

STUDIES IN CHROMIUM
COMPLEXES

"The preparation and properties of
amino base derivatives of oxalato
chromium (III) complexes."

by

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PREFACE.

The chemistry of co-ordination compounds in general has played an important role in the development of the modern theory of valency, but the properties of complex salts between chromium and organic compounds containing carboxyl and amino-groups are of additional interest because of their bearing on the theory of certain technological processes such as chromium plating and, in particular, chrome-tanning.

Owing to the rapid development of valence theory over the last two decades the technological chemist finds himself at a disadvantage vis-a-vis his academic counterpart in attempting to interpret the results of researches relating to these compounds as he must rely on the less powerful "classical" approach to his problems.

Hence the need was felt for a brief survey of modern concepts of valency in terms of wave mechanics. For a more extended study the reader may consult the appropriate references and text books.

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SUMMARY

Physical and analytical methods have been used to investigate the conditions of formation of mixed oxalato and amino-base chromium (III) complexes. The purity of these products was checked by the new technique of filter paper electrophoresis which, although requiring a relatively simple apparatus, yields excellent results.

Using this apparatus as a guide, methods have been perfected for preparing pure samples of potassium trioxalatochromiate and potassium cis- and trans-dioxalato-diaquochromiate. The products of the reactions of these compounds with ethylenediamine, propylenediamine, urea and ethylenediamine tetraacetic acid were studied with the aid of spectrophotometric, potentiometric and other methods.

From a detailed analysis of the potentiometric titration curves of the products obtained with different mole ratios of the diamino-bases and the di- and tri-oxalato chromium (III) complexes, together with the direction of migration in an electric field, it is concluded that under appropriate conditions stepwise substitution at the co-ordination positions of the chromium atom takes place. Urea under similar conditions, did not co-ordinate but decomposed gradually to cause olation. It is shown that for the bases reaction only occurs in alkaline media and the reasons for this are discussed in terms of ionic dissociation equilibria.

Trisethylenediaminochromic chloride was obtained in a pure crystalline form and the appropriate spectrophotometric data recorded. On aging in aqueous solution the complex ion was found to be unstable. Structures for the decomposition products have been tentatively suggested on the basis of the potentiometric and spectrophotometric properties of the resultant solutions.

Several known methods of preparation of mixed oxalato amino-base chromium (III) complexes were investigated, and were found to be unsatisfactory, in some cases the end products being quite different from those anticipated.

In conclusion the relative stabilities of complex ions have been discussed with particular reference to the character of the co-ordinate bonds formed (in the light of the modern concepts of valency), the ability to form chelate ring structures and the environment of the complex.

CHAPTER I.

INTRODUCTION

Modern Concepts of Valency

The classical approach to the problem of the structure of chemical compounds employed methods essentially chemical in nature. For example, through observations of the chemical composition of substances, the existence of isomers and the nature of the chemical reactions in which a substance takes part, Frankland, Kekulé and Couper formulated certain rules of valence involving directional bonds and wrote the first structural formulae for molecules. Similarly Van't Hoff and Le Bel developed the final form of classical organic stereochemistry, using the idea of tetrahedral orientation of the four valences of the carbon atom.

An extension of the structural theory of valence of Van't Hoff and Le Bel to include "co-ordinate valency" was made by Werner who found that their postulates did not explain the structure and formation of complex inorganic compounds in which the number of atoms or radicals surrounding a central atom did not correspond to the normal valency of the latter indicated by its position in the periodic classification. The nature of the forces involved in this link, however, remained as obscure as the nature of the bond in organic compounds.

In the nineteenth century the valence bond was represented by a line drawn between the symbols representing

the chemical elements, which expressed in a concise form many chemical facts, but which had only qualitative significance with regard to molecular structure. The nature of the bond was completely unknown.

