.0 ± 0.1	4.7 ± 0.2	- 6.4 ± 0.2
(c) Mole ratio	6.0 ± 0.1	5.0 ± 0.2	- 6.7 ± 0.2

It may be seen that the results of log K and ΔG^{o} obtained by both the methods are in close conformity with each other.

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REFERENCES

1. Akhmedli, M.K. and Glushchenko, E.L. — Zh. Analit. Khim. 19, 556 (1964).

2. Akhmedli, M.K., Sadykhova, A.A., Granovskaya, P.B., Lozovskaya, I.S. and Alieva, S. — Azerb. Khim. Zh. 5, 93 (1963).

3. Babko, A.K. and Kish, P.P. — Dopovidi Akad. Nauk RSR 1323 (1961).

4. Babko, A.K. and Kish, P.P. — Zh. Analit. Khim. 17, 693 (1962).

5. Babko, A.K. and Nazarchuk, T.N. — Raboty Khim Rastvorovi Kompleks Soedinenn, Akad Nauk Ukr. SS R 2, 199 (1959).

6. Babko, A.K. and Karnaukhova, N.N. — Z. Anal. Khim. 22, 868 (1967).

7. Babko, A.K. and Shtokalo, M.I. — Ukr. Khim. Zh. 29, 963 (1963).

8. Banerji, S.K. and Dey, A.K. — Proc. symp. chem. Coord. Compounds (Agra) 2, 198 (1960).

9. Beck, G. — Mikrochim. Acta 2, 9 (1937).

10. Benedetti-Pichler, A.A. and Spikes, W.F. — Mikrochem. 21, 268 (1937).

11. Benedetti-Pichler, A.A. and Spikes, W.F. — Mikrochemie, Festschr. Von Hans Molisch 36-41 (1936).

12. Bevillard, P. — Bull. Soc. Chim (France) 1509 (1955).

13. Bodov, E. — Acta. Chim. Acad. Sci.Hung. 9, 375 (1956).

14. Broda, B. — Wiadowosci Farm 63, 6-7, 15-17 (1936).

15. Burkhard, S.S. and Teresa, B.F. — Bol. Soc. Chilena Quim. (Spain) 13, 55 (1963).

16. Burriel, F. and Bolletacheo, S. — Anales real Soc. Espan fisY quim (Madrid) 50B, 957 (1954).

17. Casey, A.T. and Maddock, A.G. — J. Inorg. and Nuclear Chem. 10, 58 (1959).

18. Cauer, H. and Cauer, G. — Z. Anal. Chem. 124, 81 (1942).

19. Cervinka, J. — Chem. Listy 29, 35 (1935)

20. Dickinson, D. — Analyst 68, 106 (1943).

21. Dubsky, J.V. and Krametz, E. — Mikro Chem. 20, 57 (1936).

22. Eegriwe, E. — Z. Anal. Chem. 76, 354 (1929).

23. Feigl, F. and Krumbolz, P. — Mikro Chemie, Pregl. Festschr 77 (1929).

24. Fischer, H. — Z. Anal. Chem. 73, 54 (1928).

25. Fischer, H. — Wiss Veröff Siemens-Konzern 5, 99 (1949).

26. Flagg, J.F., Leibhajsky, H.A. and Winslow, E.H. — J. Amer. Chem. Soc. 71, 3630 (1949).

27. Flickinger, L.C. — Proc. Conf. Natl. Open Hearth Commn. Iron Steel Div. Am. Inst. Mining Met. Engrs. 27, 197 (1944).

28. Flood, H. and Smedsaas, A. — Tids. Kjemi, Bergvesen Met. 1, 150 (1941).

29. Freis, J.N. and Lauckner, H. — Z. Anal. Chem. 110, 251 (1937).

30. Grosset, T. — Ann. Soc. Bruxelles 53B, 16 (1933).

31. Gutzeit, G. — Helv. Chim. Acta 12, 713 (1929).

32. Hahn, F.L. Wolf, H. and Jäger, G. — Ber. 57B, 1394 (1924).

33. Hahn, F.L. — Mikro Chem., Pregl Festschr. 127-39 (1929).

34. Hahn, F.L. and Meyer, H. — Ber. 60B, 975 (1927).

35. Hahn, F.L. — Mikro Chemie 5, 33 (1932).

36. Harvey, A.E. and Manning, D.L. — J. Am. Chem. Soc. 72, 4488 (1950).

37. Ishidate, M. and Yamane, Y. — Chem. Pharm. Bull. (Tokyo) 8, 1116 (1960).

38. Job, P. — C.r. hebd. Séane Acad. Sci. Paris 180, 928 (1925); Annls. Chim. 9, 113 (1928).

39. Kallistratos, G., Pfau, A. and Ossowski, B. — Anal. Chim. Acta 22, 195 (1960).

40. Kelly, J.E. — U.S. Atomic Energy Commission T.LD.7568 pt.1, 87 (1958).

41. Kolthoff, I.M. — Mikro Chem., Emich. Festschr. 180-90 (1930).

42. Kolthoff, I.M. — J. Am. Pharm. Assoc. 17, 360 (1928).

43. Kolthoff, I.M. — J. Am. Chem. Soc. 50, 393 (1928).

44. Kolthoff, I.M. — Chem. Weekblad 24, 447 (1927).

45. Komarovskii, A.S. and Korenman, I.M. — Z. Anal. Chem. 94, 247 (1933).

46. Korenman, I.M., Kurina, N.V. and Emelin, E.A. — Trudy Po Khim. Tekhnol 1, 134 (1958).

47. Korenman, I.M., Ganina, V.G. and Kurina, N.V. — Tr. pa Khim-i-Khim Tekhnol 4, 761 (1961).

48. Larsen, E.M. and Hirozawa, S.T. — J. Inorg. Nucl. Chem. 3, 198 (1956).

49. Leibhafsky, H.A. and Winslow, E.H. — J. Am. Chem. Soc. 60, 1776 (1938).

50. Leibhafsky, H.A. and Winslow, E.H. — J. Am. Chem. Soc. 69, 1130 (1947).

51. Lubomir. and Kurzová, K. — Huntnické listy 14, 710 (1959).

52. McBain, J.W. — Colloid. Science (D.C.Heacth and Co. Boston) 1950.

53. Mukherji, A.K. and Dey, A.K. — Z. Anal. Chem. 155, 417 (1957).

54.	Mukherji, A.K. and Dey, A.K.	J. Inorg. Nucl. Chem. 6, 314 (1958).
54a	Mukhina, Z.S. and Aleshin. A.F.	Zavodskaya Lab. 11, 23 (1945).
55.	Nair, C.K.N. and Das gupta, A.K.	J. Sci. Ind. Research India 10, 300 (1951).
56.	Nemirovskaya, A.F.	Tr. Novocherk Polytekhn Inst. 143, 45 (1963).
57.	Pavelka, F. and Setta, G.	Mikro Chem. Ver Mikro Chim Acta 31, 73 (1943).
58.	Pavelka, F. and Setta, G.	Mikro Chem. Ver Mikro Chim Acta 31, 73 (1943).
59.	Pavlovskaya, M.P.	Tr. Kishinev. Selskokhoz. Inst. 43, 101 (1966).
60.	Pietsch, E. and Roman, W.	Z. Anorg. Allgem. Chem. 220, 219 (1934).
61.	Poluektov, N.S.	Mikro Chemie 18, 48 (1935).
62.	Purushottam, A.	Z. Analyt. Chem. 145, 425 (1955).
63.	Remirezde Verger, J.M. and Pino Perez, F.	Inform. Quim. Anal.(Madrid) 17, 39 (1963).
64.	Rienacker, G.	Z. Anal. Chem. 88, 29 (1932).
65.	Ringbom, A.	Z. Anal. Chem. 115, 332 (1938/9).
66.	Rudolph, G.A. and Flickinger, L.C.	Steel 14, 114, 131-39, 149 (1943).

67. Rudolph, G.A. and Flickinger, L.C. — Foundry 71, 168 (1943).

68. Schams, O. — Mikro Chemie 25, 16 (1938).

69. Schürman and Schob. — Chem. Z. tg. 49, 625 (1925).

70. Schrafan, I.G. — Sbstatievses Nauchn-Issled. Inst. Khim Reaktivovi Osobo Chistykh. Khim. Veshchestv 24, 158 (1961).

71. Shu-Wei Pang, Chien-Chuan Lui and Shu-Chuan Liang — Hua Hseuh Hsueh Pao 30, 160 (1964).

72. Smith, G.S. — Analyst 60, 735 (1935).

73. Smith, O.M. and Dutcher, H.A. — Ind. Eng. Chem. Anal. Ed. 6, 61 (1934).

74. Srivastava, K.C. and Banerji, S.K. — Chem. Age India 18, 295 (1967).

75. Srivastava, K.C. and Banerji, S.K. — Chem. Age India 18, 351 (1967).

76. Srivastava, K.C. and Banerji, S.K. — Chem. Age India 20, 609 (1969).

77. Srivastava, K.C. and Banerji, S.K. — Chem. Age India 18, 209 (1967).

78. Tataev, O.A. and Bagdasarov, K.N. — Elektro Khim-i-optich Metody Analiza 212 (1963).

79. Thanheiser, G. and Waterkamp, M. — Arch. Eisenhü ttenw 15, 129 (1941)

80. Thiel, A. and Von Hengel, E. — Ber. 71B, 1157 (1938).

81. Venturello, G.	Atti Accad. Sci. Torino Classe Sci. fis. mat. nat. 76, 258 (1941).
82. Von Stein, P.	Chemist. Analyst 31, 63 (1942).
83. Vosburgh, W.C. and Cooper, G.R.	J. Am. Chem. Soc. 63, 437 (1941); 64, 1630 (1942).
84. Wakamatsu, S.	Nippon Kinzoku Gakkaishi 21, 450 (1957).
85. Wakamatsu, S.	Bunseki Kagaku 7, 84 (1958).
86. Wenger, P. and Duckert, R.	Helv. Chim. Acta 25, 699 (1942).
87. Wienberg, S., Proctor, K. and Milner, O.	Ind. Eng. Chem. Anal. Ed. 17, 419 (1945).
88. Willard, H.H. and Fogg, H.C.	J. Am. Chem. Soc. 59, 40 (1937).
89. Wolter, F.J.	Iowa State Coll. J.Sci. 31, 548 (1957).
90. Yoe, J.H. and Jones, A.L.	Ind. Engng. Chem. Analyst Edu. 16, 111 (1944).

C H A P T E R IV

PHOTOMETRIC DETERMINATION OF TUNGSTEN (VI) WITH QUINALIZARIN AS A CHROMOGENIC REAGENT

The unique physical and chemical properties of tungsten have extended greatly the industrial applications of this element during the past decade. The major portion of the production of this element is used in ferrous metallurgy, in cemented carbides and for refractory metals. From the rapidly expanding fields of electronics, aerospace and catalysts have emerged new and diverse uses for this metal. Consequently there has been a universal recognition of the need for highly sensitive and accurate analytic methods for determination of tungsten in diverse types of sample materials during recent years. Some effort has also been made towards the development of analytical chemistry of tungsten in the past few years. Among the large variety of methods studied, chemical procedures based on chelate formation have been devised in an attempt to estimate small amounts of tungsten.

Since chemical analysis proper involves aqueous solutions to a great extent, it will be useful to discuss some general aspects of the behaviour of tungsten in this medium before considering its chelate formation. This discussion is limited to hexavalent tungsten (which is the common oxidation state in aqueous solution) because only its chelates are of importance in analytical chemistry. Monotungstate very easily undergoes polymerization especially in acidic solutions leading to the formation of hydrated tungsten trioxide. In accordance with the present day views on coordination in aqueous solution, the tungstate ion is explained

here as the hydroxo complex of a cationic tungstenyl(VI) ion, which may be present also in its dimeric form. These postulates enable the formation of chelates between tungsten and anionic chelating agents, to be clearly understood.

Various chelating agents have been suggested for the photometric determination and probably toluene 3, 4 dithiol (3, 5, 12, 16, 17, 22, 26, 30, 33, 36, 42, 44, 46, 47) is the most selective reagent reported so far. The reagent, however, has the disadvantage of being sensitive to oxidation and is destroyed by strong oxidants (7). Another selective reagent is benzoin anti-oxime (31, 48, 39). It precipitates tungsten in acidic media. It is reported that 1:1 chelate which is formed is only slightly soluble in chloroform (18). A recent study, however, reveals that a chelate containing two moles of the reagent per tungsten atom is extracted from 0.5 F hydrochloric acid by a solution of the reagent in chloroform (32). After precipitation or extraction tungsten has been determined photometrically with thiocyanate (32), hydroquinone (45) or toluene 3-4 dithiol (22).

Various other reagents including 8-quinoline selenol(37), 8 quinolinol (10, 19, 35, 11, 13, 29, 27, 14, 9, 1, 2, 43, 8, 34), thioglycolic acid (2, 5, 6), pyrocatechol (28, 40) and Stilbazogall I (21) have also been recommended.

Halmekoski (15) studied the application of protocatechualdehyde in the spectrophotometric determination of tungsten. He noted that the colour is developed at room

temperature at pH 7.0, and measured the absorption at 340 nm. Iron (III), molybdenum (VI), titanium (IV), uranium (VI) and vanadium (V) interfere.

Horák and Okáč (20) observed that 3, 4, 5 - trihydroxy benzene-sulfonic acid yields a red coloured complex in strongly acidic media and employed the spectrophotometric method for working out details of the use of this reagent in the determination of tungsten in steel and alloys.

Kiboku and Yoshimura elaborated a photometric method for determining tungsten using tannic acid as chromogenic reagent (23) and determinated 18 to 56 µg of tungsten at 390 nm in solutions of pH 6.8. A photometric procedure for tungsten with stilbazo as chromogenic reagent has also been elaborated (24).

Dey and Coworkers (4, 38) have utilized Alizarin Red S for the photometric determination of tungsten. The colour is best developed at pH 3.5 to 6.0 and is stable for at least 48 hours. Maximal absorbance occurs at 470 nm. 25 to 650 µg of tungsten has been determined in a total volume of 50 ml. Many other metal ions give similar reaction with Alizarin Red S.

A close inspection of the chelating agents for tungsten so far studied reveals that only a few elements serve as donor atoms, namely, sulphur, oxygen, nitrogen and selenium. At least two donor atoms must be present in a ligand molecule in order to yield a chelate ring. Of all the combinations

possible the following five systems with tungsten as the central atom in a chelate ring have actually been encountered so far.

- S - W - S	- O - W - N
- O - W - S	- Se- W - N
- O - W - O	

The tungsten chelates with sulfur and nitrogen or two nitrogen as donors have not been reported.

A comparison of the strength of these five known ring arrangements has not been published although it is of great practical significance. It seems evident that the bonding of tungsten to oxygen is stronger than that of sulfur or selenium. Nitrogen is bonded more weakly.

A large variety of chelating agents can be devised, at least theoretically by attaching either two or more identical donor atoms or different donor atoms or groups in appropriate positions to a basic structure. Although many of the arrangements have been realized in the existing chelating agents, the possibilities are not exhausted and so further studies will reveal new and valuable compounds.

The presence of oxygen atoms in a reagent renders the tungsten chelate more stable, thereby increasing the selectivity for this metal. It may be added that these not only influence the stability of chelates but may also affect other analytically important properties, including colour and

solubility and hence quinalizarin may prove valuable for the determination of tungsten.

Srivastava and Banerji (41) have recently reported that quinalizarin is very sensitive to vanadium (V), Titanium (IV), Molybdenum (VI) and Tungsten (VI) and in this work they have examined the possibility of using this reagent for the first time for the spectrophotometric determination of Tungsten on a micro scale.

Experimental

Standard solutions were prepared by dissolving sodium tungstate BDH (AnalaR) in double distilled water. A purified sample of quinalizarin (BDH reagent grade) was used for the preparation of a 0.001 M stock solution in redistilled ethyl alcohol.

The first set of experiments were performed to record absorption curves i.e. to determine the spectral region of the maximum absorption of the complex. In another set of experiments, the influence of pH, the effect of reagent concentration, temperature and stability of the colour was studied.

To investigate the validity of Beer's law a fixed quantity of the reagent solution was taken and varying quantities of the metallic salt solution added. The mixtures were raised to a constant volume and kept for 30 minutes to

attain equilibrium. The intensity of the colour was measured with a Hilger Uvispek. Spectrophotometer (with 1 cm. glass cell). The experiments were conducted at room temperature. The interference of various cations and anions were also noted.

Absorption curves

When an aqueous solution of Tungsten (VI) is mixed with a solution of quinalizarin, a wine red complex is immediately formed. Fig. 4.1 shows the absorption curves of quinalizarin and its tungsten complex. The absorption curves of tungsten complex obtained with a reagent blank as reference has an absorption maximum at 530 nm. Some of the typical results are given below in Table. 4.1.

Table 4.1

Concentration of sodium tungstate = 2.0×10^{-5} M.

Concentration of Quinalizarin(QZR) = 1.0×10^{-4} M.

pH of solutions = 6.0

Wavelength nm	Optical density of complex (A)	Optical density of QZR (B)	Difference in optical density (A-B) = C
400	0.390	0.405	-
410	0.430	0.450	-
420	0.460	0.492	-
430	0.500	0.540	-

contd.

Table 4.1 contd.

Wavelength nm	Optical density of complex (A)	Optical density of QZR (B)	Difference in optical density (A-B) = C
440	0.525	0.572	-
450	0.540	0.580	-
460	0.560	0.575	-
470	0.570	0.565	0.005
480	0.590	0.552	0.038
490	0.605	0.545	0.060
500	0.620	0.535	0.085
510	0.610	0.515	0.095
520	0.600	0.480	0.120
530	0.595	0.450	0.145
540	0.555	0.425	0.130
550	0.505	0.395	0.110
560	0.436	0.356	0.080
570	0.368	0.318	0.050
580	0.320	0.280	0.040
590	0.260	0.244	0.016
600	0.200	0.200	0.000
610	0.120	0.120	0.000
620	0.050	0.050	0.000

The effect of pH

The effect of pH on the absorbance of the solutions was examined by measuring the absorbances of the mixtures containing

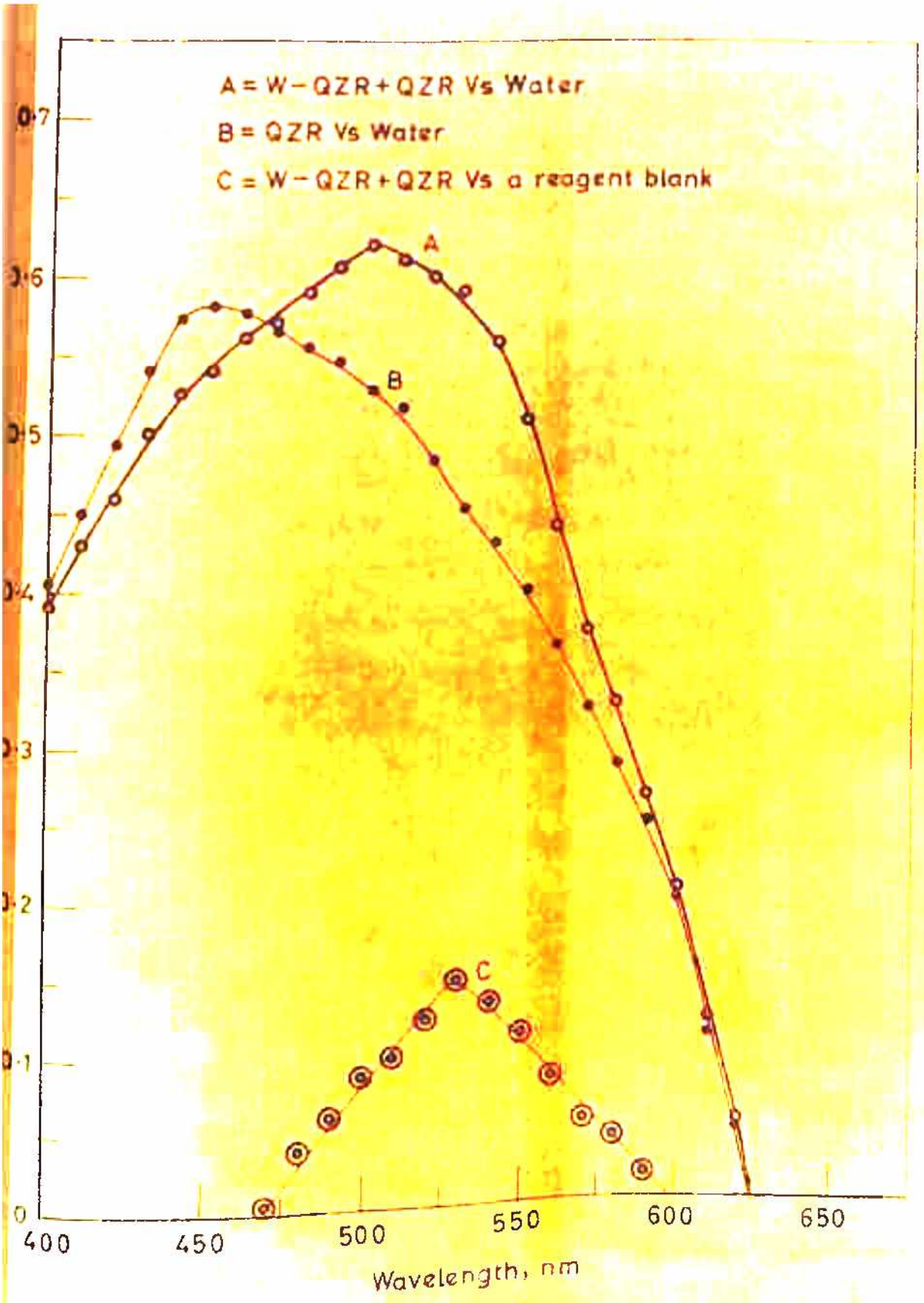


Fig._ 4·1 Absorption curves of Tungsten (VI)–Quinalizarin complex at pH: 6·0; W: $2·0 \times 10^{-5}$ M; QZR: $1·0 \times 10^{-4}$ M

0.5 ml. of 1 x 10^{-3}M tungsten solution and 2.5 ml. of a 1 x 10^{-3}M solution of quinalizarin. From Fig. 4.2 and table 4.2 it is apparant that the maximum absorbance is obtained in the pH range 6.0 and 6.3 when measured at 530 nm against the reagent blank.

Table 4.2

Concentration of Sodium Tungstate = 2.0 x 10^{-5}M

Concentration of Quinalizarin = 1.0 x 10^{-4}M

pH	5.0	5.5	5.8	6.0	6.3	6.8
Optical density per cm 530 nm.	0.100	0.130	0.140	0.148	0.150	0.120

The effect of the amount of Quinalizarin

A study of the effect of the reagent concentration at a pH 6.0 and 530 nm indicated that there should be be a fivefold molar excess of Quinalizarin over Tungsten (VI) concentration. (Fig. 4.3).

The stability of colour

It was observed that the order of addition of reactants had no appreciable effect on the absorbance. The colour formation is instantaneous and the intensity of the colour remained constant for more than forty eight hours. A study of the effect of temperature indicated that the

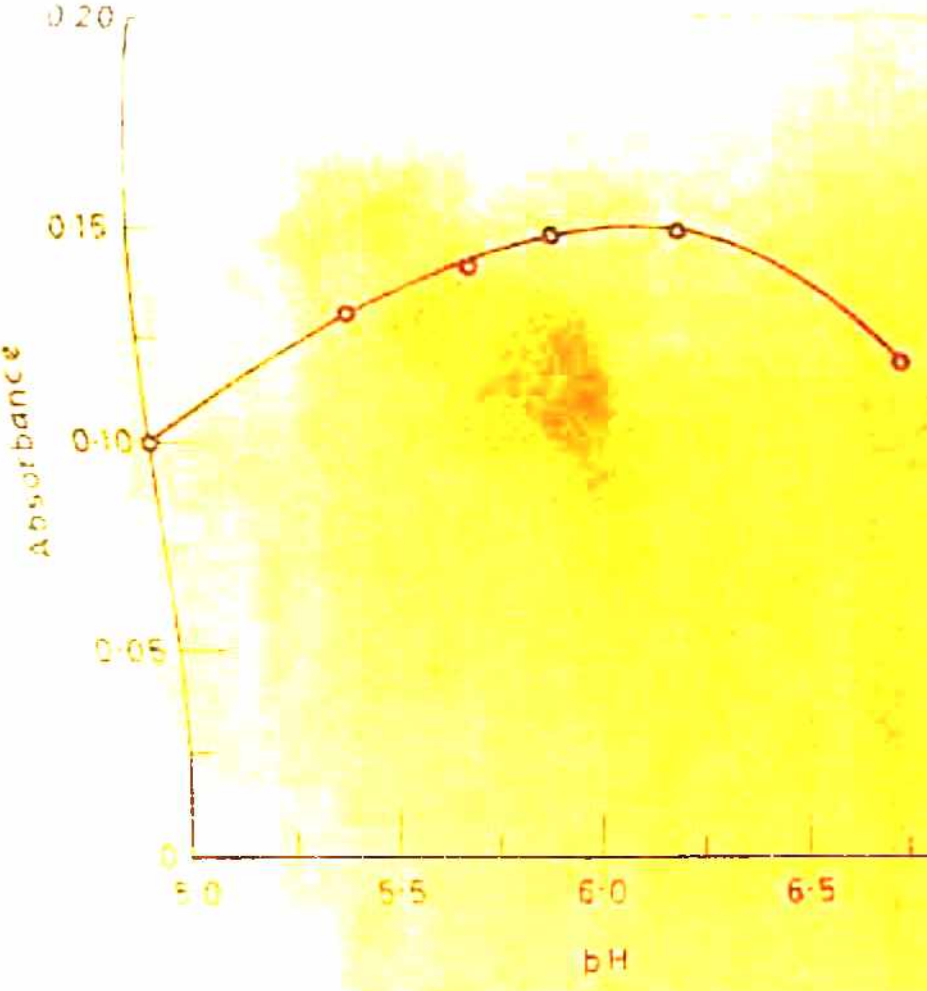


Fig.— 4·2 Effect of pH

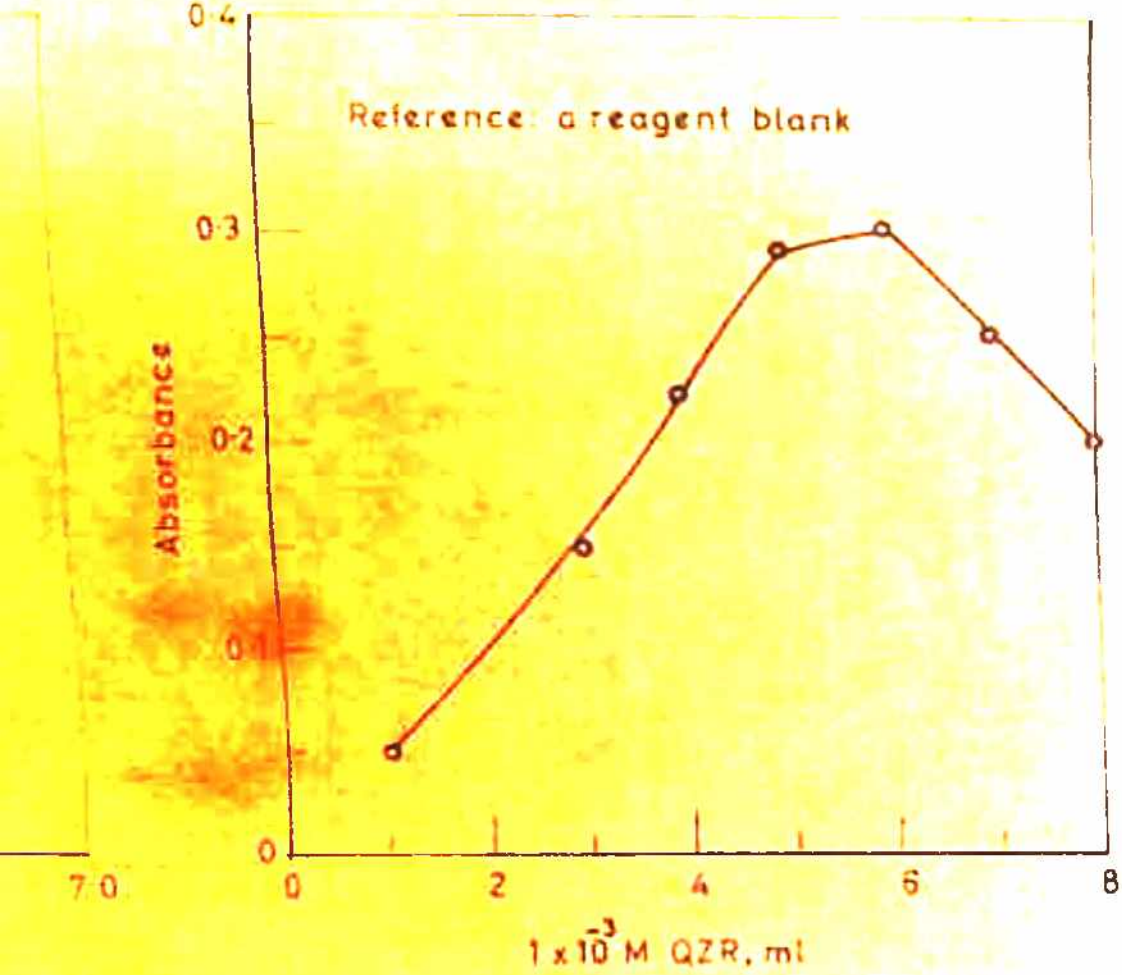


Fig _ 4 3 Effect of amount of Quinalizarin at pH: 6·0 ; W: 4·0 x 10^{-5} M

absorbance remained constant when the temperature was varied from 30 - 60°C.

Beer's law range

The concentration range over which colour system obeys Beer's law was obtained by adopting the conventional method in which the concentration of tungsten is plotted against absorbance. The range of adherence to Beer's law was found to be 0.74 to 5.88 ppm of tungsten (VI) at 530 nm and pH 6.0.

The effective range of photometric determination found out by Ringborn plot was 1.47 to 5.15 ppm of tungsten. The relative errors involved for different values of percentage transmittance from the Rinborn plot were computed using Ayres equation (3a) and it was found that the relative error is minimum when the transmittance is 32. The molar extinction coefficient determined at 530 nm was 7875.

Sensitivity of colour reaction

The sensitivity of colour reaction as defined by Sandell was 0.0261 $\mu g/cm^2$ at 530 nm. The practical sensitity corresponding to an absorbance change of 0.01 units was 0.261 $\mu g/cm^2$.

The effect of Diverse Ions

The effect of diverse ions was examined with a solution

containing 55.2 µg of tungsten and diverse ions. The pH of the solution was adjusted to 6.0 ± 0.1. Of the 25 cations tested lead (II), alumnium (III), yttrium (III), lanthanum (III), iron (III), thorium (IV), zirconium (IV), titanium(IV), vanadium (V), uranium (VI), and molybdenum (VI) interfere with the tungsten determination while common divalent cations did not interfere.

Anions such as chloride, nitrate and sulphate do not interfere. Large amounts of fluoride, tartrate and citrate reduce the absorbance considerably. Oxalate, NTA and EDTA inhibit the formation of complex when added in large amounts.

Discussion

Reagents like toluene 3, 4 dithiol (3, 5, 12, 16, 17, 22, 26, 30, 33, 36, 42, 44, 46, 47) and benzoin anti-oxime (31, 48, 39) are highly selective for tungsten. Other reagents which have been used for determination of tungsten are 8 quinoline selenol (37), 8 quinolinol (10, 19, 35, 11, 13, 29, 27, 14, 9, 1, 2, 43, 8, 34), thioglycolic acid(25, 6) pyrocatechol (28, 40), stilbazogall I (21) protocatechual-dehyde (15), 3, 4, 5 trihydroxy benzene sulphonic acid (20), Tannic acid (23), stilbazo (24) and Alizarin red S (4, 38). Of these reagents 8 quinolinol, thioglycolic acid, protocate-chualdehyde, tannic acid and stilbazo are found to be the

most sensitive to tungsten. The present method using Quinalizarin is very sensitive; it is comparable in sensitivity with the method using 8 quinolinol or the thioglycolic acid.

Procedure

The use of Quinalizarin as a reagent for the photometric determination of tungsten when present alone in minute quantities may be recommended. The solution should be suitably diluted or concentrated so as to contain 1.5 to 5.0 ppm of tungsten. Introduce a five fold excess of freshly prepared ethanolic solution of Quinalizarin. Allow the solution to stand for 5 minutes and adjust the pH to 6.0. Read the absorbance at 530 nm. and calculate the weight of tungsten present from a previously prepared calibration curve.

Composition and Stability

The composition of the chelate was established by (I) the method of continuous variations and (II) mole ratio method. A large number of observations made and some of the typical results are plotted in the figures 4.4 - 4.6.

Table 4.3 summarises the results on the composition as arrived at from the examination of figures 4.4 and 4.5, when the method of continuous variation was employed, using absorbances measurements. In the figures, c represents the

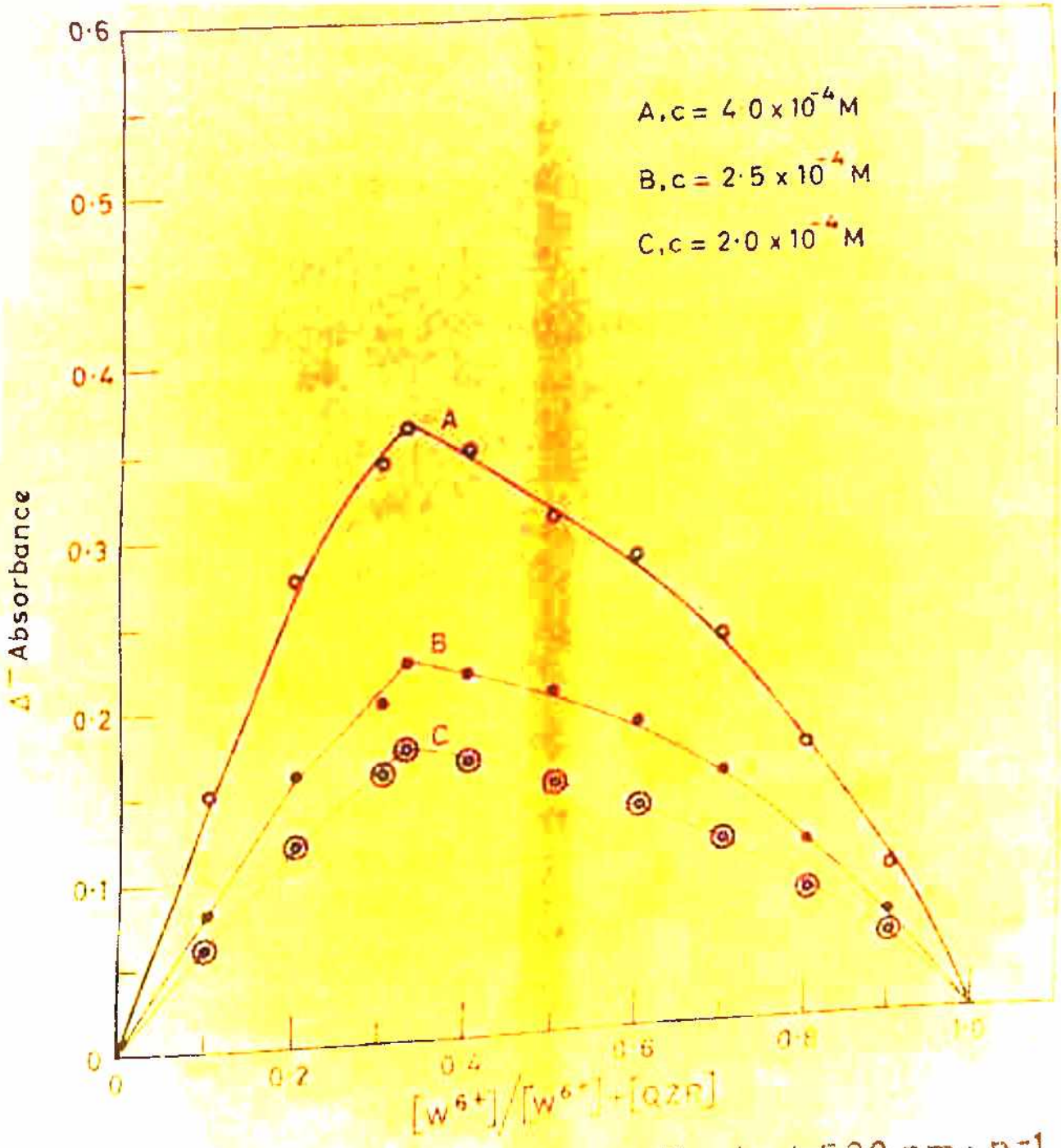


Fig._ 4·4 Continuous variation method at 530 nm; p=1

pH: 6·0

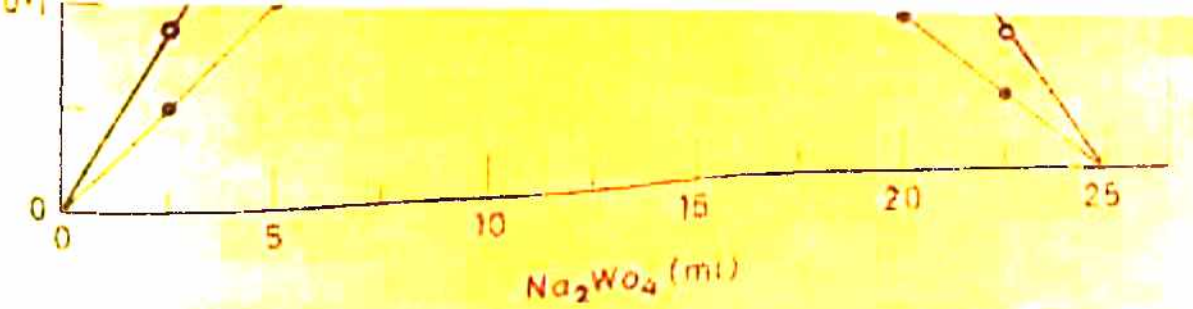
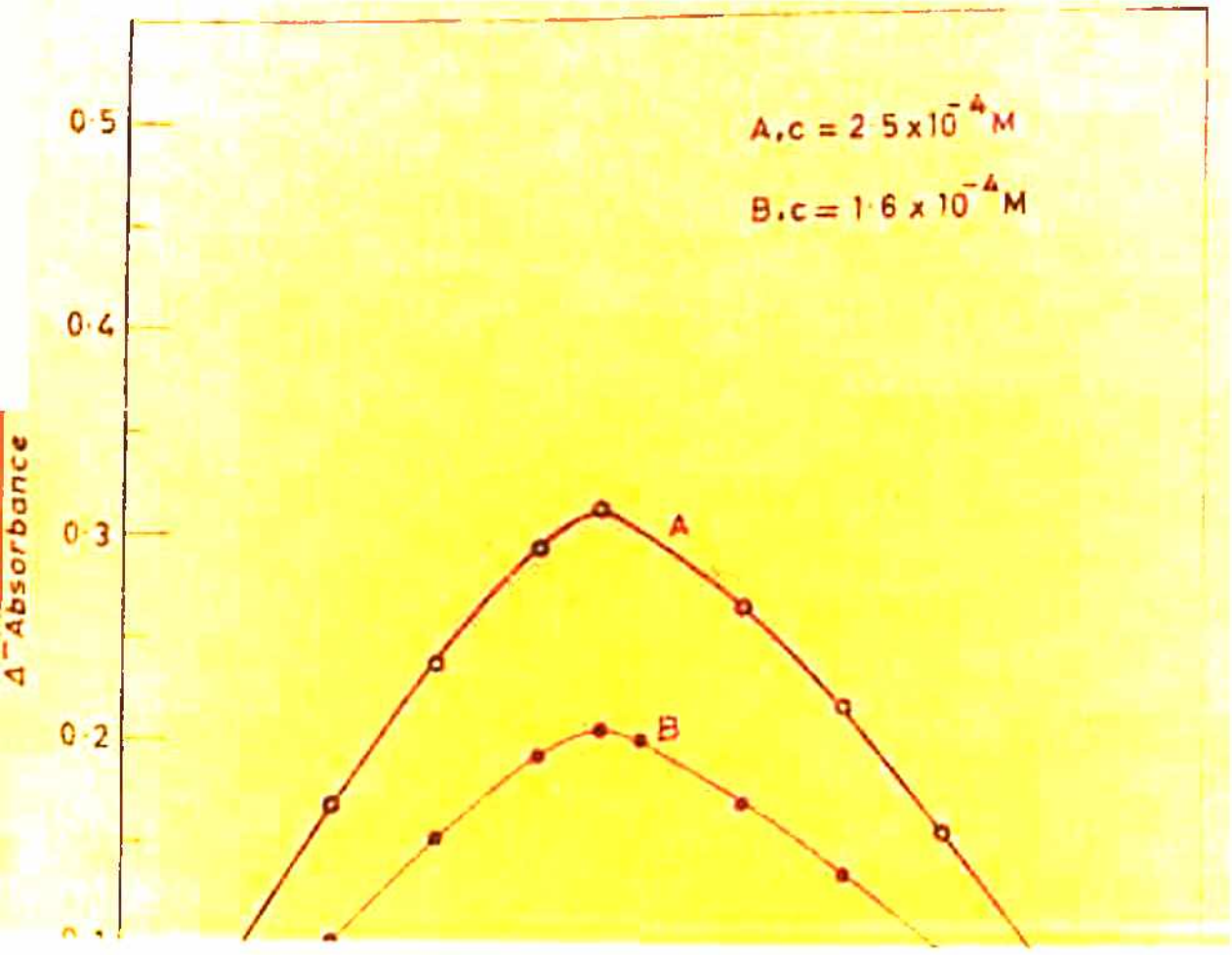


Fig._ 4·5 Continuous variation method at 530 nm;
p = 2 ; pH: 6·0


A, c = 2·5 x 10⁻⁴ M
B, c = 1·6 x 10⁻⁴ M
0·5
0·4
0·3
0·2
A
B
Δ⁻ Absorbance

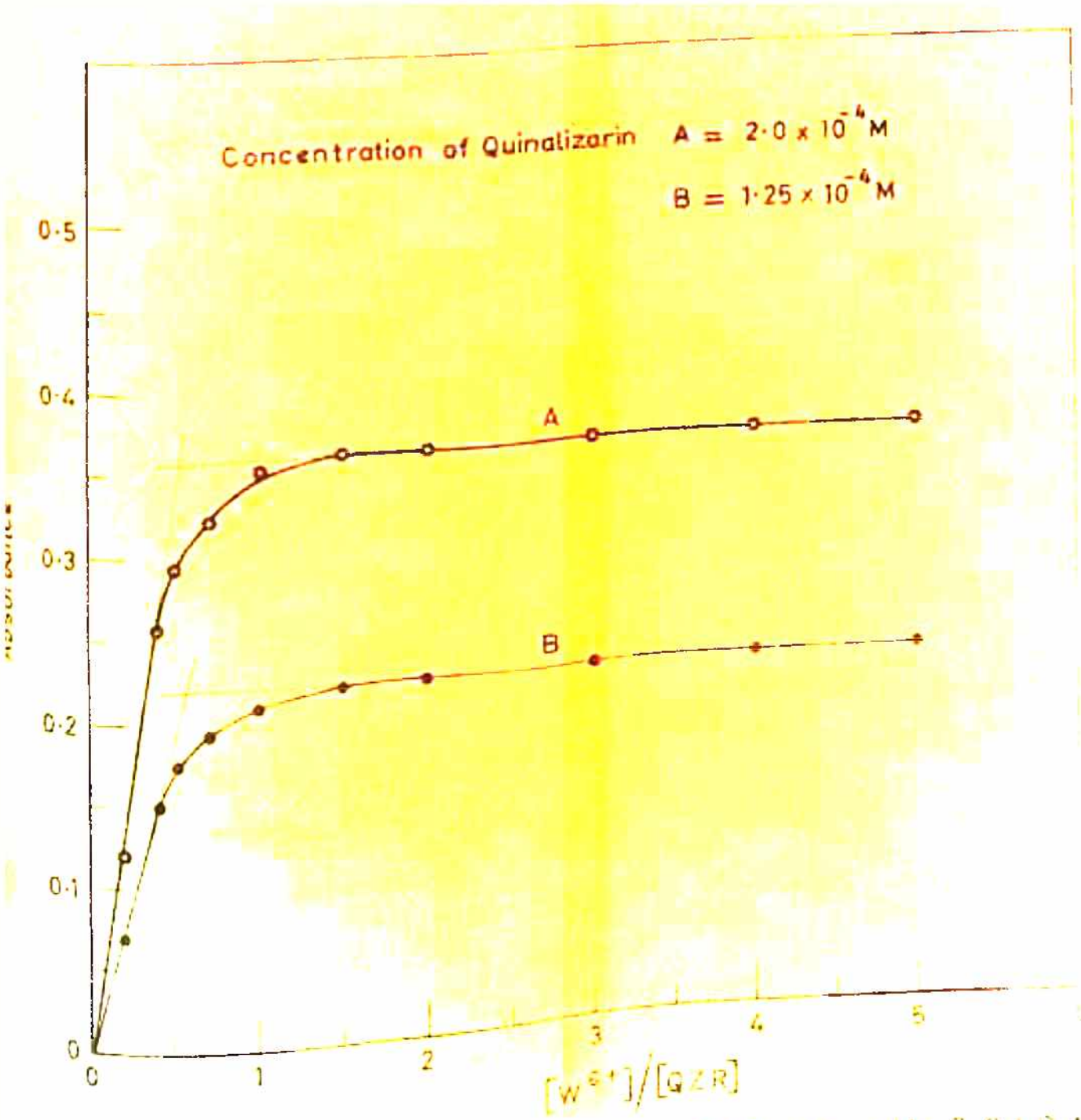


Fig._4·6 Mole ratio method at 530 nm; pH: 6·0±0·1

concentration of tungsten and p, the ratio c'/c, c' being the concentration of Quinalizarin.

Table 4.3

Figure	Curve	c x 10^4 (M)	p	Wave-length nm	Volume of W(VI) at peak (ml)	Composition of the chelate W(VI):QZR
4.4	A	4.0	1.0	530	8.33	1:2
	B	2.5	1.0	530	8.33	1:2
	C	2.0	1.0	530	8.33	1:2
4.5	A	2.5	2.0	530	11.5	1:2
	B	1.6	2.0	530	11.5	1:2

It is clear from the above table that the ratio of tungsten to Quinalizarin in the chelate is 1:2 and hence, it may be represented as $W(QZR)_2$. Results obtained by the mole ratio method (Fig. 4.6) corroborate the same composition of the chelate.

Log K (K =equilibrium constant at pH 6.0) was determined by the method of continuous variation, using nonequimolecular solutions as well as by the mole ratio method, and the values were found to be 9.0 and 9.1 respectively.

Suggestions on the structure of the chelate

It is not possible to derive definite information on

the basis of the experimental results mentioned above regarding the structure of the chelate except that the ion exchange studies show that the chelate of tungsten is anionic.

REFERENCES

1. Alimarin, I.P., Petrukhin, O.M. and Zolotov, Yu. A. — Zh. Analit. Khim, 17, 544 (1962).

2. Alimarin, I.P. and Zolotov, Yu. A. — Talanta, 9, 891 (1962)

3. Allen, S.H. and Hamilton, M.B. — Anal. Chim. Acta, 7, 483 (1952).

3a. Ayres, G.H. — Anal. Chem., 21, 652 (1949).

4. Banerji, S.K. and Dey, A.K. — Z. Anal. Chem. 179, 30 (1961).

5. Bickford, C.F., Jones, W.S. and Keene, J.S. — J. Am. Pharm. Assoc. Sci. Ed., 37, 255 (1948).

6. Buchar, V.M. — Nature, 191, 489 (1961).

7. Clark, L.J. and Axley, J.H. — Anal. Chem., 27, 2000 (1955).

8. Eberle, A.R. — Anal. Chem, 35, 669 (1963).

9. Fleck, H.R. — Analyst, 62, 378 (1937).

10. Freiser, H. — Chemist Analyst, 50, 94 (1961).

11. Gorbach, G. and Pobl, F. — Mikrochemie Mikrochim Acta 38, 258 (1951).

12. Greenberg, P. — Anal. Chem., 29, 896 (1957)

13. Halberstadt, S.	Z. Anal. Chem, 92, 86 (1933)
14. Halberstadt, S.	Compt. Rend. 205, 987 (1937).
15. Halmekoski, J.	Suomen Kemistilehti; 35, 81 (1962).
16. Headridge, J.B. and Dixon, E.J.	Analyst, 87, 32 (1962).
17. Hobart, E.W. and Hurley, E.P.	Anal. Chim. Acta 27, 144 (1962).
18. Hoenes, H.J. and Stone, K.G.	Talanta, 4, 250 (1960).
19. Hoffmann, J.I.	Chemist Analyst, 49, 126 (1960)
20. Horák, J. and Okáč, A.	Collection cZech. Chem. Commun. 29, 188 (1964).
21. Ishii, H. and Einaga, H.	Bull. Chem. Soc. Japan 39 (1) 193 (1966).
22. Jeffrey, P.G.	Analyst, 81, 104 (1956).
23. Kiboku, M. and Yoshimura, C.	Bunseki Kakaku 7, 488 (1958).
24. Kleiner, K.E. and Klibus, A. Ch.	Thesis Rept. First All Union Congress on Organic Reagents in Analytical Chemistry, 1956.
25. Kono, N. and Ozawa, T.	Tokyo - to Ritsukogyo Shoreikan Hokoku, 15, 59 (1963).

26. Machlan, L.A. and Hague, J.L. — J. Res. Natl. Bur. Std. 59, 415 (1957).

27. Magee, R.J. and Witwit, A.S. — Anal. Chim. Acta 29, 517 (1963).

28. Martini, A. — Mikrochemie, 6, 63 (1928); 12, 112 (1932).

29. Nieriker, R. and Treadwell, W.D. — Helv. Chim. Acta, 29, 1472 (1946).

30. North, A.A. — Analyst, 81, 660 (1956).

31. Otterson, D.A. and Graab, J.W. — Anal. Chem. 30, 1282 (1958).

32. Peng, P.Y. and Sandell, E.B. — Anal. Chim. Acta 29, 325 (1963).

33. Reed, D.V., Wilson, H.R. and Goward, G.W. — U.S.A.E.C. Rept WAPDCTA (GLA) 620, 1958.

34. Rehák, B. and Malinek, M. — Z. Anal. Chem., 153, 166 (1956).

35. Riley, J.P. — Anal. Chim. Acta 21, 317 (1959).

36. Scharrer, K. and Eberhardt, W. — Z. Pflauzenernaehr. Dueng. Bodenk 73, 115 (1956).

37. Sekido, E. Fernando, Q. and Zavrazhnova, D.M. — Zh. Analit. Khim. 16, 442 (1961).

38. Sinha, S.N. and Dey, A.K. — Z. Anal. Chem. 183, 182 (1961).

39. Skewes, H.R. — Australian J. Appl. Sci., 10, 464 (1959).

40. Sommer, L. — Z. Anal. Chem., 187, 7 (1962).

41. Srivastava, K.C. and Banerji, S.K. — Chemical Age of India 18 (3), 209 (1967).

42. Stepanova, N.A. and Yakunina, G.A. — Zh. Analit. Khim., 17, 858 (1962).

43. Stolyarov, K.P. — Vest. Leningr. Univ. Ser. Fiz. i-Khim. 22(4), 140 (1963).

44. Stonhill, L.G. — Chemist Analyst, 47, 68 (1958)

45. Sverak, J. — Z. Anal. Chem., 201, 12 (1964).

46. U.K.A.E.A. — Rept. PGR - 25 (S), 1959

47. Wood, D.F. and Clark, R.T. — Analyst, 83, 326 (1958).

48. Yagoda, H. and Fales, H.A. — J. Am. Chem. Soc., 60, 640 (1938).

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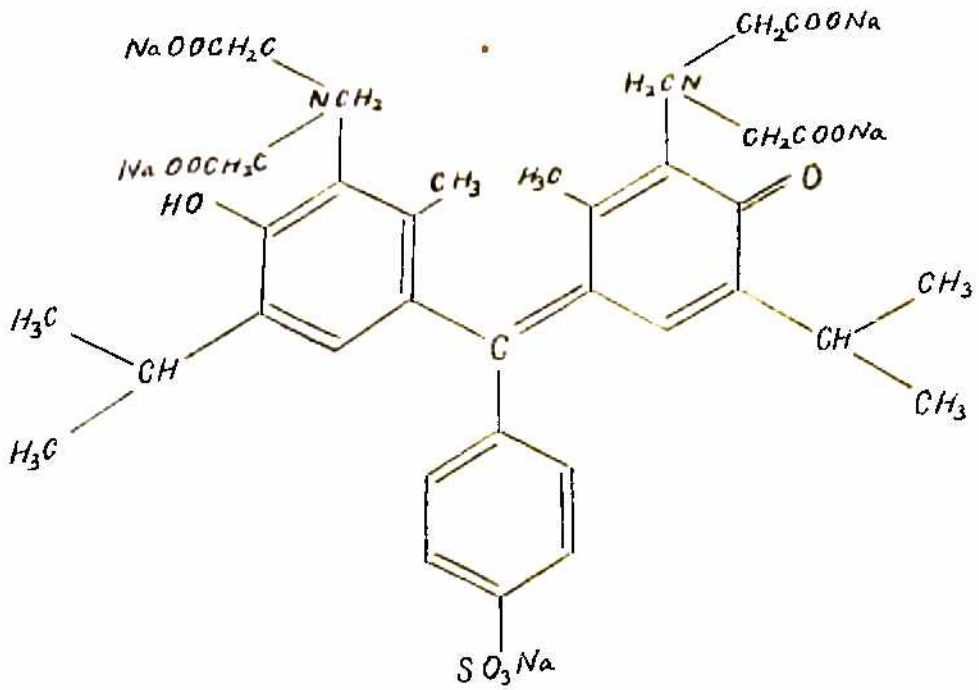
CHAPTER V

CHELATES OF SOME METAL IONS WITH METHYLTHYMOL BLUE

After the development of the indicator known variously as phthalein complexone, phthalein purple or metalphthalein(8), several extremely useful metallochromic indicators, such as xylenol orange (39) were synthesised by similar processes. In this series methylthymol blue (3, 3'-bis [N, N-bis (carboxy methyl) amino methyl] thymolsulfonphthalein appears(40) to have useful properties. It is usually supplied as penta sodium salt and is represented by the following structure.



Methylthymol blue penta sodium salt

As an indicator in complexometric titration it behaves like xylenol orange (41, 42, 43, 44). The ratio of the stability of the metal complexes of methylthymol blue to

that of the corresponding complexes with EDTA is favourable, the colour changes involved are sharp and an excellent visual indication is secured.

Methylthymol blue has a structural relation to metal indicator of the type of pyrocatecholviolet (54) and may be obtained by the replacement of the 3 and 3' phenolic groups with methylene nitrilodiacetate group. It may be used either in acid or in alkaline medium. Thus in 1 M HNO_3 bismuth may be selectively titrated with EDTA, the end point being marked by a change from blue to yellow. Thorium may be titrated similarly at pH 3, and scandium in a pyridine-HNO_3 buffer (pH 5.0). In an acid medium treated with an excess of hexamine, at pH 6-7, cadmium, cobalt-II, lanthanum, lead, mercury(II) and zinc yield good end points; in alkaline media the end point is marked by a change from blue to colourless (or faint grey) in the titration of cadmium, cobalt, lead, magnesium, manganese II and zinc at pH 10.0 in an ammonia - ammonium chloride buffer and of barium, calcium and strontium at pH 12.0 in a sodium hydroxide medium. The indicator is of value for calcium at pH 12.0 and of mercury II in a hexamine-buffered medium. The indicator may be used as an aqueous solution, but this is very unstable and it is best used as a dispersion in KNO_3. Care must be taken not to let the pH exceed 12.5. Above this value the indicator itself is blue.

Pribil (63) has reported that this indicator is "blocked" by small (trace) amounts of copper, cobalt and

nickel etc. but it may be protected by the addition of O-phenanthroline.

Soběslavský, Dudak and Tepla (69) have recommended it chiefly as a chelatometric indicator for the determination of calcium and magnesium in serum. The indicator has been used for the selective determination of zinc (37) in slightly acid medium, ferrous iron (48) at pH 4.5 - 6.0 and calcium in modified cast iron (20) at pH 11.5.

Gattow and Schoff (29) report that by using pyrocatechol violet as reference indicator in the titration of bismuth with EDTA, methylthymol blue gives acceptable results. A comparison of a number of indicators including methylthymol blue for the direct chelatometric micro determination of rare earths have been studied (35) and it has been found that xylenol orange and 4-(2 thiazolyl-azo) resorcinol are best for chelatometric micro determination of rare earths as they can be used over a wider titratable range. A study of 14 indicators for complexometric determination of manganese reveales that methylthymol blue (64) is one of the best indicators if large amounts of manganese are determined with complexone III.

Methylthymol blue has also been suggested as a metallochromic indicator in EDTA titrations for Aluminium(30), Chromium (33), gallium and indium (34) and Zirconium (81).

Pozsgay-Kovacs (62) has differentiated between the two compounds marketed under the same name "methylthymol blue",

on the basis of circular chromatograms of the two substances giving quite different pictures and allowing easy identification by comparison with authentic sample. He has pointed out that a mixture of methyl red and thymol blue (sold by Edward Gurr Ltd., London) should not be confused with the chromogenic agent, methylthymol blue.

It may be noted that methylthymol blue gives a bathochromic shift on combination with the ions of about sixty-five elements, but this behaviour is of practical importance for only about forty-five elements. The shift is of advantage in the application of the compound as metal indicator but unfavourable for use as selective chromogenic agent. Methylthymol blue is used in aqueous and homogeneous water organic solvent media. Its reaction with many metal ions under conditions of highest photometric sensitivity proceeds at a low rate, owing to appreciable hydrolysis of the metal ion.

The commercial products are usually contaminated with the starting material for the synthesis and with intermediates (60, 67). The purest products can be secured as the free acids. The preparation of methylthymol blue involves the Mannichcondensation of thymol blue (that is thymol sulfonphthalein) with iminodiacetic acid and formaldehyde (45, 46). The products may be purified chromatographically with cellulose and ion exchange resin columns. The monosubstituted product of the reaction, semimethylthymol blue (86) may also be separated. The purity of the sodium salt of methylthymol blue may also be evaluated by chromatography.

The best product shows Rf value about zero (cf. semi methylthymol blue 0.16 - 0.60).

To obtain the free acid, dissolve 1 gram of the sodium salt in 25 ml of distilled water, and pass the solution through a column filled with an appropriate, strongly acidic cation exchange resin (such as Dowex 50 w or Amberlite I R-120) placed in the hydrogen form. Evaporate the effluent in vacuo to dryness, and dry at 100°C for 5 hours.

The various acid dissociation steps of methylthymol blue are of great importance for its application as photometric reagent. The acid dissociation constants are given in Table 5.1.

Table 5.1

Pka, n values of acid dissociation constants of Methylthymol blue (47,65,22,71,1)*

Reagent	Pka, n								
n =	1	2	3	4	5	6	7	8	9
	-1.76	-1.11	0.78	1.13	2.60	3.24	7.2	11.1	13.4

*ionic strength = 0.2 M sodium nitrate

$$Ka, n = [H_9 - nL]\,[H]/[H_9 - n + 1L]$$

$$pKa, n = -\log Ka, n$$

The constants Ka, 9 and Ka, 8 express the dissociation of the two phenolic groups. Their values are relatively small, because the phenolic protons form hydrogen bridge bonds with the nitrogen of the tertiary amino groups. The constants Ka, 7 to Ka, 4 correspond to the dissociation of the carboxyl groups. The dissociation related to Ka, 7 is mainly responsible for the colour change.occuring in alkaline medium. The colour change is from yellow to blue. The constants Ka, 3 and Ka, 2 express the dissociation of the protonated tertiary amino groups. The equilibrium corresponding to constant Ka, 2 is mainly responsible for the colour change from violet to yellow in acidic medium. The last constant Ka, 1 express the deprotonisation of the sulfonate group.

Methylthymol blue has also been employed as a chromogenic agent in the photometric determination of some metal ions in the last few years. The photometric determinations can be done in pH range 0.0 to 6.0 because of the colour effects due to protonization or deprotonization of the reagent. Methylthymol blue also shows a well developed bathochromic minimum to allow the pH range 11.5 to 12.5 to be used for the photometric determination of certain metal ions such as calcium, strontium and barium. Some metal ions of the first and second group react also with methylthymol blue at pH 11.5 to 12.5 but it has been observed that the colour effects are too small for application to photometric determinations.

The reaction of methylthymol blue with zirconium has

been studied extinsively by a number of workers (53, 9, 10, 11, 12, 24, 78, 73, 13). Its high sensitivity makes it interesting for analytical purposes. In a comparative study of sixteen chromogenic agents for zirconium xylenol orange and methylthymol blue were found to be the best (11). Methylthymol blue forms 1:1 and 2:1 (metal-ligand) complex with zirconium (13, 24). The determination with MTB has been used for the analysis of zirconium-alloys (53), zirconium in slicates (10).

Cheng (24) has reported that a 2:1 complex is formed in the reaction of hafnium with MTB at pH 3.0 and MTB is more sensitive for the determination of hafnium than xylenol orange. A photometric procedure for hafnium with this reagent has been proposed (24). A straight calibration curve is obtained which, however, may not pass through the origin (due to side complexation effect). Interfering ions include bismuth, iron (III), tin (IV), zirconium, thorium, niobium (V), molybdenum (VI), vanadium (IV), titanium (IV), citrate, phosphate, oxalate, fluoride, NTA and EDTA. Iron (III) may be masked by ascorbic acid. Zirconium and molybdenum(VI) by hydrogen peroxide (24).

The interaction between methylthymol blue and thorium has been investigated by Vasilenko and Shanya (83). At pH 5.0 a blue complex having maximum absorbance at 580 nm is formed. The metal ligand ratio in the complex is 1:2. A spectrophotometric method has been developed for the determination of thorium (83) in the presence of 5000 fold

amounts of uranium (VI). A molar absorptivity of 5.5 x 10^4 liters/mole cm has been computed at 580 nm. More recently an extraction photometric procedure has been elaborated by Otomo(61). The complex is extracted at pH 2.5 - 3.0 with butyl alcohol from a solution containing 1, 3 diphenyl guanidine and the absorbance is measured at 590 nm. The molar absorptivity is 6.6 x 10^4 liters/mole - cm. The sensitivity is given as 0.0036 $\mu g/cm^2$ for absorbance = 0.001. This demonstrates the unusually high sensitivity of this reagent to thorium. Beer's law is followed in the range 0.3 - 3.0 $\mu g/ml$ thorium.

Methylthymol blue forms 1:1 complex with titanium(IV) (27). The colour changes observed with titanium (III) are feeble. The sensitivity of the titanium (IV) reaction is increased considerably in the presence of hydrogen peroxide, owing to the formation of a strongly absorbing ternary titanium (IV) - peroxo - MTB complex (50) from which a molar composition of 1:1:1 was established.

A large number of communications describe the reaction of methylthymol blue with yttrium and the lanthanides and their analytical applications (59, 66, 72, 2, 3, 14, 4, 55, 15, 16).

The reagent forms 1:1 complex with yttrium (59) and lanthanides (66, 3, 2). All complexes obey Beer's law. In the pH range 5.5 to 6.0 the principal absorbance maximum is at 605 to 610 nm. In the determination of yttrium and

lanthanides, bivalent and polyvalent metal ions interfere. Interfering anions include fluoride, phosphate, oxalate, carbonate, tartrate, citrate, NTA and EDTA. A preliminary separation of yttrium and lanthanides from other elements is necessary by paper chromatography or ion exchange. The formation constant of complexes of rare earth elements with MTB has been given by Mal'Kova and Fateeva (55). A comparative study involving sixteen photometric reagents for ytterbium has shown that Arsenazo III, Xylenol orange, Stilbazo and methylthymol blue are the best (15, 16).

Tikhonov (74) has used methylthymol blue for the photometric determination of aluminium at pH 3.0 to 4.0 with absorbance measurements at 590 nm. The chelate has a metal ligand ratio 1:1 and a molar absorptivity of 1.9×10^4 liters/mole cm. Beer's law is obeyed upto 0.4 m gm of aluminium in 100 ml of solution. The interference of various metals such as titanium, vanadium, chromium, zirconium, gallium, nickel, copper and beryllium can be eleminated by the addition of complexon (III).

The method has been applied for determining aluminium in products of titanium industry. Fluoride ion destroys the complex. In the determination manganese, zinc, copper, nickel are masked with complexon (III). The interference of titanium, iron, vanadium and zirconium can be removed by extracting their cupferron complexes with chloroform. The sensitivity of determination is 0.002 per cent and the relative error is 5.3 per cent (75).

Tonosaki and Sakai (79) have established the formation of a 1:1 complex between methylthymol blue and gallium with an absorbance maximum at 565 nm at pH 1.5 to 1.8 and the formation of a 1:2 complex with an absorbance maximum at 515 nm at pH 4.5 to 5.5. Akhmedli and Glushchenko have made a comparative study of sixteen organic reagents for the photometric determination of gallium in aqueous and nonaqueous media and found that in aqueous medium the most suitable are pyrocatechol violet, xylenol orange and methylthymol blue (5). A method of determining trace amounts of gallium has been devised (79). Diverse anions and complexing agents such as oxalate, NTA and EDTA interfere seriously (79) in determination of gallium.

Methylthymol blue gives with indium 1:1 complex(17,18), Babko and Kish (17) studied the suitability of twenty reagents for the photometric determination of indium and found that methylthymol blue, xylenol orange, 1 - (2-pyridylazo) 2 naphthol, 4 - (2-pyridylazo) resorcinol and quercetin were the most satisfactory. In a further communication they have examined the spectrophotometric characteristics of sixteen reagents that form coloured compounds with indium and report that xylenol orange, methylthymol blue and eriochrome cyanine gave the best results (18).

Methylthymol gives coloured complexes with thallium (III), but the bathochromic effect with thallium (I) is very small. At pH 2 complexes with metal to ligand ratios of 2:1 (619 nm), 1:1 (574 and 533 nm) and 1:3 (495 nm) are formed.

At pH 5.0 complexes with the composition 1:2 and 1:4 are found to exist in addition to 2:1 and 1:1 (6). The Beer's law for the 1:1 complex solutions is obeyed at thallium(III) concentrations of 1.6 to 10 μg/ml (7).

Tikhonov and coworkers have reported (76) that vanadium reacts with methylthymol blue at pH 3.5 in the molar ratio 1:1. The molar absorptivity of the complex is 1.6×10^4 at 590 nm. A photometric procedure for determination of vanadium in titanium slags has been developed (76).

Lassner and Coworkers have employed methylthymol blue for the detection of niobium (V) as a mixed complex with hydrogen peroxide (51, 50, 52). The reaction is highly selective and sensitive. Recently methylthymol blue has been proposed as a chromogenic agent for the determination of niobium in the presence of oxalate, tartrate and fluoride at pH 1-2 with absorbance measurements at 560 nm. A 1:1 complex is formed. The colour remains stable in niobium oxalate ratio 1:30 and slightly decreases up to ratio 1:80. The molar absorptivity at 30 fold excess of ammonium oxalate is 13×10^3. Beer's law is obeyed in the range 5 to 50 μg/ml niobium. This method has been applied to the determination of niobium in uranium, tungsten and uranium alloys (28).

Babko and Shtokalo (19) reported that methylthymol blue gives with tantalum (V) a coloured complex at pH 2.0 to 4.0 but the reaction has not yet been applied to photometric determination.

Magnesium forms 1:1 complex with methylthymol blue. The reaction with methylthymol blue has been thoroughly investigated by Metcalfe (57). A photometric procedure of determining magnesium with methylthymol blue has been devised (57). The complex is formed in an alcohol water medium buffered to pH 10.8 with ammonia - ammonium chloride solution. The molar absorptivity is 1.5×10^4 liters/mole cm. Up to 1000 µg of iron (III) (reduced with ascorbic acid), 5000 µg of nickel, 1000 µg of Cobalt (II), 1000 µg of Cadmium, 1000 µg of Zinc and 5000 µg of Copper (II) do not interfere (57).

Iritani and Miyahara have developed a method for the determination of mercury (II) with methylthymol blue (36) but it is of little practical importance because of its low sensitivity. Recently Tikhonov (77) has studied the complexes of some divalent metals such as magnesium, calcium, iron (II), manganese, zinc, nickel, lead with methylthymol blue spectrophotometrically and reports that all of them form 1:1 complex with methylthymol blue.

According to Cheng (25) chromium (III) gives coloured complexes with xylenol orange and methylthymol blue in the pH range 3 to 5. The reaction of xylenol orange is more sensitive than methylthymol blue (25). The interaction between methylthymol blue and iron (III) has been investigated by Tonosaki (80). In the range 0.07 to 1 M $HClO_4$ a 1:1 complex is formed with its absorption maximum at 580 nm and

in the pH range 4.5 to 5.5 a complex with a metal reagent ratio 1:2 is formed with an absorption maximum at 520 nm. The molar absorptivity of the two complexes is 1.5 x 10^4 and 1.4 x 10^4 liters/mole cm. respectively. In both complexes Beer's law is obeyed over the range 5 to 50 µg of iron (III) in 25 ml (80). Borislav and Coworkers (21) have concluded from recent studies that iron (III) and MTB form two complexes with metal ligand ratio 1:1 and 1:2. The absorption maxima are at 610 nm (1:1) and 515 nm for (1:2), the molar absorptivity being 1.73 x 10^4 and 3.21 x 10^3 liters/mole cm. respectively. The molar absorptivities for the complexes of iron (III) reported by these workers (80, 21) show a marked difference. The differences seems to be related to varying purity and to the commercial source of the reagents used. It may be stated here that some workers express the sensitivity in terms of absolute molar absorptivity of the complex formed, which is usually of little significance for the spectrophotometric sensitivity of a given determination, because its value is generally considerably higher than that of net molar absorptivity at a given total concentration of the metal ion, derived from an absorbance measurement versus a blank containing the same concentration of the reagent.

The thorium complexes with methylthymol blue (32, 82) have been applied to the indirect determination of fluoride. Recently Wilson and Cooke have used methylthymol blue for the detection of trace amounts of fluoride ion (84). The chromogenic reactions of methylthymol blue with many metal

ions have been reported by Budesinsky (23).

A systematic study of the coloured chelates of methylthymol blue and their analytical applications in the photometric determination of cations has been undertaken by us in these laboratories. Srivastava and Banerji have observed that methylthymol blue also produces colour with various other metallic ions and in a recent communication (70) they have reported the new colour reactions, effect of pH on the reagent and the conditions for the reaction of some metal ions with the reagent. It is interesting to note that inspite of the enormous amount of work done on the use of the reagent in photometric analysis, no systematic study of the composition stability and other characteristics of the coloured chelates appears to have been made so far. The present study was, therefore, undertaken to establish the composition, stability and optimum conditions for the photometric determination of hexavalent uranium, pentavalent vanadium and bivalent iron with methylthymol blue as a chromogenic reagent.

EXPERIMENTAL

Variation of the colour of methylthymol blue with hydrogen ion concentration of the medium

A standard solution of methylthymol blue was prepared

by dissolving purified Eastman reagent (penta sodium salt) in distilled water. To measured amounts of the solution acid or alkali was added and the total volume raised to 25 ml. The pH of the solutions was measured with Beckman H2 pH meter. The absorption spectra were studied with a Hilger Uvispek spectrophotometer and glass cells of 1 cm thickness. The experiments were conducted at 25° at a constant ionic strength of 0.1 M $NaClO_4$. The various absorption maxima shown by the reagent at different pH are presented in figure 5.1 and summarised in Table 5.2.

Table 5.2

Shift of λ_{max} with change in pH of Methylthymol blue

pH	Region of maximum absorption, nm
1.0 - 7.0	436
7.1 - 7.5	436
9.0 -10.0	580
11.0 -13.0	605

Colour formation with inorganic cations

For studying colour reactions with metallic ions a 1×10^{-3} M solution of methylthymol blue was prepared in distilled water. Solutions of various metallic salts, using analytical grade reagents, were prepared of 0.01 M concentration

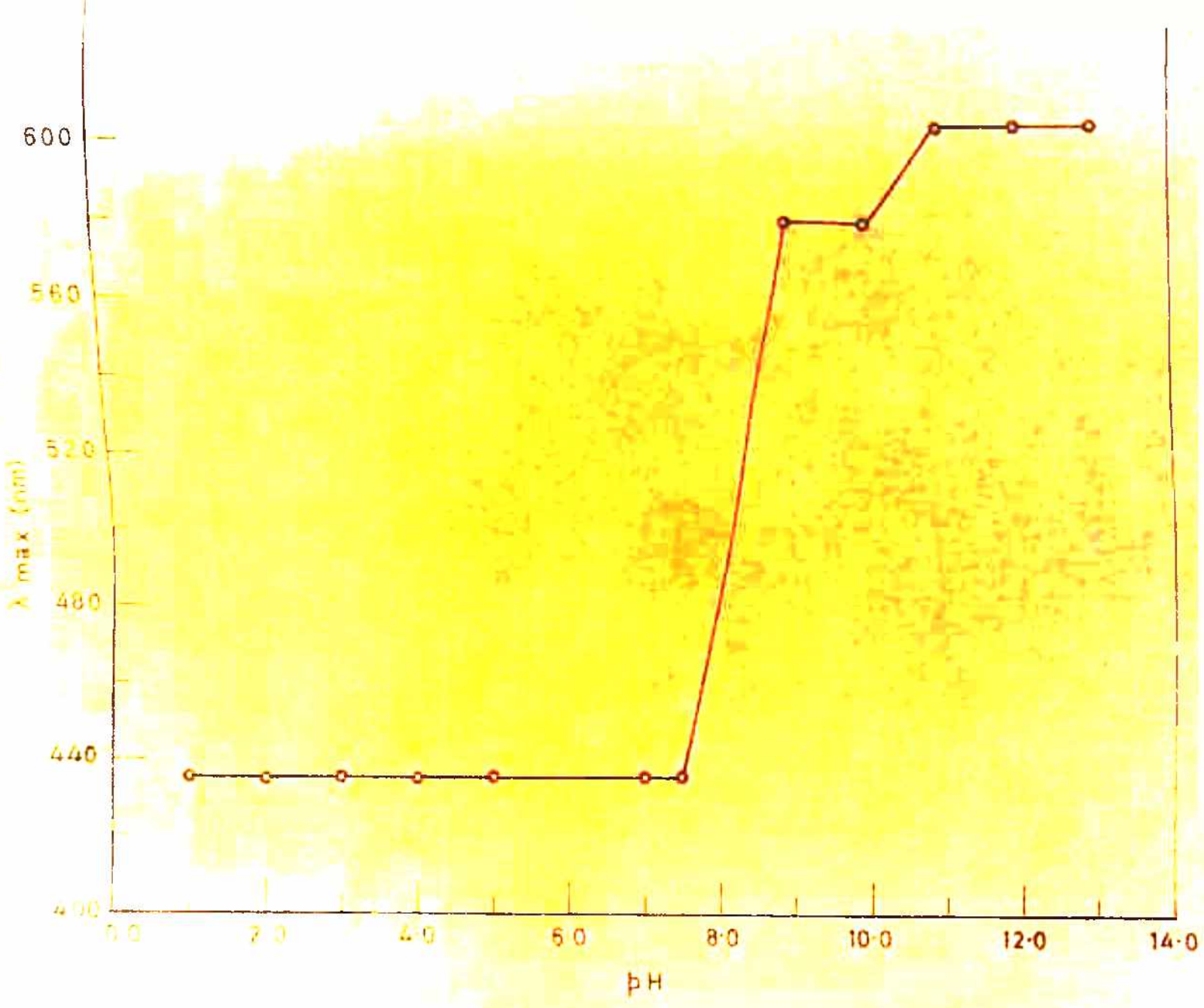


Fig _ 5·1 Variation of λ max with pH of Methylthmol blue $c' = 5 \cdot 0 \times 10^{-5} M$

in distilled water, acid being added in several cases to prevent hydrolysis.

In several test tubes 1 ml of the solutions were taken and 1 ml of the reagent solution and 2 ml of the buffer solution were added to each and the colour was noted visually. The colour was compared with a blank prepared in the same manner. Table 5.3 records the conditions for the reaction of various metal ions with methylthymol blue.

Table 5.3

Reactions of metal ions with Methylthymol Blue

Metal ion	Coloration	pH	Buffer	λ_{max} nm	Net molar absorptivity liters/mole cm.
Copper II	Blue	5.8	HMT-HNO_3	600	32,000
Beryllium	Red	5.0	HMT-$HClO_4$	500	13,250
Magnesium	Blue	10.8	NH_4Cl-NH_4OH	610	15,200
Calcium	Blue	11.4	KoH	610	20,300
Strontium	Blue	11.5	KoH	610	11,500
Barium	Blue	11.6	KoH	610	4,000
Zinc	Blue	6.0	HMT-HNO_3	600	12,500
Mercury(II)	Blue	6.0	HMT-HNO_3	630	10,100
Aluminium	Pink	3.0	ACOH-ACONa	590	19,000
Scandium	Purple red	3.0	ACOH-ACONa	570	9,300

contd.

Table 5.3 contd.

Metal ion	Coloration	pH	Buffer	λ_{max} nm	Net molar absorptivity liters/mole cm.
Gallium	Pink	1.5	HNO_3	570	12,800
Indium	Blue	3.4	ACOH-ACONa	600	18,000
Yttrium	Blue	5.8	HMT-HNO_3	610	18,500
Lanthanum	Blue	5.8	HMT-HNO_3	610	17,800
Cerium	Blue	6.5	HMT-HNO_3	600	21,000
Thulium	Blue	6.0	ACOH-ACONa	608	21,000
Ytterbium	Blue	5.8	HMT-HNO_3	570	21,000
Lutetium	Blue	6.0	ACOH-ACONa	606	23,000
Titanium(IV)	Blue	3.0	ACOH-ACONa	600	11,000
Zirconium	Blue	1.5	$HClO_4$	580	21,700
Hafnium	Blue	1.5	$HClO_4$	570	18,700
Thorium	Blue	5.0	$ACONH_4$	580	55,000
Lead(II)	Blue	5.8	HMT-HNO_3	600	19,500
Vanadium(V)	Blue	4.5	HMT-$HClO_4$	590	17,125
Niobium(V)	Brown	2.0	$C_4H_6O_6$-HCOOH	560	13,000
Chromium(III)	Yellow	3.0	ACOH-ACONa	490	11,500
Uranium(VI)	Red	6.7	HMT-HNO_3	510	10,625
Iron (III)	Blue	2.0	$HClO_4$	580	15,000
Iron (II)	Red	5.8	HMT-$HClO_4$	510	12,000
Cobalt(II)	Blue	5.8	HMT-HNO_3	600	9,100
Nickel	Blue	5.8	HMT-HNO_3	600	11,000
Palladium(II)	Red	2.0	$HClO_4$	530	21,250

HMT = Hexamethylene tetramine

ACOH = Acetic acid

ACONa = Sodium acetate

$C_4H_6O_6$ = Tartric acid.

Methylthymol blue yields coloured chelates with copper, beryllium, calcium, strontium, lead, vanadium (V), uranium(VI), iron (II) and palladium(II) besides those already reported in the literature.

Behaviour of the reagent as colloidal electrolyte:

Before performing experiments on composition and stability of the metal chelates involving methylthymol blue, it was thought necessary to investigate the behaviour of aqueous solutions of the reagent. This was essential, because deviations in the composition of the chelate from true stoichiometry were observed in many cases. Hence, electrical conductance studies were performed with aqueous solutions of methylthymol blue. The results established the behaviour of the reagent as colloidal electrolyte. The curve between the square root of concentration and equivalent conductance is not linear and resembles that of colloidal electrolyte recorded by McBain (56). The temperature of zero conductance of methylthymol blue lies at $-16.5^{o}C$ and the temperature coefficient per degree centigrade per 100 of conductance at $35^{o}C$ provides values between 1.35 and 1.95. These observations are in close conformity with those of Mushran and Prakash (58),

who, during their work on a number of colloidal systems, found that, in general, the temperature of zero conductance of true electrolytes lies at about $-40^{\circ}C$, whereas in the case of colloidal systems this temperature ranges between $-15^{\circ}C$ and $-35^{\circ}C$. Similar observations were reported by Shivapuri and Prakash (68) who sought to establish the colloidal nature of some acidic and basic dyes. According to Mushran and Prakash the temperature coefficient per degree centigrade per 100 of conductance at $35^{\circ}C$, in colloidal systems and colloidal electrolytes is mostly found to be around 2.0.

On the basis of the above results, it was concluded that aqueous solution of methylthymol blue behaves as a colloidal electrolyte and due to this, deviations in the composition of the chelates from true stoichiometry are encountered. Many workers have ignored this aspect while explaining the behaviour of such reagents, and attributed the non-stoichiometric ratio of the composition of the chelates to be due to the hydrolysis of the metal ions (49). Our work suggests that the colloidal characteristics of the chelating agent also play a significant role while determining the composition of the metal chelates, and because of this often non-stoichiometric ratios are arrived at. For physicochemical measurements in solution, therefore, it is advisible to work with extremely dilute solutions, because only then the chelating agent would behave as a true electrolyte (26). Consequently, during the present studies, solutions of concentration of the order of $10^{-4}M$ and $10^{-5}M$ have been

employed, and at this dilution, the reagent behaves as a true electrolyte and the compositions determined are therefore the true stoichiometric ratios.

Uranium (VI) - Methylthymol Blue System

The penta sodium salt of 3, 3' - Bis { [N, N - bis (carboxy methyl) amino] methyl } - thymol sulphon phthalein (trivial name methylthymol blue, abbreviated as MTB) forms coloured chelates with a number of metal ions in acidic solution and has received extensive attention as a metal indicator for chelatometric titrations. In the last few years it has also been employed as a chromogenic agent in the photometric determination of various metals. No systematic work seems to have been done on the metal chelates of methylthymol blue with regard to composition and stability. The reagent possesses pronounced chelating tendencies due to the presence of chromogenic phthalein group with two iminodiacetate groups. The 2 nitrogen donors and 4 acetate groups in the molecule may greatly effect the order of stability of metal chelates. Detailed studies have, therefore, been made regarding the composition, stability and analytical applications of the chelates of methylthymol blue. This study deals with the investigation of the chelate of uranium(VI) ion. The results of the continuous variation method the mole ratio

method and the slope ratio method show a complex consisting of one molecule of methylthymol blue to one uranium (VI) ion.

EXPERIMENTAL

Standard solutions of uranyl acetate (BDH AnalaR) and purified sample of Eastman methylthymol blue (penta sodium salt) were prepared in double distilled water, in view of the strong complexing nature of carbonate with uranyl ions, care being taken to exclude carbondioxide.

A hexamine - nitric acid buffer and sodium perchlorate (E. Merck) was used to maintain a constant ionic strength.

Conditions of study

All experiments were performed at 30°C ± 0.1°C. The pH of all the mixtures prepared for the measurements was kept at 6.7 ± 0.1 by addition of hexamine - nitric acid buffer. The ionic strength of the system was maintained at 0.1 M with sodium perchlorate.

Absorption curves

When a buffered, aqueous solution of uranium is mixed with a methylthymol blue solution, a red complex is immediately

formed. Fig. 5.2 shows the absorption curves of methylthymol blue and its uranium complex. The absorption curve of the uranium complex obtained with a reagent blank as reference has an absorption maximum at 510 nm. Some of the typical results are given in Table.5.4.

Table 5.4

Concentration of uranyl acetate = 2.0×10^{-5}M

Concentration of Methylthymol blue = 2.0×10^{-4}M

pH of solutions = 6.7

Wavelength nm	Optical density of complex (A)	Optical density of MTB (B)	Difference in optical density A - B = C
400	0.920	1.180	-
410	1.050	1.280	-
420	1.250	1.420	-
430	1.350	1.570	-
440	1.450	1.560	-
450	1.500	1.500	-
460	1.450	1.450	-
470	1.330	1.330	-
480	1.250	1.200	0.050
490	1.200	1.080	0.120
500	1.040	0.880	0.160
510	0.930	0.720	0.210
520	0.820	0.640	0.180
530	0.740	0.580	0.160
540	0.680	0.550	0.130
550	0.660	0.560	0.100
560	0.670	0.590	0.080
570	0.660	0.615	0.045
580	0.670	0.640	0.030
590	0.620	0.600	0.020
600	0.590	0.580	0.010
610	0.440	0.435	0.005
620	0.340	0.330	-
630	0.240	0.230	-
640	0.160	0.150	-
650	0.080	0.070	-

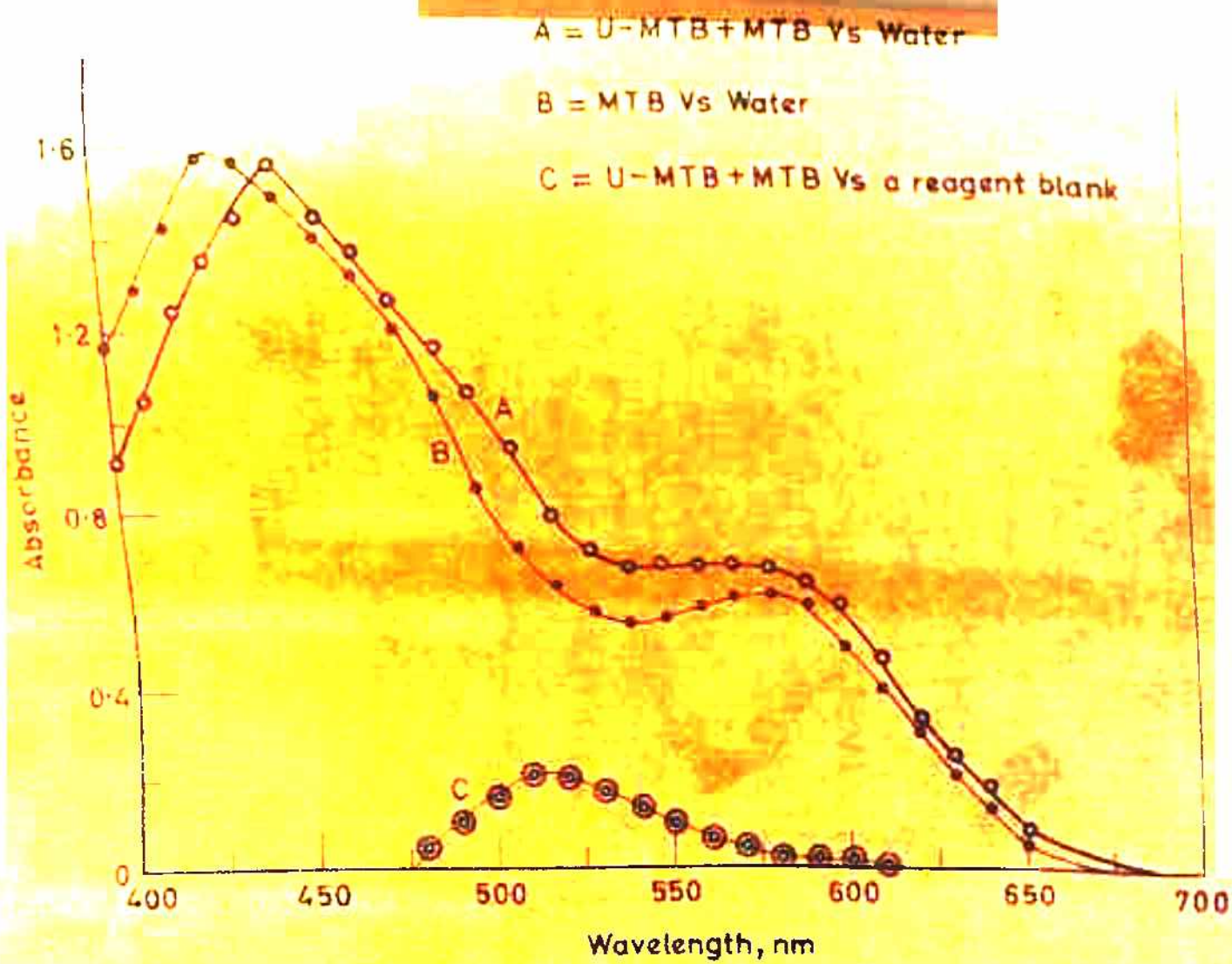


Fig._ 5·2 Absorption curves of MTB and its Uranium complex at pH:6·7; μ: 0·1 $NaClO_4$; U. $2{\cdot}0 \times 10^{-5}$M; MTB: $2{\cdot}0 \times 10^{-4}$M

Effect of pH: The effect of pH on the absorbance of the solution was examined by measuring at 510 nm, the absorbance of solution containing 94 μg of uranium and 4 ml of a 1×10^{-3}M solution of methylthymol blue. From table 5.5 and figure 5.3 it was found that the maximum absorbance is obtained in the pH range 6.6 to 6.8.

Table 5.5

Concentration of uranyl acetate = 1.6×10^{-5} M

Concentration of MTB = 1.6×10^{-4} M

pH	6.2	6.3	6.4	6.6	6.7	6.8	6.9	7.0
Optical density per cm (510 nm)	0.105	0.125	0.135	0.165	0.165	0.165	0.164	0.140

Effect of Methylthymol Blue: The effect of the reagent concentration was studied with solutions containing a given amount of uranium and varying amounts of a 1×10^{-3} M solution of methylthymol blue. The pH values of the solution was kept constant at 6.7 and the absorbance measurements were carried out at 510 nm. It was found that a constant absorbance is obtained when tenfold molar excess of the reagent solution is used.