The development of atomic theory and in particular the knowledge that atoms consist of positively charged nuclei and negatively charged electrons led to the revival of the electrostatic theory of Berzelius by Kossel. However electrostatic forces do not provide a complete explanation of the stability of ionic compounds, the valency forces in organic compounds, or the valency forces of simple molecules such as H_2 , O_2 , N_2 etc. The first attempt to explain the formation of such covalent or homopolar compounds was made by Lewis in his electronic theory of the chemical bond (1). Lewis discussed not only the formation of ions by the completion of stable shells of electrons around the atomic nucleus (on the Bohr model of the atom) but also the formation of a chemical bond, now called the covalent bond, by the sharing of two electrons between two atoms. He further emphasised the importance of the phenomena of the pairing of unshared as well as shared electrons and of the stability of the group of eight electrons (shared or unshared) about the lighter atoms.

The refinement of the electronic theory of valence into its present form has been due almost entirely to the development of the theory of quantum mechanics, which has not only provided a method for the calculation of the properties of simple molecules, leading to the complete

elucidation of the phenomena involved in the formation of a covalent bond between two atoms, but has also introduced into chemical theory a new concept, that of resonance.

While the quantum theory of Planck, as extended to atomic structure by Bohr, Sommerfeld and others, has proved to be of inestimable value in the analysis of atomic spectra, other methods of representing atomic processes have been developed which are in still better agreement with the experimental facts. In 1923 de Broglie put forward a new theory of quantum dynamics, which at the outset met with little success. In the hands of Schrödinger the theory was developed and extended. At about the same time Heisenberg put forward an independent theory of quantum mechanics or matrix mechanics which was so successful that it attracted wide attention.

In order to understand what is meant by the term co-ordination in relation to the inorganic metal complexes it is essential to know something about the modern concepts of valency. Accordingly a brief account of these concepts is given below.

When atoms change from a state of higher energy to one of lower energy, they may do so by transferring their excess energy to some other particle which collides with them. Generally, however, no such particle is present, and the excess energy is radiated in the form of a quantum. This phenomena results in optical spectra.

Spectra have been observed since the time of Newton, but it was not until 1879 that any order was found

among the large numbers of lines found in the spectra. In that year it was found that the successive pairs of lines in the spectrum of sodium vapour were alternately sharp and diffuse, no matter how good the spectroscope used to view them. Later Hartley measured the separation of the doublets in terms of frequency instead of wavelength (which can be measured directly by diffraction methods), and since that time it has been the practice to express spectroscopic data in terms of frequency, or more usually in terms of the wave number, which is the number of waves per centimeter.

Eventually Rydberg put the subject on a sound footing as far as the experimental side went by observing that the lines in many spectra fell into series which could be fitted very well to a formula of the type

$$\overline{V}_n = \overline{V}_\infty - \frac{R}{(n + \alpha)^2}$$

Where $\overline{V}_n$ is the wave number of the n^{th} line in the series, R is a universal constant called the Rydberg constant, and α is a constant for a given series in a given spectrum. It will be observed that for a large n the value tends to a limit which is $\overline{V}_\infty$, which is therefore called the series limit. Eventually four series of lines were found in various spectra, called, from their properties, the sharp, principal, diffuse and fundamental series respectively. It is from these observations that the letters s, p, d and f used in the sublevel notation of atoms arise. It is now

realised that each of these series corresponds to a particular type of energy level in the atom or molecule.

de Broglie brought forward the idea of the association of wave properties with ordinary particles of matter, such as electrons and protons. He proposed the equation

$$\lambda = h/m v$$

for the wavelength of waves (λ) associated with a particle of mass m travelling with speed v . This is analogous to the equation for light

$$\lambda = h/m c$$

Extending this idea, Schrödinger derived a wave equation which gives a complete description of a particle in space (2, 3).

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (W - V) \psi = 0$$

where x, y, z = co-ordinates of the particle.

m = mass of the particle.

h = Planck's constant.

W = total energy

V = potential energy.

ψ = "wave function"

This wave mechanical treatment involves the employment of boundary conditions, i.e. that ψ shall be single-valued, finite and continuous throughout configuration space. When

these are applied it is found that certain energy levels only can exist for a system (eigenvalues). Thus on a firm mathematical basis is derived the hitherto arbitrary condition of quantisation.