The Stability of the Colour

The colour of the chelate did not depend on reaction

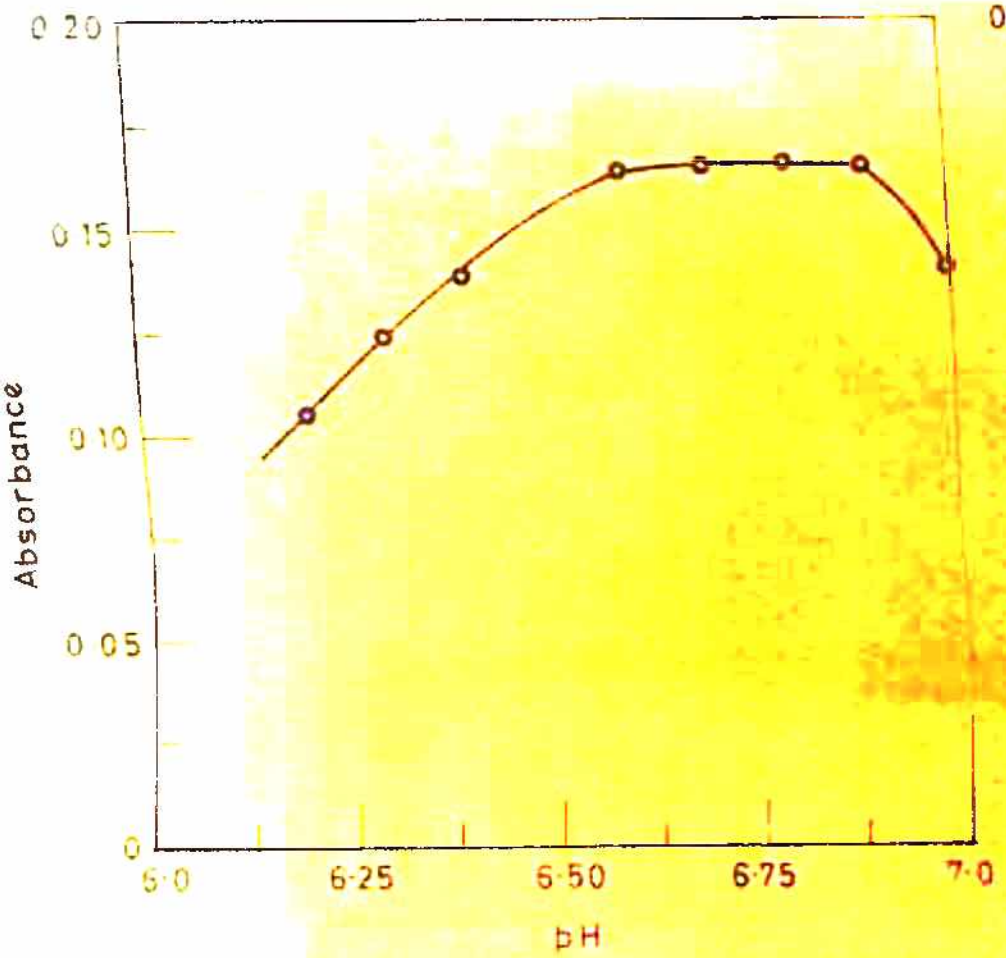


Fig._ 5·3 Effect of pH; MTB: $1{\cdot}6 \times 10^{-4}$ M
U: 94 µg

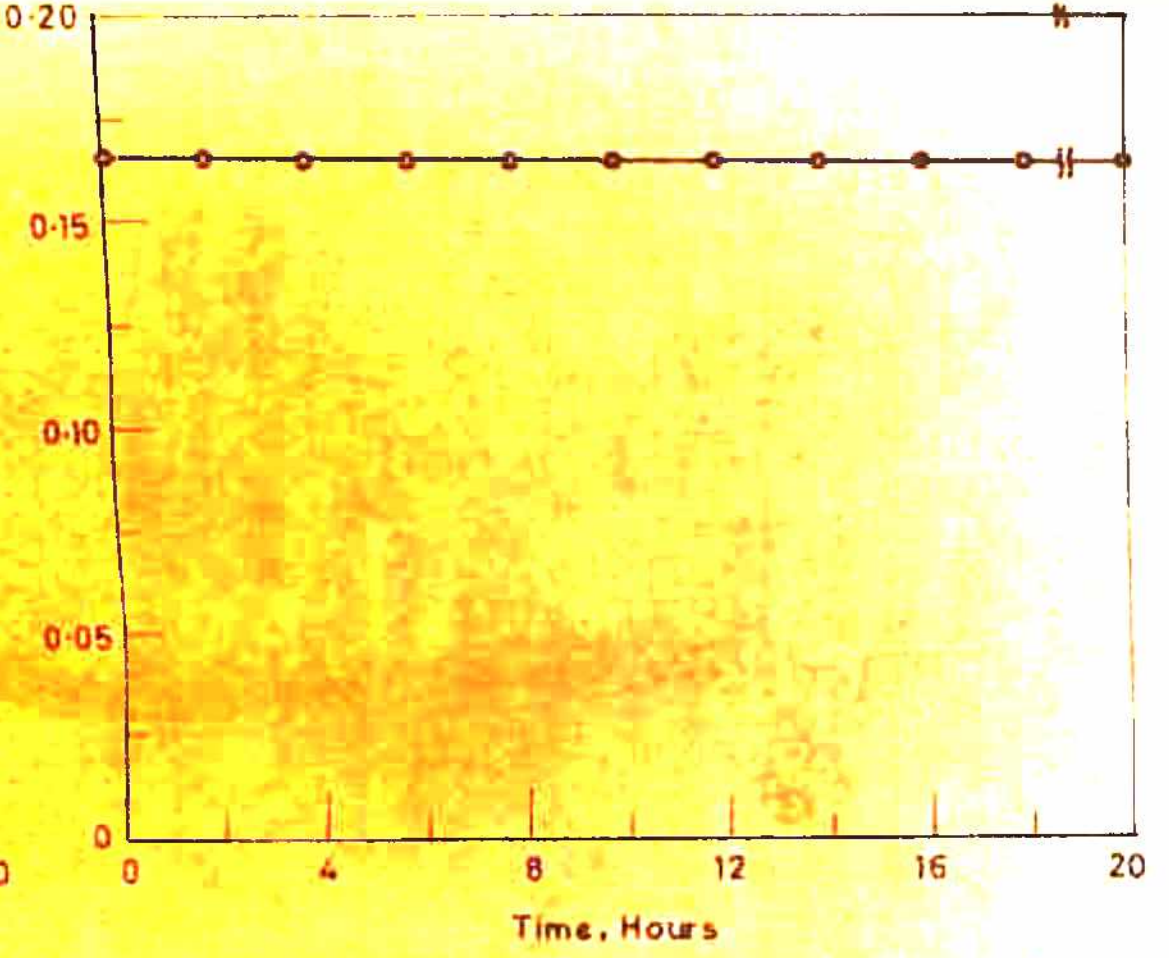


Fig._ 5·4 Stability of colour MTB: $1{\cdot}6 \times 10^{-4}$ M
U: 94 µg

time and assumed its full intensity within less than five minutes at room temperature. Heating beyond 35° reduces the colour intensity. The complex is stable and the absorbance remains constant for a period of over 18 hours (fig. 5.4).

The order of the Addition of Reagents:

Varying the order in which the reagents were added had no significant effect on the results. In all cases the colour was completely developed within 2 minutes.

Adherence to Beer's law: Beer's law is obeyed in the range from 10 to 94 µg (0.4 to 3.76 ppm) of uranium at 510 nm. The optimum concentration range for the determination of uranium by the Ringbom method was found to be 0.8 to 2.4 ppm. Under the conditions of spectrophotometric determination. The net molar absorptivity was found to be 10,625 at 510 nm.

COMPOSITION OF THE CHELATE

Job's method: Job's method of continuous variation (38) was adopted for the determination of the composition of the complex. The total volume in each case was kept at 25 ml. The pH was kept at 6.7 ± 0.1 and ionic strength 0.1 M with $NaClO_4$. The absorbance of the mixture and chelating agent was measured at two different wave lengths 510 and 530 nm. Measurements, using equimolecular and nonequimolecular solutions in large numbers, were taken. The results are given in tables 5.6 to 5.19 and in figures 5.5 to 5.9. The

figures indicate the difference between the absorbance of the mixture and that which would be shown by the metal and the chelating agent, if no chelation took place. The difference is plotted against the composition of the mixtures.

Table 5.6

Concentration of uranyl acetate (c) = 4.0×10^{-4} M

Concentration of MTB (c') = 4.0×10^{-4} M

pH = 6.7 ± 0.1

λ = 510 nm

$p = c'/c$ = 1

peak at 1:1 (Fig. 5.5 curve A)

Volume of uranyl acetate ml	Volume of MTB ml	Optical density of mixture (a)	Optical density of MTB (b)	Difference in optical density (a-b)
0	25	1.420	1.420	0.000
2.5	22.5	1.425	1.300	0.125
5.0	20.0	1.395	1.150	0.245
7.5	17.5	1.360	1.000	0.360
10.0	15.0	1.340	0.850	0.490
12.5	12.5	1.265	0.725	0.540
15.0	10.0	1.055	0.570	0.485
17.5	7.5	0.795	0.400	0.395
20.0	5.0	0.565	0.305	0.260
22.5	2.5	0.255	0.125	0.130

Table 5.7

Concentration of uranyl acetate (c) = 3.33×10^{-4} M

Concentration of MTB (c') = 3.33×10^{-4} M

pH = 6.7 ± 0.1, λ = 510 nm, p = c'/c = 1

peak at 1:1 (Fig. 5.5 curve B)

Volume of uranyl acetate ml	Volume of MTB ml	Optical density of mixture (a)	Optical density of MTB (b)	Difference in optical density (a-b)
0	25	1.120	1.120	0.000
2.5	22.5	1.130	1.025	0.105
5.0	20.0	1.090	0.885	0.205
7.5	17.5	1.030	0.730	0.300
10.0	15.0	1.010	0.620	0.390
12.5	12.5	0.985	0.550	0.435
15.0	10.0	0.835	0.450	0.385
17.5	7.5	0.620	0.320	0.300
20.0	5.0	0.433	0.235	0.198
22.5	2.5	0.210	0.115	0.095

Table 5.8

Concentration of uranyl acetate (c) = 2.0×10^{-4} M

Concentration of MTB (c') = 2.0×10^{-4} M

pH = 6.7 ± 0.1, λ = 510 nm, p = c'/c = 1

peak at 1:1 (Fig. 5.5 curve C)

0	25	0.720	0.720	0.000
2.5	22.5	0.726	0.666	0.060
5.0	20.0	0.705	0.575	0.130
7.5	17.5	0.695	0.500	0.195
10.0	15.0	0.668	0.420	0.248
12.5	12.5	0.640	0.360	0.280
15.0	10.0	0.530	0.280	0.250
17.5	7.5	0.402	0.196	0.206
20.0	5.0	0.280	0.150	0.130
22.5	2.5	0.130	0.065	0.065

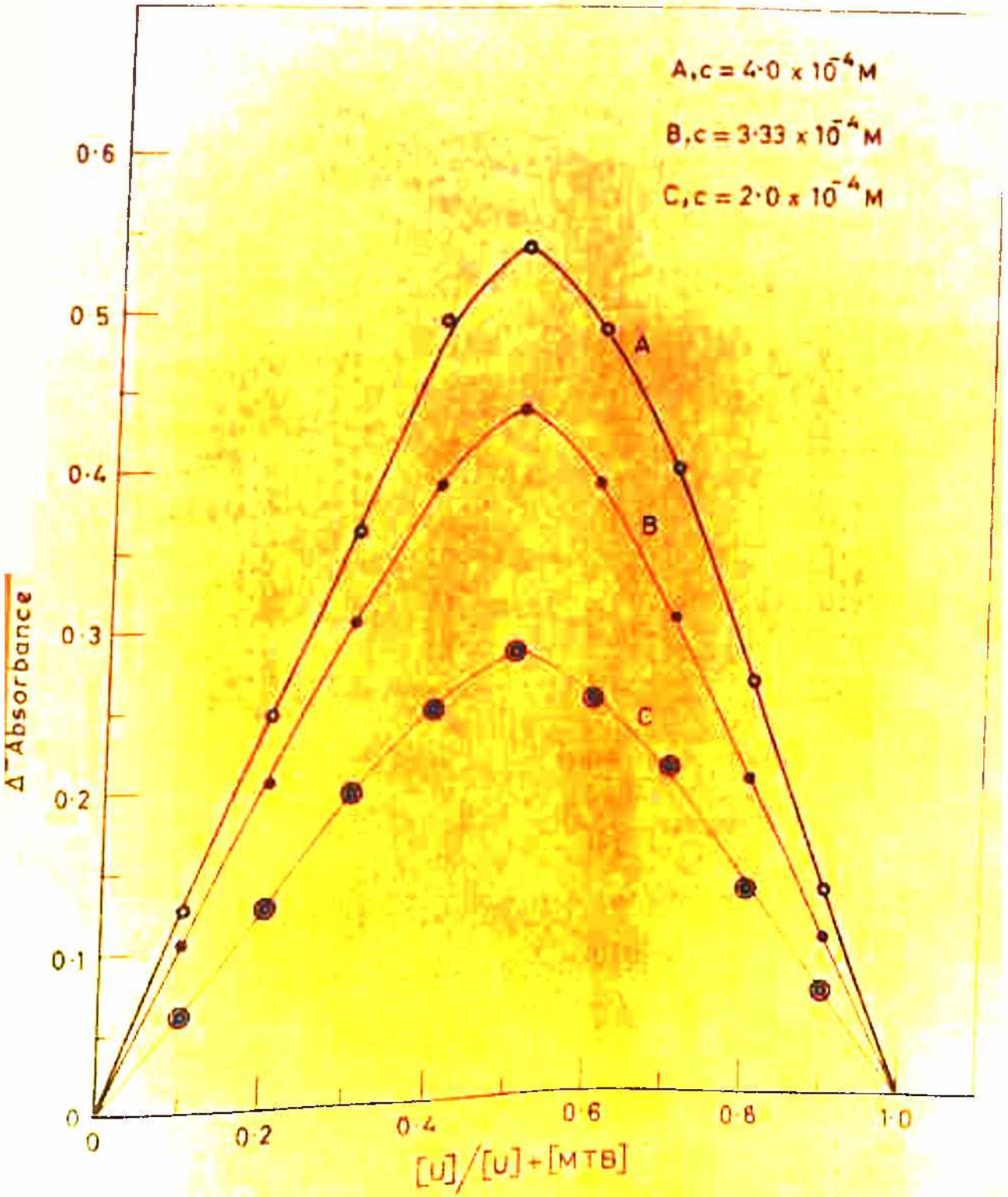


Fig._ 5·5 Continuous variation method at 510 nm ;
p=1; pH: 6·7±0·1; μ: 0·1 $NaClO_4$

Table 5.9

Concentration of uranyl acetate (c) = 1.60×10^{-4} M

Concentration of MTB (c') = 1.60×10^{-4} M

pH = 6.7 ± 0.1, λ = 510 nm, p = c'/c = 1

peak at 1:1 (Fig. 5.6 curve A)

Volume of uranyl acetate ml	Volume of MTB ml	Optical density of mixture (a)	Optical density of MTB (b)	Difference in optical density (a-b)
0	25	0.545	0.545	0.000
2.5	22.5	0.550	0.500	0.050
5.0	20.0	0.540	0.435	0.105
7.5	17.5	0.520	0.360	0.160
10.0	15.0	0.505	0.310	0.195
12.5	12.5	0.490	0.265	0.225
15.0	10.0	0.420	0.220	0.200
17.5	7.5	0.325	0.155	0.170
20.0	5.0	0.220	0.115	0.105
22.5	2.5	0.105	0.055	0.050

Table 5.10

Concentration of uranyl acetate (c) = 1.25×10^{-4} M

Concentration of MTB (c') = 1.25×10^{-4} M

pH = 6.7 ± 0.1, λ = 510 nm, p = c'/c = 1

peak at 1:1 (Fig. 5.6 curve B)

	25	0.390	0.390	0.000
0	22.5	0.395	0.355	0.040
2.5	20.0	0.390	0.305	0.085
5.0	17.5	0.385	0.255	0.130
7.5	15.0	0.375	0.225	0.150
10.0	12.5	0.360	0.185	0.175
12.5	10.0	0.315	0.160	0.155
15.0	7.5	0.245	0.120	0.125
17.5	5.0	0.165	0.080	0.085
20.0	2.5	0.080	0.045	0.035
22.5				

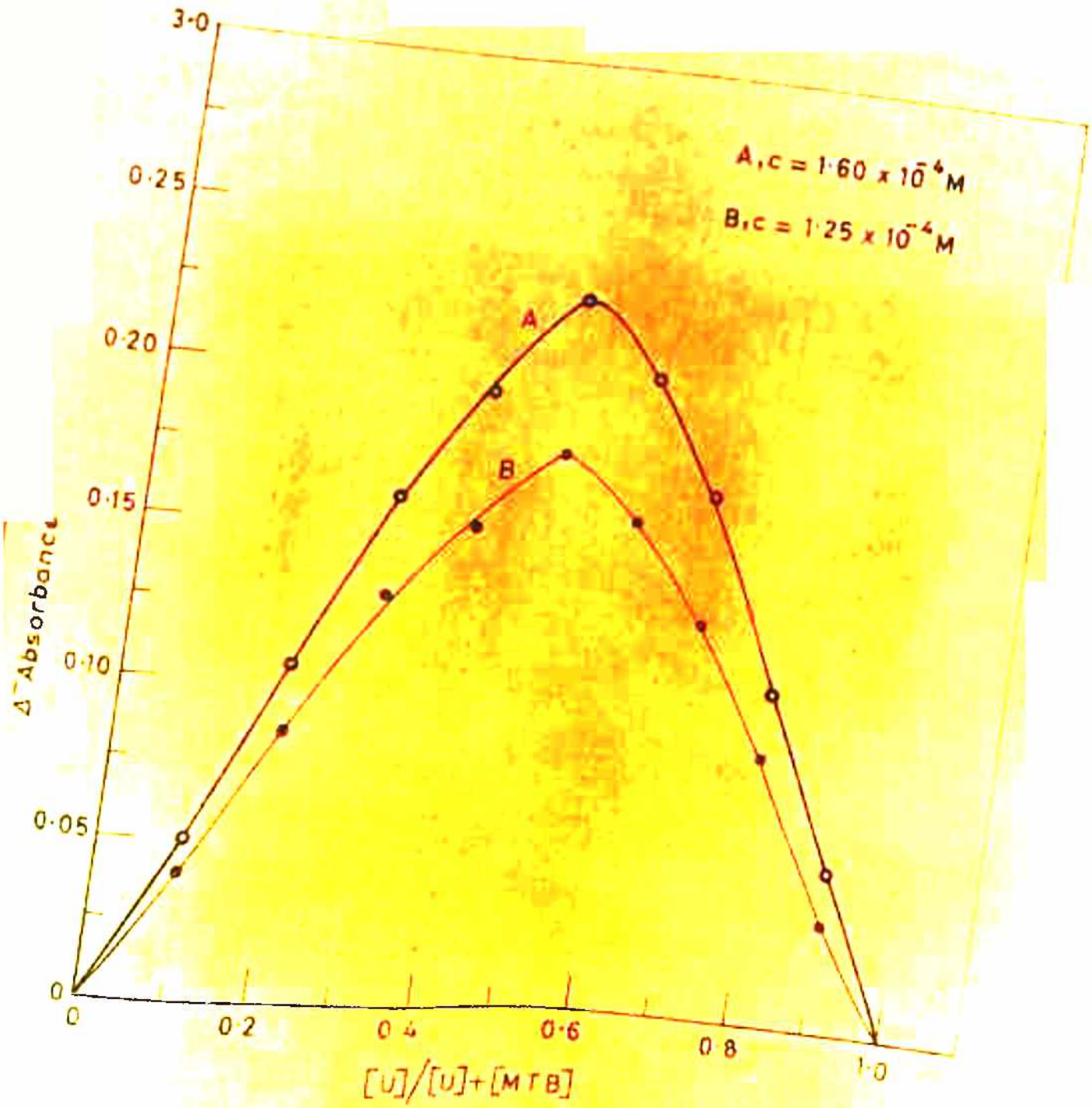


Fig._ 5·6 Continuous variation method at 510 nm; $p = 1$; pH: 6·7 ± 0·1; μ 0·1 $NaClO_4$

Table 5.11

Concentration of uranyl acetate (c) = 4.0×10^{-4} M

Concentration of MTB (c') = 4.0×10^{-4} M

pH = 6.7 ± 0.1, λ = 530 nm, p = c'/c = 1

peak at 1:1 (Fig. 5.7 curve A)

Volume of uranyl acetate ml	Volume of MTB ml	Optical density of mixture (a)	Optical density of MTB (b)	Difference in optical density (a-b)
0	25	1.165	1.165	0.000
2.5	22.5	1.175	1.075	0.100
5.0	20.0	1.098	0.900	0.198
7.5	17.5	1.060	0.780	0.280
10.0	15.0	1.030	0.680	0.350
12.5	12.5	0.980	0.575	0.405
15.0	10.0	0.800	0.445	0.355
17.5	7.5	0.600	0.310	0.290
20.0	5.0	0.425	0.205	0.220
22.5	2.5	0.240	0.110	0.130

Table 5.12

Concentration of uranyl acetate (c) = 3.33×10^{-4} M

Concentration of MTB (c') = 3.33×10^{-4} M

pH = 6.7 ± 0.1, λ = 530 nm, p = c'/c = 1

peak at 1:1 (Fig. 5.7 curve B)

0	25	0.970	0.970	0.000
2.5	22.5	0.980	0.895	0.085
5.0	20.0	0.910	0.750	0.160
7.5	17.5	0.875	0.650	0.225
10.0	15.0	0.855	0.570	0.285
12.5	12.5	0.795	0.480	0.315
15.0	10.0	0.640	0.370	0.270
17.5	7.5	0.480	0.260	0.220
20.0	5.0	0.330	0.170	0.160
22.5	2.5	0.200	0.105	0.095

Table 5.13

Concentration of uranyl acetate (c) = 2.0×10^{-4} M

Concentration of MTB (c') = 2.0×10^{-4} M

pH = 6.7 ± 0.1, λ = 530 nm, p = c'/c = 1

peak at 1:1 (Fig. 5.7 curve C)

Volume of uranyl acetate ml	Volume of MTB ml	Optical density of mixture (a)	Optical density of MTB (b)	Difference in optical density (a-b)
0	25	0.570	0.570	0.000
2.5	22.5	0.580	0.530	0.050
5.0	20.0	0.555	0.445	0.110
7.5	17.5	0.540	0.385	0.155
10.0	15.0	0.535	0.335	0.200
12.5	12.5	0.505	0.285	0.220
15.0	10.0	0.410	0.220	0.190
17.5	7.5	0.320	0.150	0.170
20.0	5.0	0.210	0.100	0.110
22.5	2.5	0.105	0.055	0.050

Table 5.14

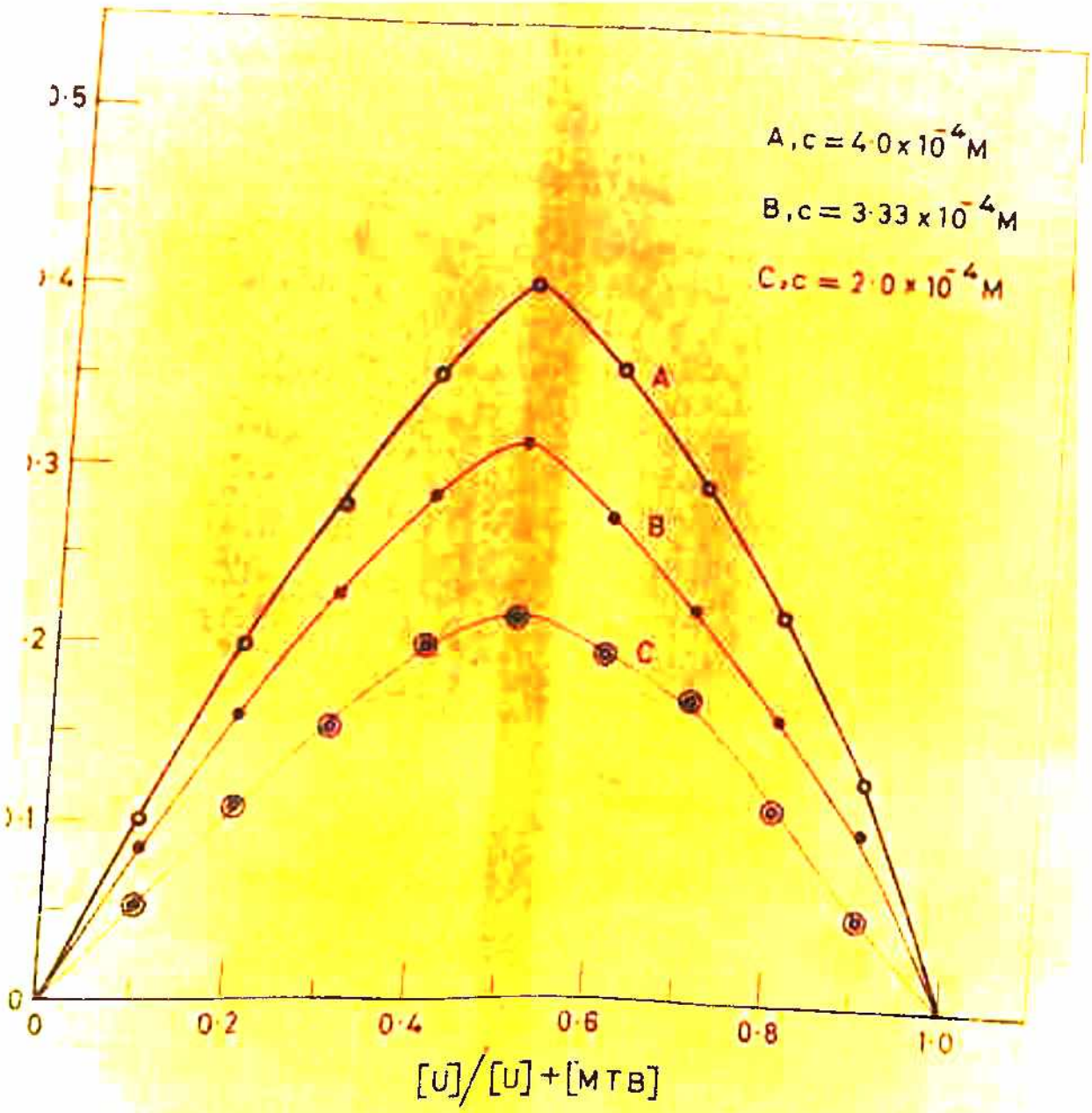
Concentration of uranyl acetate (c) = 4.0×10^{-4} M

Concentration of MTB (c') = 1.0×10^{-4} M

pH = 6.7 ± 0.1, λ = 510 nm, p = c'/c = 0.25

peak at 1:1 (Fig. 5.8 curve A)

	25	0.355	0.355	0.000
0	22.5	0.515	0.330	0.185
2.5	22.0	0.540	0.315	0.225
3.0	21.0	0.550	0.295	0.255
4.0	20.0	0.525	0.275	0.250
5.0	17.5	0.485	0.245	0.240
7.5	15.0	0.430	0.210	0.220
10.0	12.5	0.365	0.175	0.190
12.5	10.0	0.300	0.142	0.158
15.0	7.5	0.210	0.095	0.115
17.5	5.0	0.145	0.075	0.070
20.0	2.5	0.070	0.035	0.035
22.5				



1.— 5·7 Continuous variation method at 530 nm; p=1; pH: 6·7±0·1; μ: 0·1 $NaClO_4$

Table 5.15

Concentration of uranyl acetate (c) = 2.0×10^{-4} M

Concentration of MTB (c') = 1.0×10^{-4} M

pH = 6.7 ± 0.1, λ = 510 nm, p = c'/c = 0.5

peak aat (Fig. 5.8 curve B)

Volume of uranyl acetate ml	Volume of MTB ml	Optical density of mixture (a)	Optical density of MTB (b)	Difference in optical density (a-b)
0	25	0.355	0.355	0.000
2.5	22.5	0.420	0.330	0.090
5.0	20.0	0.440	0.275	0.165
7.0	18.0	0.445	0.250	0.195
7.5	17.5	0.450	0.245	0.205
9.0	16.0	0.415	0.220	0.195
10.0	15.0	0.398	0.210	0.188
12.5	12.5	0.335	0.175	0.160
15.0	10.0	0.272	0.142	0.130
17.5	7.5	0.190	0.095	0.095
20.0	5.0	0.140	0.075	0.065
22.5	2.5	0.070	0.035	0.035

Table 5.16

Concentration of uranyl acetate (c) = 1.66×10^{-4} M

Concentration of MTB (c') = 2.50×10^{-4} M

pH = 6.7 ± 0.1, λ = 510 nm, p = c'/c = 1.5

peak at 1:1 (Fig. 5.8 curve C)

0	25	0.860	0.860	0.000
2.5	22.5	0.880	0.800	0.080
5.0	20.0	0.835	0.690	0.145
7.5	17.5	0.825	0.630	0.195
10.0	15.0	0.735	0.505	0.230
12.5	12.5	0.685	0.430	0.255
14.0	11.0	0.635	0.370	0.265
14.5	10.5	0.625	0.355	0.270
15.0	10.0	0.603	0.335	0.268
16.0	9.0	0.555	0.295	0.260
17.5	7.5	0.485	0.240	0.245
20.0	5.0	0.350	0.180	0.170
22.5	2.5	0.165	0.080	0.085

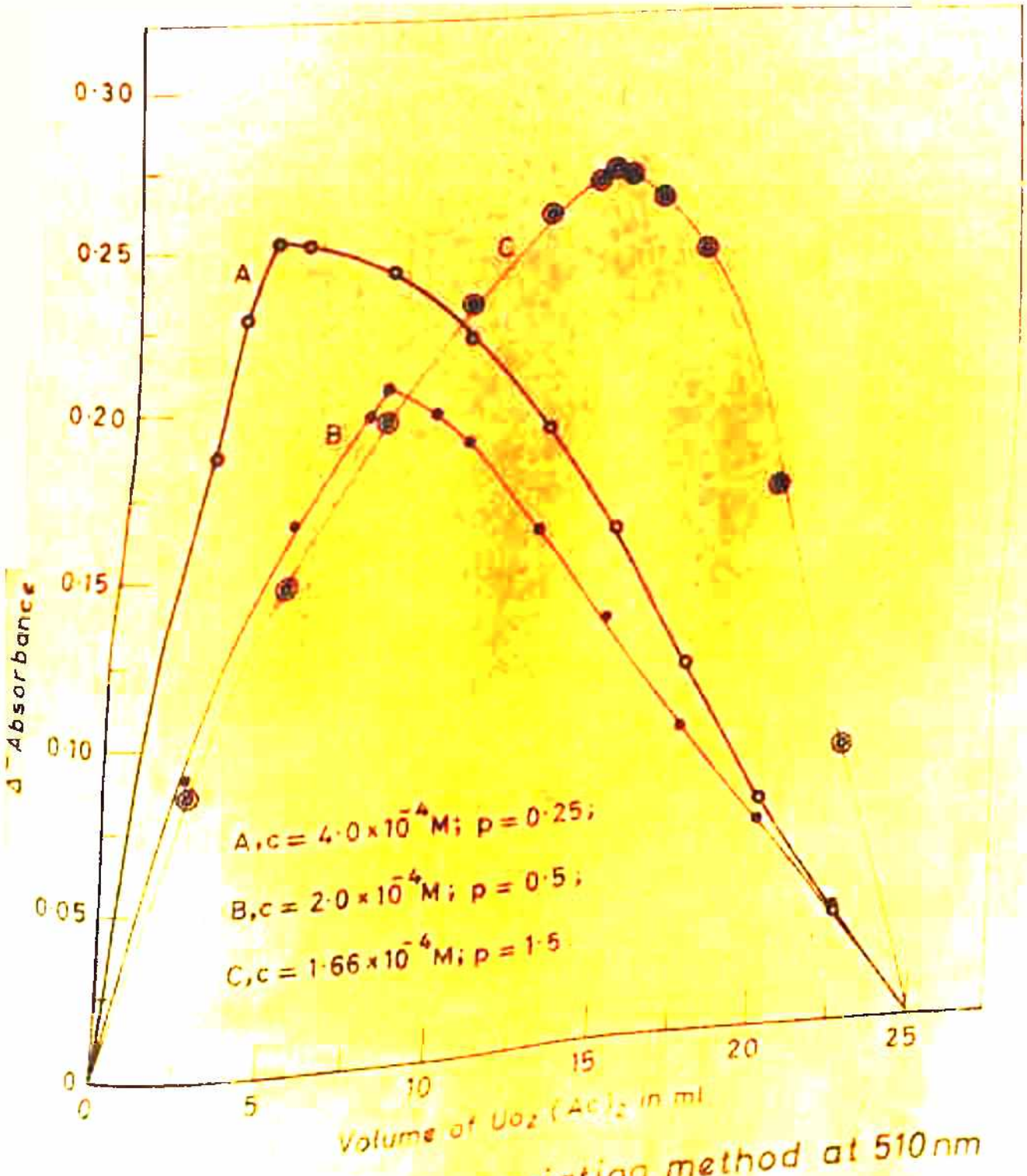


Fig._ 5·8 Continuous variation method at 510 nm

pH 6·7 ± 0·1; μ - 0·1 Na ClO4

Table 5.17

Concentration of uranyl acetate (c) = 4.0×10^{-4} M

Concentration of MTB (c') = 1.0×10^{-4} M

pH = 6.7 ± 0.1, λ = 530 nm, p = c'/c = 0.25

peak at 1:1 (Fig. 5.9 curve A)

Volume of uranyl acetate ml	Volume of MTB ml	Optical density of mixture (a)	Optical density of MTB (b)	Difference in optical density (a-b)
0	25	0.280	0.280	0.000
2.5	22.5	0.415	0.260	0.155
3.0	22.0	0.440	0.255	0.185
4.0	21.0	0.466	0.240	0.226
5.0	20.0	0.450	0.225	0.225
7.5	17.5	0.405	0.190	0.215
10.0	15.0	0.355	0.165	0.190
12.5	12.5	0.300	0.140	0.160
15.0	10.0	0.240	0.110	0.130
17.5	7.5	0.170	0.075	0.095
20.0	5.0	0.120	0.055	0.065
22.5	2.5	0.058	0.030	0.028

Table 5.18

Concentration of uranyl acetate (c) = 2.0×10^{-4} M

Concentration of MTB (c') = 1.0×10^{-4} M

pH = 6.7 ± 0.1, λ = 530 nm, p = c'/c = 0.5

peak at 1:1 (Fig. 5.9 curve B)

0	25	0.280	0.280	0.000
2.5	22.5	0.340	0.260	0.080
5.0	20.0	0.350	0.215	0.135
7.0	18.0	0.352	0.192	0.160
7.5	17.5	0.355	0.190	0.165
9.0	16.0	0.333	0.178	0.155
10.0	15.0	0.310	0.165	0.145
12.5	12.5	0.265	0.140	0.125
15.0	10.0	0.210	0.110	0.100
17.5	7.5	0.153	0.075	0.078
20.0	5.0	0.110	0.055	0.055
22.5	2.5	0.055	0.030	0.025

Table 5.19

Concentration of uranyl acetate (c) = 1.66×10^{-4} M

Concentration of MTB (c') = 2.50×10^{-4} M

pH of mixtures = 6.7 ± 0.1

λ = 530 nm

$p = c'/c$ = 1.5

peak at 1:1 (Fig. 5.9 curve C)

Volume of uranyl acetate ml	Volume of MTB ml	Optical density of mixture (a)	Optical density of MTB (b)	Difference in optical density (a-b)
0	25	0.710	0.710	0.000
2.5	22.5	0.725	0.660	0.065
5.0	20.0	0.675	0.550	0.120
7.5	17.5	0.640	0.480	0.160
10.0	15.0	0.615	0.420	0.195
12.5	12.5	0.575	0.355	0.220
14.0	11.0	0.535	0.305	0.230
14.5	10.5	0.525	0.290	0.235
15.0	10.0	0.507	0.275	0.232
16.0	9.0	0.480	0.255	0.225
17.5	7.5	0.395	0.190	0.205
20.0	5.0	0.273	0.125	0.148
22.5	2.5	0.132	0.065	0.067

Mole ratio method

The mole ratio of uranium to reagent was confirmed by the mole ratio method (85) at pH 6.7 ± 0.1. In this work each solution was 1×10^{-4} M in the total concentration of methylthymol blue. The results are shown in table 5.20, fig. 5.10 which indicates that 1:1 complex is formed between uranium and the reagent.

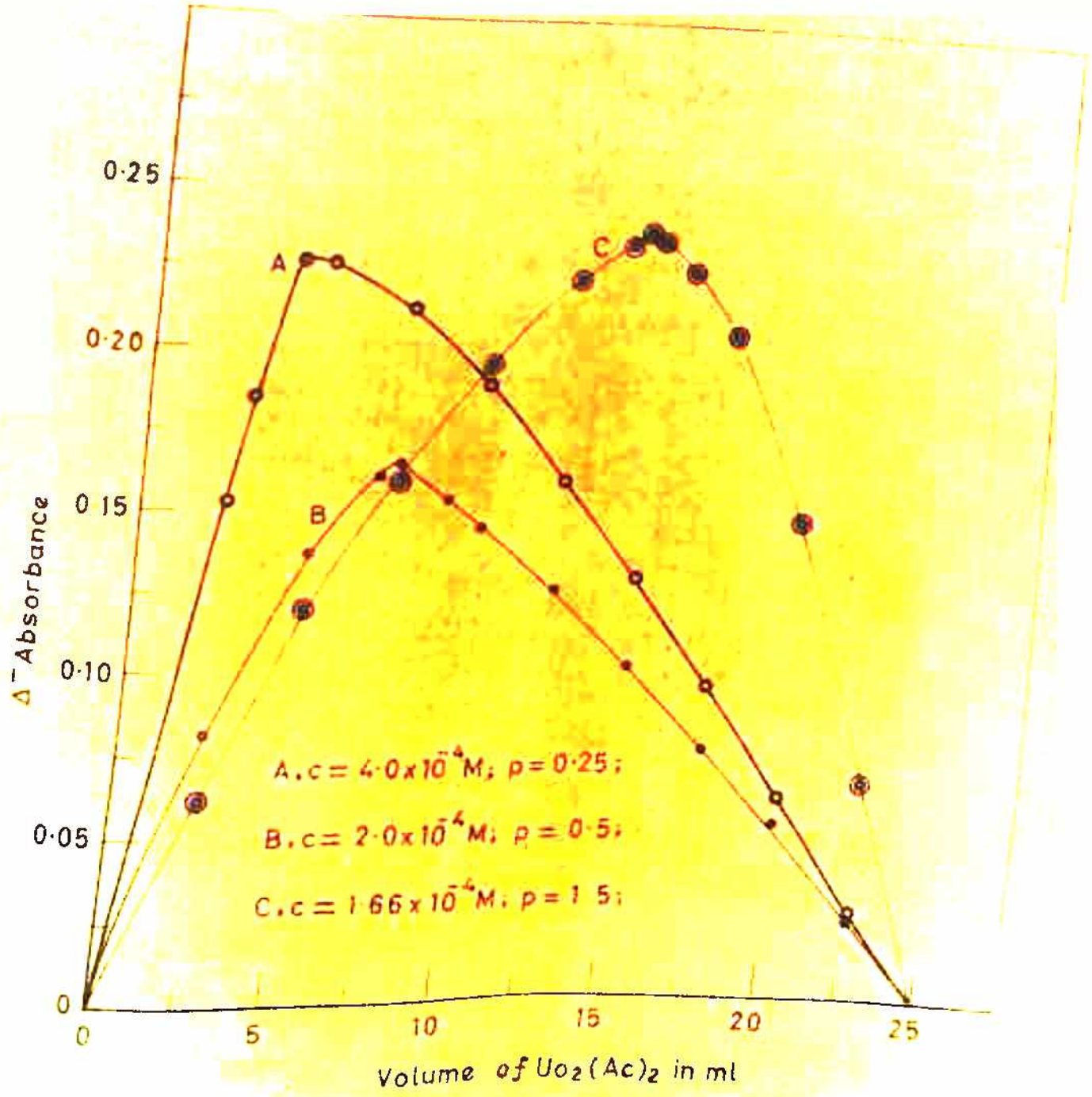


Fig._ 5·9 Continuous variation method at 530 nm;
pH: 6·7±0·1; μ: 0·1 $NaClO_4$

Table 5.20

Concentration of uranyl acetate = 1.0×10^{-3} M

Concentration of MTB = 1.0×10^{-3} M

pH = 6.7 ± 0.1

Total volume made up = 25 ml

Break at 1:1 (Fig. 5.10 curve A and B)

Volume of uranyl acetate ml	Volume of MTB ml	Ratio U : MTB	Optical density of mixture 510 nm	Optical density of mixture 530 nm
0.25	2.50	0.1 : 1.0	0.375	0.365
0.75	2.50	0.3 : 1.0	0.440	0.410
1.25	2.50	0.5 : 1.0	0.500	0.450
1.75	2.50	0.7 : 1.0	0.552	0.490
2.00	2.50	0.8 : 1.0	0.580	0.505
2.25	2.50	0.9 : 1.0	0.625	0.525
2.50	2.50	1.0 : 1.0	0.650	0.540
3.00	2.50	1.2 : 1.0	0.665	0.560
3.75	2.50	1.5 : 1.0	0.690	0.580
5.00	2.50	2.0 : 1.0	0.720	0.605
6.25	2.50	2.5 : 1.0	0.740	0.620
7.50	2.50	3.0 : 1.0	0.760	0.630
10.00	2.50	4.0 : 1.0	0.770	0.640
12.50	2.50	5.0 : 1.0	0.770	0.650
15.00	2.50	6.0 : 1.0	0.770	0.650

Slope ratio method (31)

The concentration of the variable component was 5.0×10^{-4} M. The volume of the variable component was from 1 to 12.5 ml in the presence of 12.5 ml of excess concentration 2.0×10^{-4} M of the constant component. The total volume in each was kept at 25 ml. The pH of the solution was maintained at 6.7 ± 0.1. The absorbance was noted at 510 and 530 nm. Figure 5.11 shows the measured absorbance at 510 and 530 nm plotted against the volume of the variable component. The slopes of

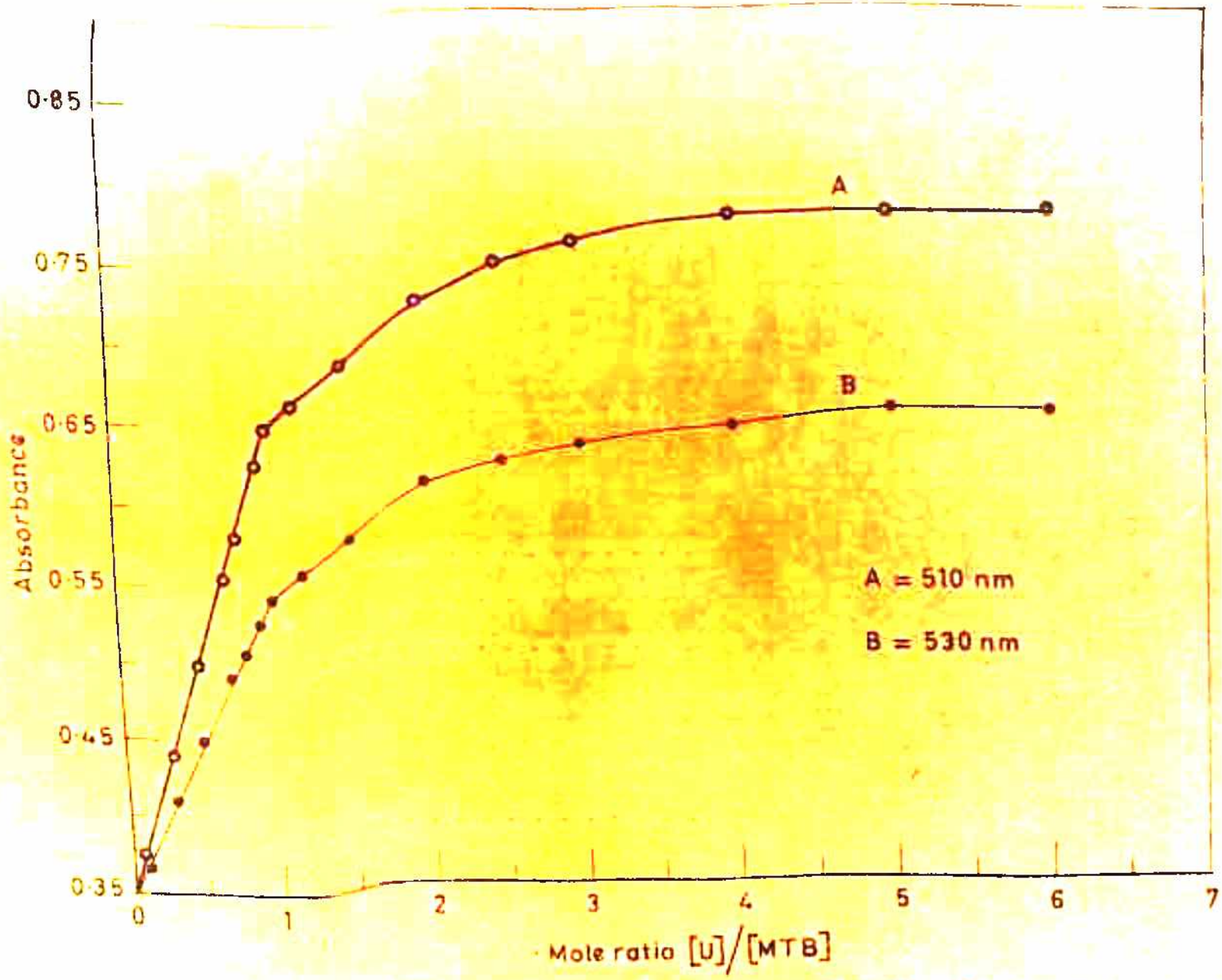


Fig. 5·10 Mole ratio method at pH 6·7±0·1; μ: 0·1 $NaClO_4$; MTB: $1·0 \times 10^{-4}$ M

the two straight lines in each case gave the uranium methylthymol blue ratio as 1:1. Some typical results are given in table 5.21 and 5.22.

Table 5.21

Concentration of excess component (MTB) = 2.0×10^{-4} M

Volume of excess component (MTB) = 12.5 ml

Concentration of variable component (uranyl acetate) = 5.0×10^{-5} M

pH of mixtures = 6.7 ± 0.1

Total volume = 25 ml

Volume of variable component (uranyl acetate)	Optical density at	
	510 nm	530 nm
1.0	0.305	0.222
2.0	0.310	0.230
3.0	0.320	0.235
4.0	0.328	0.238
5.0	0.334	0.248
6.0	0.340	0.255
7.0	0.350	0.260
8.0	0.352	0.265
9.0	0.362	0.272
10.0	0.370	0.280
11.0	0.378	0.285
12.0	0.385	0.290
12.5	0.390	0.290

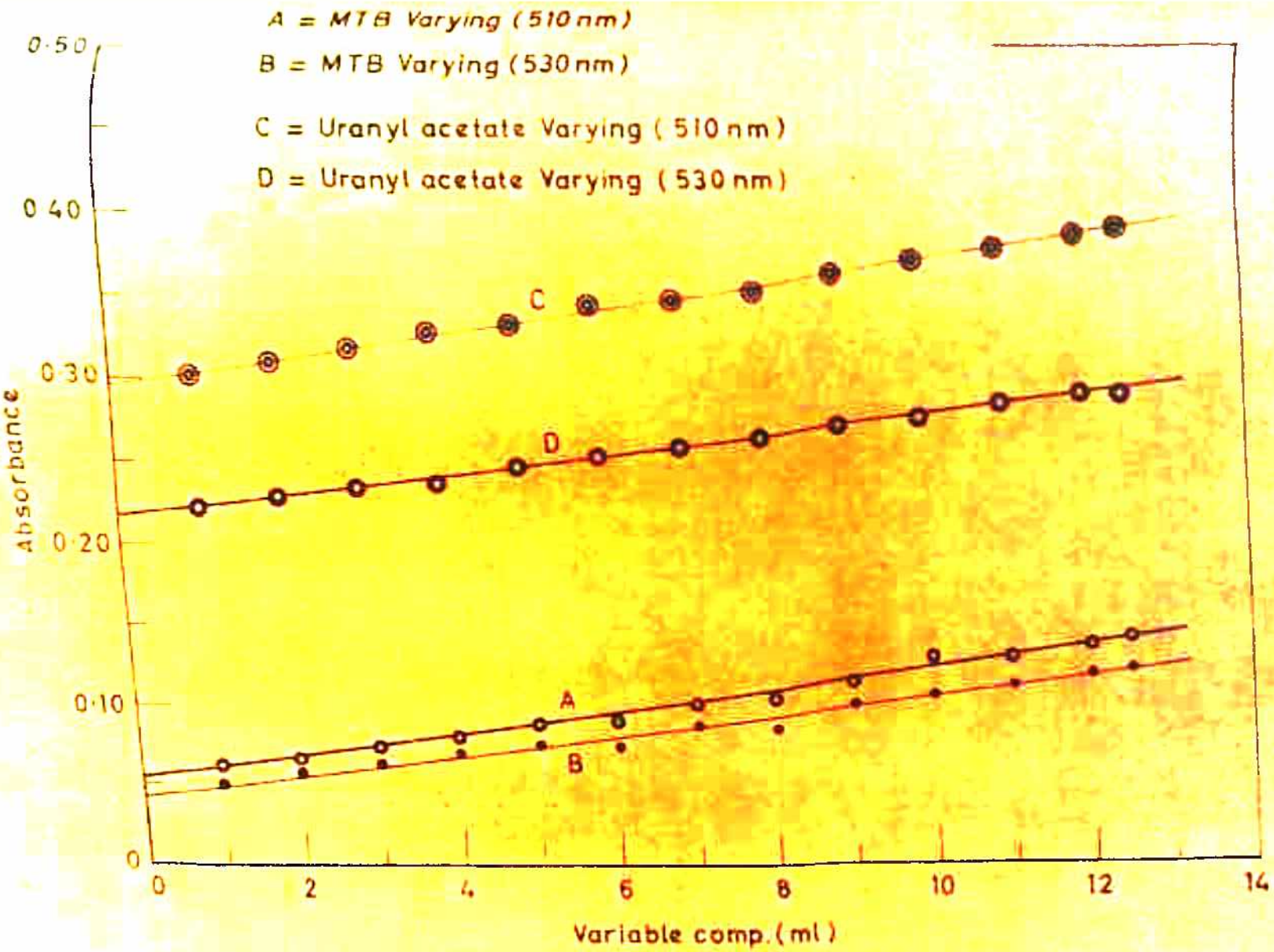


Fig. 5-11 The slop ratioemethod; pH: 6·7 ± 0·1; μ: 0·1 $NaClO_4$; $2{\cdot}0 \times 10^{-4}$ M excess component (12·5 ml) + $5{\cdot}0 \times 10^{-5}$ M variable component (x ml) + water ([12·5 − x] ml)

Table 5.22

Concentration of excess component (uranyl acetate) = 2.0×10^{-4} M

Volume of excess component (uranyl acetate) = 12.5 ml

Concentration of variable component (MTB) = 5.0×10^{-5} M

pH of mixtures = 6.7 ± 0.1

Total volume = 25 ml

Volume of variable component (MTB)	Optical density at	
	510 nm	530 nm
1.0	0.062	0.050
2.0	0.068	0.060
3.0	0.075	0.065
4.0	0.080	0.070
5.0	0.090	0.075
6.0	0.092	0.076
7.0	0.100	0.088
8.0	0.106	0.088
9.0	0.115	0.100
10.0	0.130	0.105
11.0	0.130	0.110
12.0	0.138	0.120
12.5	0.140	0.125

Calculation of the Stability Constant

The conditional stability constants were calculated by three different methods namely (a) the method of Dey and Coworkers (b) the method of continuous variation using non-equimolecular solutions and (c) the method of mole ratio.

For the calculation of K by method (a) concentrations of the metal ions used are shown in table 5.23 (p=1), Fig. 5.12. For method (b) the concentrations and the volume of the metal

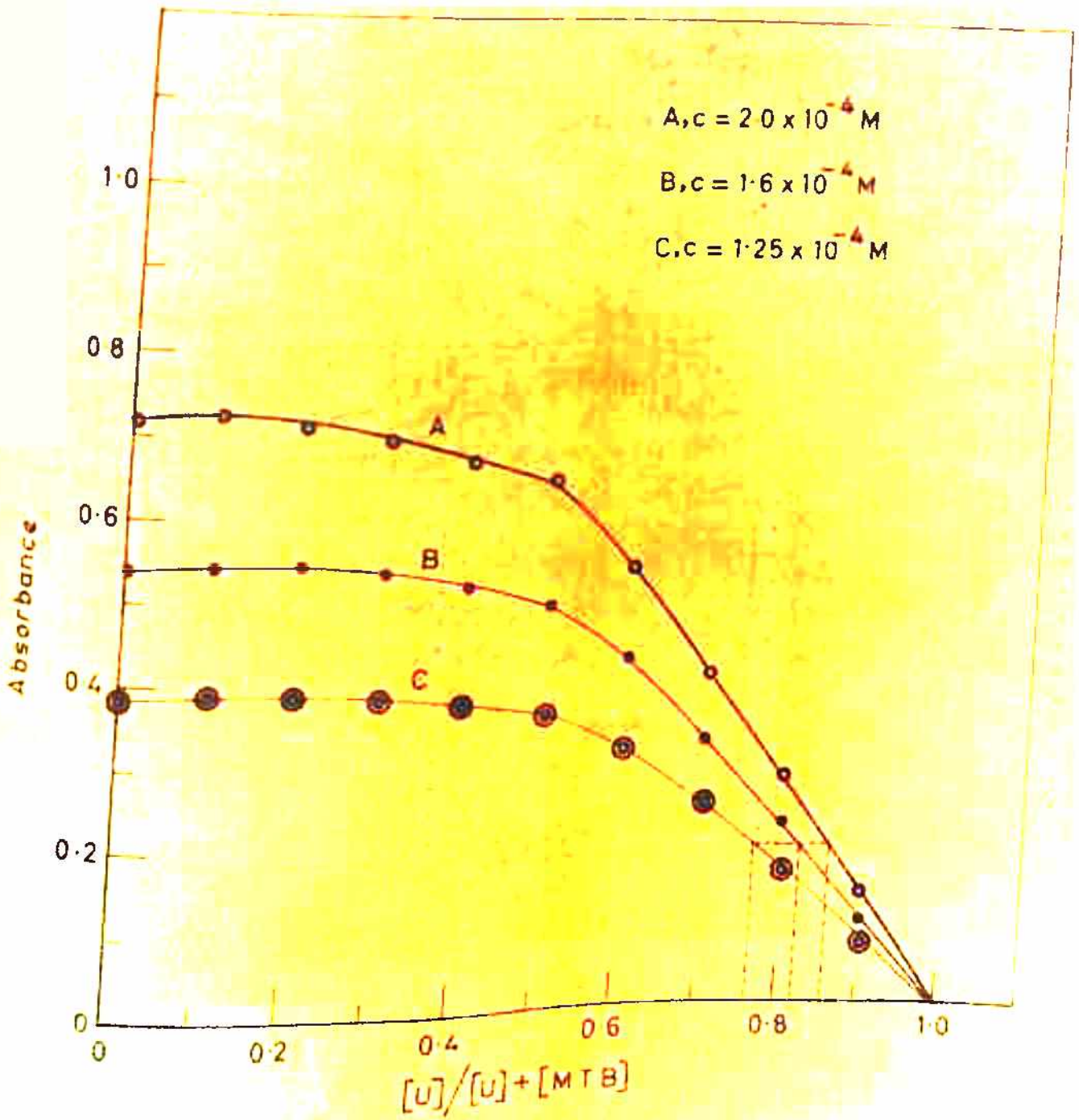


Fig._ 5·12 Determination of the Stability constant from absorbance data at 510 nm; p = 1; pH: 6·7 ± 0·1; μ: 0·1 $NaClO_4$

ion used at the peak are shown in table 5.24 (Fig. 5.8).

Table 5.23

Fig.	Curve	c x 10^4M	p	K
5.12	A	2.0	1.0	4.70 x 10^5
	B	1.6	1.0	4.5 x 10^5
	C	1.25	1.0	2.25 x 10^5

Table 5.24

Fig.	Curve	c 10^4M	p	Vol. of metal ion used at the peak	K
5.8	A	4.0	0.25	4.0	5.12 x 10^5
	B	2.0	0.50	7.5	4.0 x 10^5
	C	1.66	1.50	14.5	1.92 x 10^5

For calculation of K by method (c), the concentration, Em, Es and α are shown in table 5.25 (Fig. 5.10).

Table 5.25

Fig.	Curve	10^4c(M)	Em	Es	α	K
5.10	A	1.0	0.760	0.650	0.144	4.2 x 10^5
	B	1.0	0.630	0.540	0.142	4.2 x 10^5

Suggestions on the Structure of the Chelate:

It is not possible to derive a definite information, on the basis of the experimental results mentioned above, regarding the structure of the chelate excepting that the ion exchange adsorption studies show that the chelate of uranium is neutral.

ANALYTICAL APPLICATIONS

The effect of anions and complexing agents:

The results of examination of the influence of various anions and some complexing agents have been represented in table 5.26 Chloride, nitrate, and sulphate ions do not interfere, even at high concentration. Phosphate, fluoride, tartrate and citrate give negative errors at higher concentrations. Oxalate, NTA and EDTA interfere with the colour reaction because they form more stable complexes with uranium than methylthymol blue.

Table 5.26

Effect of Anions and Complexing Agents

Uranium taken = 94 µg

Anion or complexing agent added, µ mol		Uranium found	Deviation µg
Cl^-	200	94	± 0.0
	500	94.5	+ 0.5

contd.

Table 5.26 contd.

Anion or complexing agent added, μ mol		Uranium found	Deviation μg
F^-	1	92.6	- 1.4
	5	89	- 5.0
NO_3^-	100	94	± 0.0
	200	94.5	+ 0.5
SO_4^{2-}	100	94.5	+ 0.5
	250	94	± 0.0
$C_2O_4^{2-}$	5	91	- 3.0
	20	85	- 9.0
$C_4H_4O_6^{2-}$	5	91	- 3.0
	10	89	- 5.0
PO_4^{3-}	5	83	-11.0
	10	74	-20.0
$C_6H_5O_7^{3-}$	0.2	92.5	- 1.5
	1.0	88.5	- 5.5
NTA	0.5	93.5	- 0.5
	2.5	84	-10.0
EDTA	0.01	88	- 6.0
	0.05	59	-35.0

The Effect of Cations:- Methylthymol blue is a selective agent for certain cations when it is used in a relatively strong medium. However, in a slightly acid or neutral medium it reacts with many metal cations to give red or reddish violet complexes, indicating that a suitable masking agent must be used to increase the selectivity.

Of the 25 cations tested, Aluminium(III), Bismuth(III), Chromium(III), Copper(II), Iron(III), Palladium(II), Thorium(IV), Titanium(IV), Vanadium(V), Zirconium(IV), Gallium(III), Yttrium(III), Lanthanum(III) disturb the estimation. The interfering bivalent cations can be effectively masked by EDTA. The interference of Iron(III) can be eleminated by the addition of reducing agent such as ascorbic acid.

The Standard Procedure for the Determination

An aliquot of the standard uranium solution was introduced into a 25 ml volumetric flask. 2.5 ml of a pH 6.7 buffer, 1.0 ml of a 1 x 10^{-3}M methylthymol blue solution and the volume was adjusted to 25 ml by addition of distilled water and was allowed to stand for about 30 minutes to attain equilibrium. The absorbance of the solution was measured against a reagent blank at 510 nm.

D I S C U S S I O N

For obtaining a purified sample of methylthymol blue suitable for photometric analysis, the mono substituted

product of the reaction, semimethylthymol blue was separated using cellulose and ion exchange columns. The Rf value of the penta sodium salt of methylthymol blue was found to be 0.05 - 0.15. The molar absorptivity of the purified sample at λ_{max}, 436 nm was found to be 1.88 + 0.02 x 10^4 at pH 5.0.

The reagent is a dye consisting of Na^+ ions as cations and an anion of high molecular weight. Such dyes do not behave as true electrolytes. Hence a study of the aqueous solution of the reagent was undertaken and it was found that methylthymol blue (penta sodium salt) behaves as a colloidal electrolyte. The temperature of zero conductance lies at -16.5^o and the temperature coefficient per degree centigrade per hundred of the conductance at 35^oC provides values between 1.35 and 1.95; hence extremely dilute solutions of the order of $10^{-4}M$ were employed in these investigations.

During preliminary studies it was noted in table 5.3 that methylthymol blue forms a red complex in aqueous solution with uranium(VI).

In the present investigation the composition, stability and optimum conditions for the photometric determination of uranium(VI) with methylthymol blue as a chromogenic agent have been studied in detail using spectrophotometric method.

The composition of the uranium methylthymol blue complex as determined by the methods of (1) continuous

variation (tables 5.6 to 5.19, figures 5.5 to 5.9) (2) mole ratio method (table 5.20, figure 5.10) and (3) slope ratio method (table 5.21 to 5.22, figure 5.11) indicate that only one uranium methylthymol blue complex is formed and that the mole ratio of methylthymol blue to uranium in this complex is 1:1.

The stability constants have been calculated using the method of (a) Dey and Coworkers (b) continuous variation method and (c) mole ratio method. The results are shown in table 5.27. The free energy change of formation has also been calculated with the help of the expression.

$$\Delta G^{o} = -RT\ln k$$

Table 5.27

Method	pH	ionic strength	log K	ΔG^{o} at 30° (K cal)
(a) Dey and Coworkers	6.7 ± 0.1	0.1 M ($NaClO_4$)	5.6 ± 0.1	-7.7 ± 0.1
(b) Continuous variation	6.7 ± 0.1	0.1 M ($NaClO_4$)	5.5 ± 0.2	-7.6 ± 0.2
(c) Mole ratio	6.7 ± 0.1	0.1 M ($NaClO_4$)	5.7 ± 0.2	-7.9 ± 0.2

Methylthymol blue has been proposed for the spectrophotometric determination of uranium (70a). A red complex, whose net molar absorptivity is 10,625 at 510 nm is

formed. Beer's law is obeyed within the limits of 0.4 and 3.76 ppm. The effects of pH, reagent concentration and interfering ions are described.

VANADIUM (V) - METHYLTHYMOL BLUE SYSTEM

Methylthymol blue (MTB) has been used as a metallochromic indicator and a reagent for the photometric determination of various metals, but the composition and stability of its coloured chelates have not yet been reported upon. It forms very stable coloured chelates in solution with a large number of metal ions under appropriate conditions. This investigation deals with the composition and stability of vanadium-methylthymol blue chelates and indicates the possibilities of analytical applications.

EXPERIMENTAL

Reagents

Vanadium (V) solution: A 0.001M solution was prepared by dissolving the requisite amounts of ammonium vanadate (Merck) in double distilled water. The strength of the solution was chekced by titration with a standard iron (II) solution.

Methylthymol Blue Solution: An aqueous 0.001 M solution was prepared from purified Eastman methylthymol blue (penta sodium salt).

Ionic Strength:- All investigations were carried out at a constant ionic strength of 0.1 M, maintained by addition of the required amount of 1 M $NaClO_4$ solution.

Buffer Solution:- A hexamine perchloric acid mixture was prepared by dissolving 4 gm of hexamine in water and by adding a perchloric acid solution in order to bring the pH to a desired value and making up the solution to 100 ml.

Behaviour of the reagent as a colloidal electrolyte

Methylthymol blue (penta sodium salt) was found to behave as a colloidal electrolyte; hence extremely dilute solutions of the order of 10^{-4} M were employed in these investigations, and compositions determined under these conditions adhering to the true stoichiometric ratios.

Absorption Curves

When aqueous solution of vanadium(V) is mixed with methylthymol blue solution a blue complex is formed at pH 4.0 with excess of metal ions while a red complex is formed at pH 6.0 with excess of MTB. Figure 5.13 and 5.14 show the absorption curves of methylthymol blue and its vanadium(V) complex. The absorption curves obtained with a regent blank has an absorption maximum at 590 and 520 nm, respectively. Some of the typical results are given in table 5.28 and 5.29.

Table 5.28

Concentration of Ammonium Vanadate = 8.0×10^{-5} M

Concentration of Methylthymol blue = 4.0×10^{-5} M

pH of solutions = 4.5

Wavelength nm	Optical density of complex (A)	Optical density of MTB (B)	Difference A - B = C
400	0.288	0.324	-
410	0.276	0.360	-
420	0.265	0.385	-
430	0.254	0.390	-
440	0.235	0.380	-
450	0.220	0.350	-
460	0.220	0.306	-
470	0.224	0.258	-
480	0.236	0.212	0.024
490	0.246	0.166	0.080
500	0.265	0.135	0.130
510	0.300	0.105	0.195
520	0.330	0.080	0.250
530	0.365	0.065	0.300
540	0.410	0.060	0.350
550	0.480	0.055	0.425
560	0.530	0.050	0.480
570	0.635	0.045	0.590
580	0.745	0.040	0.705
590	0.800	0.035	0.765
600	0.780	0.030	0.750
610	0.675	0.025	0.650
620	0.505	0.020	0.485
630	0.310	0.010	0.300
640	0.200	0.000	0.200
650	0.110	0.000	0.105
660	0.055	0.000	0.050
670	0.028	0.000	0.025
680	0.020	0.000	0.020

Table 5.29

Concentration of Ammonium Vanadate = 4.0×10^{-5} M

Concentration of MTB = 3.2×10^{-4} M

pH of solutions = 6.5

400	2.050	2.250	-
410	2.160	2.360	-

Table 5.29 contd.

Wavelength nm	Optical density of Complex (A)	Optical density of MTB (B)	Difference A - B = C
420	2.300	2.520	-
430	2.380	2.620	-
440	2.460	2.600	-
450	2.390	2.420	-
460	2.300	2.100	0.200
470	2.200	1.900	0.300
480	2.080	1.680	0.400
490	1.940	1.520	0.420
500	1.840	1.300	0.540
510	1.680	1.080	0.600
520	1.520	0.900	0.620
530	1.400	0.800	0.600
540	1.300	0.780	0.520
550	1.220	0.780	0.440
560	1.135	0.800	0.335
570	1.050	0.840	0.210
580	1.000	0.870	0.130
590	0.900	0.820	0.080
600	0.780	0.760	0.020
610	0.600	0.600	0.000
620	0.400	0.400	0.000

Effect of pH

Measurements at different pH values indicate that the blue complex shows maximum absorbance in pH range 4.0 - 4.7 and the red complex between 6.0 and 6.5, λ_{max}, remaining constant within these ranges of pH. The results are given in table 5.30 to 5.31 and represented in figures 5.15 to 5.16.

Table 5.30

Concentration of Ammonium Vanadate = 8.0×10^{-5} M
Concentration of Methylthymol blue = 4.0×10^{-5} M

pH	3.5	4.0	4.5	4.7	5.0
Optical density per cm (590 nm)	0.650	0.765	0.765	0.765	0.644

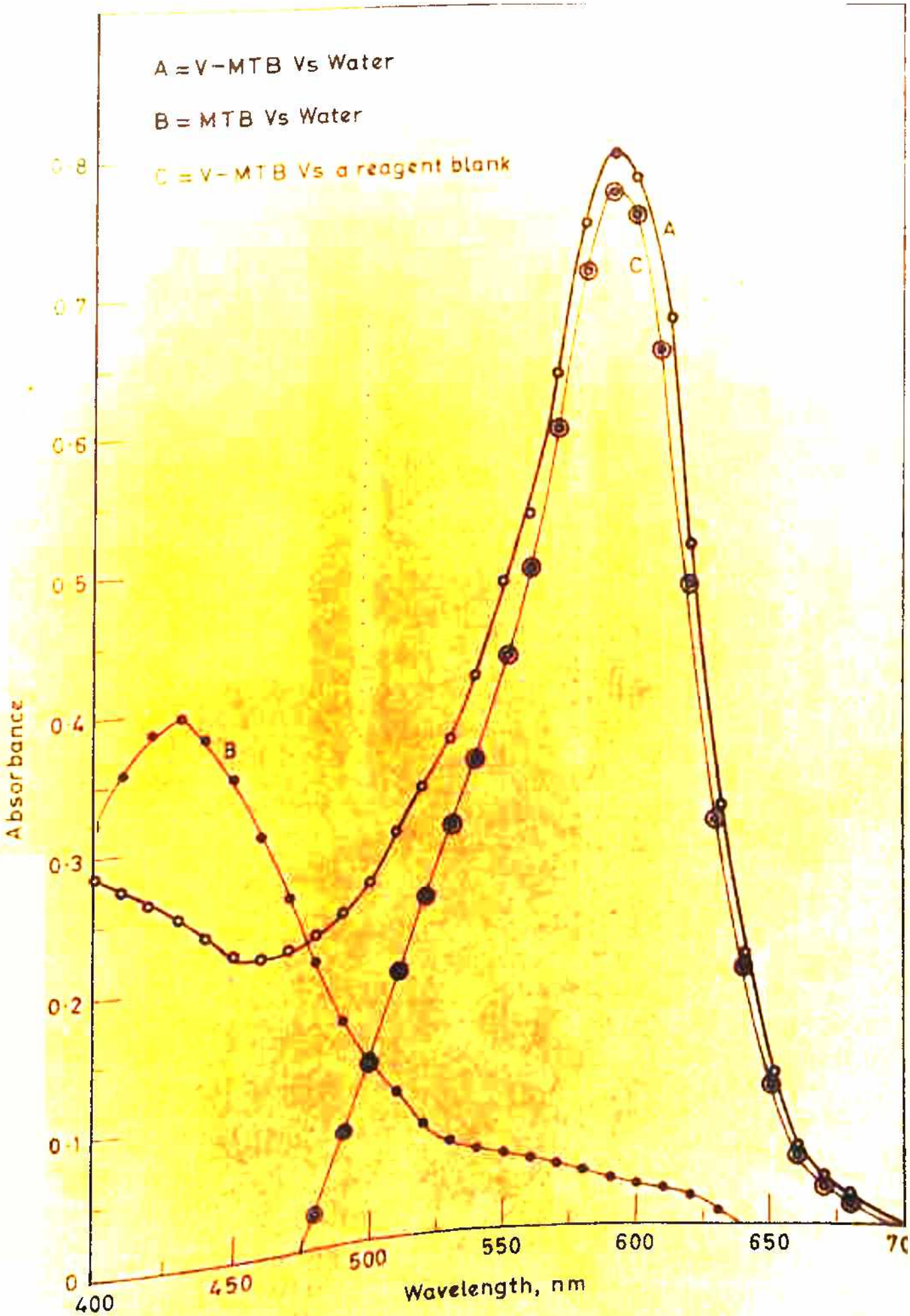


Fig._ 5·13 Absorption curves of Methylthymol blue and its vanadium complex at pH: 4·5 ; μ: 0·1 $NaClO_4$; vanadium · $8·0 \times 10^{-5}$ M ; MTB: $4·0 \times 10^{-5}$ M

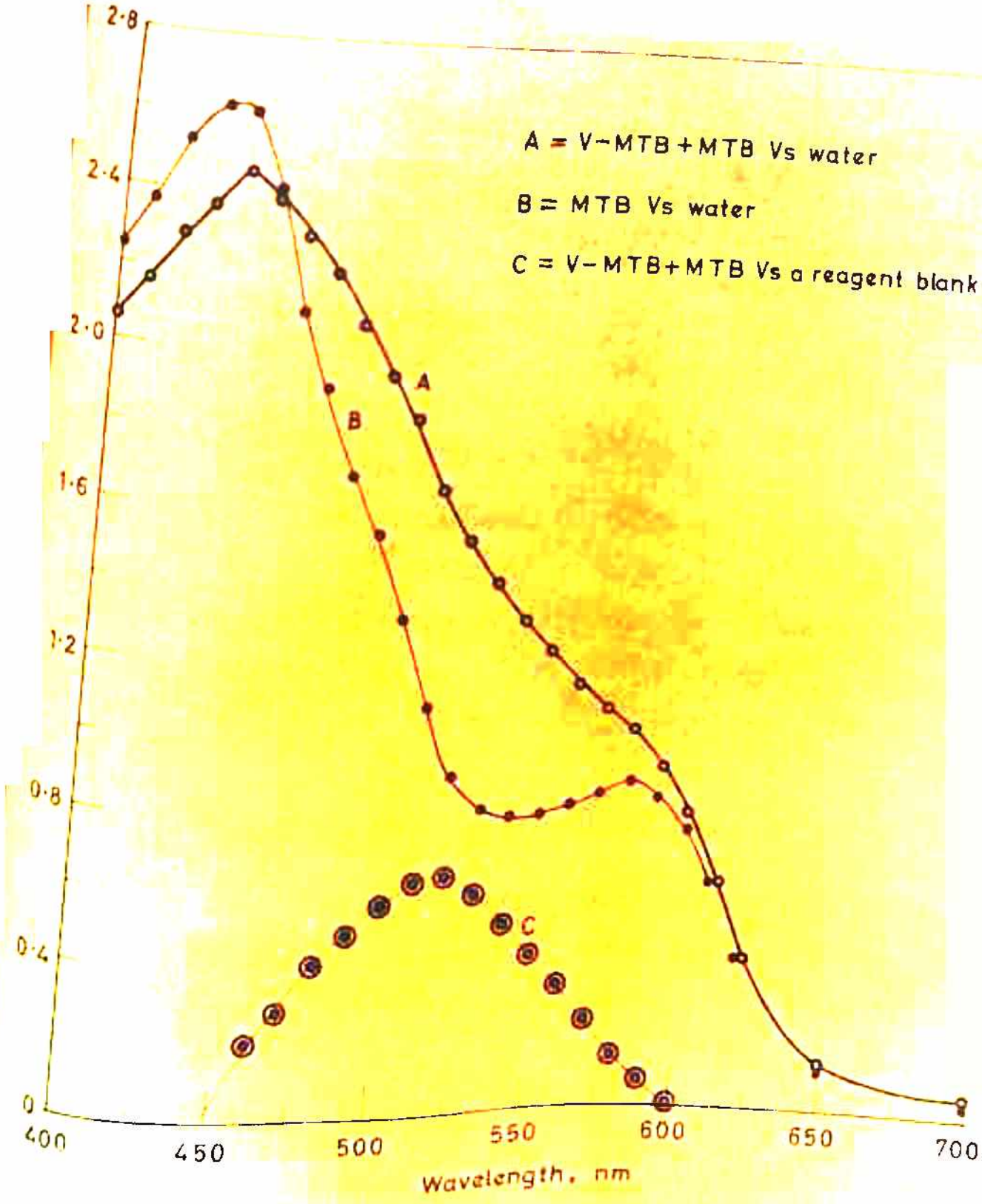


Fig. 5.14 Absorption curves of Methylthymol blue and its Vanadium complex at pH 6·0 ; μ : 0·1 $NaClO_4$; Vanadium: $4{\cdot}0 \times 10^{-5}$ M ; MTB: $3{\cdot}2 \times 10^{-4}$ M

Table 5.31

Concentration of Ammonium Vanadate = 4.0×10^{-5} M

Concentration of Methylthymol Blue = 3.2×10^{-4} M

pH	5.2	5.5	5.9	6.0	6.3	6.5
Optical density per cm(590 nm)	0.490	0.520	0.590	0.620	0.620	0.620

Effect of reagent concentration

The absorbance values of mixtures of metal colutions with varying ratios of MTB at pH 6.0 and at 520 nm showed that maximum colour formation was attained only when the mixtures contained greater than eightfold excess of the reagent with respect to the metal solutions.

Effect of time on the colour of the chelate

Colour formation was instantaneous and the intensity remained constant for at least four hours. However, all mixtures were kept for one hour to attain equilibrium.

Order of addition of reagent

No significant change was observed when the order of addition of the reagents was alternated.

Effect of temperature on the colour stability of the chelate

A study of the effect of temperature indicates that

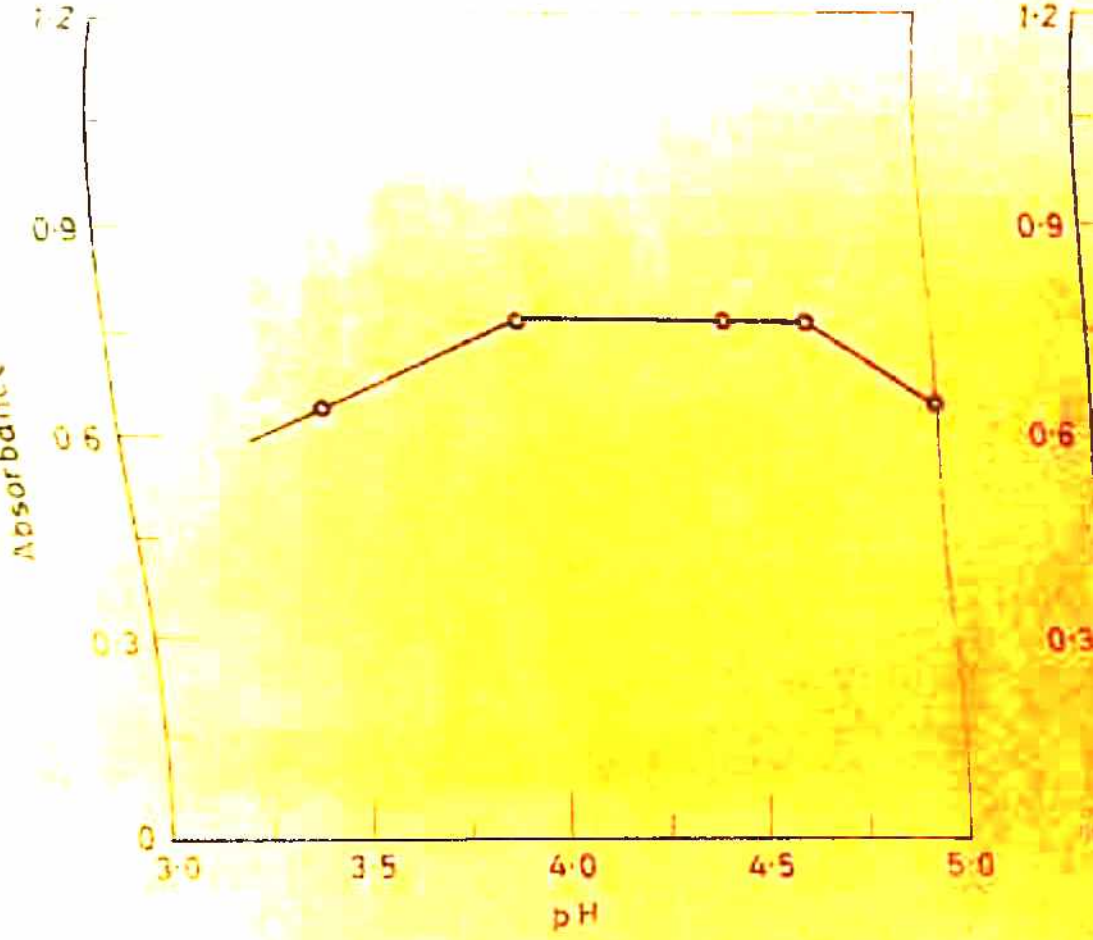


Fig : 5·15 _ Effect of pH

V : $8{\cdot}0 \times 10^{-5}$ M ; MTB : $4{\cdot}0 \times 10^{-5}$ M

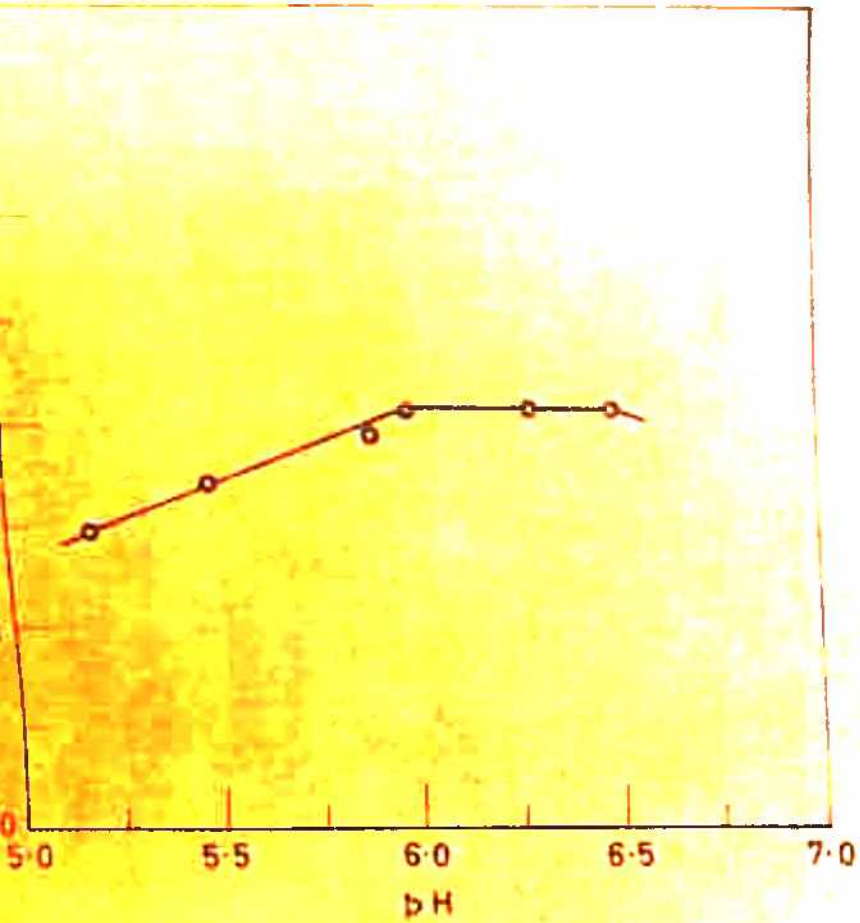


Fig: 5·16_Effect of pH

V: $4{\cdot}0 \times 10^{-5}$ M; MTB: $3{\cdot}2 \times 10^{-4}$ M

the absorbance of the blue complex decreases when the temperature is varied from 30° to 60°C and when the absorbance remains constant in the case of the red complex up to 60°C.

COMPOSITION OF THE CHELATES

(i) Complex with absorption maxima at 590 nm

Job's method of continuous variation

In order to determine the composition of the coloured complex, Job's method of continuous variation was adopted. The total volume in each case was kept 25 ml. The pH of the solutions in the case of mixtures containing both the components were measured. The optical densities were noted at 590 nm at pH 4.5. The results are given in tables 5.32 to 5.36 and represented graphically in figures 5.17 to 5.18, which indicate that a 1:1 complex is formed between vanadium and MTB at pH 4.5.

Table 5.32

Concentration of Ammonium Vanadate(c) = 8.0×10^{-5} M

Concentration of MTB (c') = 8.0×10^{-5} M

pH = 4.5 ± 0.1, λ = 590 nm, p = c'/c = 1

peak at 1:1 (Fig. 5.17 curve A)

Volume of Ammonium Vanadate ml	Volume of MTB ml	Optical density of mixture (a)	Optical density of MTB (b)	Difference in optical density (a-b)
0	25	0.075	0.075	0.000
2.5	22.5	0.240	0.070	0.170
5.0	20.0	0.395	0.065	0.330
7.5	17.5	0.515	0.060	0.455
10.0	15.0	0.620	0.050	0.570
12.5	12.5	0.683	0.035	0.648
15.0	10.0	0.610	0.030	0.580
17.5	7.5	0.485	0.025	0.460
20.0	5.0	0.360	0.020	0.340
22.5	2.5	0.200	0.010	0.190

Table 5.33

Concentration of Ammonium Vanadate(c) = 5.0×10^{-5} M

Concentration of MTB (c') = 5.0×10^{-5} M

pH = 4.5 ± 0.1, λ = 590 nm, p = c'/c = 1

peak at 1:1 (Fig. 5.17 curve B)

0	25	0.050	0.050	0.000
2.5	22.5	0.135	0.045	0.090
5.0	20.0	0.210	0.040	0.170
7.5	17.5	0.280	0.035	0.245
10.0	15.0	0.350	0.030	0.320
12.5	12.5	0.395	0.020	0.375
15.0	10.0	0.345	0.015	0.330
17.5	7.5	0.272	0.012	0.260
20.0	5.0	0.195	0.010	0.185
22.5	2.5	0.105	0.005	0.100

Table 5.34

Concentration of Ammonium Vanadate (c) = 4.0×10^{-5} M

Concentration of MTB (c') = 4.0×10^{-5} M

pH = 4.5 ± 0.1, λ = 590 nm, p = c'/c = 1.

peak at 1:1 (Fig. 5.17 curve C)

Volume of Ammonium Vanadate (ml)	Volume of MTB (ml)	Optical density of mixture (a)	Optical density of MTB (b)	Difference in optical density (a-b)
0	25	0.035	0.035	0.000
2.5	22.5	0.100	0.030	0.070
5.0	20.0	0.165	0.025	0.140
7.5	17.5	0.230	0.020	0.210
10.0	15.0	0.285	0.015	0.270
12.5	12.5	0.330	0.010	0.320
15.0	10.0	0.293	0.008	0.285
17.5	7.5	0.235	0.005	0.230
20.0	5.0	0.160	0.000	0.160
22.5	2.5	0.075	0.000	0.075

Table 5.35

Concentration of Ammonium Vanadate (c) = 2.0×10^{-4} M

Concentration of MTB (c') = 1.0×10^{-4} M

pH = 4.5 ± 0.1, λ = 590 nm, p = c'/c = 0.5

peak at 1:1 (Fig. 5.18 curve A)

0	25	0.095	0.095	0.000
2.5	22.5	0.465	0.085	0.380
5.0	20.0	0.790	0.080	0.710
5.5	19.5	0.858	0.078	0.780
7.0	18.0	0.835	0.075	0.760
8.5	16.5	0.810	0.070	0.740
10.0	15.0	0.745	0.060	0.685
12.5	12.5	0.645	0.045	0.600
15.0	10.0	0.540	0.040	0.500
17.0	7.5	0.400	0.030	0.370
20.0	5.0	0.260	0.025	0.235
22.5	2.5	0.132	0.012	0.120

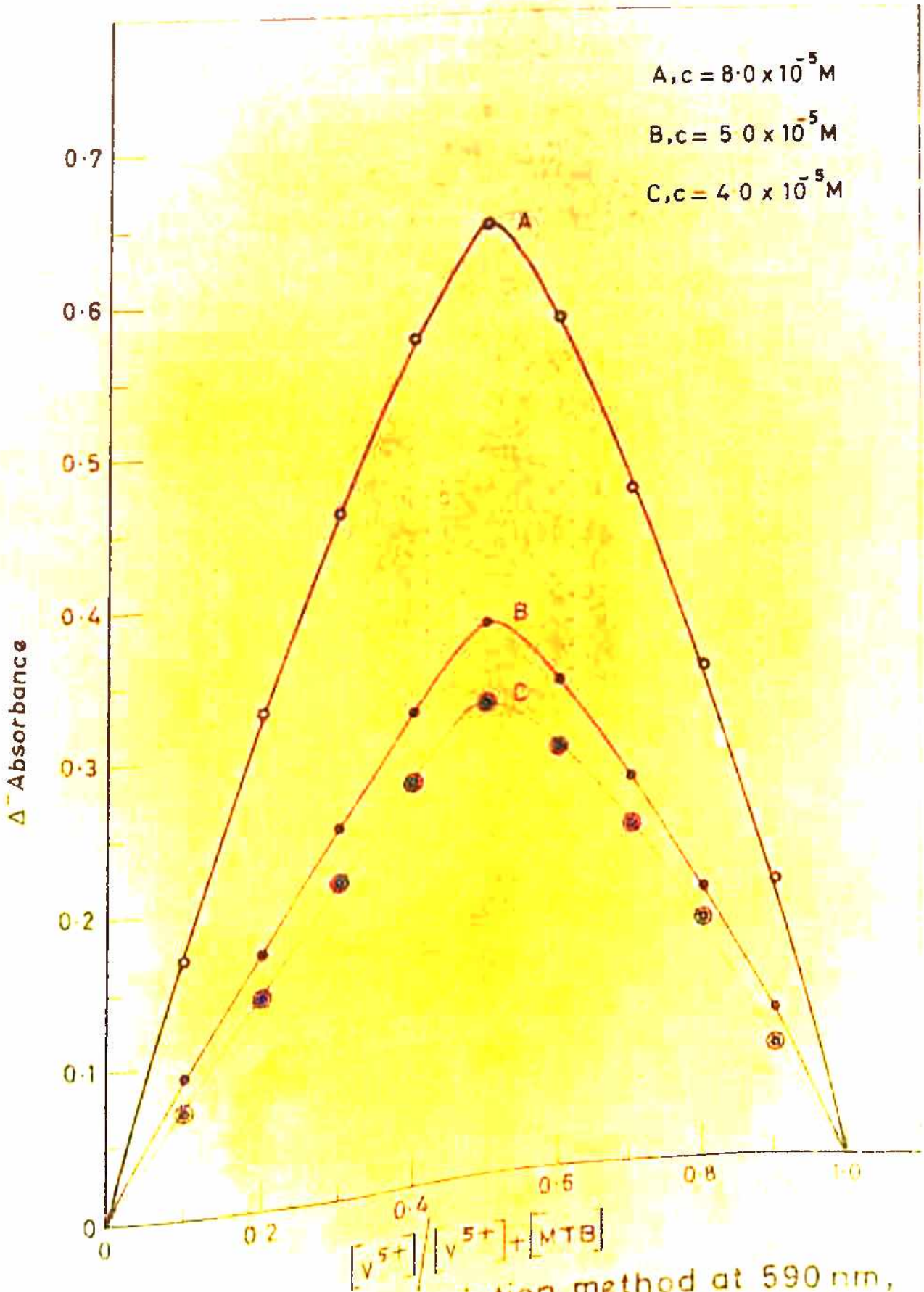


Fig — 5·17 Continuous variation method at 590 nm, p=1, pH: 4·5 ± 0·1; μ: 0·1 $NaClO_4$

Table 5.36

Concentration of Ammonium Vanadate (c) = 1.0×10^{-4} M

Concentration of MTB (c') = 2.0×10^{-4} M

pH = 4.5 ± 0.1, λ = 590 nm, p = c'/c = 2.0

peak at 1:1 (Fig. 5.18 curve B)

Volume of Ammonium Vanadate (ml)	Volume of MTB (ml)	Optical density of mixture (a)	Optical density of MTB (b)	Difference in optical density (a-b)
0	25	0.185	0.185	0.000
2.5	22.5	0.290	0.170	0.120
5.0	20.0	0.400	0.160	0.240
7.5	17.5	0.495	0.145	0.350
10.0	15.0	0.575	0.115	0.460
12.5	12.5	0.675	0.095	0.580
15.0	10.0	0.750	0.080	0.670
15.5	9.5	0.735	0.075	0.660
16.0	9.0	0.710	0.070	0.640
17.5	7.5	0.620	0.060	0.560
20.0	5.0	0.425	0.045	0.380
22.5	2.5	0.225	0.025	0.200

Mole ratio method

The mole ratio of Vanadium to the reagent was confirmed by the mole ratio method at pH 4.5 ± 0.1. In this work, each solution was 4.0×10^{-5} M in the total concentration of methylthymol blue. The results are shown in table 5.37, fig. 5.19 which indicate that 1:1 complex is formed between

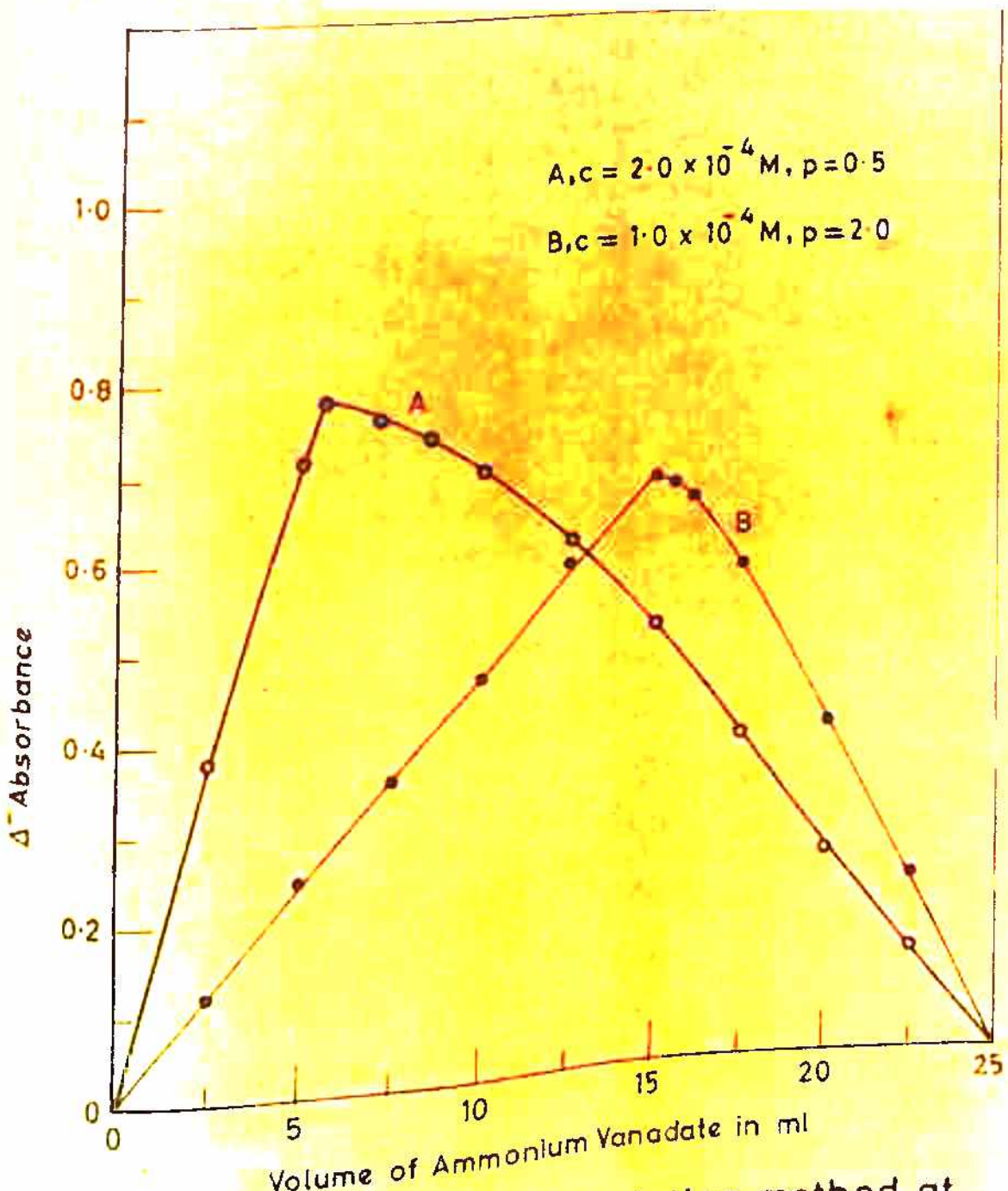


Fig._ 5·18 Continuous variation method at 590 nm; pH: 4·5 ± 0·1, μ 0·1 $NaClO_4$

vanadium and the reagent.