To translate the appropriate mathematical equations for any system into some mental concept it is necessary to derive some "material" meaning of Ψ , since we think in terms of matter and space. In actual fact the distribution of matter in space and time, that is, the concept of "where a particle is at a particular time" is not so straightforward from the wave mechanical point of view as in classical mechanics. It is found that Ψ^2 - the square of the amplitude - represents the intensity distribution of matter, and may be regarded as a probability function.

The wave equation is not completely soluble for a system involving more than two particles. However, certain approximations may be made namely, that the nuclei are fixed in space for molecules, and that electrons do not interact, thus permitting solution of the wave equation.

The application of the wave equation to the hydrogen atom has been presented in detail by Pauling, Wilson and others (2, 3, 4).

One of the cardinal points which emerges from the treatment of a many-electron system by the wave mechanical method is this : all electrons must enter into the wave equation in an entirely equivalent manner; if any two electrons are interchanged in the eigenfunctions, the

probability distribution functions must be entirely unchanged. This is a statement of the fact that electrons are entirely indistinguishable from each other. As a result of this we have the Pauli Exclusion Principle :

"The eigenfunctions representing all naturally occurring states of systems must be antisymmetric in all pairs of electrons".

This means that no two electrons may have the same four quantum numbers. The Bohr-Sommerfeld theory of the atom only made arbitrary provision for this.

Just as in atomic theory, the theory of more complex atoms can be understood on the basis of the structure of the simplest atom, hydrogen, so in molecular theory the hydrogen molecule has served as the starting point for more complex molecules.

The application of wave mechanics to the hydrogen molecule was carried out by Hund and Mulliken (5) who used the function :

$$\Psi = N \left[\Psi_A(1) \cdot \Psi_A(2) + \Psi_B(1) \cdot \Psi_B(2) + \Psi_A(1) \cdot \Psi_B(2) + \Psi_A(2) \cdot \Psi_B(1) \right]$$

and Heitler and London (5, 6, 7, 8) who used the function :

$$\Psi = C \left[\Psi_A(1) \cdot \Psi_B(2) + \Psi_A(2) \cdot \Psi_B(1) \right]$$

where C = constant

N = constant

A and B are the nuclei

(1) and (2) denote the electrons.

The difference between these two treatments lies in the presence of two additional terms in the Hund-Mulliken function. The first corresponds to both electrons on nucleus A while the second to both electrons on nucleus B. These two terms are called the "ionic terms" while the other two, corresponding to one electron on each nucleus are "homopolar terms".

Solution of these functions reveals evidence pointing to the fact that it is the possibility of "resonance" or, indeed the mere fact that electrons are indistinguishable which is mainly responsible for the stability of the hydrogen molecule, and by induction, of all other molecules.

The necessity of the electrons having opposite spins in the bond was one of the most immediately striking results of the Heitler-London treatment. When dealing with molecular structures, it is found that the vast majority do in fact behave very much as if they had two electrons with opposed spins in each single bond. For molecules which do not behave in this way (which, according to the molecular orbital theory, is because in this case the assignment of an integral number of electrons, particularly two, to each bond is not as stable as a fractional assignment) it is convenient to write down the nearest structure in terms of ordinary bonds. Generally, several such structures may be written down, each of which in some way corresponds to some special property of the substance studied. In effect particular solutions to the problem

in terms of electron pair bonds are taken as approximations to the true eigenfunctions. The statement that "a molecule resonates between structures A, B etc" is in fact a statement of the inadequacy of the mathematical solution rather than of any particular property of the molecule.

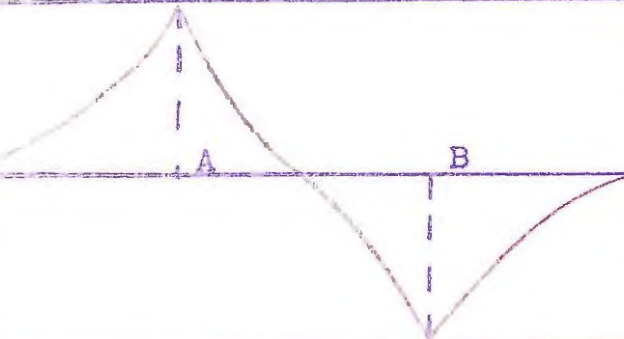
The concept of Resonance and its applications has been dealt with fully by various authors (6, 7, 9).