Table 5.37

Concentration of Ammonium Vanadate = 1.0×10^{-3} M

Concentration of MTB = 1.0×10^{-3} M

pH of mixtures = 4.5 ± 0.1

Volume made up = 25 ml

Break at 1:1 (Fig. 5.19 curve A and B)

Volume of Ammonium Vanadate (ml)	Volume of MTB (ml)	Ratio V : MTB	Optical density of mixture against blank	
			590 nm	610 nm
0.50	1.00	0.5 : 1.0	0.340	0.240
0.80	1.00	0.8 : 1.0	0.540	0.400
1.00	1.00	1.0 : 1.0	0.600	0.500
1.20	1.00	1.2 : 1.0	0.675	0.560
1.50	1.00	1.5 : 1.0	0.735	0.605
1.80	1.00	1.8 : 1.0	0.760	0.640
2.00	1.00	2.0 : 1.0	0.775	0.660
2.50	1.00	2.5 : 1.0	0.780	0.680
3.00	1.00	3.0 : 1.0	0.780	0.680
3.50	1.00	3.5 : 1.0	0.780	0.680
4.00	1.00	4.0 : 1.0	0.780	0.680
4.50	1.00	4.5 : 1.0	0.785	0.685
5.00	1.00	5.0 : 1.0	0.785	0.685
5.50	1.00	5.5 : 1.0	0.785	0.685
6.00	1.00	6.0 : 1.0		

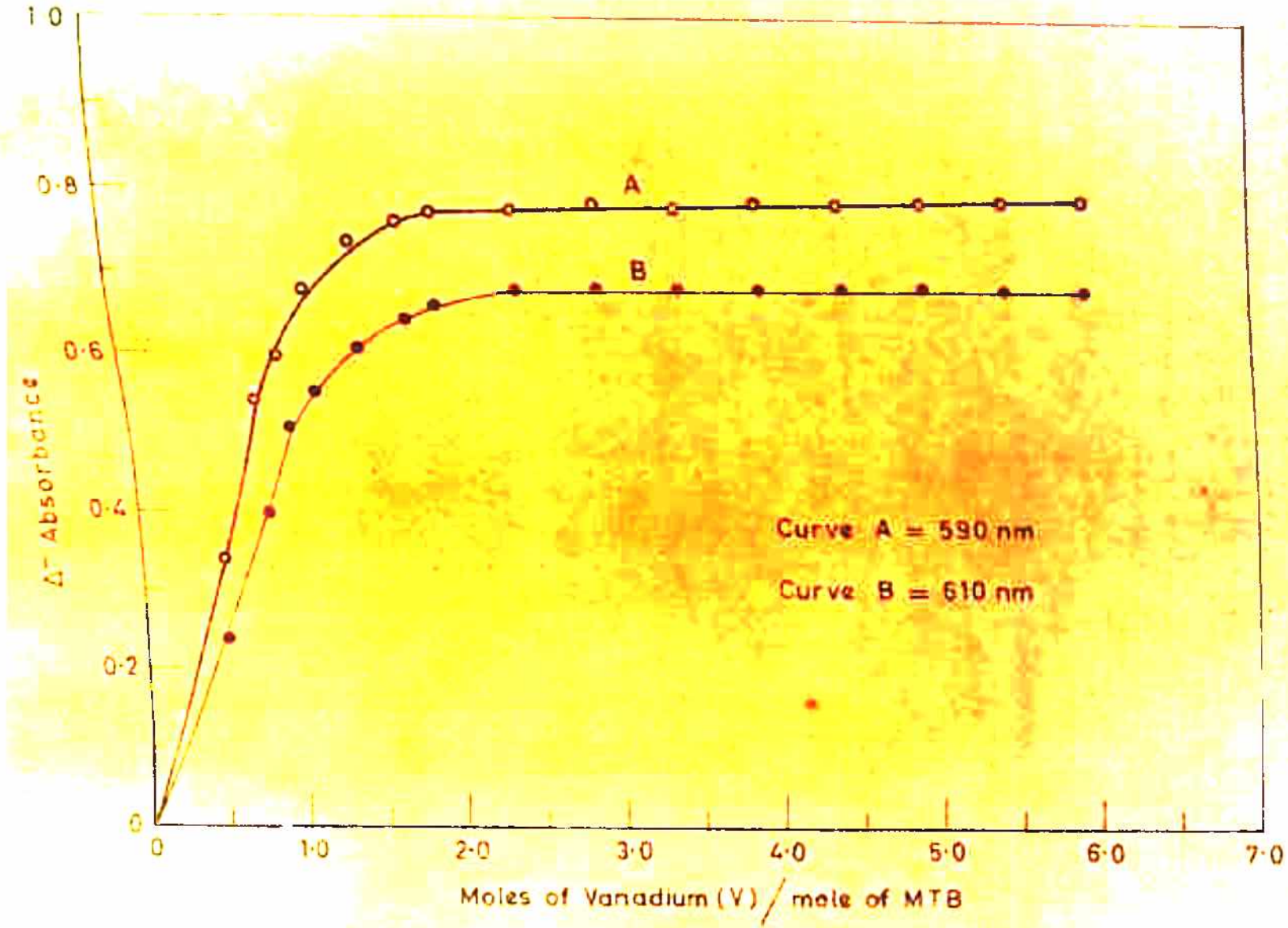


Fig._ 5·19 Mole ratio method, MTB: 4.0×10^{-5} M; pH: 4·5±0·1; μ: 0·1 $NaClO_4$

(ii) The complex with an absorption maximum at 520 nm

The composition was established by (I) the method of continuous variation and (II) the mole ratio method.

The method of continuous variation

The composition of vanadium - methylthymol blue complex at pH 6.0 by the continuous variation method was found to be 1:2. The results are given in tables 5.38 to 5.42 and represented graphically in figures 5.20 and 5.21.

Table 5.38

Concentration of Ammonium Vanadate (c) = 2.5×10^{-4} M

Concentration of MTB (c') = 2.5×10^{-4} M

pH = 6.0 ± 0.1, λ = 520 nm, p = c'/c = 1

peak at 1:2 (Fig. 5.20 curve A)

Volume of Ammonium Vanadate (ml)	Volume of MTB (ml)	Optical density of mixture (a)	Optical density of MTB (b)	Difference in optical density (a-b)
0	25	0.800	0.800	0.000
2.5	22.5	1.005	0.740	0.265
5.0	20.0	1.025	0.630	0.395
7.5	17.5	1.050	0.570	0.480
8.33	16.67	1.010	0.520	0.490
10.0	15.0	0.870	0.440	0.430
12.5	12.5	0.725	0.370	0.355
15.0	10.0	0.570	0.275	0.295
16.67	8.33	0.485	0.225	0.260
17.5	7.50	0.405	0.180	0.225
20.0	5.0	0.265	0.125	0.140
22.5	2.5	0.135	0.055	0.080

Table 5.39

Concentration of Ammonium Vanadate (c) = 2.0×10^{-4} M

Concentration of MTB (c') = 2.0×10^{-4} M

pH = 6.0 ± 0.1, λ = 520 nm, p = c'/c = 1.

peak at 1:2 (Fig. 5.20 curve B)

Volume of Ammonium Vanadate (ml)	Volume of MTB (ml)	Optical density of mixture (a)	Optical density of MTB (b)	Difference in optical density (a-b)
0	25	0.660	0.660	0.000
2.5	22.5	0.800	0.585	0.215
5.0	20.0	0.810	0.490	0.320
7.5	17.5	0.825	0.440	0.385
8.33	16.67	0.815	0.420	0.395
10.0	15.0	0.715	0.370	0.345
12.5	12.5	0.585	0.300	0.285
15.0	10.0	0.465	0.230	0.235
16.67	8.33	0.390	0.180	0.210
17.5	7.5	0.330	0.150	0.180
20.0	5.0	0.240	0.125	0.115
22.5	2.5	0.115	0.050	0.065

Table 5.40

Concentration of Ammonium Vanadate (c) = 1.0×10^{-4} M

Concentration of MTB (c') = 1.0×10^{-4} M

pH = 6.0 ± 0.1, λ = 520 nm, p = c'/c = 1

peak at 1:2 (Fig. 5.20 curve C)

	25	0.325	0.325	0.000
0	22.5	0.395	0.290	0.105
2.5	20.0	0.400	0.240	0.160
5.0	17.5	0.410	0.220	0.190
7.5	16.67	0.400	0.205	0.195
8.33	15.0	0.355	0.185	0.170
10.0	12.5	0.290	0.150	0.140
12.5	10.0	0.230	0.115	0.115
15.0	8.33	0.190	0.090	0.100
16.67	7.5	0.160	0.075	0.085
17.5	5.0	0.110	0.055	0.055
20.0	2.5	0.050	0.020	0.030
22.5				

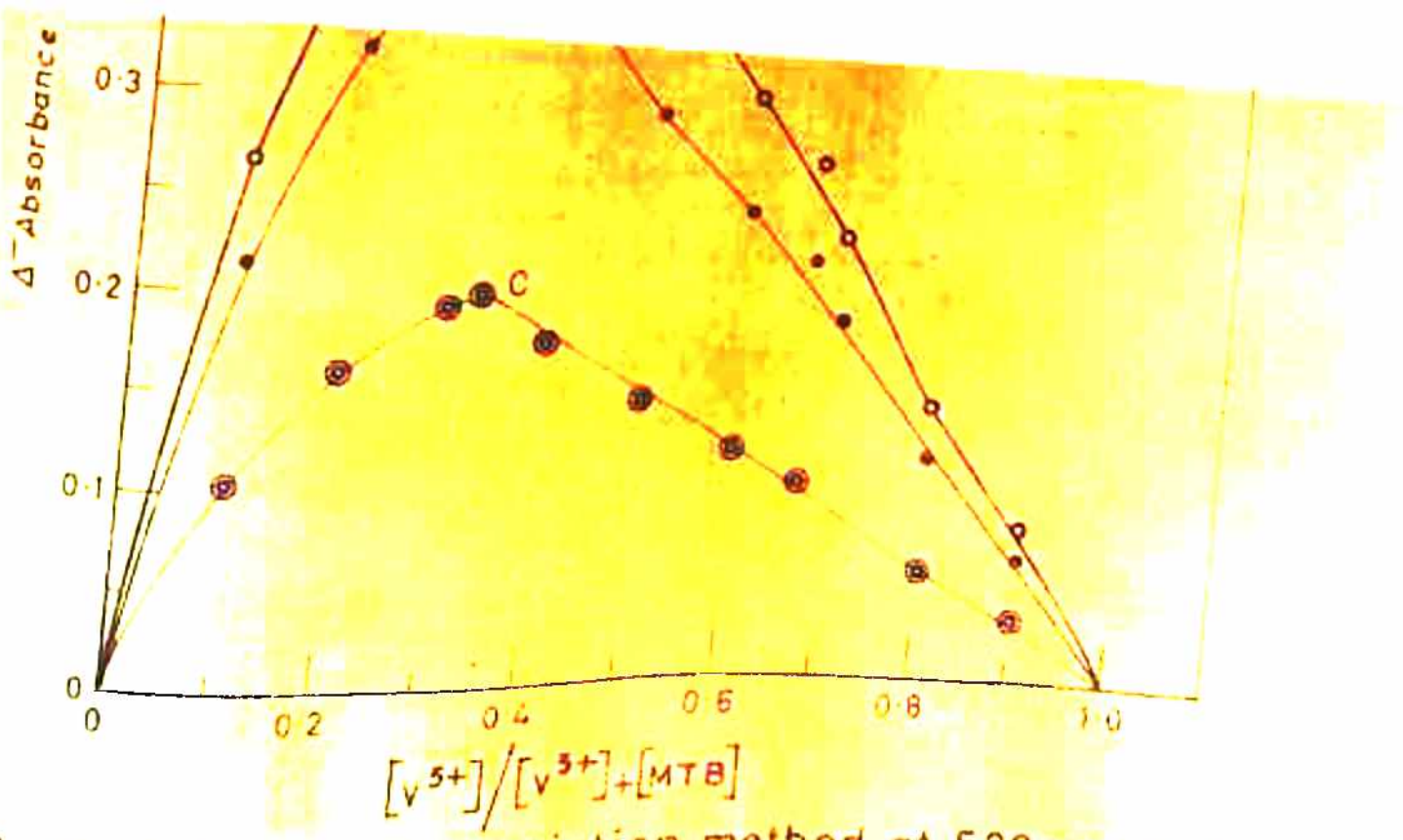


Fig. – 5·20 Continuous variation method at 520 nm; p:1, pH: 6·0±0·1, μ:0·1 $NaClO_4$

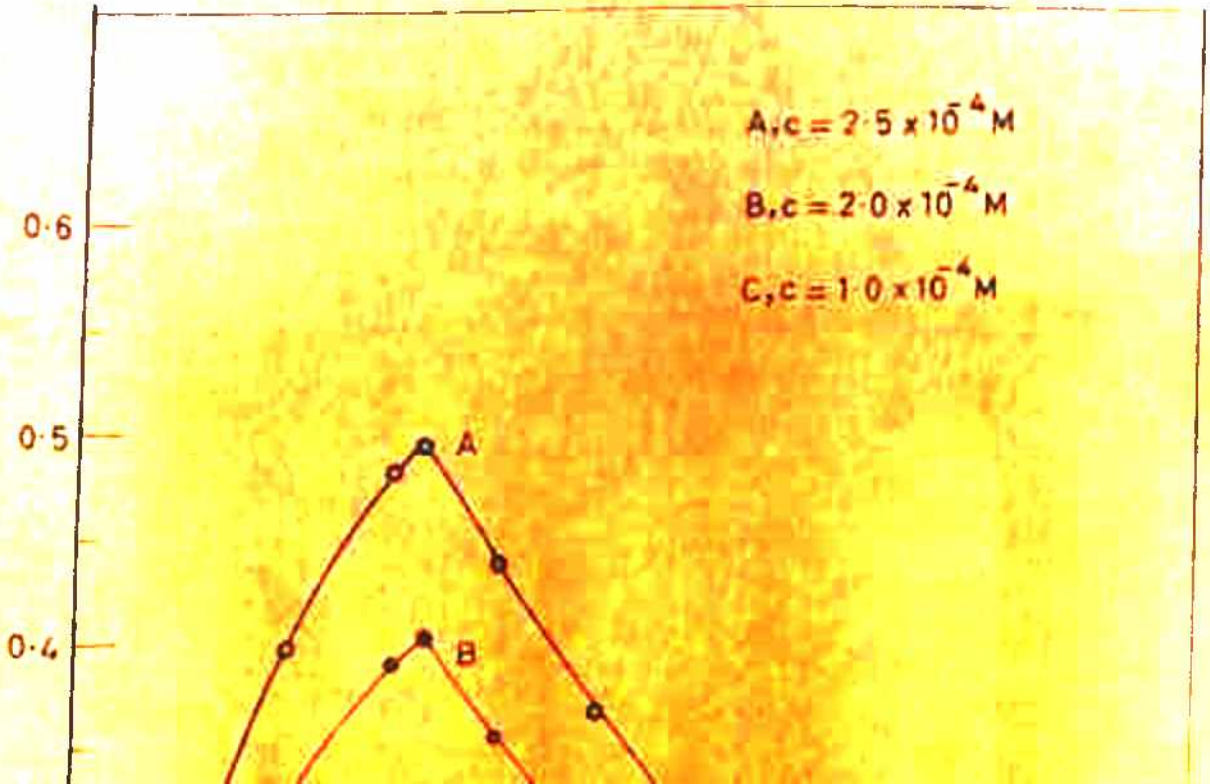

A, c = 2·5 x 10⁻⁴ M
B, c = 2·0 x 10⁻⁴ M
C, c = 1·0 x 10⁻⁴ M
0·6
0·5
0·4
A
B

Table 5.41

Concentration of Ammonium Vanadate (c) = 1.25×10^{-4} M

Concentration of MTB (c') = 2.5×10^{-4} M

pH = 6.0 ± 0.1, λ = 520 nm, p = c'/c = 2.0

peak at 1:2 (Fig. 5.21 curve A)

Volume of Ammonium Vanadate (ml)	Volume of MTB (ml)	Optical density of mixture (a)	Optical density of MTB (b)	Difference in optical density (a-b)
0	25	0.800	0.800	0.000
2.5	22.5	0.920	0.740	0.180
5.0	20.0	0.930	0.630	0.300
7.5	17.5	0.950	0.570	0.380
8.33	16.67	0.960	0.520	0.440
10.0	15.0	0.970	0.440	0.530
11.0	14.0	0.975	0.425	0.550
12.0	13.0	0.980	0.390	0.590
12.5	12.5	0.950	0.370	0.580
15.0	10.0	0.755	0.275	0.480
16.67	8.33	0.615	0.225	0.390
17.5	7.5	0.530	0.180	0.350
20.0	5.0	0.365	0.125	0.240
22.5	2.5	0.165	0.055	0.110

Table 5.42

Concentration of Ammonium Vanadate (c) = 1.0×10^{-4} M

Concentration of MTB (c') = 2.0×10^{-4} M

pH = 6.0 ± 0.1, λ = 520 nm, p = c'/c = 2.0

peak at 1:2 (Fig. 5.21 curve B)

0	25	0.660	0.660	0.000
2.5	22.5	0.705	0.585	0.120
5.0	20.0	0.720	0.490	0.230
7.5	17.5	0.750	0.440	0.310
8.33	16.67	0.765	0.415	0.350
10.0	15.0	0.775	0.370	0.405
11.0	14.0	0.785	0.350	0.435
12.0	13.0	0.790	0.325	0.465
12.5	12.5	0.755	0.300	0.455
15.0	10.0	0.550	0.230	0.320
16.67	8.33	0.415	0.180	0.235
17.5	7.5	0.370	0.150	0.220
20.0	5.0	0.265	0.125	0.140
22.5	2.5	0.110	0.050	0.060

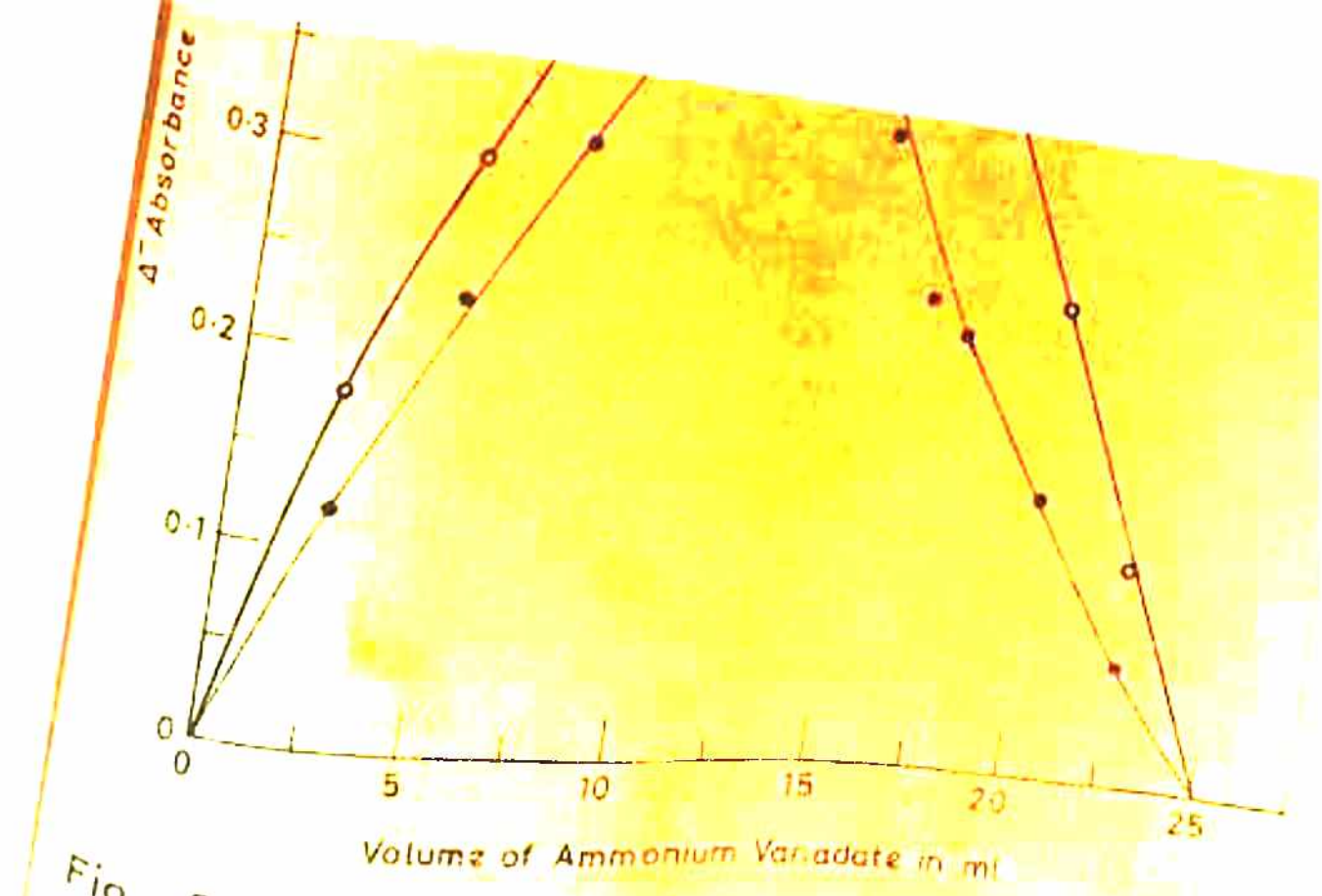
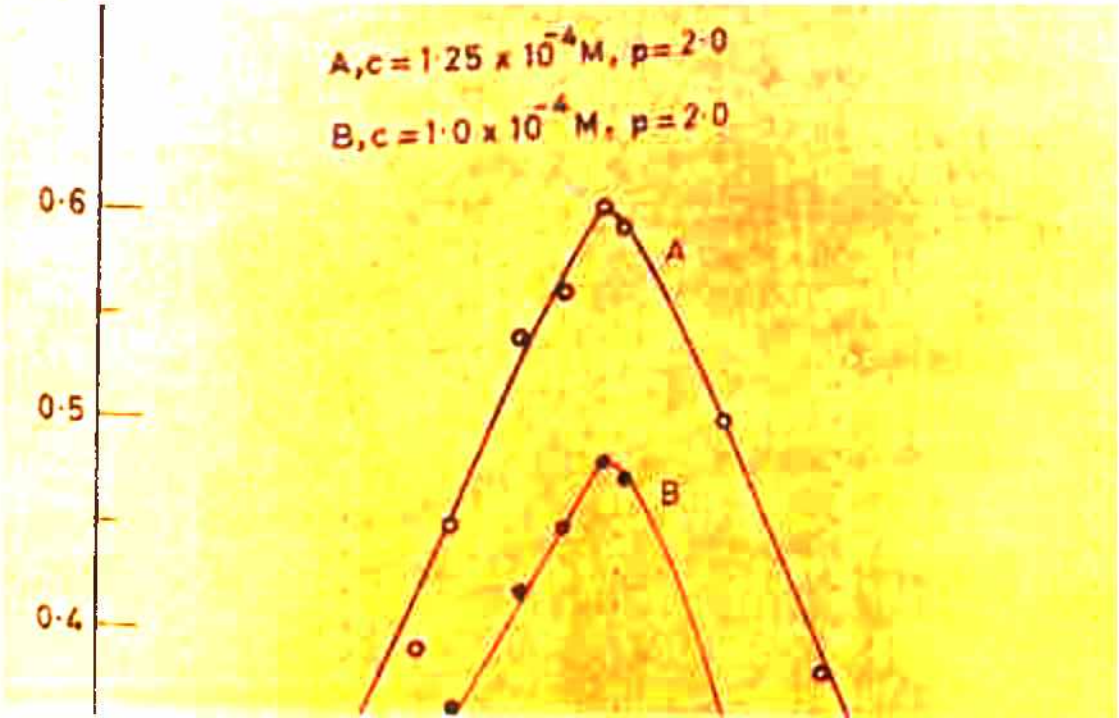


Fig.— 5·21 Continuous variation method at 520 nm; pH: 6·0±0·1; μ : 0·1 $NaClO_4$


A, c = 1·25 x 10⁻⁴ M, p = 2·0
B, c = 1·0 x 10⁻⁴ M, p = 2·0
0·6
0·5
0·4
A
B

Mole Ratio Method: The mole ratio of vanadium to the reagent was confirmed by the mole ratio method at pH 6.0 ± 0.1. In this work, each solution was 1.6×10^{-4} M in the total concentration of methylthymol blue. The results are shown in table 5.43, fig. 5.22, which indicate that 1:2 complex is formed between vanadium and the reagent.

Table 5.43

Concentration of Ammonium Vanadate = 1.0×10^{-3} M

Concentration of MTB = 1.0×10^{-3} M

pH = 6.0 ± 0.1

Volume made up = 25 ml

Break at 1:2 (Fig. 5.22 curve A and B)

Volume of Ammonium Vanadate (ml)	Volume of MTB (ml)	Ratio V : MTB	Optical density of mixture against blank 520 nm
	4.0	0.25 : 1.0	0.525
1.0	4.0	0.40 : 1.0	0.875
1.6	4.0	0.50 : 1.0	1.020
2.0	4.0	0.625: 1.0	1.100
2.5	4.0	0.75 : 1.0	1.150
3.0	4.0	0.875: 1.0	1.160
3.5	4.0	1.0 : 1.0	1.160
4.0	4.0	1.125: 1.0	1.160
4.5	4.0	1.25 : 1.0	1.160
5.0	4.0	1.375: 1.0	1.160
5.5	4.0	1.50 : 1.0	1.160
6.0	4.0	1.625: 1.0	1.165
6.5	4.0	1.75 : 1.0	1.165
7.0	4.0	1.875: 1.0	1.165
7.5	4.0	2.0 : 1.0	1.165
8.0			

Calculation of the Stability Constant

The stability constants were calculated by three

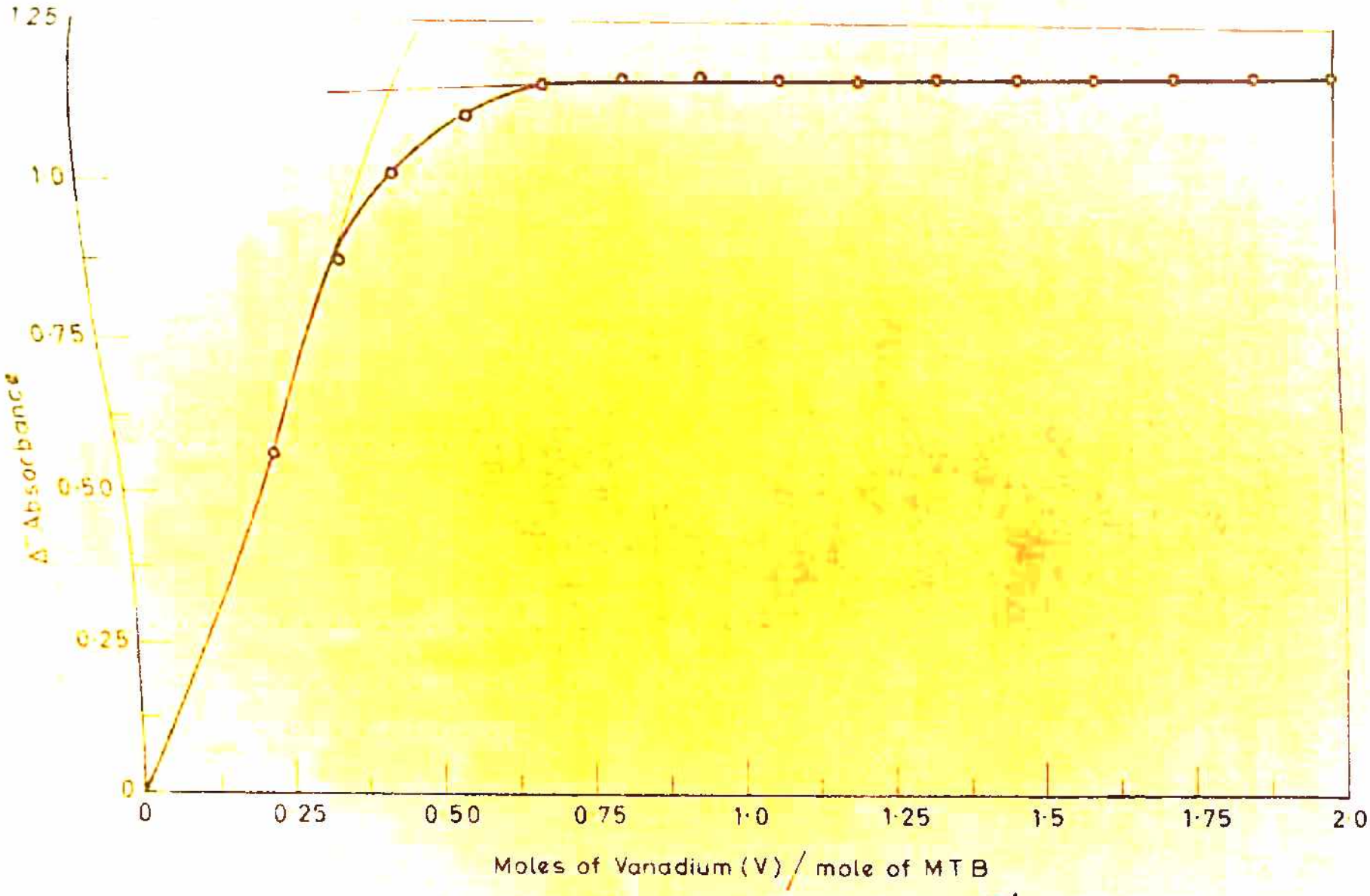


Fig. 5·22 Mole ratio method at : 520 nm ; MTB : $1{\cdot}6 \times 10^{-4}$ M; pH: $6{\cdot}0 \pm 0{\cdot}1$; μ: 0·1 $NaClO_4$

different methods, namely,

(a) the method of Dey and Coworkers,
(b) the method of continuous variation using nonequimolecular solutions, and
(c) the method of mole ratio.

The method of calculation has been the same as explained earlier in Chapter 2.

ANALYTICAL APPLICATIONS

Experiments were performed to test the suitability of the chelate for photometric determination of vanadium. Beer's law is obeyed in the range of 35.7 to 56 ppm in the case of blue chelate and in the range 5.1 to 56 ppm in the case of red chelate. The reaction is sensitive, the molar absorptivities being 17125 and 15000 for 1:1 and 1:2 complex respectively.

Copper, aluminium, iron(III), yttrium, lanthanum, uranium(VI), thorium, zirconium, oxalate and EDTA interfere in the determination. The reducing substances such as iron(II) should not be present, because they reduce vanadium (V) to vanadium(IV).

Discussion

The present investigation deals with the study of chelate formation of vanadium(V) with methylthymol blue (MTB). It has been established that, depending on the pH of the

solution, vanadium(V) reacts with methylthymol blue to form two complexes, with metal-ligand ratios of 1 to 1 and 1 to 2. Table. 5.44 summarises the results on the composition of the chelates arrived at from the examination of figures 5.17 to 5.18 and 5.20 and 5.21 when the method of continuous variation was employed using absorbance measurements. In the legends, c represents the concentration of Ammonium Vanadate and p the ratio c'/c (c' being the concentration of MTB).

Table 5.44

Figure	Curve	pH	10^4c (M)	p	Wave-length nm	Vol. of Ammonium Vanadate at Peak (ml)	Composition of the chelate V : MTB
5.17	A	4.5 ± 0.1	0.8	1	590	12.5	1 : 1
	B	4.5 ± 0.1	0.5	1	590	12.5	1 : 1
	C	4.5 ± 0.1	0.4	1	590	12.5	1 : 1
5.18	A	4.5 ± 0.1	2.0	0.5	590	5.5	1 : 1
	B	4.5 ± 0.1	1.0	2.0	590	15.0	1 : 1
5.20	A	6.0 ± 0.1	2.5	1.0	520	8.33	1 : 2
	B	6.0 ± 0.1	2.0	1.0	520	8.33	1 : 2
	C	6.0 ± 0.1	1.0	1.0	520	8.33	1 : 2
5.21	A	6.0 ± 0.1	1.25	2.0	520	12.0	1 : 2
	B	6.0 ± 0.1	1.0	2.0	520	12.0	1 : 2

The results show that at pH 4.5 a 1:1 complex is formed

while at pH 6.0 a 1:2 complex is formed between Vanadium(V) and the reagent. Results obtained by the mole ratio method (Fig. 5.19 and 5.22) corroborate the composition of the chelate.

The stability constants have been calculated by three different methods and the results are shown in table 5.45. The values of the change in free energy of formation (ΔG^{o}) have also been calculated).

Table 5.45

Apparent stability constants of the chelates

Chelate	Method	pH	Ionic strength	log K (30°C)	ΔG^{o} at 30°C (K Cals)
Vanadium (V) MTB	Dey and Coworkers	4.5 ± 0.1	0.1 M $NaClO_4$	4.2 ± 0.15	- 5.8 ± 0.2
	Continuous variation	4.5 ± 0.1	0.1 M $NaClO_4$	4.6 ± 0.1	- 6.4 ± 0.2
	Mole Ratio	4.5 ± 0.1	0.1 M $NaClO_4$	4.4 ± 0.2	- 6.1 ± 0.3
Vanadium (V) MTB	Dey and Coworkers	6.0 ± 0.1	0.1 M $NaClO_4$	10.2 ± 0.1	-14.1 ± 0.2
	Continuous variation	6.0 ± 0.1	0.1 M $NaClO_4$	10.4 ± 0.2	-14.4 ± 0.3
	Mole ratio	6.0 ± 0.1	0.1 M $NaClO_4$	10.4 ± 0.2	-14.1 ± 0.3

The optimum pH range between which the chelate is stable, range of concentration for adherence to Beer's law, the value of molecular extinction coefficient have been given in the table 5.46.

Table 5.46

Optimum conditions for the photometric determination of Vanadium(V) by MTB

Wavelength maximum nm	Optimum pH range	Range for adherence to Beer's law (ppm)	Range for effective photometric determination (ppm)	Molecular extinction coefficient
590	4.0 - 4.7	35.7 - 56.0	40.8 - 51.0	17125
520	6.0 - 6.5	5.1 - 56.0	15.3 - 40.8	15000

IRON (II) - METHYLTHYMOL BLUE SYSTEM

Methylthymol blue has found use as complexometric indicator and as reagent for the spectrophotometric determination of inorganic ions. It forms stable, coloured chelates with a large number of metal ions. It has been found that, depending on the pH value of the solution, iron (II) reacts with methylthymol blue to form two complexes, with metal ligand ratios of 1:1 and 1:2 and that these reactions are applicable to the spectrophotometric determination upto 40 μg of iron (II) in 25 ml.

Experimental

Reagents:- Ferrous ammonium sulphate, analaR grade, BDH was used for the preparation of iron (II) solutions. Purified Eastman methylthymol blue (penta-Na-Salt) was dissolved in double distilled water.

A hexamethylene tetramine perchloric acid mixture was used for the adjustment of pH values.

Solutions of diverse ions were prepared by dissolving the respective compounds (all reagent grade chemicals) in distilled water in appropriate concentrations.

Absorption curves:- When a buffered, aqueous solution of iron(II) is mixed with excess of methylthymol blue solution

at pH 5.8, a red complex is formed while a beautiful green complex is formed at pH 2.5 with excess of metal ions. Figures 5.23 and 5.24 show the absorption curves of methylthymol blue and its iron(II) complex. The absorption curves obtained with a reagent blank havean absorption maximum at 510 and 600 nm respectively some of the typical results are given in Table 5.47 and 5.48.

Table 5.47

Concentration of Ferrous ammonium sulphate = 4.0×10^{-5}M

Concentration of MTB = 3.2×10^{-4}M

pH = 5.8

Wavelength nm	Optical density of Complex (A)	Optical density of MTB (B)	Difference A-B = C
400	2.120	2.200	-
410	2.200	2.355	-
420	2.320	2.510	-
430	2.420	2.610	-
440	2.540	2.550	-
450	2.500	2.420	0.080
460	2.280	2.160	0.120
470	2.060	1.900	0.160
480	1.920	1.680	0.240
490	1.680	1.360	0.320
500	1.488	1.100	0.388
510	1.250	0.850	0.400
520	1.045	0.680	0.365
530	0.865	0.540	0.325
540	0.700	0.420	0.280
550	0.620	0.380	0.240
560	0.528	0.340	0.188
570	0.465	0.325	0.140
580	0.405	0.305	0.100
590	0.330	0.270	0.060
600	0.284	0.240	0.044
610	0.221	0.185	0.036
620	0.160	0.130	0.030
630	0.118	0.090	0.028
640	0.075	0.050	0.025

Table 5.48

Concentration of Ferrous ammonium sulphate = 4.0×10^{-5} M

Concentration of MTB = 4.0×10^{-5} M

pH = 2.5

Wavelength nm	Optical density of complex (A)	Optical density of MTB (B)	Difference A-B = C
400	0.302	0.320	-
410	0.340	0.360	-
420	0.355	0.380	-
430	0.360	0.390	-
440	0.365	0.380	-
450	0.345	0.350	-
460	0.305	0.306	-
470	0.274	0.258	0.016
480	0.242	0.212	0.030
490	0.222	0.170	0.052
500	0.200	0.135	0.065
510	0.185	0.105	0.080
520	0.180	0.080	0.100
530	0.175	0.065	0.110
540	0.180	0.060	0.120
550	0.195	0.055	0.140
560	0.205	0.050	0.155
570	0.222	0.042	0.180
580	0.235	0.035	0.200
590	0.260	0.025	0.235
600	0.280	0.020	0.260
610	0.255	0.015	0.240
620	0.210	0.010	0.200
630	0.170	0.005	0.165
640	0.115	0.000	0.115
650	0.080	0.000	0.080
660	0.050	0.000	0.050
670	0.025	0.000	0.025
680	0.010	0.000	0.010

Effect of pH:- The effect of pH on the absorbance of the solutions was examined by measuring, at two wavelengths, 510 and 600 nm, the absorbance of solution containing 0.5 ml of 1×10^{-3}M of iron solution (28 µg of iron) and 4 ml (for

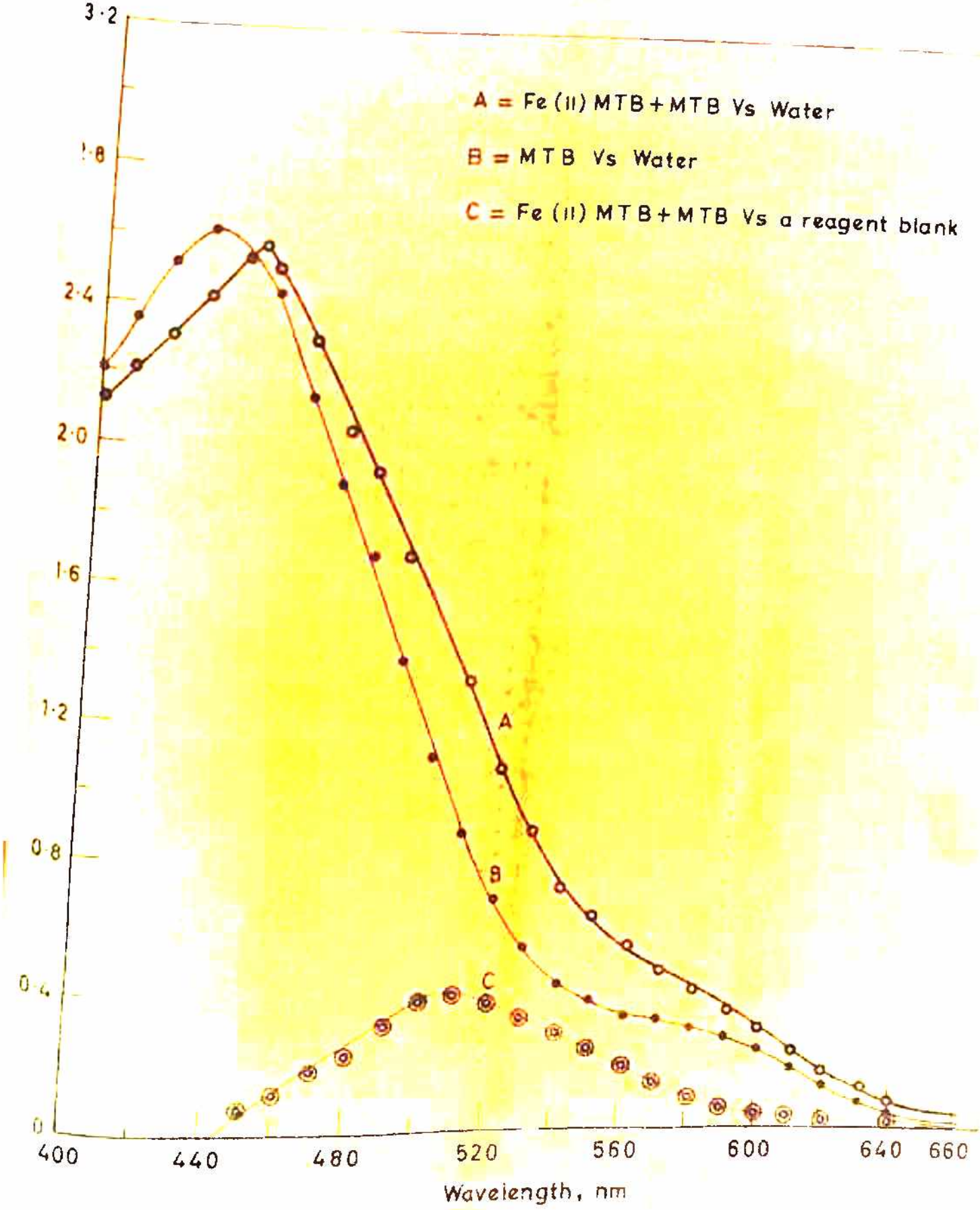


Fig. 5·23 Absorption curves of Methylthymol blue and its Iron (II) complex at pH: 5·8, MTB: $3{\cdot}2 \times 10^{-4}$ M; Fe(II). $4{\cdot}0 \times 10^{-5}$ M

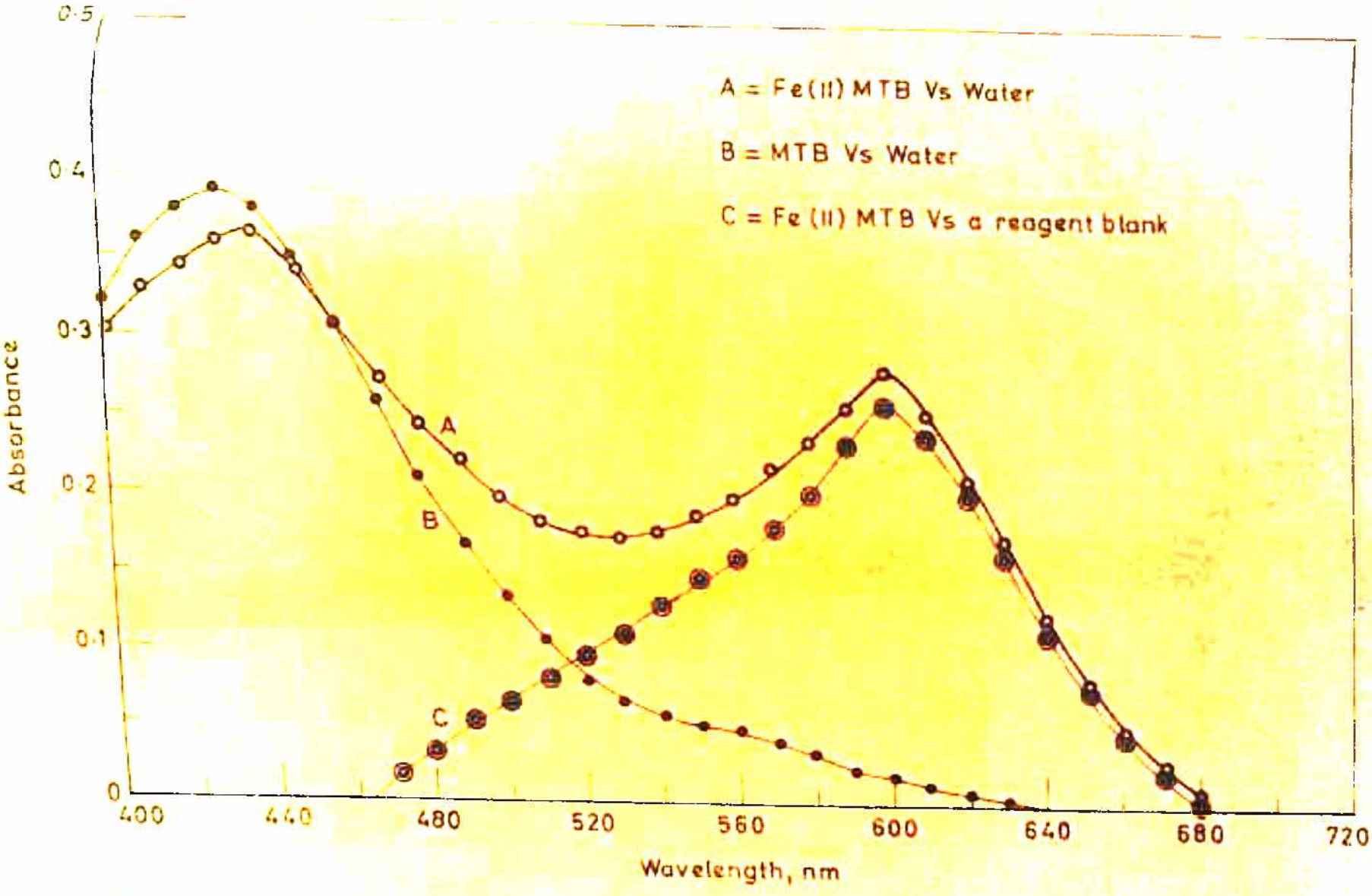


Fig _ 5 24 Absorption spectra of Methylthymol blue and its Iron (II) complex at pH: 2·5, MTB: $4 \cdot 0 \times 10^{-5}$ M; Fe (II) : $4 \cdot 0 \times 10^{-5}$ M

red complex) or 0.5 ml (for green complex) of a 1×10^{-3} M solution of methylthymol blue. From Fig. 5.25 and tables 5.49 and 5.50 it is apparent that the maximum absorbance is obtained in the pH range 5.5 to 5.8 when measured at 510 nm and from 2.2 to 2.5 when measured at 600 nm against the reagent blank.

Table 5.49

Concentration of Ferrous ammonium sulphate = 2.0×10^{-5} M
Concentration of MTB = 1.6×10^{-4} M

pH	5.2	5.5	5.8	6.0	6.4
Optical density per cm (510 nm)	0.202	0.212	0.212	0.210	0.200

Table 5.50

Concentration of Ferrous ammonium sulphate = 2.0×10^{-5} M
Concentration of MTB = 2.0×10^{-5} M

pH	2.2	2.5	2.8	3.7	4.4	5.0
Optical density per cm (600 nm)	0.120	0.120	0.112	0.110	0.106	0.100

Effect of Reagent Concentration

A study of the effect of the reagent concentration at a pH 5.8 and 510 nm indicated that there should be an eight-fold molar excess of MTB over iron(II) concentration.