The extent of the contribution of each eigenfunction to the "resonance hybrid" depends on the associated energy level. An eigenfunction corresponding to a high energy level, i.e. an unstable configuration of the molecule, will have a small coefficient in the linear combination, and it will contribute only to a small extent to the final function.

The theory of valency founded on the Heitler-London treatment of the hydrogen molecule is often called "the method of valence bond wave functions" (6, 10). The main tenets of this theory are :

- (i) Only electrons of opposite spin can form a bond.
- (ii) An electron which is paired in one of the atoms may become available for bond formation if enough energy is set free during the combination to unpair it and promote it to the lowest available orbital which is unoccupied.
- (iii) A stable bond will not be formed if the total quantum number n of the electron is changed during this process.

FIG. 1

	Atomic orbital function, $\psi_A(1)$
	Atomic orbital function $\psi_B(1)$
	$\psi_A(1) + \psi_B(1)$ Proportional to Symmetric Function.
	$[\psi_A(1) + \psi_B(1)]^2$ Proportional to probability distribution function
	Electron density for Symmetric Function
	$\psi_A(1) - \psi_B(1)$ Proportional to Antisymmetric Function
	$[\psi_A(1) - \psi_B(1)]^2$ Proportional to probability distribution function
	Electron density for Antisymmetric Function

Of this Coulson (11) has to say, "a study of recent literature shows that the molecular orbital method of valence, originally rather neglected, is now receiving more attention than the alternative method of valence bond structures, first introduced by Heitler and London (8) and so lucidly developed by Pauling (7)." A comparative study of the two methods, has been given by Van Vleck and Sherman (12).

The Slater-Pauling Theory of Directed Valence may now be considered. In the symmetric orbital eigenfunction, which, as shown by the Heitler-London and Hund-Mulliken treatments of the hydrogen molecule, leads to bond formation, there is a high electron density between the two nuclei. On the other hand the antisymmetric eigenfunction shows zero probability, and hence no bond formation, between the two nuclei. This is shown graphically in Fig. 1. Pauling extended this concept by postulating that the direction in which a chemical bond will be formed is that in which there will be a maximum probability of finding the bonding electrons between the two bonded nuclei, i.e. the direction in which the probability distribution functions overlap most. Probability distribution patterns are best represented by polar diagrams (2, 3, 4, 7) and in Pauling's method we look for the particular directions in which these diagrams "stick out" most.

Pauling also adopted the reasonably simple assumption that the strength of a bond will be proportional to the product of the eigenfunctions concerned in forming

the bond. In his own words (7), "It is expected that of two orbitals in an atom the one which can overlap more with an orbital of another atom will form the stronger bond with that atom, and, moreover, the bond formed by a given orbital will tend to be in that direction in which the orbital is concentrated".

In the type of bond envisaged by the earlier theory of Kossel, both electrons of what might otherwise have been a covalent bond belong completely to one atom, resulting in the formation of two ions of opposite charge. From the point of view of wave mechanics this amounts to saying that one of the ionic terms in an expression of the type of the Hund-Mulliken function contributes practically everything to the eigenfunction for the bond, the other terms contributing nothing.

In the general case the difference of electronegativity of the two atoms bound together is not large enough to produce a perfectly electrovalent bond, nor is it zero, so as to produce a perfectly covalent homopolar bond. We may represent the situation by a linear combination of atomic orbitals (L.C.A.O.) of the type of the expanded Hund-Mulliken function :

$$\Psi = c [\psi_A(1) \cdot \psi_B(2) + \psi_A(2) \cdot \psi_B(1)] + a [\psi_A(1) \cdot \psi_A(2)] + b [\psi_B(1) \cdot \psi_B(2)]$$

where different coefficients for the two ionic terms are allowed. If A is more electronegative than B, then a will