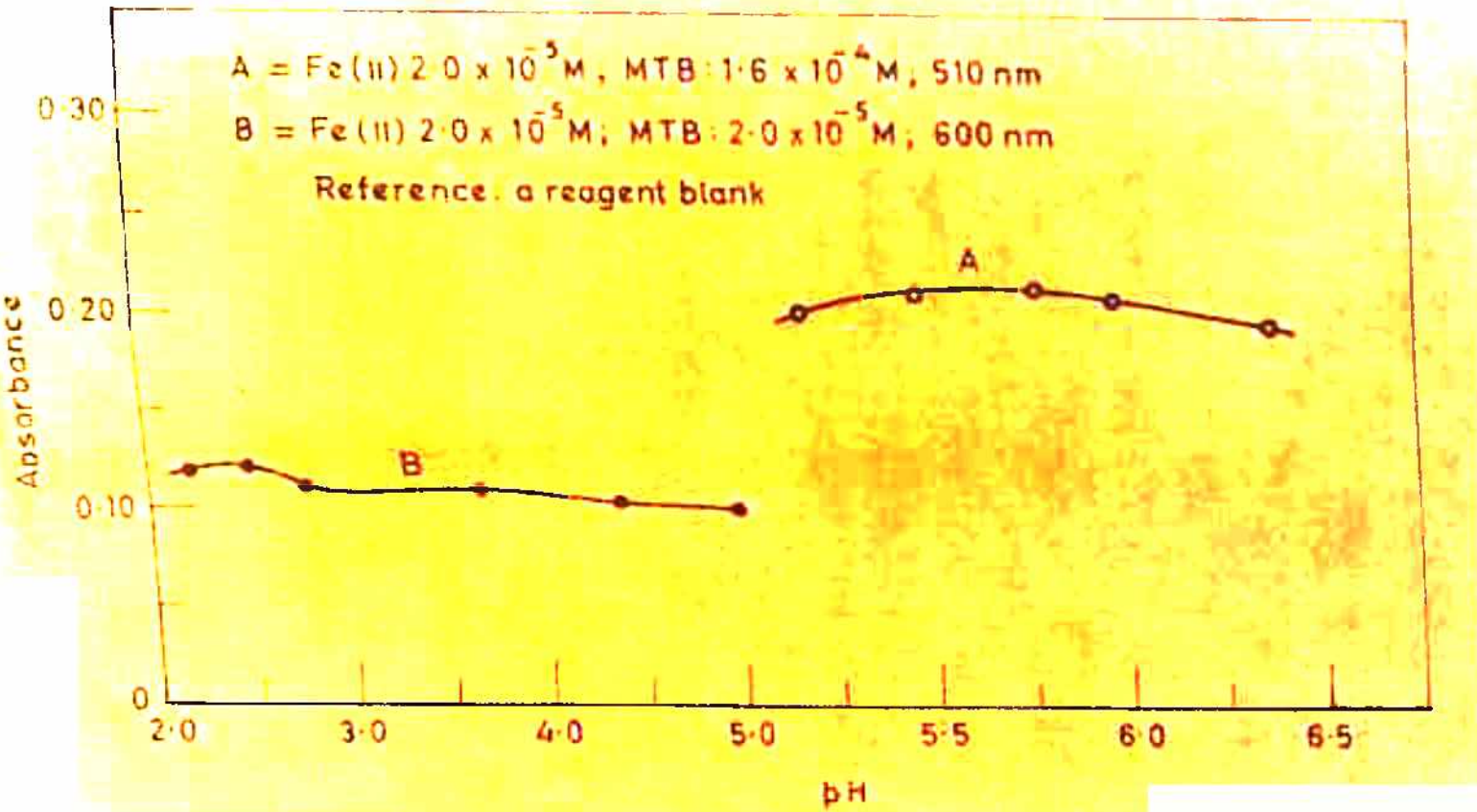


Fig. 5·25 Effect of pH

The Stability of Colour:- It was found that the order of adding the reagents has no significant effect upon the absorbance. The development of colour is almost instantaneous in both cases and the absorbance remained constant for more than 10 hours, either at pH 5.8 or at 2.5. A study of the effect of temperature indicates that the absorbance of red complex remain constant when the temperature was increased to 60°C while decrease in absorbance was noticed in the case of the green complex on increasing the temperature to 60°.

THE COMPOSITION OF THE CHELATES

Mole ratio method:- The mole ratio of iron(II) to the reagent was confirmed by the mole ratio method at pH 5.8 and 2.5. In this work at pH 5.8 each solution was 1×10^{-4} M in the total concentration of methylthymol blue while at pH 2.5 the total concentration was 4.0×10^{-5} M. The results are shown in tables 5.51 and 5.52, figs. 5.26 and 5.27 indicating that at pH 5.8 a 1:2 complex is formed while at pH 2.5 a 1:1 complex is formed between iron (II) and the reagents.

Table 5.51

Concentration of Ferrous ammonium sulphate = 1.0×10^{-3}M

Concentration of MTB = 1.0×10^{-3}M

pH = 5.8, Volume made up = 25 ml.

Break at 1:2 (Fig. 5.26)

Volume of Ferrous ammonium sulphate (ml)	Volume of MTB (ml)	Ratio Fe(II) : MTB	Optical density of mixture against blank at 510 nm
0.25	2.5	0.1 : 1.0	0.070
0.50	2.5	0.2 : 1.0	0.145
0.75	2.5	0.3 : 1.0	0.210
1.00	2.5	0.4 : 1.0	0.285
1.25	2.5	0.5 : 1.0	0.355
1.50	2.5	0.6 : 1.0	0.360
1.75	2.5	0.7 : 1.0	0.362
2.00	2.5	0.8 : 1.0	0.365

Table 5.52

Concentration of Ferrous ammonium sulphate = 1.0×10^{-3}M

Concentration of MTB = 1.0×10^{-3}M

pH = 2.5, Volume made up = 25 ml.

Break at 1:1 (Fig. 5.27)

0.2	1.0	0.2 : 1.0	0.05
0.5	1.0	0.5 : 1.0	0.125
0.8	1.0	0.8 : 1.0	0.200
1.0	1.0	1.0 : 1.0	0.260
1.3	1.0	1.3 : 1.0	0.275
1.5	1.0	1.5 : 1.0	0.280
1.7	1.0	1.7 : 1.0	0.280
2.0	1.0	2.0 : 1.0	0.282
2.5	1.0	2.5 : 1.0	0.285
3.0	1.0	3.0 : 1.0	0.288
4.0	1.0	4.0 : 1.0	0.290
5.0		5.0 : 1.0	0.295

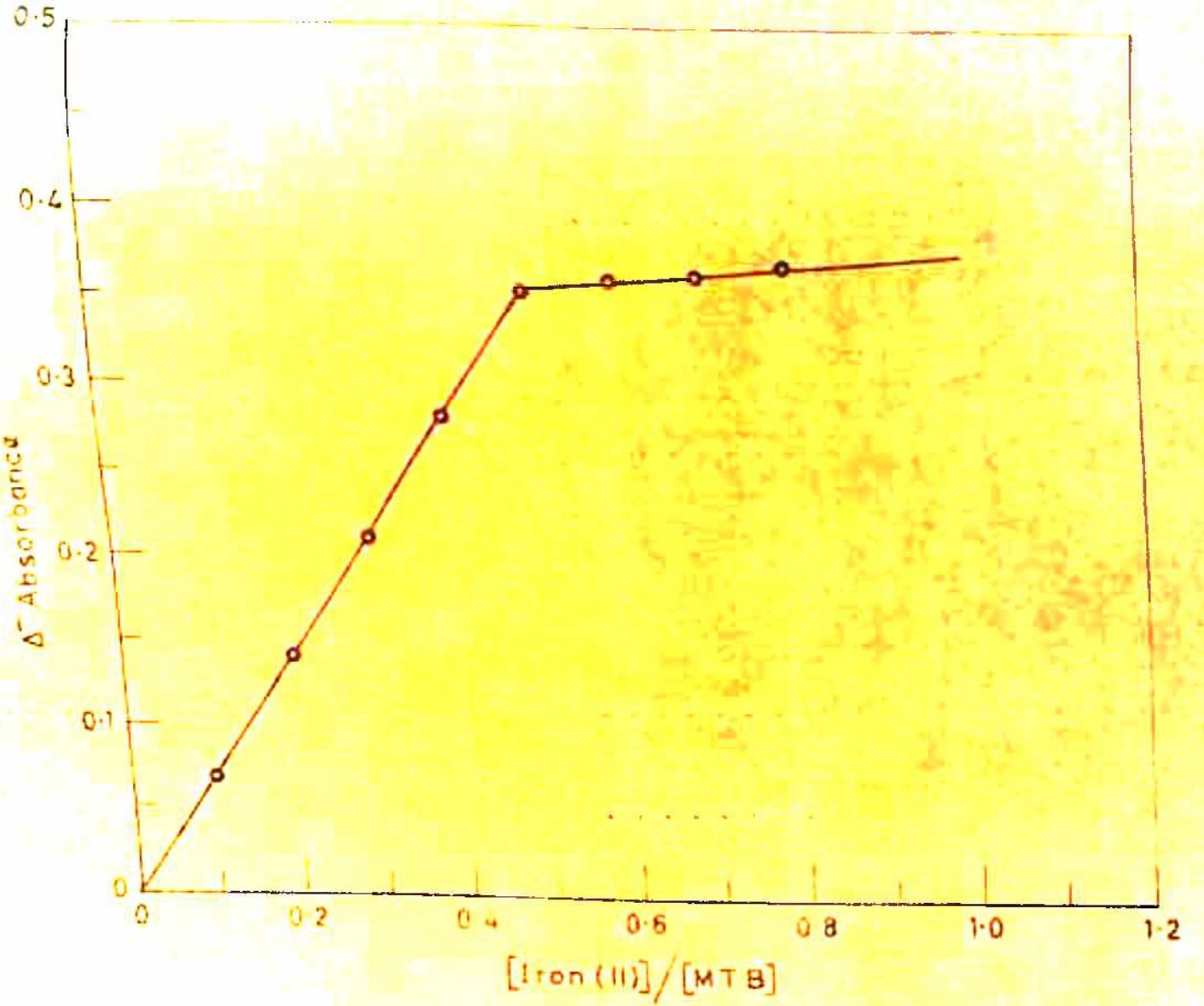


Fig._ 5·26 Mole ratio method at 510 nm; pH: 5·8, MTB: $1{\cdot}0 \times 10^{-4}$ M

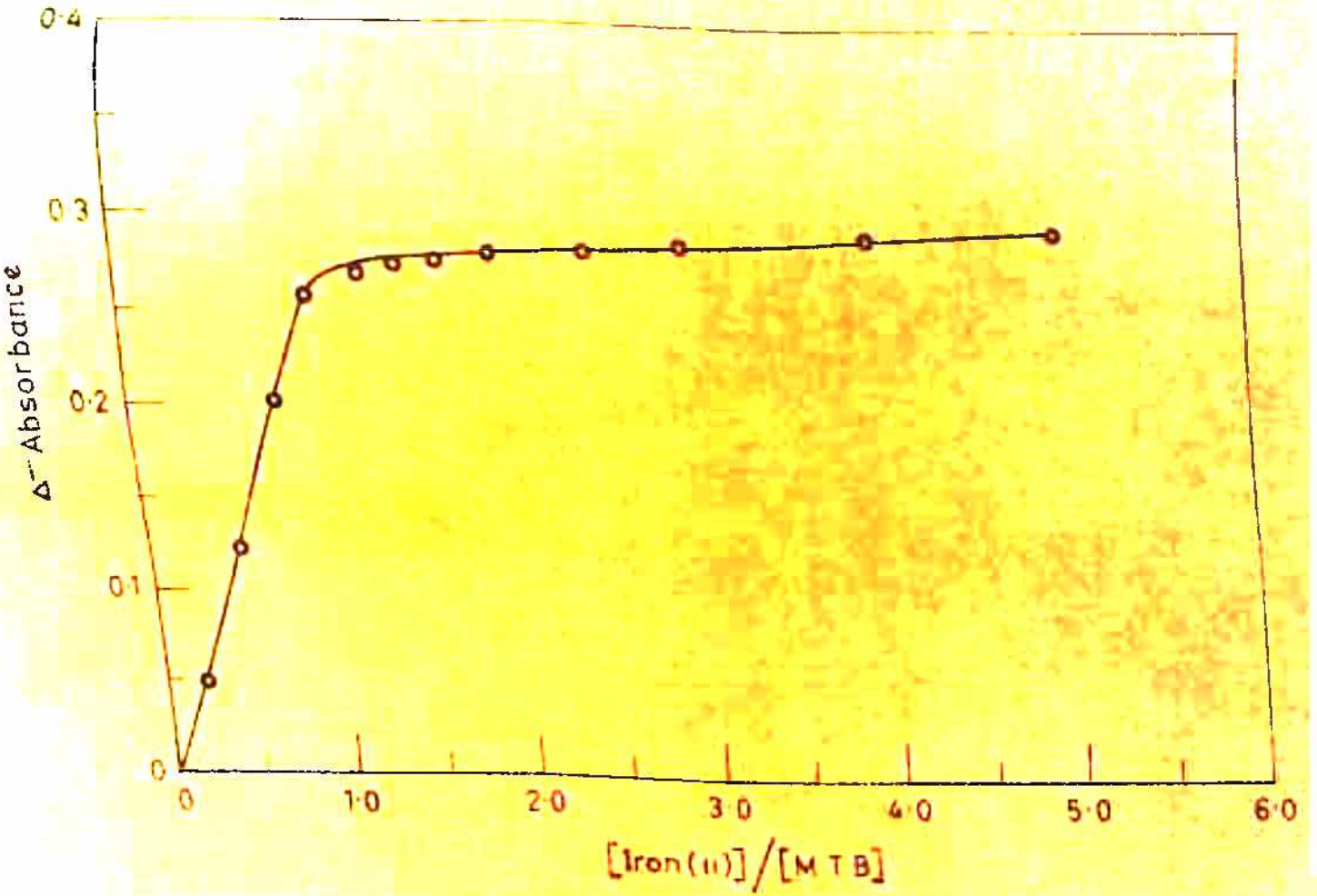


Fig: 5·27 _ Mole ratio method. MTB: $4{\cdot}0 \times 10^{-5}$ M; pH 2·5; 600nm

Evaluation of the Stability Constants

The conditional stability constants were calculated from the absorbance data by the mole ratio method. The values of log K are 9.6 ± 0.1 and 5.6 ± 0.1 for the 1:2 and 1:1 complex respectively. The corresponding values of $\triangle G^{o}$ at 30° are - 13.2 ± 0.2 and - 7.6 ± 0.2.

ANALYTICAL APPLICATIONS

Calibration curves:- From the foregoing results, two optimum conditions for determining iron(II) were found. The procedure for preparing the calibration curve was as follows. An aliquot of the standard iron(II) was pipetted into a 25 ml volumetric flask. The pH was adjusted to 5.8 or 2.5 as the case may be. To the solution 8 ml or 1 ml of a 1 x 10^{-3}M methylthymol blue solution was added, and the resulting solutions were made up to 25 ml with distilled water. After about 30 minutes the absorbance of the solution was measured at 510 or 600 nm against the reagent blank.

The results shown in figure 5.28 indicate that Beer's law is followed by solutions containing upto atleast 40 µg of iron. The net molar absorptivity of the two complexes was found to be 12,000 at 510 and 6550 at 600 nm.

The effect of foreign ions:- Chloride, nitrate and sulphate do not interfere upto atleast 100 µ mol, tartrate and citrate upto 25 µ mol, fluoride and phosphate upto 10 µ mol. Oxalate,

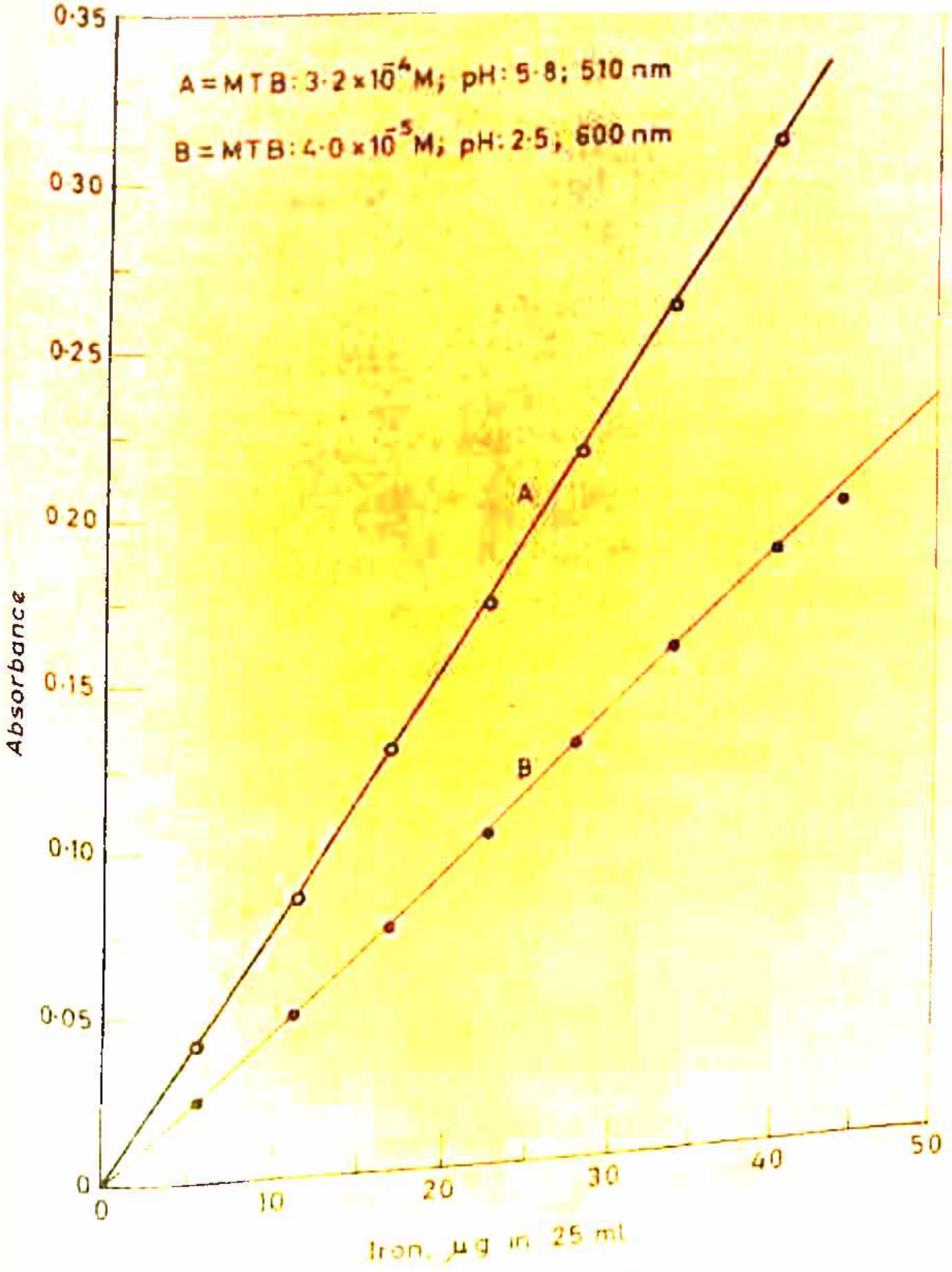


Fig._5·28 Calibration curves.

NTA and EDTA interfere with the colour reaction, even when only trace amounts are present.

Of the 25 cations tested aluminium, gallium, indium, thallium, bismuth, iron(III), thorium, vanadium and zirconium, gave a positive error, while some of the common divalent cations did not interfere.

Discussion

The reaction between iron(II) and methylthymol blue has been studied spectrophotometrically in an attempt to establish the optimum conditions for determining small amounts of iron. Depending on the pH value of a solution, iron (II) reacts with methylthymol blue to form two complexes, with metal ligand ratios of 1 to 1 and 1 to 2. Table 5.53 summarises the results of the composition and stability.

Table 5.53

Complex	pH	Composition	log K	ΔG° at 30° (K Cal)
Fe(II) - MTB	5.8	1 : 2	9.6 ± 0.1	- 13.2 ± 0.2
Fe(II) - MTB	2.5	1 : 1	5.6 ± 0.1	- 7.6 ± 0.2

The optimum pH range between which the complex is stable, range of concentration for adherence to Beer's law,

the value of molecular extinction coefficient have been given in table 5.54.

Table 5.54

Optimum conditions for the photometric determination of iron (II) with MTB

Wavelength maximum nm	Optimum pH range	Range for adherence to Beer's law (ppm)	Range for effective photometric determination (ppm)	Molecular extinction coefficient
600	2.2 - 2.5	5.6 - 40.0	11.2 - 28.0	6,550
510	5.5 - 5.8	5.6 - 40.0	11.2 - 33.6	12,000

REFERENCES

1. Akhmedli, M.K. and Babaeva, T.R. — Uch. Zap. Azerb. Gos. Univ. Ser. Khim. Nauk 3, 31 (1965).

2. Akhmedli, M.K. Granovskaya, P.B. and Islamov, S.U. — ibid, 1, 16 (1967).

3. Akhmedli, M.K. and Granovskaya, P.B. — Ukr. Khim. Zh. 31, 615 (1965).

4. Akhmedli, M.K. and Granovskaya, P.B. — Azerb. Khim. Zh. 5, 105 (1965).

5. Akhmedli, M.K. and Glushchenko, E.L. — Zh. Analit. Khim. 19, 556 (1964).

6. Akhmedli, M.K. Bashirov, E.A. and Sadykhova, A.M. — Uch. Zap. Azerb, Gos. Univ. Ser. Khim. Nauk 3, 25 (1965).

7. Akhmedli, M.K. and Sadykhova, A.M. — Zh. Neorg. Khim. 12, 476 (1967).

8. Anderegg, G. Flaschka, H. Sallmann, R. and Schwarzenbach, G. — Helv. Chim. Acta 37, 113 (1954).

9. Babko, A.K. and Vasilenko, V.T. — Ukrain, Khim. Zhur. 26, 514 (1960)

10. Babko, A.K. and Vasilenko, V.T. — Zavodskaya Lab. 27, 640 (1961).

11. Babko, A.K. and Vasilenko, V.T. — Ukrain, Khim. Zhur. 27, 396 (1961).

12. Babko, A.K. and Gridchina, G.I. — Zh. Neorgan. Khim. 7, 889 (1962).

13. Babko, A.K. and Shtokalo, M.I. — Ukr. Khim. Zh. 28, 293 (1962).

14. Babko, A.K. and Vdovenko, M.E. — ibid, 32, 209 (1966).

15. Babko, A.K. Akhmedli, M.K. and Granovskaya, P.B. — ibid, 32, 879 (1966).

16. Babko, A.K. Akhmedli, M.K. and Granovskaya, P.B. — ibid, 32, 1015 (1966).

17. Babko, A.K. and Kish, P.P. — Dopovidi Akad. Nauk. Ukr. R.S.R. 1323 (1961).

18. Babko, A.K. and Kish, P.P. — Zh. Analit, Khim 17, 693 (1962).

19. Babko, A.K. and Shtokalo, M.I. — Ukr. Khim. Zh. 29, 963 (1963).

20. Bezugli, D.V. and Amsheeva, A.A. — Zh. Analit. Khim 17, 1045 (1962).

21. Borislav, K Donka, K. and Petrana, N. — Talanta 15, 525 (1968).

22. Budĕšinsky, B — Z. Anal. Chem. 207, 247 (1965).

23. Budesinsky, B — Chelates in analytical chemistry Marcel Dekkar, Inc, New York 1967 Vol. 1 page 22.

24. Cheng, K.L. — Anal. Chim. Acta 28, 41 (1963).

25. Cheng, K.L. — Talanta 14, 875 (1967).

26. Dey, A.K. — J. Colloid. Sci, 3, 473 (1948).

27. Doowon Park and Cheong Nam Lee — Dachan Hwahak Hwoejee 7, 229 (1963).

28. Elinson, S.V. and Mirzoyan, N.A. — Zh. Anal. Khim. 21, 1436 (1966).

29. Gattow, G. and Schott, D. — Z. Anal. Chem. 188, 10 (1962).

30. Geyer, R. and Bormann, R. — Z. Chem. 7, 30 (1967).

31. Harvey, A.E. and Manning, D.L. — J. Am. Chem. Soc. 72, 4488 (1950).

32. Hluchan, E. and Mayer, J. — Chem. Zvesti 17, 569 (1963).

33. Horiuchi, Y. and Ichizyo, O. — Iwate Daigaku Kogakubu Kenekyu Hokoku 19, 91 (1966).

34. Horiuchi, Y. and Ichizyo, O. — ibid, 20, 43 (1967).

35. Hung, S. and Jen, H. — HuaHSuch HSueh Pao, 31, 91 (1965).

36. Iritani, N. and Miyahara, T — Bunseki Kagaku 12, 1183 (1963).

37. Janonšek, I. and Studlar, K. — Collection Czech. Chem. Commun. 24, 799 (1959).

38. Job, P. — C.r. acad. Sci.,Paris 180, 928 (1925); Ann. Chim. (10) 9, 113 (1928); (11) 6, 97 (1936).

39. Korbl, J. and Pribil, R. — Chemist Analyst 45, 162 (1956).

40. Korbl, J. and Pribil, R. — Listy 51, 1061 (1957).

41. Korbl, J. Pribil, R. and Emr. A. — Chem. Listy 50, 1440 (1956).

42. Korbl, J. and Pribil, R. — Chem. Anal 45, 102 (1956).

43. Korbl, J. and Pribil, R. — Chem. and Ind (London) 233, 1957.

44. Korbl, J. — Nove Komplexometricke indikatory, Chemapol, Prague 1958.

45. Korbl, J. — Czech Pats 89, 173 (March 1959) 91, 363 (Aug. 1959) U.S. Patent 2980, 696 (April 1961) Brit. Pat. 858, 019 (January 1961).

46. Korbl, J. — Chem. Listy 51, 1304 (1957) Collection Czech. Chem. Commun. 23,1789 (1957).

47. Korbl, J. and Kakac, B — Chem. Listy 51, 1680 (1957) Collection Czech. Chem. Commun. 23, 889 (1958)

48. Koros, E. — Proc. Intern. Symposium Micro Chem, Brimingham Univ. 474, 1958.

49. Larsen, E.M. and Hirozawa, S.T. — J. Inorg. Nucl. Chem. 3, 198 (1956).

50. Lassner, E. and Pueschel, R. — Mikrochim. Ichnoanal Acta 753 (1964).

51. Lassner, E. — Chemist Analyst 51, 14 (1962)

52. Lassner, E. and Puschel, R. — Mikro Chim. Ichnoanal Acta 950 (1963).

53. Lukyanov, V.F. and Knyazeva, E.M. — Zavodskaya Lab. 26, 263 (1960).

54. Malat, M. Suk, V. and Ryba, O. — Chem. Listy 48, 203 (1954) Collection Czech. Chem. Commun. 19, 258 (1954).

55. Malkova, V.T. and Fateeva, N.A. — Zh. Neorg. Khim 13, 2094 (1968).

56. McBain, J.W. — Colloid Science, Boston Heath and Co. 1950.

57. Metcalfe, J. — Analyst 90, 409 (1965).

58. Mushran, S.P. and Prakash, S. — J. Physic. Chem. 50, 251 (1946).

59. Okada, H, Kaneko, K. and Goseki, S. — Bunseki Kagaku 12, 822 (1963).

60. Olson, D.C. and Margerum D.W. — Anal. Chem. 34, 1299 (1962).

61. Otomo, M. — Nippon Kegaku Zasshi 89, 503 (1968).

62. Pozsgay-Kovacs, E. — Gyogyszereszet 7, 210 (1963).

63. Přibil, R. — Talanta 3, 91 (1959).

64. Radko, V.A. Yakimets, E.M. and Vladimirtsev, I.F. — Zh. Analit. Khim. 20, 955 (1965).

65. Řehák, B. and Korbl, J. — Collection Czech. Chem. Commun. 25, 797 (1960).

66. Serdyuk, L.S. and Smirnaya, V.S. — Zh. Analit. Khim. 20, 161 (1965).

67. Siemroth, J. — Private Communication 1965.

68. Shivapuri, T.N. and Prakash, S. — Current Sci. 18, 403 (1949).

69. Sobéslavský, C. Dudek, J. and Tepla, E. — Časopis Lékařů Českých 98, 279 (1959).

70. Srivastava, K.C. and Banerji, S.K. — Chem. Age, India 20, 609 (196

70a. Srivastava, K.C. and Banerji, S.K. — Microchem. J. 13, 626 (1968).

71. Tereshin, G.S., Rubinshtein, A.R. and Tananaev, I.V. — Zh. Analit. Khim 20, 1082 (1965).

72. Tereshin, G.S. Rubinshtein, A.R. and Tananaev, I.V. — ibid, 20, 1086 (1965).

73. Tikhonov, V.N. — ibid, 21, 1172 (1966).

74. Tikhonov, V.N. — ibid, 21, 275 (1966).

75. Tikhonov, V.N. and Grankina, M. Ya. — Zavodsk, Lab. 32, 278 (1966).

76. Tikhonov, V.N. Grankina, M. Ya and Veringora, V.P. — Zh. Anal. Khim. 22, 359 (1967).

77. Tikhonov, V.N. — ibid, 22, 658 (1967).

78. Tolmachev, V.N. Goltsberg, I.M. and Konkin, V.D. — ibid, 22, 950 (1967).

79. Tonosaki, K. and Sakai, K. — Bunseki Kagaku 14, 495 (1965).

80. Tonosaki, K. — Bull. Chem. Soc. Japan 39, 425 (1966).

81. Tselinskii, Yu. K. and Lapitskaya, E.V. — Ukr. Khim. Zh. 34, 189 (1968).

82. Uhlíř, Z. — Chem. Zvesti 18, 756 (1964).

83. Vasilenko, V.D. and Shanya, M.V. — Zh. Analit. Khim. 20, 636 (1965).

84. Wilson, A.D. and Cooke, J.R. — Analyst 91, 135 (1966).

85. Yoe, J.H. and Jones, A.L. — Ind. Eng. Chem. Anal. Ed., 16, 111 (1944).

86. Yoshino, T. Imada, H. Oshikuwano, T. and Iwasa, K. — Talanta 16, 151 (1969).

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CHAPTER VI

METHYLTHYMOL BLUE AS A REAGENT FOR THE PHOTOMETRIC DETERMINATION OF TRACES OF SOME BIVALENT METALS

Since methylthymol blue was first prepared by Körbl and Přibil (17) as a metallochromic indicator, this reagent has widely been used by a number of investigators in complexometric titrations. However, in the last few years it has also been employed by a few workers as a chromogenic agent in the photometric determination of metals such as zirconium (18, 2) yttrium (24, 38), lanthanum (24) mercury(13), thorium (25, 44), gallium (40), magnesium (21), iron (41) and aluminium (39).

In a recent communication from this laboratory, Srivastava and Banerji (37) have reported the formation of coloured chelates of various metals with this reagent and have suggested that it would be profitable to try this reagent for other photometric estimations as well. In the present investigation they have attempted to evaluate the applicability of methylthymol blue as a spectrophotometric reagent for various metal cations. From the results obtained, a new spectrophotometric method for the determination of beryllium, lead, and palladium is proposed.

Experimental

Solutions of metallic salts of analytical grade a

of Eastman methylthymol blue (penta sodium salt) reagent were prepared in double distilled water and standardized by the usual methods. The first set of experiments were performed to record absorption curves i.e. to determine the spectral region of the maximum absorption of the complex. In another set of experiments, the influence of pH, effect of reagent concentration, temperature and stability of the colour was studied.

To investigate the validity of Beer's law, in the systems a fixed quantity of the reagent solutions was taken and varying quantities of the metallic salt solutions added. The mixtures were raised to a constant volume and kept for 30 minutes to attain equilibrium. The intensity of the colour was measured with a Hilger Uvispek spectrophotometer (with 1 cm glass cell). The experiments were conducted at room temperature. The interference of various cations and anions was also noted. In the next set of experiments the composition and the stability of the complexes formed was determined.

Beryllium-Methylthymol Blue System

Methylthymol blue reacts with many metal ions in a weakly or a slightly acid medium to form red or reddish violet complexes, and it also reacts with beryllium ions to give a red coloration. The reaction is applied to the spectrophotometric determination of trace amounts of beryllium. The purpose of this study is to find optimum

conditions under which upto 9 μg of beryllium can be determined, to ascertain the effect of diverse ions on the determination, and to determine the composition and the stability constant of the complex formed.

Absorption Curves

When buffered, aqueous solution of beryllium is mixed with a methylthymol blue solution, a red complex is immediately formed. Fig. 6.1 shows the absorption curves of methylthymol blue and its beryllium complex. The absorption curves of the beryllium complex obtained with a reagent blank as reference has an absorption maximum at 500 nm. Some of the typical results are given below in table 6.1

Table 6.1

Beryllium perchlorate = 4.0×10^{-5}M

Methylthymol blue = 4.0×10^{-4}M

pH of the solutions = 5.0

Wavelength nm	Optical density of complex (A)	Optical density of MTB (B)	Difference in optical density (A-B) = C
400	2.30	2.48	-
410	2.44	2.62	-
420	2.60	2.78	-
430	2.72	2.90	-
440	2.84	2.84	0.00
450	2.80	2.76	0.04
460	2.70	2.58	0.12
470	2.60	2.40	0.20
480	2.36	2.04	0.32
490	2.04	1.60	0.44
500	1.62	1.10	0.52
510	1.28	0.80	0.48

contd.

Table 6.1 contd.

Wavelength nm	Optical density of complex (A)	Optical density of MTB (B)	Difference in optical density (A-B) = C
520	0.96	0.56	0.40
530	0.65	0.37	0.28
540	0.50	0.28	0.22
550	0.38	0.22	0.16
560	0.28	0.16	0.12
570	0.22	0.14	0.08
580	0.16	0.12	0.04
590	0.11	0.10	0.01
600	0.08	0.09	-
610	0.05	0.06	-
620	0.04	0.05	-

The Effect of pH and Choice of Buffer

The pH is very important because the reagent functions as an acid-base indicator. The effect of pH on the colour development of the complex was investigated by measuring the absorbance of mixtures containing 9 μg (1.0 μ mol) of beryllium and 10.0 μ mol of the reagent at different pH values; the results are represented in table 6.2, fig. 6.2, from which it can be seen that the optimum pH range for analytical purposes lies between 5.0 and 5.5.

Table 6.2

Beryllium perchlorate = 4.0×10^{-5}M

Methylthymol Blue = 4.0×10^{-4}M

pH	3.6	4.0	4.4	4.8	5.0	5.25	5.5	5.8
Optical density per cm (500 nm)	0.310	0.400	0.460	0.515	0.530	0.530	0.525	0.475

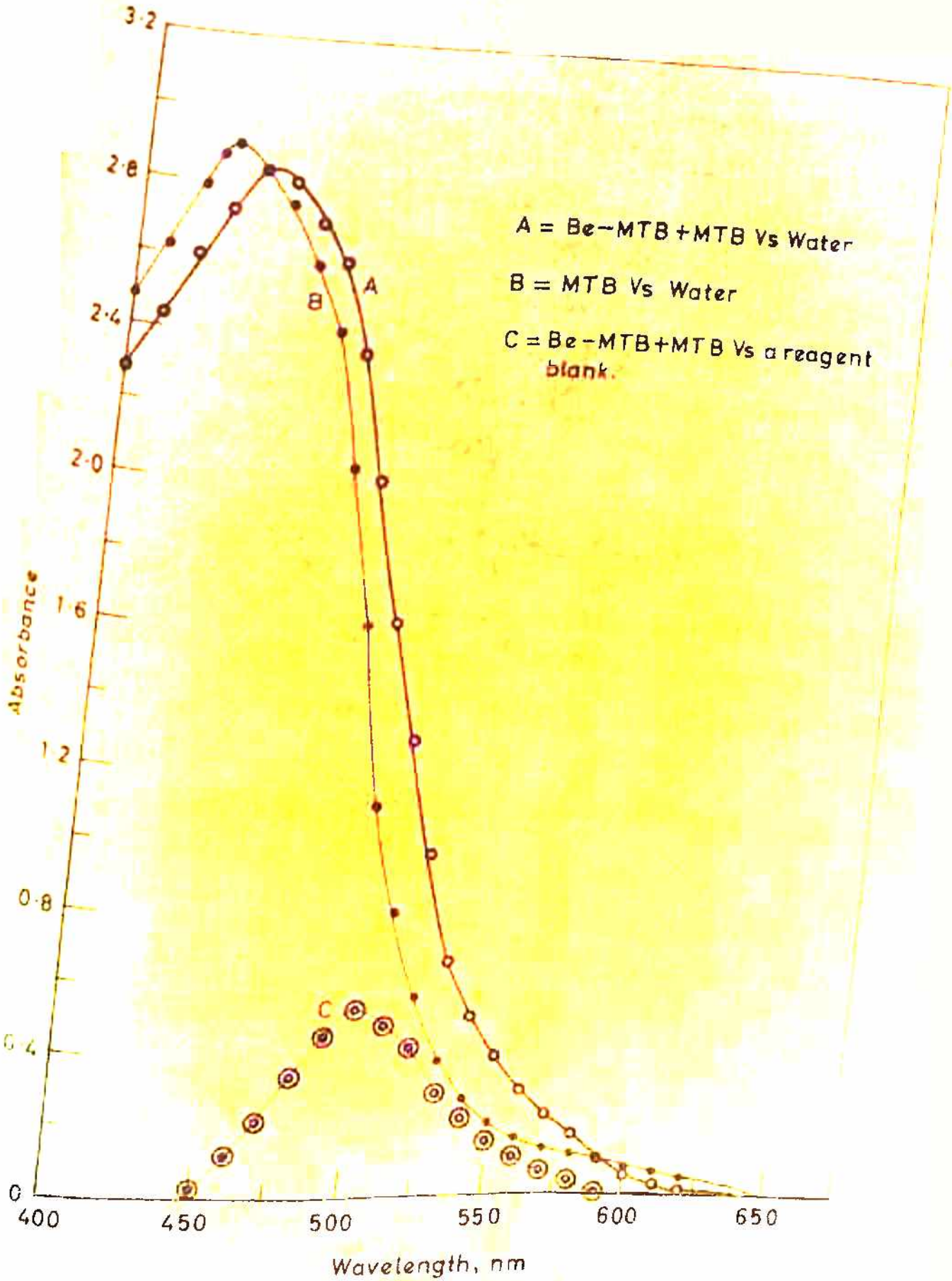


Fig. 6·1 Absorption curves of Methylthymol blue and its beryllium complex at pH: 5·0, Be: 9 µg; MTB: $4·0 \times 10^{-4}$ M

Initially an acetate buffer was used to maintain the pH within this optimal range, but the observed absorbance was always found to be lower than that obtained with the hexamethylene tetramine perchloric acid buffer. This may be due to the fact that acetate forms a complex with beryllium, rendering it ionically unavailable. The buffer system, hexamethylene tetramine perchloric acid was employed, which has a great buffering capacity in the pH range from 4 to 7.

The Effect of the Reagent Concentration

A study of the effect of the reagent concentration at pH 5.0 and 500 nm indicated that there should be ten fold molar excess of methylthymol blue over beryllium concentration.

The Colour Stability

The intensity of the colour increases with rise in temperature, the maximum colour development is attained within 20 minutes when the mixture is heated to 80°C in a water bath. The absorbance remains constant for at least 8 hours after this at pH 5.0. The order of addition of the reagent was found to be of no significance.

Calibration Curve

The analytical potentiality of the procedure was checked against the Lambert Beer law performance of the colour system (Fig.613). Calibration curve showed linearity in the

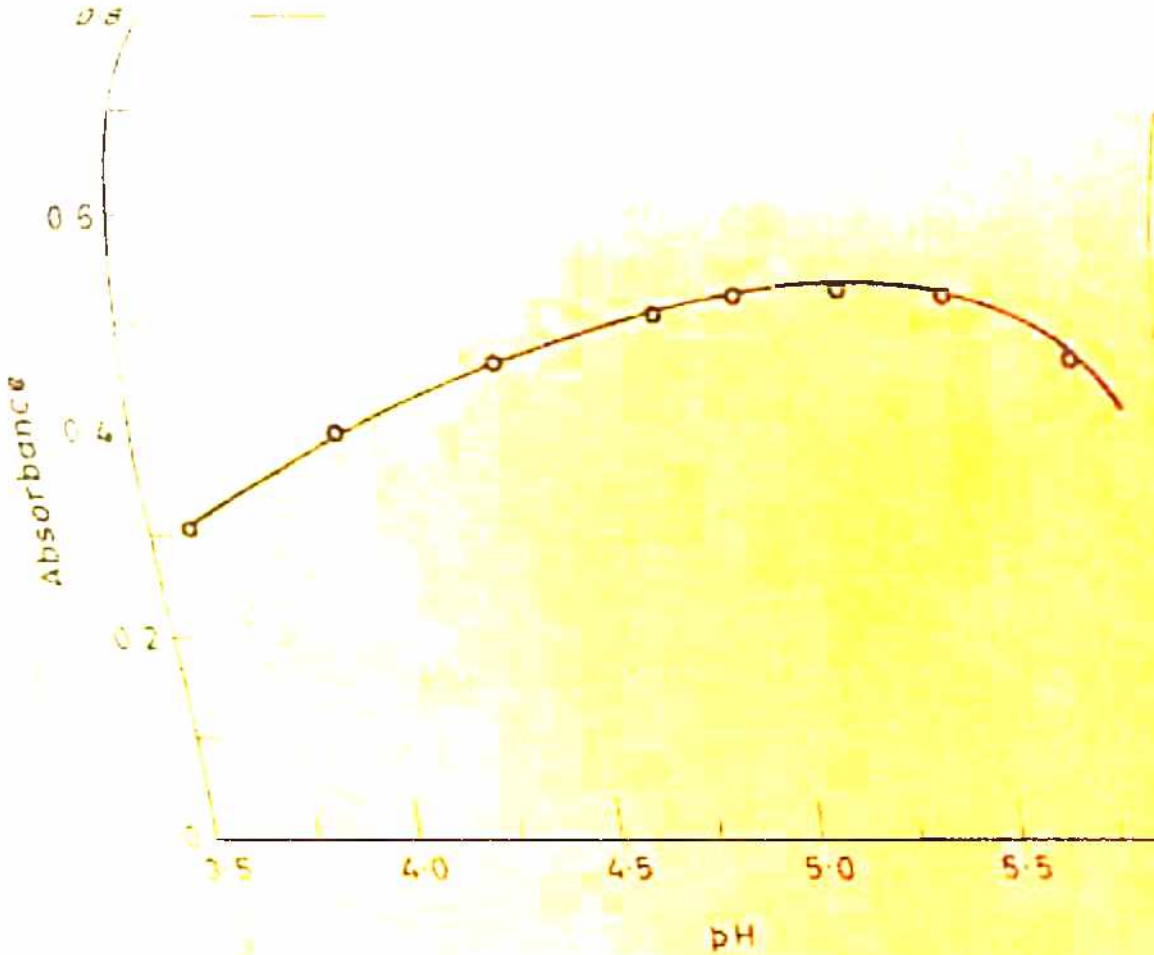


Fig._ 6·2 Effect of pH; MTB: 4.0×10^{-4} M, Be : 9 µg

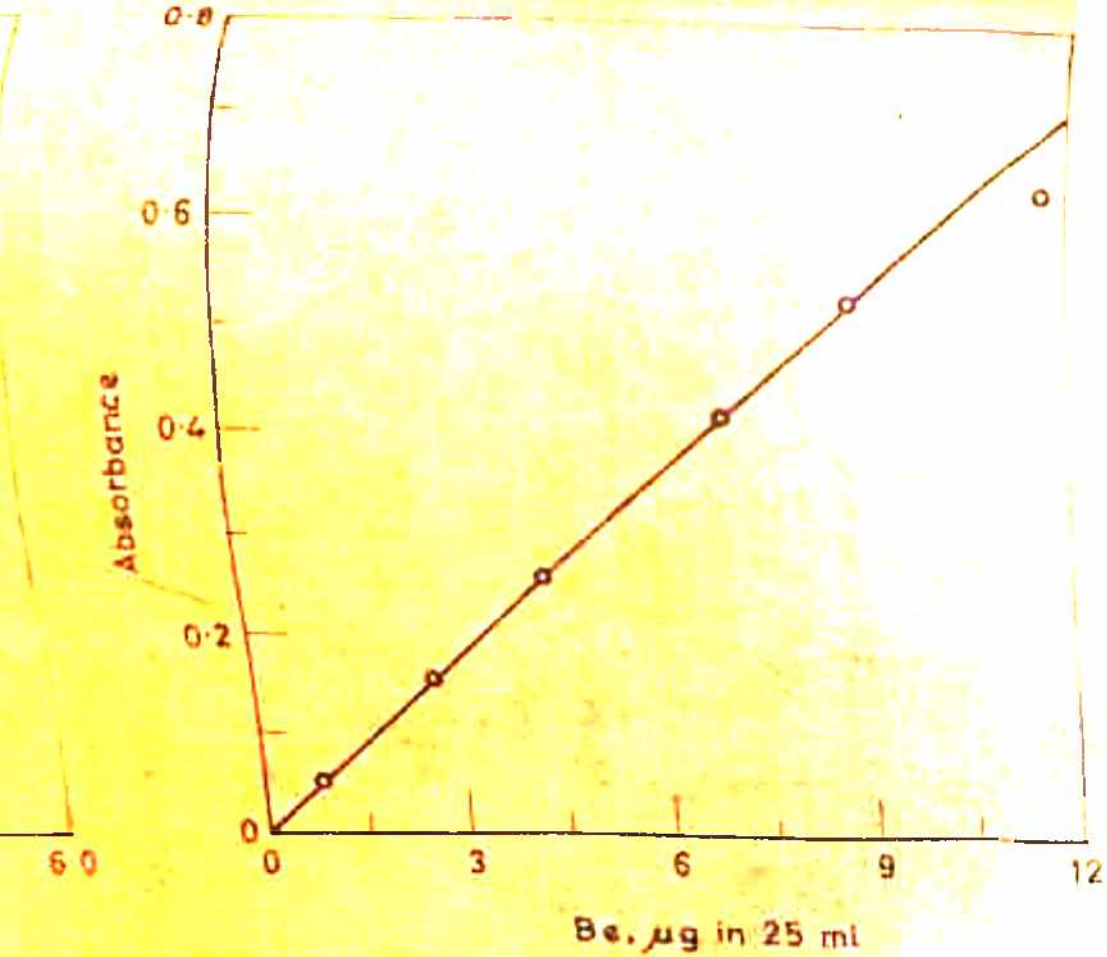


Fig._6·3 Calibration curve at 500 nm;
MTB: $4{\cdot}0 \times 10^{-4}$ M; pH: 5·0

range 0.9 to 9 μg of beryllium with net molar absorptivity ε 500 nm = 13.250. The sensitivity of the reaction as expressed by Sandell's notation (31) is 0.00066 μg of beryllium per cm^2. An examination of the data presented in table 6.2a shows that MTB is considerably more sensitive than some conventional colorimetric reagents.

Table 6.2a

Sensitivity of colorimetric reagents for beryllium

Reagent	Maximal absorption nm	Sensitivity index	Reference
Methylthymol blue	500	0.00066	
Acetylacetone	295	0.001	30
Chrome Azurol S	575	0.0004	35
Eriochrome cyanine R	512	0.004	12
Fast Sulfon Black F	630	0.001	4
Alkannin and naphthazarin	-	0.005	43
2-phenoxyquinizarin - 3, 4 disulfonic acid	550	0.01	28
Quinizarin -2-sulfonic acid	575	0.005	6
Sodium chlorophenol azo 1, 8 dihydroxy naphthalene 3, 6 disulfonate	610	0.0008	42
Xylenol orange	495	0.0006	26

The Effect of anions and Complexing Agents

The effect of anions and complexing agents was studied

as usual and the tolerance limits were determined. The latter denotes the maximum permissible concentration of the foreign ion in the solution under investigation, which would affect the optical density by less than ± 3 per cent. The results are given in table 6.3

Table 6.3

The effect of anions and complexing agents

Beryllium taken 9 μg

Anion or complexing agent added, μ mol		Relative error per cent	Tolerance limit μ mol
Cl^-	100	± 0.0	
	250	+ 1.1	large excess
F^-	2	- 3.3	1.8
	5	- 8.8	
NO_3^-	100	± 0.0	large excess
	250	± 0.0	
SO_4^{2-}	100	+ 2.2	150
	200	+ 4.0	
$C_2O_4^{2-}$	5	- 5.5	2.7
	20	-14.3	
$C_4H_4O_6^{2-}$	10	± 0.0	68
	25	- 1.1	

contd.

Table 6.3 contd.

Anion or complexing agent added, μ mol		Relative error per cent	Tolerance limit μ mol
PO_4^{3-}	5	- 6.5	2.3
	10	-12.1	
$C_6H_5O_7^{3-}$	2	-13.2	0.4
		-28.6	
NTA	1	± 0.0	
	5	- 2.2	6.8
EDTA	0.5	± 0.0	
	2.5	- 2.2	3.4

The effect of cations

Methylthymol blue is a selective reagent for certain cations when it is used in a relatively strong acid medium. However, in a slightly acid medium it reacts with many metal cations to give blue, red or reddish violet complexes, indicating that a suitable masking agent must be used to increase the selectivity. Disodium salt of EDTA was chosen for this reason. The common bivalent ions can be masked by EDTA as shown in table 6.4. The following cationic interferences could not be masked: aluminium, bismuth, thorium and zirconium.

Table 6.4

Masking effect of EDTA

Beryllium taken : 9.0 μg

Cations added : each 2.0 μ mol

EDTA added : 2.5 μ mol

Cations	Relative error per cent	Tolerance limit μ mol
Mg^{2+}	- 2.2	2.7
Zn^{2+}	- 1.1	5.4
Cd^{2+}	± 0.0	Large excess
Hg^{2+}	- 1.1	5.4
Cu^{2+}	- 2.2	2.7
Pb^{2+}	- 3.3	1.8
Mn^{2+}	- 0.5	12.0
Pd^{2+}	- 2.2	2.7
Co^{2+}	± 0.0	Large excess
Fe^{3+}	+ 1.1	5.4
Bi^{3+}	+ 6.6	0.8
La^{3+}	+ 3.3	1.6

Discussion

Some sensitive reagents, including Morin (32, 33, 34), 1, 4 Dihydroxy anthraquinone (18), 8-Hydroxy quinaldine (22), Acetylacetone (30), Chrome Azurol S (35, 36), Eriochrome Cyanine R (12), Fast Sulfon Black F (4), Alkannin and naphthazarin (43), 2 phenoxyquinizarin 3, 4 disulfonic acid (28), Quinizarin - 2-sulphonic acid (6), Sodium chlorophenol azo 1, 8 dihydroxy naphthalene 3, 6 disulfonate (42) and Xylenol Orange (26) have been used for the determination of beryllium. Out of these reagents, morin, 1, 4 dihydroxy anthraquinone and 8 hydroxy quinaldine have been used as fluorometric reagents for beryllium. Of the reagents which react with beryllium to form water soluble complexes, chrome azurol S, Sodium chlorophenol azo, 1, 8 dihydroxy naphthalene, 3, 6 disulfonate and xylenol orange are found to be the most sensitive to beryllium. The present method using methylthymol blue is very sensitive and is comparable with the sodium chlorophenol azo, 1, 8 dihydroxy naphthalene 3,6 disulfonate or the xylenol orange method in sensitivity.

Procedure

An aliquot of the standard beryllium solution was introduced in a 25 ml volumetric flask, 5 ml of a pH 5.0 buffer, 10 ml of a 1 x 10^{-3}M methylthymol blue solution and then a small amount of water was added to make the solution

about 20 ml. The solution was heated in a water bath at 80°C for 20 minutes, cooled with running water, diluted with water and made up. The resulting solution was kept for about 30 minutes in a thermostat at 30 ± 0.5°C. The absorbance of the solution was measured against a reagent blank at 500 nm.

Composition and Stability of the Complex

The composition of the beryllium methylthymol blue complex was determined by two methods, the method of continuous variations (15), and the mole ratio method (45). The results are presented in Figs. 6.4 and 6.5 from which it is evident that beryllium forms a 1:1 complex with MTB at pH 5.0. The conditional stability constant of the complex obtained by calculations based on the mole ratio data was found to be 7.7×10^5 at 30 ± 0.5°C and pH 5.0.

Lead-Methylthymol Blue System

A new, spectrophotometric method for the determination of a trace of lead has been developed. It is based upon the formation of a blue lead (II) complex of methylthymol blue, which was synthesised by Körbl et al and which has recently been used as a reagent for the determination of some inorganic ions.

Absorption Curves

When solutions containing lead (II) and methylthymol

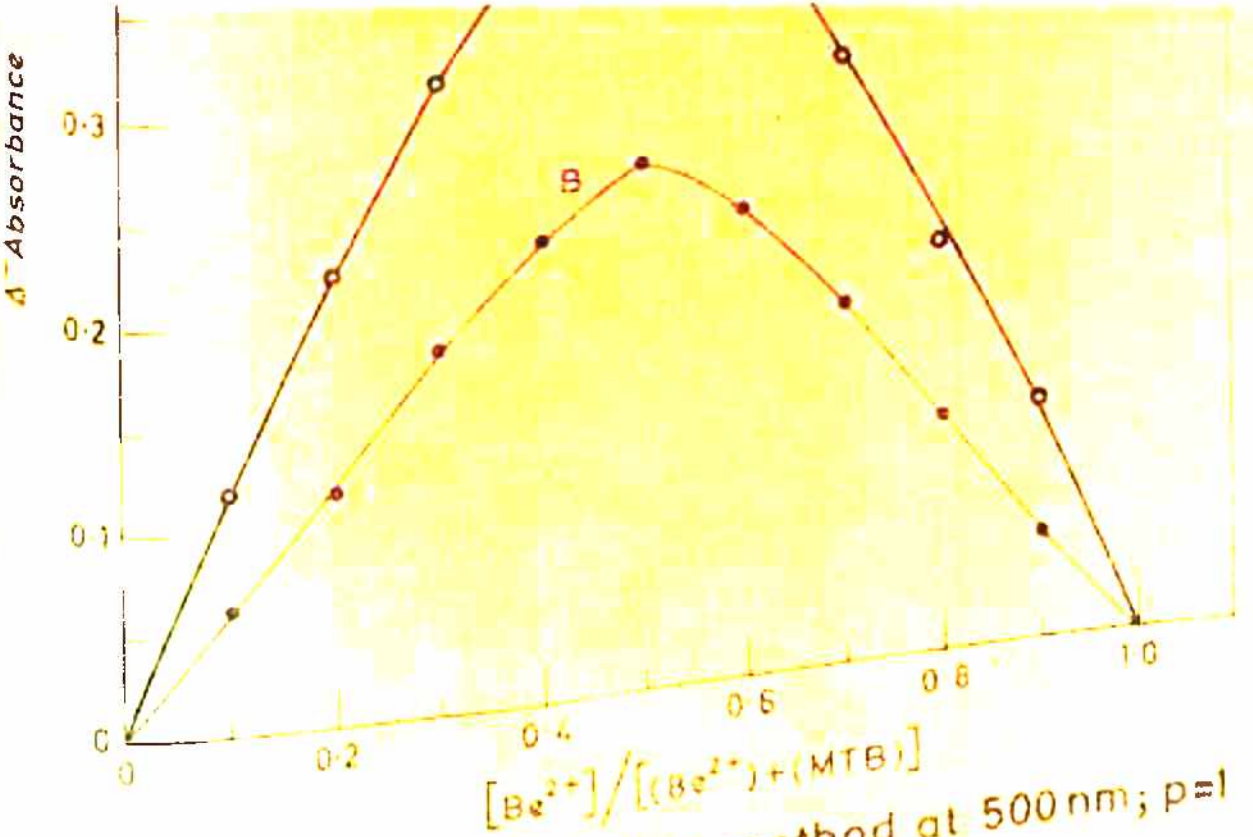
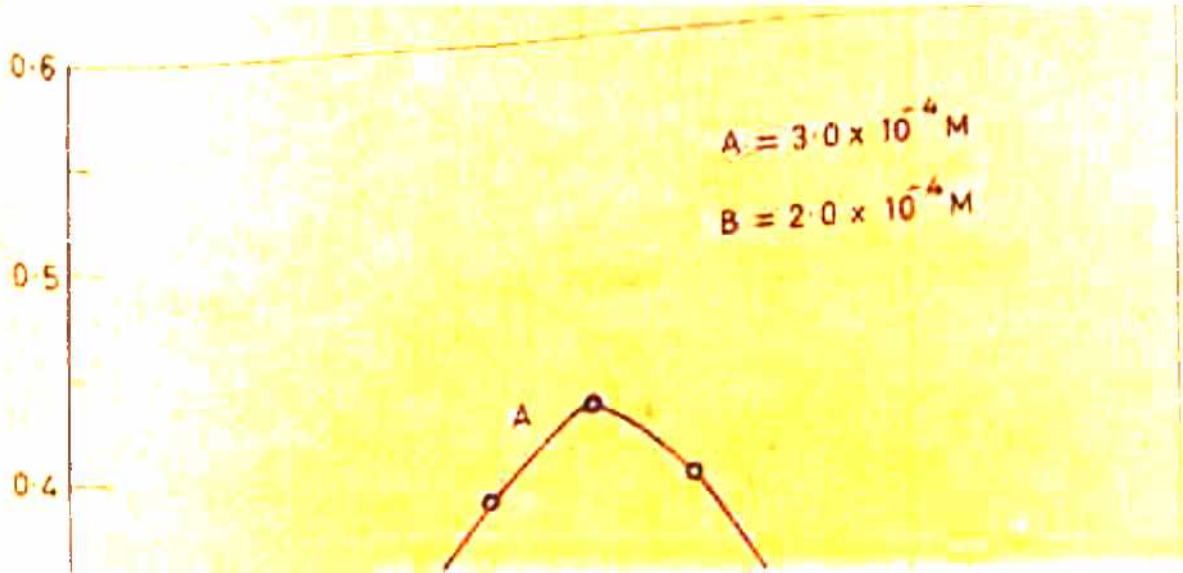


Fig. 6·4 Continuous variation method at 500 nm; p=1

pH: 5·0


0·6
0·5
0·4
A = 3·0 x 10⁻⁴ M
B = 2·0 x 10⁻⁴ M
A

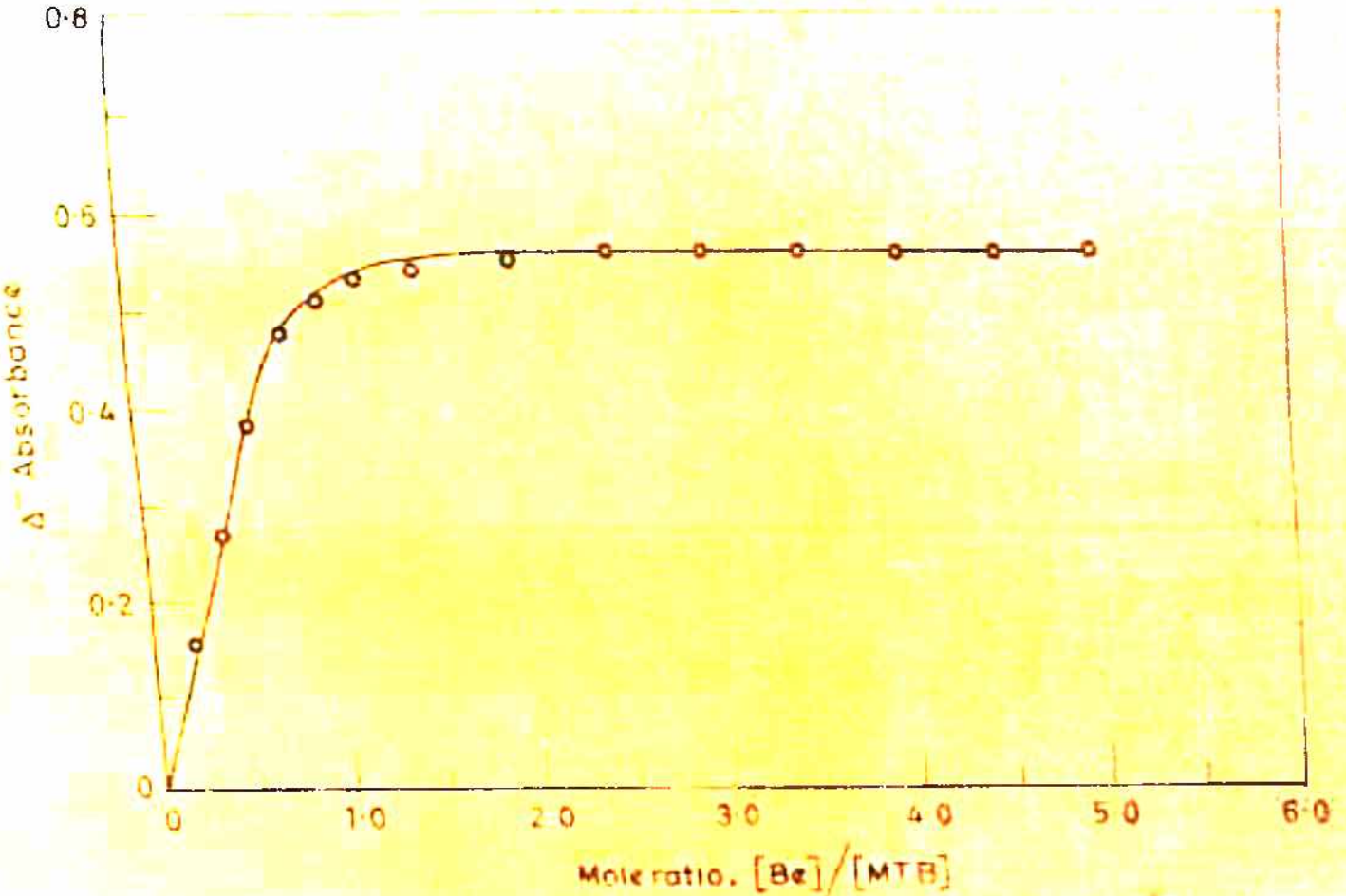


Fig._ 6·5 Mole ratio method at 500 nm; pH: 5·0; MTB: 2×10^{-4} M

blue in equimolecular amounts are mixed, a blue colour appears immediately at pH 5.8. Fig. 6.6 shows the absorption curves of methylthymol blue and its lead complex. The absorption curve of lead complex obtained with a reagent blank as reference has an absorption maximum at 600 nm. Some of the typical results are given below in table 6.5.

Table 6.5

Lead Acetate = 4.0×10^{-5}M

Methylthymol blue = 4.0×10^{-5}M

pH = 5.8

Wavelength nm	Optical density of complex (A)	Optical density of MTB (B)	Difference in optical density A-B = C
400	0.240	0.326	-
410	0.206	0.368	-
420	0.170	0.388	-
430	0.150	0.396	-
440	0.136	0.384	-
450	0.146	0.348	-
460	0.157	0.308	-
470	0.190	0.266	-
480	0.222	0.222	-
490	0.258	0.180	0.078
500	0.300	0.150	0.150
510	0.350	0.122	0.228
520	0.396	0.102	0.294
530	0.450	0.090	0.360
540	0.520	0.078	0.442
550	0.584	0.074	0.510
560	0.670	0.068	0.602
570	0.739	0.062	0.677
580	0.802	0.056	0.746
590	0.810	0.050	0.760
600	0.825	0.042	0.783
610	0.756	0.036	0.720
620	0.480	0.020	0.460
630	0.310	0.010	0.300
640	0.174	0.000	0.165
650	0.098	0.000	0.090
660	0.058	0.000	0.055
670	0.045	0.000	0.040
680	0.040	0.000	0.030
690	0.020	0.000	0.016
700	0.015	0.000	0.010

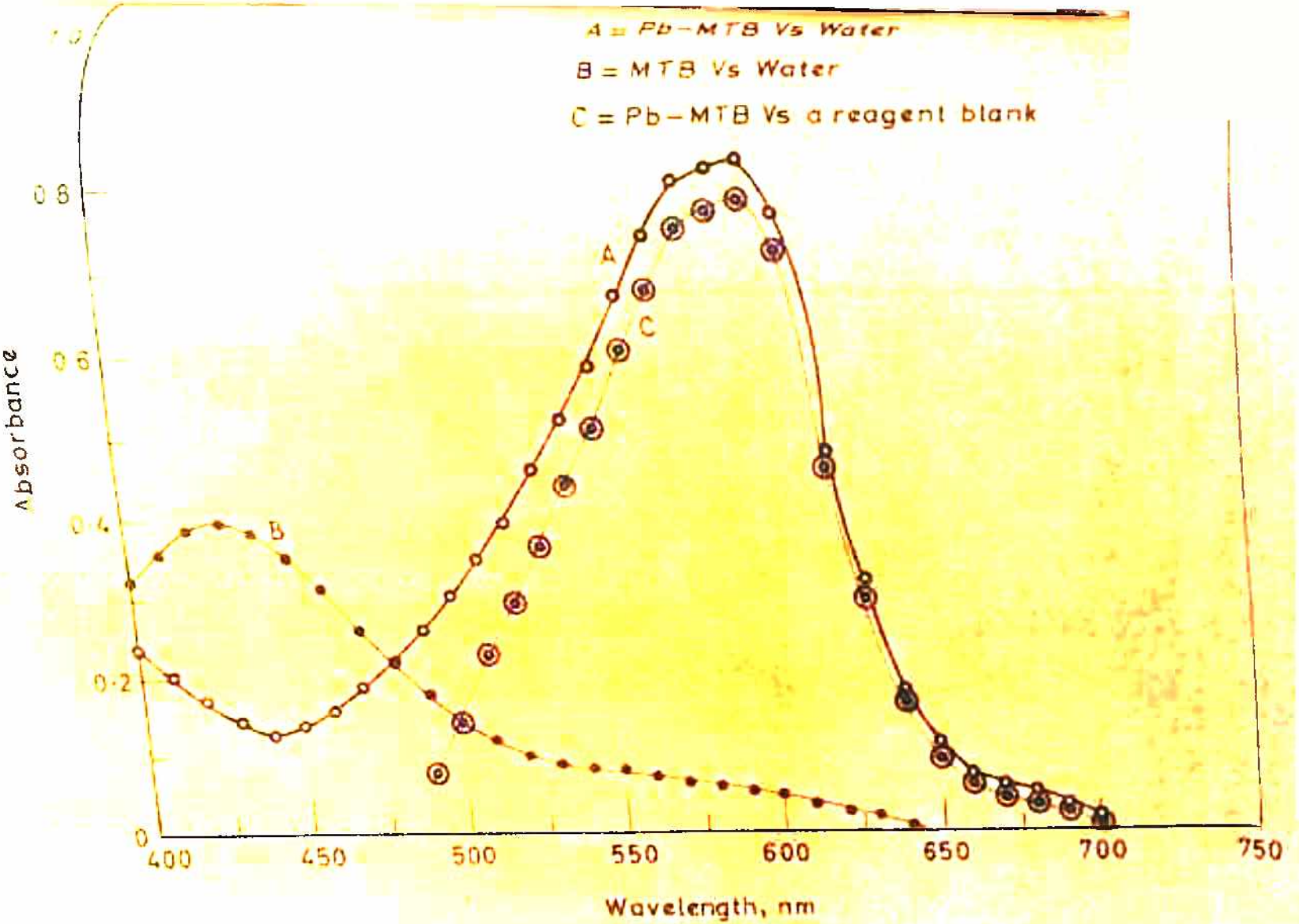


Fig _ 6·6 Absorption curves of Methylthymol blue and its Lead complex at pH: 5·8; Pb: $4 \cdot 0 \times 10^{-5}$ M; MTB: $4 \cdot 0 \times 10^{-5}$ M

The Effect of pH

The effect of pH of the colour development of the complex was investigated by measuring the absorbance of the mixtures containing 100 μg of lead and 0.5 ml of a 1×10^{-3}M solution of methylthymol blue at different pH values; the results are shown in fig. 6.7, table 6.6 from which it can be seen that the optimum pH range for analytical purposes lies between 5.8 and 6.0.

Table 6.6

Concentration of lead acetate = 2.0×10^{-5}M

Concentration of MTB = 2.0×10^{-5}M

pH	5.2	5.5	5.6	5.8	6.0	6.25	6.4
Optical density per cm (600 nm)	0.22	0.34	0.36	0.39	0.39	0.38	0.37

Hexamethylene tetramine-nitric acid buffer was used for obtaining pH 5.8

The effect of the reagent concentration

It was observed that the complex is formed on mixing equimolecular solutions and maximal absorbance values are obtained with 3 fold excess of the metal ion.

The colour stability

The colour of the complex develops immediately at room temperature and the absorbance remains constant for at least 12 hours after preparation at pH 5.8. A study of the effect of temperature indicated that the absorbance decreases on increasing the temperature to 60°C.

Calibration Curves

The calibration curves for the lead determination were prepared with solutions containing no fluoride or 40 μ mol of fluoride. In both the curves shown in fig. 6.8, linear relationships between absorbance and concentration are found to hold upto 200 μg (8 ppm) of lead at pH 5.8. The optimum concentration range was then determined by Ringbom (29) procedure and was found to lie between 20 to 100 μg (0.8 to 4.0 ppm) of lead. At the measured wavelength the net molar absorptivity of the complex was found to be 19,500.

The Effect of Diverse Ions

The effect of diverse ions on the determination of lead was then examined at pH 5.8 and the tolerance limit was calculated in each case. The tolerance limit was tentatively defined as the concentration of the foreign ion which affects the absorbance of the system by less than $\pm$ 3 per cent. The results are summarised in table 6.7

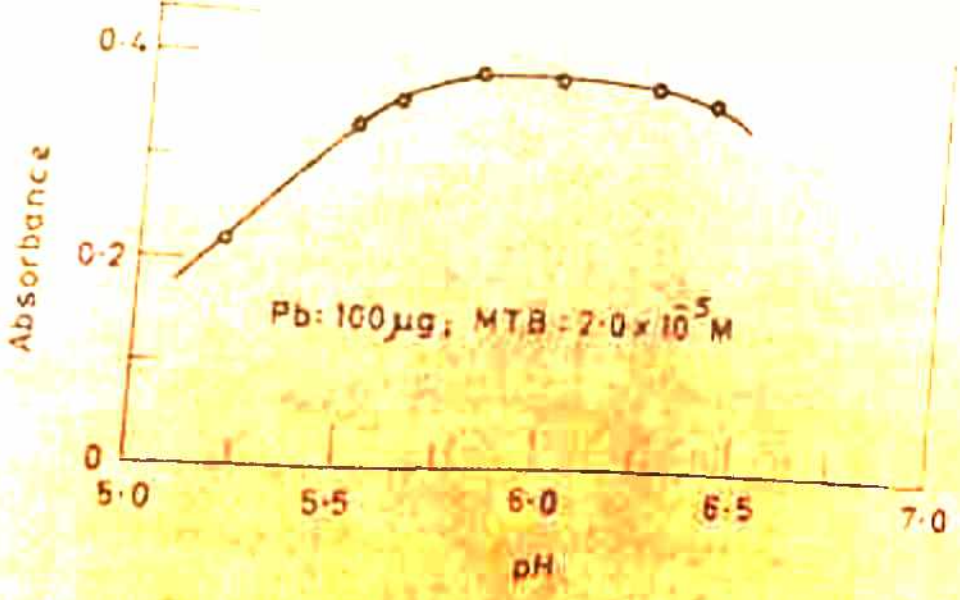


Fig.-6·7 Effect of pH

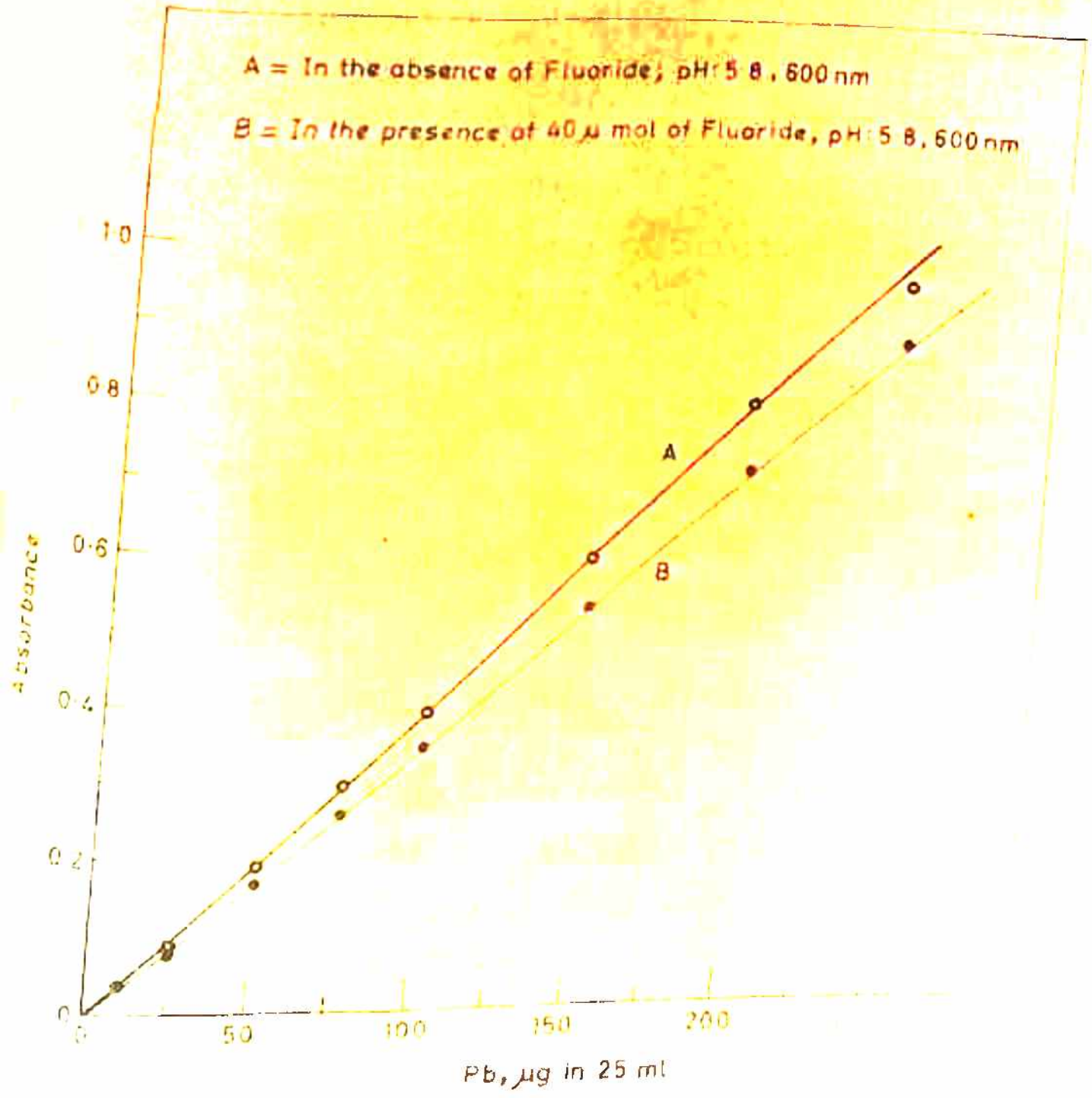


Fig.-6·8 Calibration curves

from which it may be seen that Bismuth (III), Iron (III), Thorium (IV), Zirconium (IV), NTA and EDTA interfere in even the smallest concentrations examined, but that some interfering cations including Aluminium (III), Thorium(IV) and Zirconium (IV), are partly masked by adding 40 μ mol of potassium fluoride. The interference of iron (III), palladium (II) and thallium (III), can be eleminated by the addition of such a reducing agent as ascorbic acid.

Table 6.7

Effect of Diverse Ions

pb taken = 100 μg

Diverse ion	μ mol	Relative error percentage	Tolerance limit μ mol
Al(III)	1.0	+ 5.8	0.50
	1.0*	- 1.2	2.50
Bi(III)	1.0	+20.6	0.16
Cd(II)	1.0	- 0.3	Large excess
Ce(III)	1.0	+ 0.4	Large excess
Co(II)	1.0	± 0.0	Large excess
Cr(III)	1.0	- 0.2	Large excess
Cu(II)	1.0	+ 1.8	1.6
Fe(III)	1.0	+30.6	0.1
	1.0*	- 0.5	Large excess

contd.

Table 6.7 contd.

Diverse ion	μ mol	Relative error percentage	Tolerance limit μ mol
Ga(III)	1.0	+ 0.7	4.2
Hg(II)	1.0	- 0.2	Large excess
Mn(II)	1.0	± 0.0	Large excess
Ni(II)	1.0	- 0.4	Large excess
Pd(II)	1.0	+ 3.1	1.0
	1.0 **	- 0.5	Large excess
Th(IV)	1.0	+37.6	0
	1.0*	+18.3	0
Ti(V)	1.0	+ 1.3	2.4
Tl(III)	1.00*	- 0.2	Large excess
U(VI)	1.0	+ 0.4	Large excess
V(V)	1.0	- 0.5	Large excess
Zn(II)	1.0	± 0.0	Large excess
Zr(IV)	1.0	+11.0	0.2
	1.0*	+ 5.6	0.6
F^-	10	- 2.9	10
	25	- 5.7	
	100	-19.3	Large excess
Cl^-	500	- 0.2	Large excess
NO_3^-	100	± 0.0	Large excess
	200	± 0.0	200
SO_4^{2-}	500	- 7.2	0.5
$C_2O_4^{2-}$	2.0	-12.9	contd.

Table 6.7 contd.

Diverse ion	μ mol	Relative error percentage	Tolerance limit μ mol
$C_4H_4O_6^{2-}$	25	- 1.8	45
$C_6H_5O_7^{3-}$	10	- 0.4	75
NTA	0.2	-27.6	0
EDTA	0.2	-20.0	0

* 40 μ mol of F^- added.

** 40 μ mol of F^- and 2.0 ml of 3 per cent ascorbic acid added.

Discussion

With a net molar absorptivity of 19,500, the technique compares favourably with those at present in use for the spectrophotometric determination of lead. It has been found that MTB is considerably more sensitive than some conventional colorimetric reagents, although it lacks selectivity.

Procedure

To a sample solution containing lead in a 25 ml volumetric flask, 2.5 ml of hexamethylene tetramine nitric acid buffer, a given amount of methylthymol blue solution

and a small amount of water were added to make the volume about 20 ml. When sample solution contained Aluminium(III), Thorium(IV) or Zirconium(IV) about 40 μ mol of Potassium fluoride was added before the addition of methylthymol blue solution. The solution was mixed and allowed to stand for 30 minutes. The absorbance of the solution was then measured at the given wavelength and the amount of lead was found from the calibration curve prepared earlier.

Composition and Stability Constant

Attempts were made to establish the nature of the complex in solution and to determine the composition and formation constant of the complex.

1. Continuous Variation Method

The ratio between ligand and metal ion in the lead(II) methylthymol blue complexes was determined by the method of continuous variations in equimolecular solutions. The ratio 1:1 was found (fig. 6.9).

2. Mole ratio method

The mole ratio of lead to the reagent was confirmed by the mole ratio method at pH 5.8. In this work each solution was 4.0×10^{-5} M in the total concentration of methylthymol blue. The absorbance measurements were made

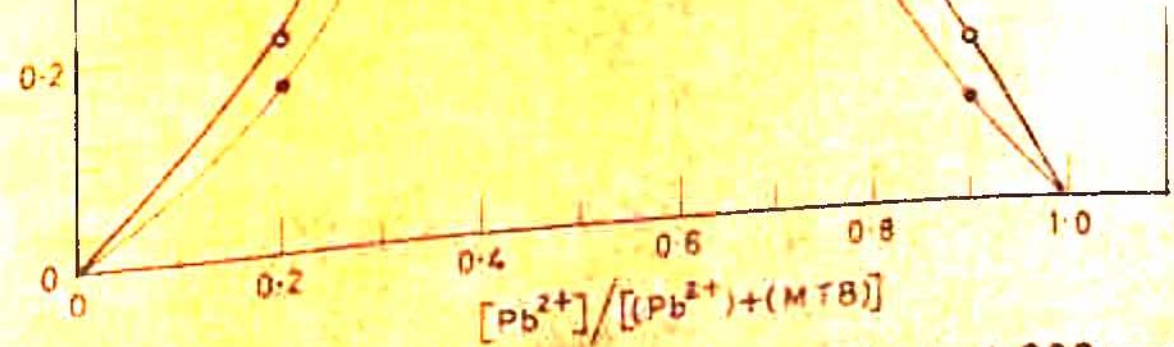
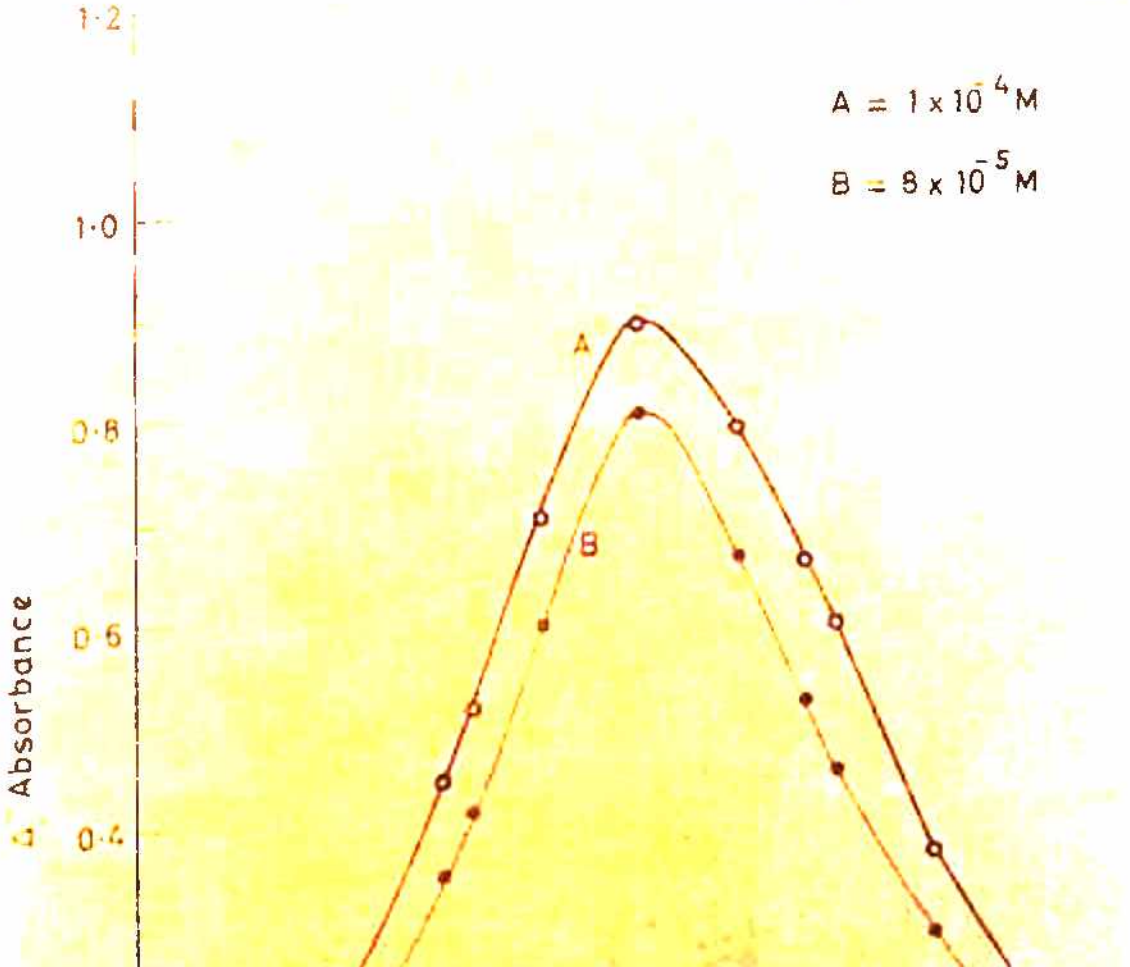


Fig.– 6·9 Continuous variation method at 600 nm; p = 1; pH: 5·8


1·2
1·0
0·8
0·6
0·4
Absorbance
A = 1 x 10⁻⁴ M
B = 8 x 10⁻⁵ M
A
B

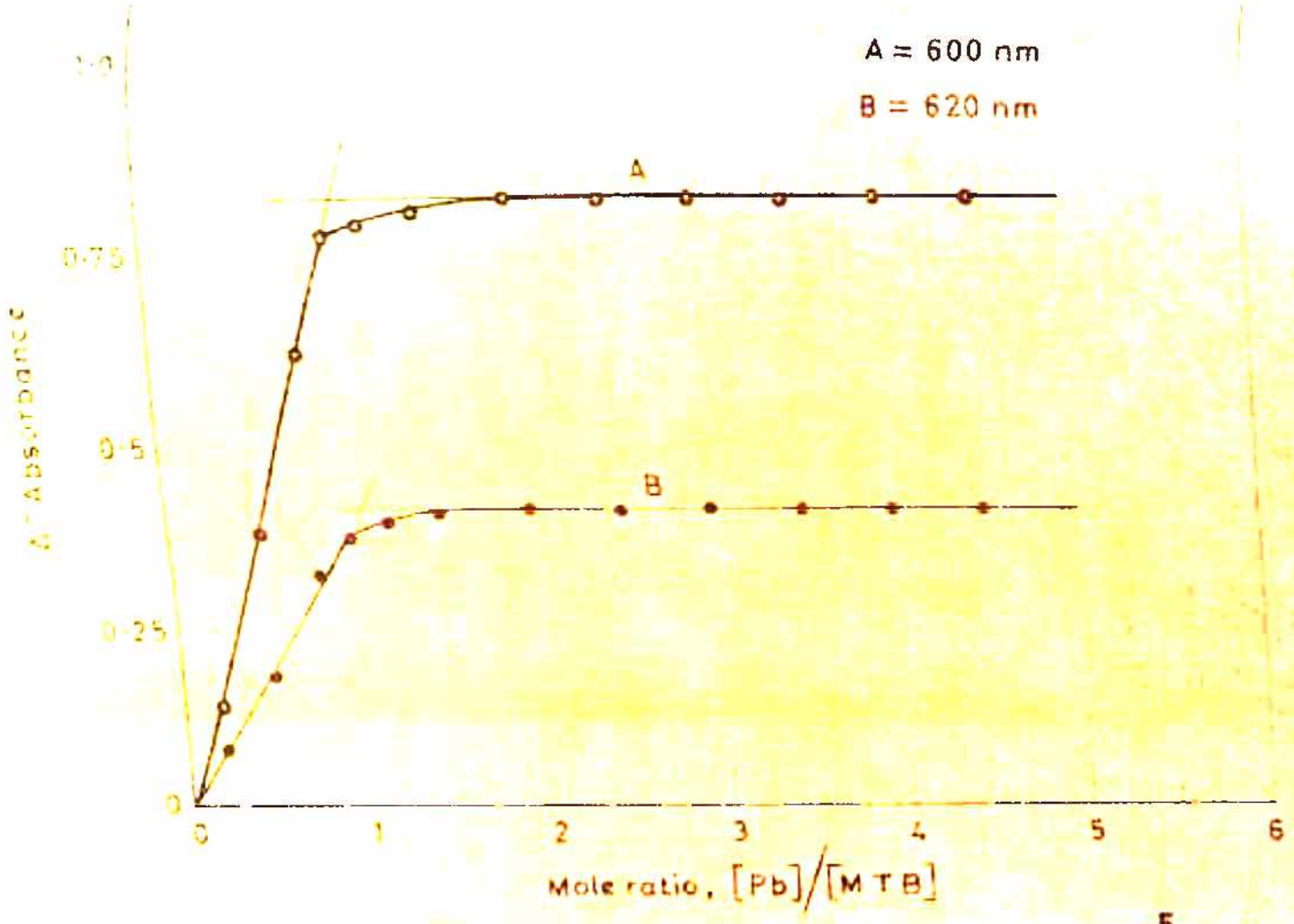


Fig._6·10 Mole ratio method; MTB: $4{\cdot}0 \times 10^{-5}$ M

at 600 and 620 nm. The results are shown in Fig. 6.10, which indicates the formation of 1:1 complex between the lead (II) and the reagent.

The stability constant was calculated from the curves shown in fig. 6.10 based on the method described by Harvey and Manning. It was found to be 5×10^5 at $30^\circ C$ and pH 5.8.

PALLADIUM METHYLTHYMOL BLUE SYSTEM

Methylthymol blue reacts with many metal ions in a weakly or a slighly acid medium to form blue, pink or reddish violet chelates. Because of the low selectivity of methyl-thymol blue, it is necessary for the practical determinations in slightly acidic media either to mask interfering ions with an appropriate masking agent or preliminary to separate these ions from the object ion. In a acidic solution of perchloric acid, however, this reagent reacts almost selectively with palladous ions, even in the presence of many other cations, to give a bright red complex with an absorption maximum at 530 nm.

This investigation presents spectrophotometric study of the reaction between palladous ion and methylthymol blue at pH 2.0 or at pH 7.3. The composition and the stability constant of the chelate have also been determined.

Absorption curves

The absorption curves of the solutions containing

palladium (II) and methylthymol blue at different pH values are shown in Figs. 6.11 and 6.12 and in Table 6.8 and 6.9. These curves were obtained by measuring the absorbance of the coloured solutions against a reagent blank which contained the same amount of methylthymol blue.

At pH 1.6 to 2.0 the solutions give essentially identical absorption curves, with one absorption maximum at 530 nm. Above pH 5, the position of maximum absorption shifts towards shorter wavelengths with an increase in pH value. Between pH 5.2 and 7.8 the solutions give absorption curves with an absorption maximum at 500 nm. Therefore, it may be concluded that, in presence of an excess of methylthymol blue, two complexes are formed between palladium (II) and the reagent

Table 6.8

Concentration of Palladium Chloride = 2.0×10^{-5}M

Concentration of Methylthymol blue = 2.5×10^{-4}M

pH of solutions:

A = 2.1 B = 2.0 C = 1.6

D = 1.4 E = 1.0

Wavelength nm	Optical density				
	A	B	C	D	E
480	0.080	0.10	0.085	0.075	0.045
490	0.170	0.20	0.180	0.154	0.080
500	0.260	0.29	0.275	0.215	0.110
510	0.325	0.36	0.342	0.260	0.150
520	0.370	0.395	0.390	0.310	0.185
525	0.384	0.418	0.405	0.335	0.200
530	0.388	0.425	0.410	0.340	0.205
540	0.360	0.392	0.370	0.310	0.178

contd.

Table 6.8 contd.