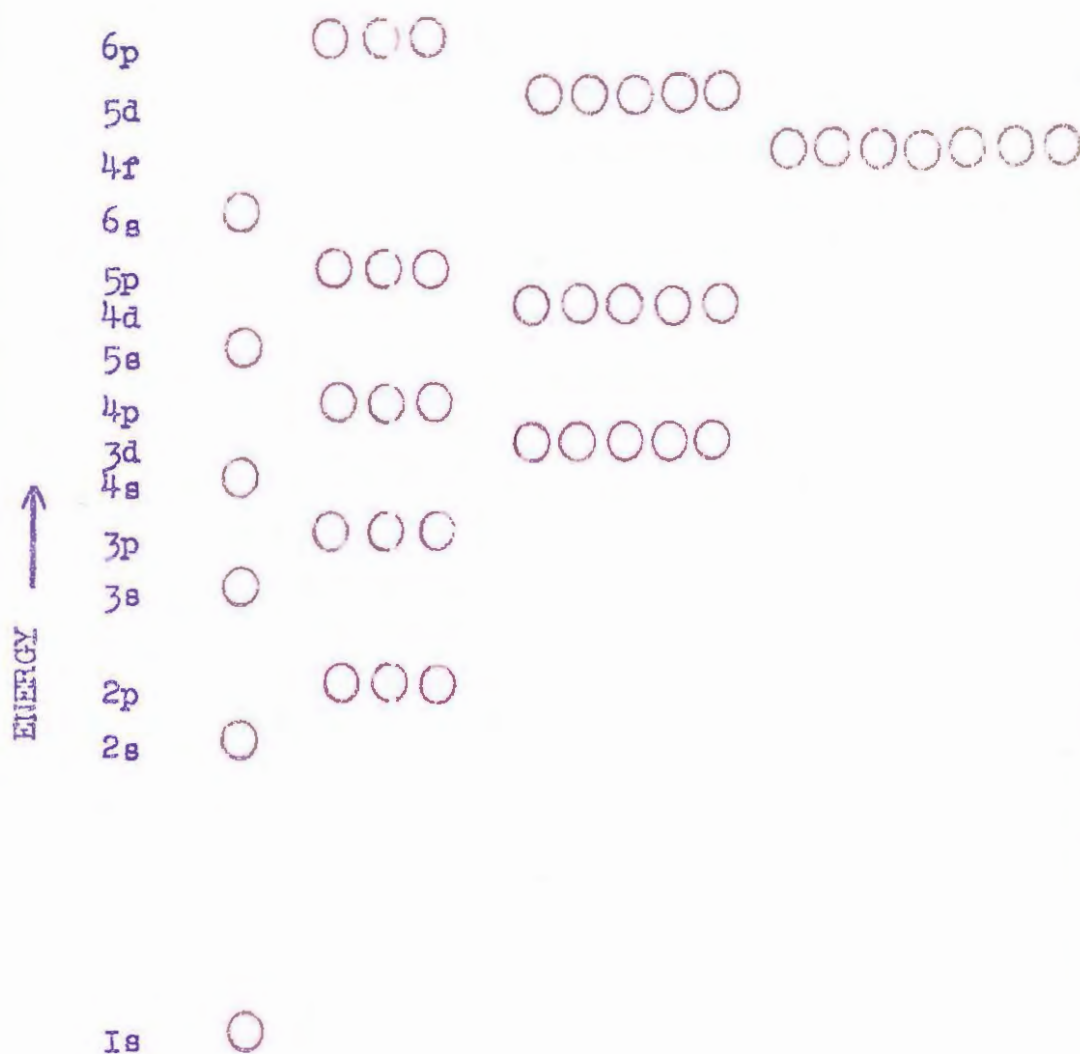


FIG. 2

The approximate stability sequence for atomic orbitals, the lowest representing the most stable orbital (1s). Each circle represents one atomic orbital, which can be occupied by one electron or by two electrons with opposed spins.

be larger than b and vice versa; if A and B are identical, a will equal b and the function becomes that used by Weinbaum for the normal covalent bond where $a = 0.256$. On this view the distinction between electrovalency and covalency is a matter of degree rather than of kind.

The treatment up to now has been essentially from the molecular orbital point of view. We may change over to the valence bond wave function method by regarding the above wave function as a linear combination of wave functions representing four different states of the molecule. The first two terms represent the ordinary Heitler-London covalent resonant state; the third term represents the ionic state A^-B^+ ; and the fourth the ionic state A^+B^- . The linear combination now represents a resonance hybrid of these three states.