Wavelength nm	Optical density				
	A	B	C	D	E
550	0.315	0.340	0.328	0.270	0.135
560	0.250	0.280	0.260	0.210	0.100
570	0.178	0.195	0.190	0.145	0.060
580	0.118	0.140	0.130	0.095	0.040
590	0.072	0.085	0.080	0.058	0.025
600	0.040	0.045	0.040	0.030	0.015

Table 6.9

Concentration of Palladium Chloride = 2.0×10^{-5} M

Concentration of Methylthymol Blue = 1.2×10^{-4} M

pH of solutions:

A = 5.2 B = 6.5

C = 7.3 D = 7.8

Wavelength nm	Optical density			
	A	B	C	D
460	0.00	0.05	0.080	0.065
470	0.04	0.120	0.156	0.130
480	0.08	0.185	0.212	0.175
490	0.130	0.230	0.258	0.218
500	0.175	0.266	0.295	0.254
510	0.170	0.260	0.289	0.245
520	0.150	0.215	0.245	0.188
530	0.140	0.197	0.205	0.146
540	0.128	0.172	0.163	0.100
550	0.118	0.141	0.120	0.075
560	0.106	0.115	0.076	0.045
570	0.095	0.090	0.040	0.020
580	0.085	0.065	0.005	0.000
590	0.068	0.050	0.000	0.000
600	0.050	0.030		
610	0.025	0.020		
620	0.010	0.000		

The effect of pH

The effect of pH on the absorbance of the solution was

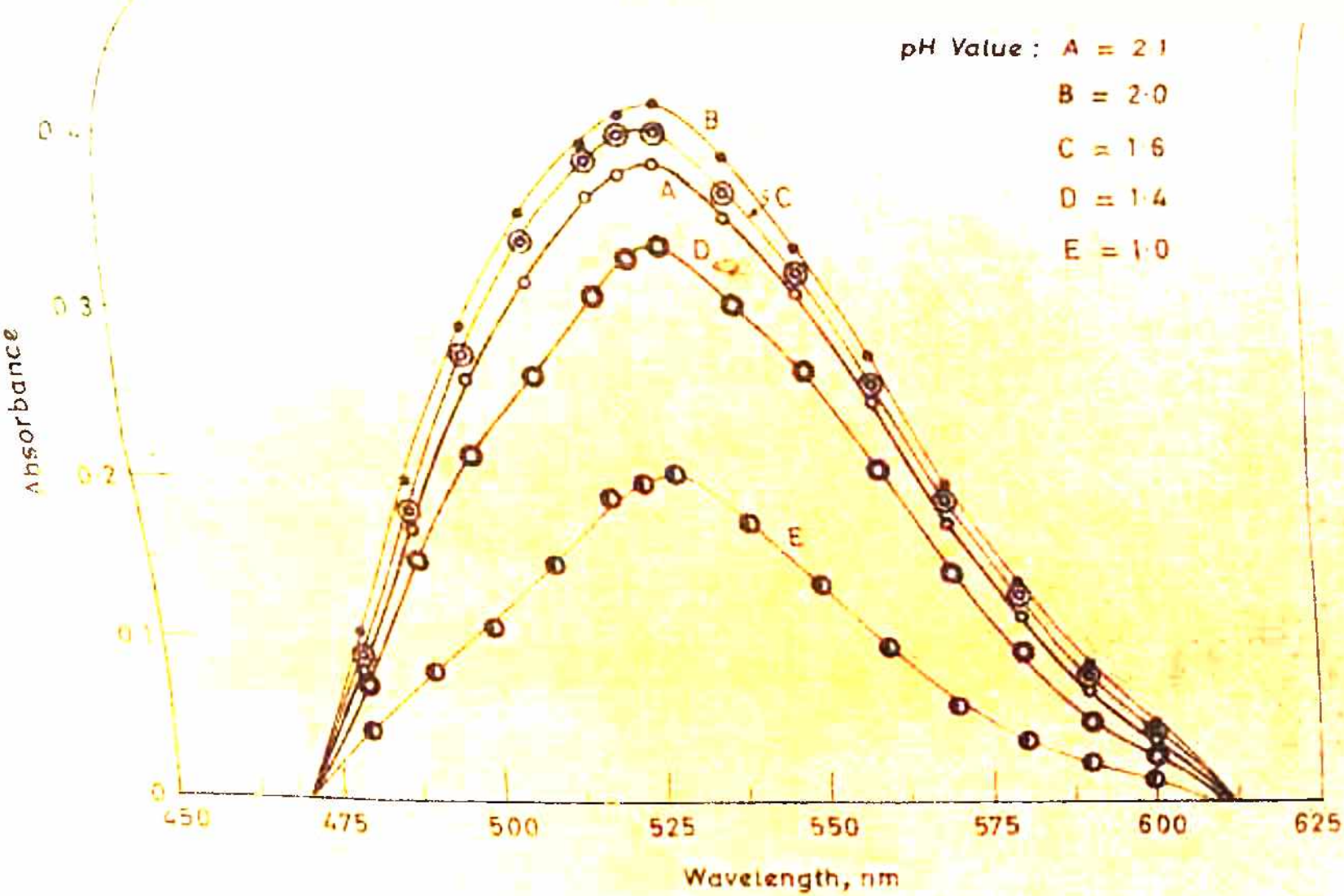


Fig._ 6·11 Absorption curves of Methylthymol blue and its Palladium complex Palladium: 50 µg, MTB: $2{\cdot}5 \times 10^{-4}$ M, A–E Palladium complex Vs a reagent blank

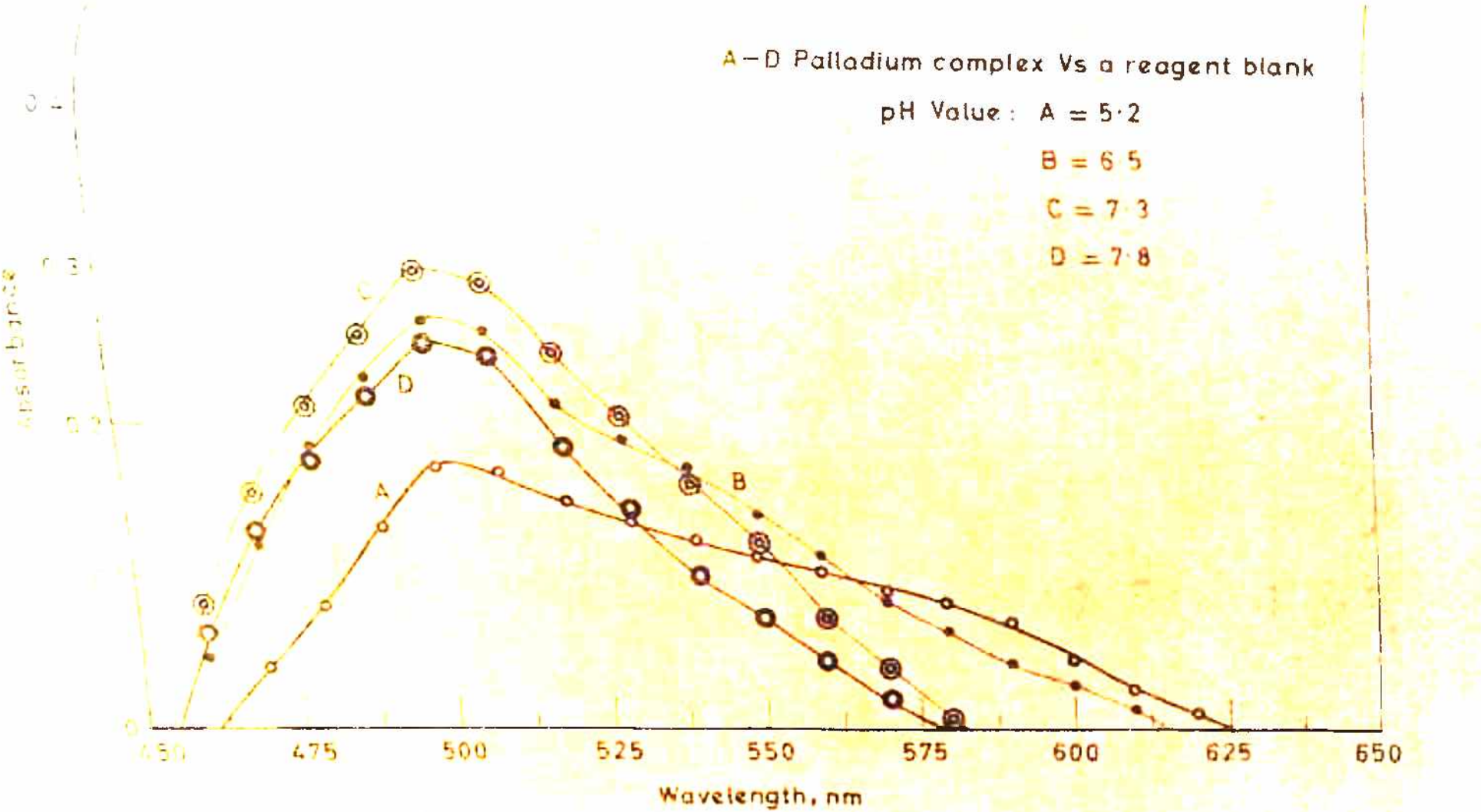


Fig – 6.12 Absorption curves of Methylthymol blue and its Palladium complex; Palladium 50 µg ; MTB · 1·2 x 10^{-4} M

examined by measuring, at two wavelengths 530 and 500 nm, the absorbance of a solution containing 50 μg of palladium and a 12 fold excess of pH 2.0 or 6 fold excess at pH 7.3 of methylthymol blue. From the curve shown in fig. 6.13 and 6.14 it was found that the maximum absorbance is obtained in the pH range from 1.6 to 2.0 when measured at 530 nm, and in the pH range from 6.8 to 7.3 when measured at 500 nm. The results are shown in table 6.10 and 6.11.

Table 6.10

Palladium Chloride = 2.0×10^{-5}M

Methylthymol blue = 2.5×10^{-4}M

pH	1.0	1.4	1.6	2.0	2.1
Optical density per cm (530 nm)	0.205	0.340	0.410	0.425	0.388

Table 6.11

Palladium Chloride = 2.0×10^{-5}M

Methylthymol blue = 1.2×10^{-4}M

pH	5.2	6.5	7.3	7.8
Optical density per cm (500 nm)	0.175	0.266	0.295	0.254

The effect of the Reagent Concentration

An excess of methylthymol blue must be added since the

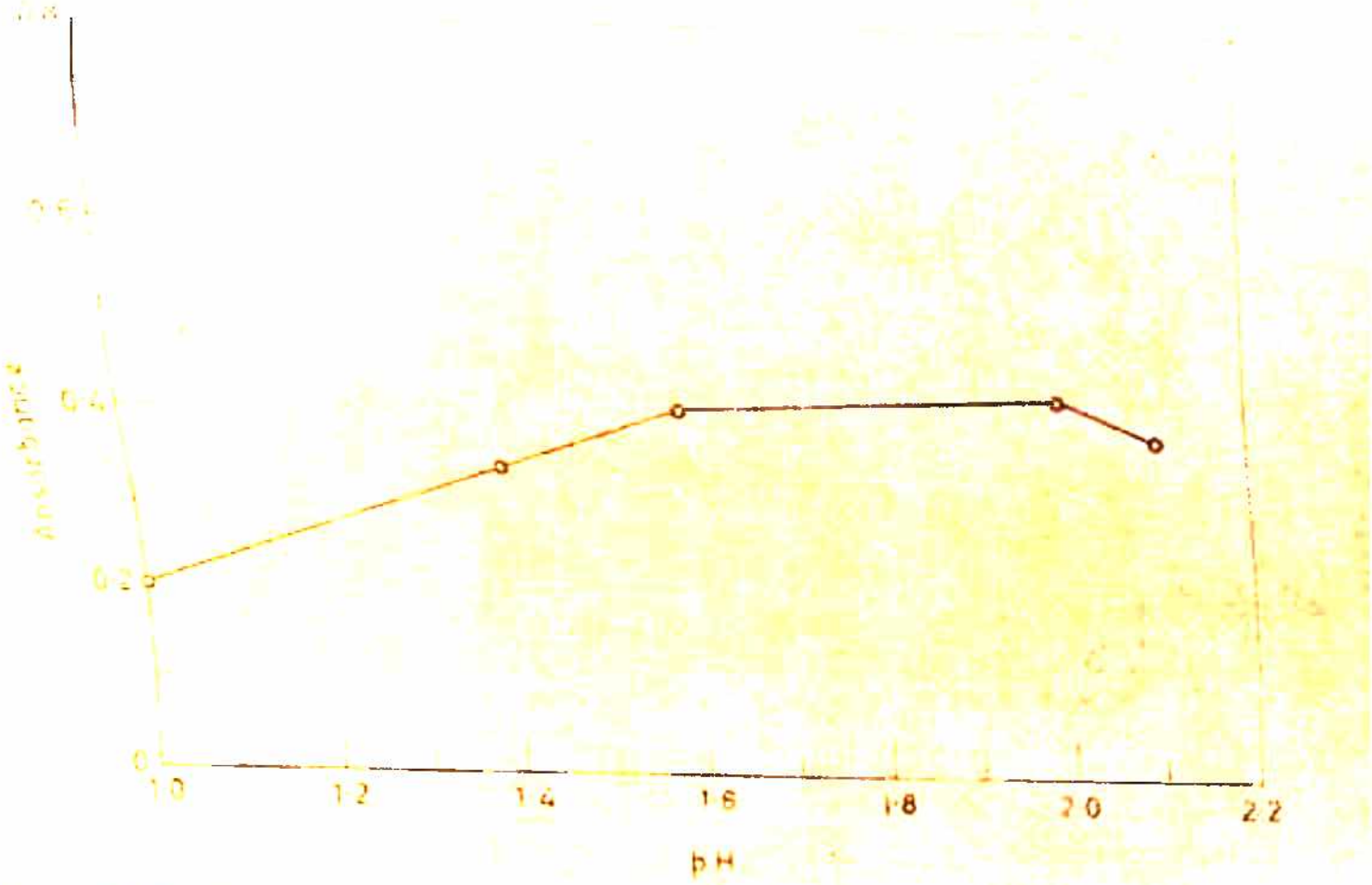


Fig - 6.13 Effect of pH at 530 nm, MTB: 2.5×10^{-4} M; Palladium: 50 µg

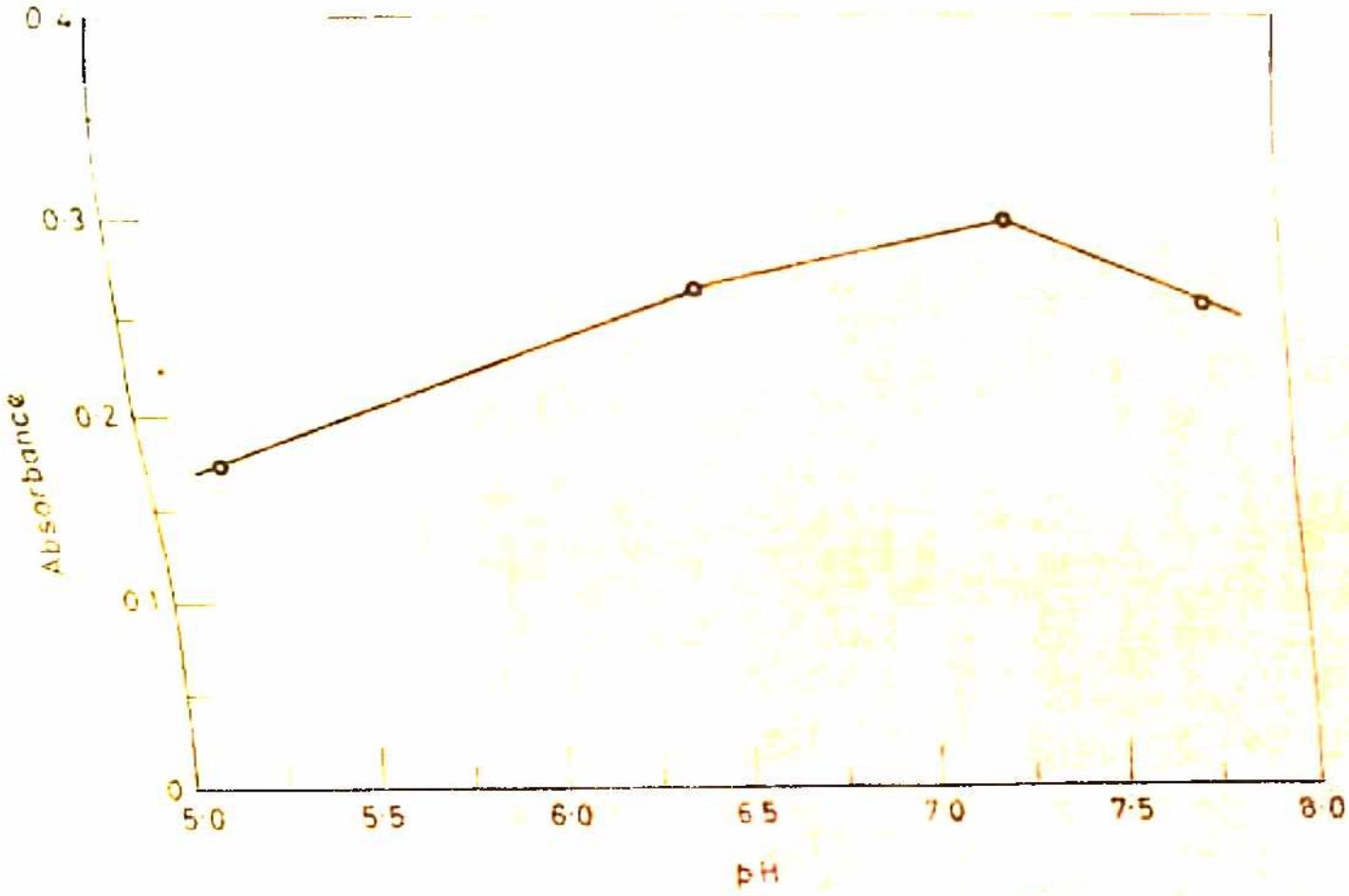


Fig._ 6·14 Effect of pH at 500 nm; MTB. $1{\cdot}2 \times 10^{-4}$ M; Palladium: 50 µg

absorbance of the complex at 530 nm and 500 nm is increased with an increased concentration of the reagent. 12 ml of 1 x 10^{-3}M solution of methylthymol blue was found to be sufficient for 100 µg (1 ml of 1 x 10^{-3}M) of palladium at pH 2.0 while at pH 7.3 only 6 ml of 1 x 10^{-3}M of methylthymol blue was sufficient for 100 µg of palladium.

The effect of heating time and the colour stability

The maximum colour development was reached when the solution had been kept at 80°C for about 20 to 30 minutes. The 20 ml of the solution contained 0.5 ml of 1 M $HClO_4$ and 6.25 ml of 1 x 10^{-3}M solution of methylthymol blue along with 50 µg of palladium. After heating the solution was cooled, transferred to a 25 ml volumetric flask and made up with distilled water. The absorbance was measured after 30 minutes, to allow equilibrium to be attained. The absorbance of the result and solution remained practically constant for at least 4 hours.

Calibration curves

As is shown in fig. 6.15, with either complex, Beer's law is obeyed over the concentration range from 10 µg to 80 µg (0.4 to 3.2 ppm) of palladium. The optimum concentration range for the determination of palladium was determined by the method described by Ringbom(29) and was found to lie between 20 to 60 µg (0.8 to 2.4 ppm). The molar absorptivity

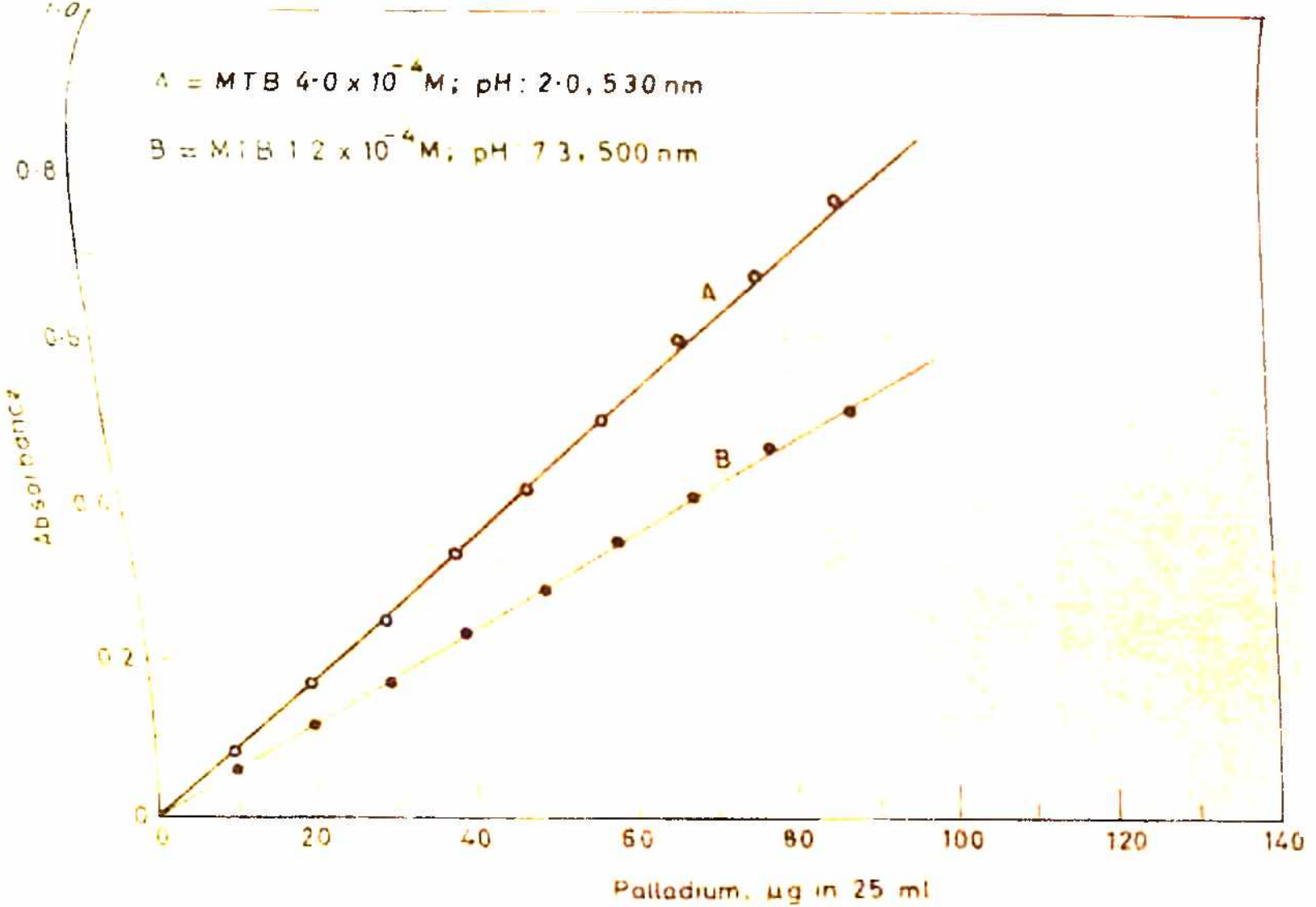


Fig._ 6·15 Calibration curves.

was 21,250 at 530 nm and 14,750 at 500 nm. The sensitivities of the methods are 0.005 μg of palladium per cm^2 at 530 nm and 0.0073 μg of palladium per cm^2 at 500 nm.

The effect of Diverse Ions

The effect of 38 diverse ions was investigated using 50 μg/25 ml of palladium (2.0 ppm) at pH 2.0. 50 μ mol of the anions such as chloride, sulphate, tartrate, oxalate and citrate and 5 μ mol of the cations such as arsenic (III), barium, beryllium, calcium, cadmium, cerium (III), chromium (III), cobalt (II), copper (II), iron (II), iron (III), lanthanum, lead, magnesium, manganese (II), mercury (II), nickel, platinum (IV), rhodium(III), strontium, uranium(VI) and zinc caused no interference. The ions causing interference are listed in table 6.12. Ther permissible amount is based on an error not exceeding (3 per cent) i.e. two times the estimate of the relative standard deviation.

Table 6.12

Effect of diverse ions on palladium determination

Palladium taken: 50 μg

Diverse ion	μ mol	Percentage relative error	Permissible amount μ mol
PO_4^{3-}	10	- 1.1	25
	25	- 2.9	
	50	- 5.7	

contd.

Table 6.12 contd.

Diverse ion	μ mol	Percentage relative error	Permissible amount μ mol
F^-	5.0	- 2.8	5
NTA	0.5	- 1.9	
	1.0	- 3.5	0.8
EDTA	0.2	-12.4	
	1.0	-41.2	0
Bi(III)	0.5	+ 0.7	2.1
Ga(III)	0.5	+ 1.8	0.8
In(III)	0.5	+ 0.4	3.7
Th(IV)	0.5	+ 8.8	0.18
	0.5*	+ 0.2	7.5
V(IV)	0.5	+ 4.6	0.3
Zr(IV)	0.5	+11.0	0.1
	0.5*	+ 5.6	0.25
Ru(III)	0.5	+ 0.5	3.0

* 1 ml of .01 M fluoride solution added.

Precision

In a series of six determinations on solutions containing 50 μg/25 ml (2.0 ppm) of palladium at pH 2.0 and rendered 2.5×10^{-4} M with respect to MTB, a relative standard deviation of 1.5 per cent was obtained.

Discussion

Several reagents have been used for the spectrophotometric determination of palladium. The most sensitive reagents have been found to be p - nitrosodiphenylamine (46), p-nitrosodimethylaniline (47), thioglycolic acid (16) potassium iodide (10) ethylenediamine tetra acetic acid (19) and nitrilotriacetic acid (7) have been used for the colorimetric determination of palladium. More recently some workers (23, 5, 20, 14, 27, 3) have suggested other reagents.

The methods using the above reagents, however, in many cases required the extraction of the palladium complexes into such an organic solvent as chloroform or toluene. A method which can be carried out in an aqueous medium and which is rapid, sensitive, selective and relatively free from interference is more desirable.

Methylthymol blue has some advantages as colorimetric reagent for palladium. No extraction of the complex is required since palladium methylthymol blue complex is water soluble, the pH for the maximum colour development can easily be adjusted, not many cations interfere and this method is comparable in sensitivity with the β-nitroso-α naphthol method (5).

Procedure

1 ml. of the sample solution (10 - 50 μg of Pd) is

taken and diluted to about 14 ml, to which 0.5 ml (1 M) $HClO_4$ and 6.25 ml (1 x 10^{-3}M) MTB is added in a flask and heated to 80°C for about 30 minutes. This is cooled and made up in a 25 ml. flask. The absorbance of this solution is determined at 530 nm and the weight of palladium is read off from the calibration curve prepared earlier under similar conditions.

The composition and stability constants of the complexes:

The compositions of the two complexes were determined by the following two methods. The method developed by Frank and Oswalt (9) and by Furman and Garner (11) was employed for determining the composition of the complex with an absorption maximum at 530 nm, and the mole ratio method was employed for determining that with an absorption maximum at 500 nm.

The complex with its absorption maximum at 530 nm

An attempt to discover the composition was made with solution with a given molar concentration of palladium at a given perchloric acid concentration, but varying methylthymol blue concentrations. If only a 1 to 1 complex is formed under certain conditions and the absorbance D, is measured against a reagent blank, the following relationship may be derived:

$$ab/D = (a+b)/(\varepsilon c - \varepsilon MTB) + 1/K'_1(\varepsilon c - \varepsilon MTB) \qquad - (6.1)$$

where a and b represents the total molar concentrations of palladium and methylthymol blue respectively ϵ_{MTB} and ϵ_c, the molar extinction coefficients of methylthymol blue and the complex respectively K_1' is defined as

$$K_1' = x/(a-x)(b-x) \qquad - (6.2)$$

where x represents the equilibrium molar concentration of the complex at a given acidity.

In Fig. 6.16 ab/D is plotted against (a+b) at five wave lengths between 500 and 540 nm. In these solutions, the concentration of palladium was 1.0×10^{-5}M while the concentration of methylthymol blue was varied from 1.25×10^{-4}M to 8.0×10^{-4}M; the pH was adjusted at 2.0. The good linearity of the curves in Fig. 6.16 supports the assumptions inherent in equation 6.1, indicating that only 1 to 1 complex is formed under the conditions investigated. The value of K_1' was calculated to be 1.18×10^4 (log K = 4.07) and at 20°C ΔG^o = - 5.46 kilo calories.

The complex with its absorption maximum at 500 nm

The mole ratio of palladium to the reagent was confirmed by the mole ratio method at pH 7.3. In this work each solution was 1×10^{-4}M in the total concentration of methylthymol blue. The results are shown in Fig. 6.17 which indicates a 1 to 2 complex is formed between palladium and the reagent. The wavelengths 500 and 530 nm were chosen.

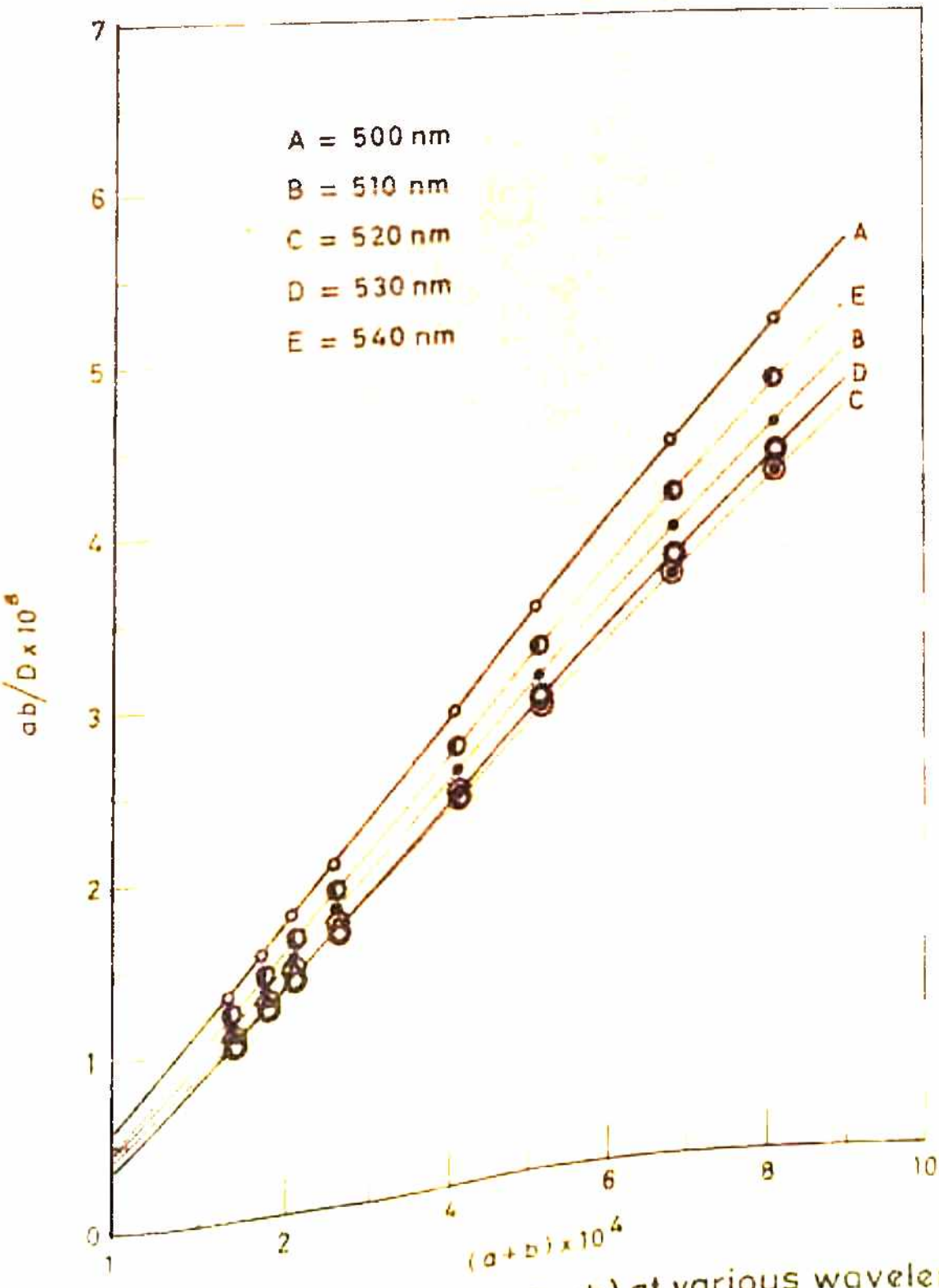


Fig._6·16 Plots of ab/D Vs (a+b) at various wavelengths
a: 1·0 x 10^{-5} M; b: 1·25 10^{-4} M – 8·0 x 10^{-4} M, pH 2·0

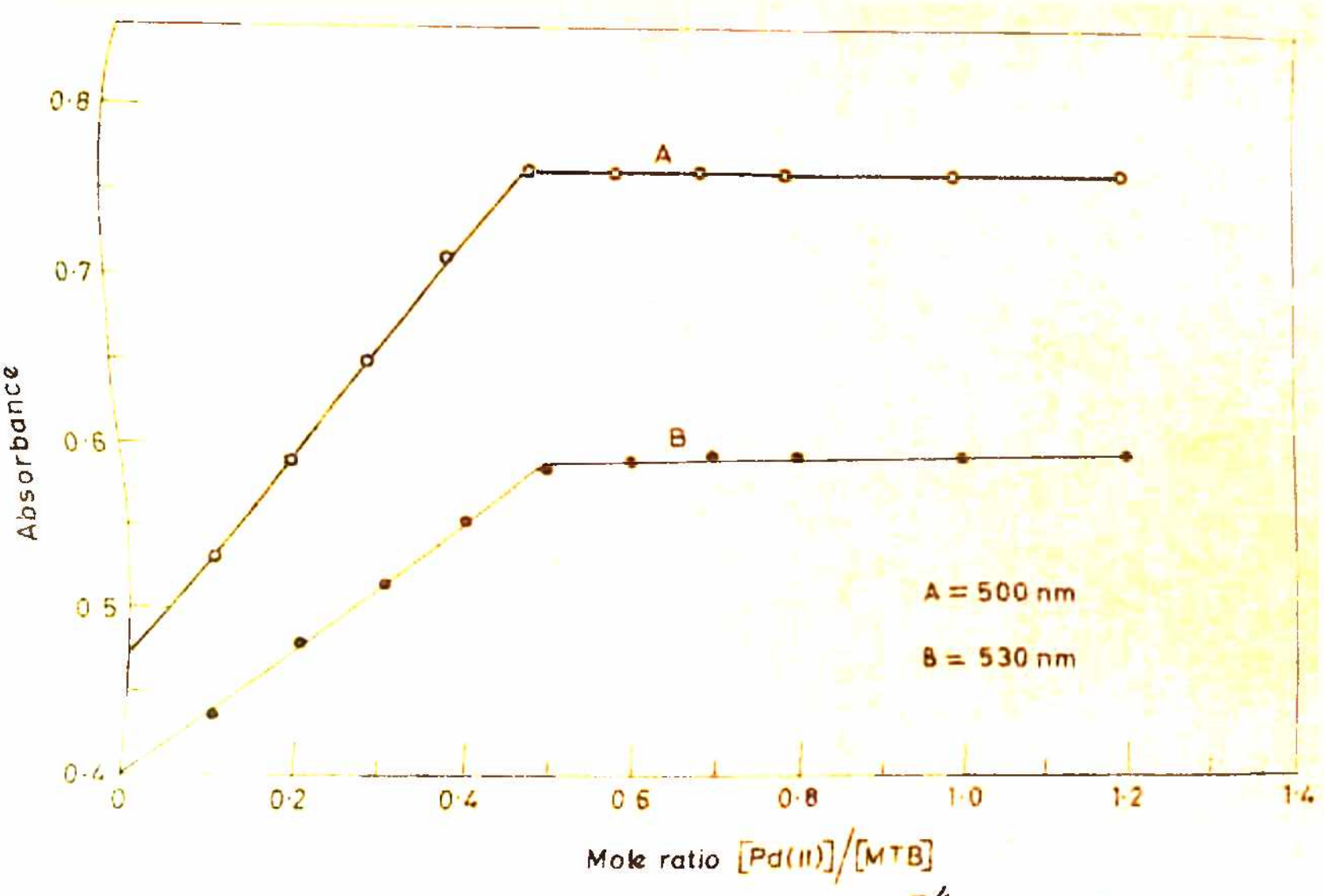


Fig._ 6·17 Mole ratio method, MTB : 1·0 x 10^{-4} M; pH: 7·3

The formation constant, as calculated by the mole ratio method was found to be 6.25×10^9 ($\log K = 9.79$) and ΔG^o at 20^oC = 13.13 kilo calories.

Nature of the complex:

Ion exchange studies have been made and these indicate that the complex formed is uncharged or neutral in character.

R E F E R E N C E S

1. Adam, J.A., Booth, E. and Strickland, J.D.H. — Anal. Chim. Acta 6, 462 (1952).

2. Babko, A.K. and Vasilenko, V.D. — Ukrain, Khim. Zhur. 26, 514 (1960).

3. Bell, C.F. and Rose, D.R. — Talanta 12, 696 (1965).

4. Cabrera, A.M. and West, T.S. — Anal. Chem. 35, 311 (1963).

5. Cheng, K.L. — Anal. Chem. 26, 1894 (1954).

6. Cucci, M.W., Neuman, W.F. and Mulryan, B.J. — Anal. Chem. 21, 1358 (1949).

7. Desideri, P. and Pantani, F. — Talanta 8, 235 (1961).

8. Fletcher, M.H., White C.E. and Sheftel, M.S. — Ind. Engg. Chem. Anal. Ed. 18, 179 (1946).

9. Frank, H.S. and Oswalt, R.L. — J. Am. Chem. Soc. 69, 1321 (1947).

10. Fraser, J.G., Beamish, F.E. and McBryde, W.A.E. — Anal. Chem. 26, 495 (1954).

11. Furman, S.C. and Garner, C.S. — J. Am. Chem. Soc. 73, 4528 (1951).

12. Hill, U.T. — Anal. Chem. 30, 521 (1958).

13. Iritani, M. and Mayahara, T. — Japan Analyst 12, 1182 (1963).

14. Jacobs, W.D., Wheeler, C.M. and Waggoner, W.H. — Talanta 9, 243 (1962).

15. Job. P. — Compt. rend., 180, 928 (1925) Ann. Chim. 9 (10), 113 (1928) 6 (11), 97 (1936).

16. Konig, O. and Crowell, W.R. — Mikro Chem. Ver Mikrochim. Acta 33, 298 (1948).

17. Körbl, J. and Přibil, R. — Collection CZech. Chem. Commun. 23, 873 (1958). Listy, 51, 1061 (1957).

18. Lukyanov, V.F. and Knyazeva, E.M. — Zavodsk, Lab. 26, 263 (1960).

19. McNevin, M.W. and Kriege, C.H. — Anal. Chem. 26, 1768 (1954).

20. Menis, O. and Rains, T.C. — Anal. Chem. 27, 1932 (1955).

21. Metcalfe, J. — Analyst 90, 409 (1965).

22. Motojima, K. — Bull. Chem. Soc. Japan 29, 75 (1956).

23. Niesch, W. — Z. Anal. Chem. 30, 142 (1954).

24. Ökada, H., Kaneko, K. and Goseki, S. — Japan Analyst 12, 822 (1963).

25. Otomo, M. — Japan Analyst 14, 229 (1965).

26. Otomo, M.	Bull Chem. Soc. Japan 38, 730 (1965).
27. Otomo, M.	Bull Chem. Soc. Japan 36(8), 889 (1963).
28. Owens, E.G. and Yoe, J.H.	Anal. Chem. 32, 1345 (1960).
29. Ringbom, A.	Z. Anal. Chem. 115, 332 (1938/9).
30. Sandell, E.B.	Colorimetric determination of traces of metals, 3rd Ed. Inter Science Publishers New York (1959) p 304-324.
31. Sandell, E.B.	Colorimetric determination of traces of metals 2nd.Ed. Inter Science Publishers, New York (1950) p 49.
32. Sill, C.W. and Willis, C.P.	Anal. Chem. 31, 598 (1959).
33. Sill, C.W.	Anal. Chem. 33, 1684 (1961).
34. Sill, C.W., Willis, C.P. and Flygare, J.K.	Anal. Chem. 33, 1671 (1961).
35. Silverman, L. and Shideler, M.E.	Anal. Chem. 30, 521 (1958).
36. Sommer, L. and Kuban, V.	Anal. Chim. Acta 44, 333 (1969).
37. Srivastava, K.C. and Banerji, S.K.	Chem. Age India 20. 609(1969).
38. Tereshin, G.S., Rubinshtein, A.R. and Tananaev, I.V.	Zh. Analit. Khim 20 (10) 1082 (1965).

39. Tikhonov, V.N. — Zh. Analit, Khim 21, 275 (1966).

40. Tonosaki, K. and Sakai, K. — Japan Analyst 14, 495 (1965).

41. Tonosaki, K. — Bull. Chem. Soc. Japan 39, 425 (1966).

42. Uesugi, K. and Katsube, Y. — Bull. Chem. Soc. Japan 39, 194 (1966).

43. Underwood, A.L. and Neuman, W.F. — Anal. Chem. 21, 1348 (1949).

44. Vasilenko, V.D. and Shanya, M.V. — Zh. Analit. Khim. 20, 636 (1965).

45. Yoe, J.H. and Jones, A.L. — Ind. Engg. Chem. Analyt. Ed. 16, 111 (1944).

46. Yoe, J.H. and Overholser, L.G. — J. Am. Chem. Soc., 61, 2058 (1939).

47. Yoe, J.H. and Overholser, L.G. — J. Am. Chem. Soc., 63, 3224 (1941).

This thesis concerns itself with the study of several metal chelates, involving quinalizarin and methylthymol blue as chelating agents. The study has been confined to the coloured chelates only, since these reagents have found application in the colorimetric determination of metals on a micro scale. The reagents investigated here are chromogenic reagents. They are known for their applications in colorimetric analysis of a few metals. It is interesting to note from the literature published on their use as analytical reagents, not much information is available on the composition and stability of the coloured chelates formed. Hence, the primary aim of the present work has been to investigate systematically, the composition and stability of the metal chelates formed in solution, while working with low concentrations. Incidentally, attempts have also been made to find further application of the reagents for micro determination of metal ions, and some of the results have been reported in this thesis.

The present work has been divided into six chapters; the last four describe the experimental results. Chapter I gives a brief introduction of coordination chemistry with particular reference to the chemistry of metal chelates. In Chapter II, methods of discerning chelate formation in solution are outlined, with special emphasis on spectrophotometric method with which the present work is concerned. For the determination of the composition of metal chelates in solution using absorbance measurements the following methods

have been employed:

(1) The method of Continuous Variation;
(2) The mole ratio method;
(3) The slope ratio method;
(4) Frank and Oswalt method (in a few cases)

The present studies have shown that the results obtained by these different methods are in good agreement, and show the utility of these methods for such studies.

The stability constant is useful for the understanding of the characteristics of a chelate (or a complex) but the determination of the thermodynamic constants is beset with difficulties and it is often convenient and valuable to determine the stoichiometric constants, which describe the stability of species, Under a given set of experimental conditions. Several methods based on absorptiometric measurements have been described for the determination of stability constant. In recent years Dey and Banerji have worked out a method based on the comparison of the composition of the constituents in a system, having identity of colour. This method is a modification of the procedure described by Anderson et al and has an advantage that it can also be applied to such systems where one of the interactants is coloured. In the present work stability constants have been calculated by the aforesaid method, by the continuous variations and by the mole ratio method. In a few cases stability constants have also been calculated with the help

of the measurements of molecular extinction coefficients. The values obtained by these methods have been found to be in good agreement with each other. From the values of the stability constants the free energy changes of formation have also been calculated.

A detailed investigation of the metal chelates of Pb(II), La(III), Fe(III) and Zr(IV) with quinalizarin (abbreviated as QZR) has been described in Chapter III. It also records the influence of the variation of the hydrogen ion concentration on the colour of the dye and the colour forming reactions of metal ions with quinalizarin. The results on the characteristics and the composition of the metal chelates are summarised in the following table.

Table I

Composition of Quinalizarin Chelates

Chelate	λ_{max} (nm)	Composition M : Ke	pH range of stability
Pb (II)-QZR	520	1 : 1	5.5 - 6.5
La(III)-QZR	530	1 : 2	6.5 - 7.8
Fe(III)-QZR	560	1 : 1	2.0 - 4.5
Zr (IV)-QZR	500	1 : 1	5.0 - 6.5

The stability constants have been calculated and the results are shown in table II.

Table II

Stability constants of Quinalizarin Chelates

Chelate	pH	Ionic strength	Temperature (°C)	Log K by the method of				ΔG^{o} (KCals)
				Dey et al	Continuous variation	Mole ratio	Molecular extinction Coeff.	
Pb(II) - QZR	6.3 ± 0.1	-	30	4.3±0.1	4.2±0.1	4.1±0.1	-	- 5.7±0.1
La(III)- QZR	6.8 ± 0.1	0.1 M ($NaClO_4$)	30	10.1±0.1	10.1±0.1	10.2±0.1	-	-14.0±0.1
Fe(III)- QZR	3.0 ± 0.1	0.1 M (KCl)	20	5.0±0.1	5.2±0.1	5.3±0.15	5.0±0.0	- 6.9±0.2
Zr(IV) - QZR	6.0 ± 0.1	-	20	4.8±0.1	4.7±0.1	5.0±0.2	-	- 6.5±0.2

In some cases it was not possible to swamp the systems with an excess of an electrolyte to obtain a medium of constant *ionic strength*, the lakes having a tendency to precipitate out in these cases.

Ion exchange studies were made to determine the nature of the charge on the chelates and it has been found that the chelates of lead(II), lanthanum(III), iron(III) and zirconium(IV) are anionic.

Chapter IV presents a brief review of the various chelating reagents for tungsten and contains the results of the application of quinalizarin for the determination of tungsten. The coloured chelate has composition of 1:2 of the components.

The optimum pH range within which the chelate is stable, range of concentration for adherence to Beer's law (ppm), effective photometric range, the value of molecular extinction coefficient and sensitivity of the system investigated have been given in the following table.

Table III

Determination of tungsten with Quinalizarin

Metal ion	pH range for the stability of the chelate	Range of concentration for adherence to Beer's law (ppm)	Effective photometric range (ppm)	Molecular extinction coefficient	Sensitivity (Sandell) $\mu g/cm^2$
W(VI)	5.0 - 6.3	0.74 - 5.88	1.47-5.15	7875	0.0261

Ion exchange studies on tungsten quinalizarin chelate indicated that the chelate is anionic in character.

The work done on the study of uranium, vanadium and iron(II) chelates of methylthymol blue has been described in Chapter V. The plan of study has been the same as with quinalizarin chelates (Chapter III). In addition to the composition and stability, analytical applications have been worked out. The results on the characteristic and composition of the metal chelates are summarised in the following table.

Table IV

Composition of Methylthymol blue chelates

Chelate	λ_{max} (nm) against reagent blank	Composition M : Ke	pH range of stability
U(VI) - MTB	510	1 : 1	6.2 - 7.0
V(V) - MTB	590	1 : 1	3.5 - 5.0
V(V) - MTB	520	1 : 2	5.2 - 6.5
Fe(II)- MTB	510	1 : 2	5.2 - 6.4
Fe(II)- MTB	600	1 : 1	2.2 - 5.0

The stability constants have been calculated by different methods and the results are shown in table V.

Table V

Stability constants of MTB chelates

Chelate	pH	ionic strength	Temperature (°C)	Log K by the method of			ΔG° (KCals)
				Dey et al	Continuous Variation	Mole ratio	
U(VI) - MTB	6.7±0.1	0.1 M ($NaClO_4$)	30	5.6±0.1	5.5±0.2	5.7±0.2	-7.7±0.2
V(V) - MTB	4.5±0.1	0.1 M ($NaClO_4$)	30	4.2±0.15	4.6±0.1	4.4±0.2	-6.1±0.3
V(V) - MTB	6.0±0.1	0.1 M ($NaClO_4$)	30	10.2±0.1	10.4±0.2	10.2±0.2	-14.1±0.3
Fe(II) - MTB	5.8±0.1	-	30	-	-	9.6±0.1	-13.2±0.2
Fe(II) - MTB	2.5±0.1	-	30	-	-	5.6±0.1	-7.6±0.2

The optimum pH range within which the chelate is stable, range of concentration for adherence to Beer's law (ppm), effective photometric range and the value of net molar absorptivity of the systems investigated have been recorded in the following table.

Table VI

Determination of Metals by Methylthymol Blue

Metal ion	Optimum pH range	Range of concentration for adherence to Beer's law (ppm)	Effective photometric range (ppm)	Net molar absorptivity
U(VI)	6.6-6.8	0.4 - 3.76	0.6-3.5	10,625
V(V)	4.0-4.7	35.7- 56.0	40.8-51.0	17,125
V(V)	6.0-6.5	5.1 -56.0	15.3-40.8	15,000
Fe(II)	5.5-5.8	5.6-40.0	11.2-33.6	12,000
Fe(II)	2.2-2.5	5.6-40.0	11.2-28.0	6,500

Chapter VI deals with methylthymol blue as a photometric reagent in the determination of beryllium, lead and palladium ions. Conditions for proper utilization of the reagent, have been ascertained and the procedures by which traces of metals can be determined photometrically have been recommended. The interference caused by the presence of a large number of ions have been studied and the tolerance limits of the various foreign ions have been determined.