The above considerations show that the so-called co-ordination valency postulated by Werner is in fact a special type of bond, the incidence of which should be predictable from the electronic structure of the reacting molecules.

In modern terms, various energy levels, which are related to the four types of spectral lines derived from spectroscopic data, are associated with a particular atom.

The approximate stability sequence for atomic orbitals, each corresponding to a particular energy level, is given in Fig. 2; the lowest circle representing the most stable orbital ($1s$). Each circle represents one

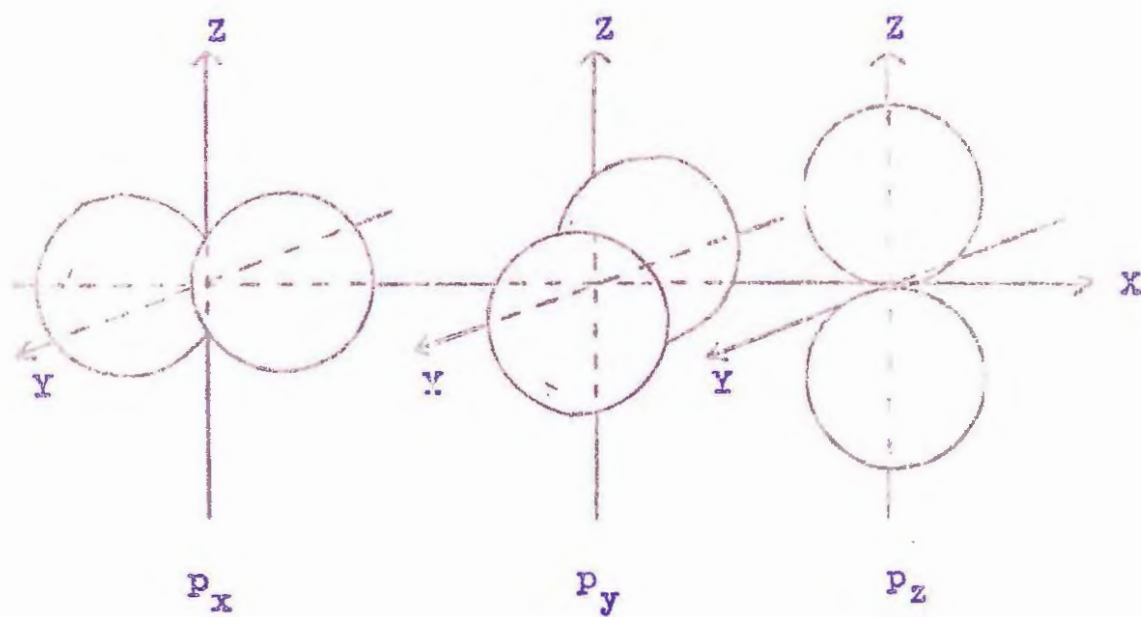
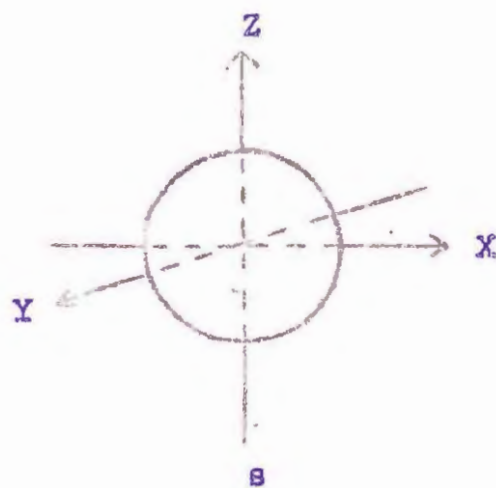


FIG. 3

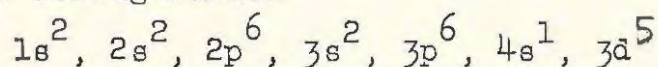
Representation of the relative magnitudes of
s and p orbitals in dependence on angle.

atomic orbital, which can be occupied either by one electron or by two electrons with opposed spins.

Tables of electron configurations of atoms in their normal states are given by Pauling (7), Glasstone (13) and Syrkin and Dyatkina (4).

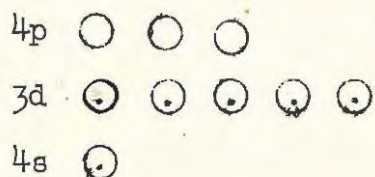
The different stable orbitals of an atom which can be used for bond formation do not differ very much from one another in their dependence on the effective radius of the orbital, but they show a great difference in their angular distribution. This can be seen from Fig. 3, representing the angular distribution of an s orbital and the three p orbitals. The s orbital is spherically symmetrical, and so can form a bond in one direction as well as in any other, whereas the three p orbitals are directed along the three axes and will tend to form bonds in these directions. Moreover, the p orbitals are concentrated in these directions and have magnitudes $\sqrt{3}$ times as great as that of an s orbital, so far as angular dependence is concerned. Since the radial part of an s orbital and that of the p orbitals of the same shell do not differ much, the p orbitals can overlap the orbital of another atom more effectively than can the s orbital of the same shell; p bonds are stronger than s bonds.

The chromium atom in the ground state has the electronic configuration

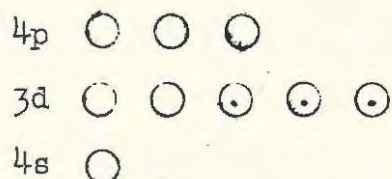


Considering the orbitals which will be involved in bond

formation we have



while the chromic ion is



resulting in six empty orbitals. According to Pauling, these orbitals can be filled by electrons from other ions or molecules, the result being a complex or co-ordination compound. The six new bonds formed in this way are the so-called $d^2 s p^3$ "hybrid bonds" which are directed towards the corners of a regular octahedron.

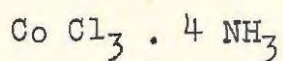
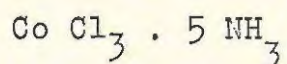
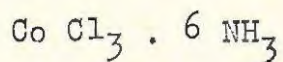
Relative Stability of Co-ordination Compounds

Having established the theoretical basis of co-ordination compounds it is now possible to give a general discussion of the chemical behaviour of these compounds with particular reference to those of chromium.

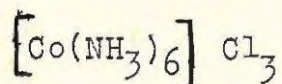
As with Arrhenius' theory of electrolytic dissociation, the experimental evidence leading to Werner's Co-ordination theory was based on specific ionic reactions, electrical conductivity and the determination of molecular weights.

To quote an example, Werner found that three ammoniates of trivalent cobalt are obtainable from an

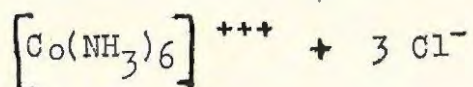
ammonical solution of cobaltous chloride on oxidation with atmospheric oxygen, namely :



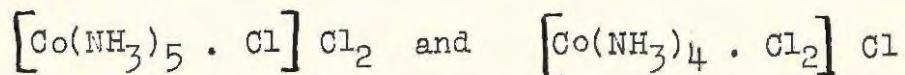
He called these the cobaltammines and found that ammonia could not be expelled from them by alkali. In other words, the ammonia must be very firmly bound. Consider $\text{Co Cl}_3 \cdot 6 \text{ NH}_3$ which precipitates all its chlorine with silver nitrate, exhibits a specific molar conductivity corresponding to dissociation into four ions, and gives a freezing-point depression about four times as large as would be expected for the undissociated molecule $\text{Co Cl}_3 \cdot 6 \text{ NH}_3$. On these grounds the molecule is written as



and dissociates in solution to give the ions :

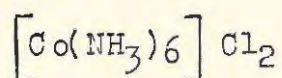


By similar deductions the other two cobaltammines are written as :



Inspection of the formulae of the above cobalt co-ordination compounds reveals the important fact that in

every case cobalt is linked to six atoms or groups. The co-ordination number 6 is also found in numerous other complex compounds, not only in those which have the metal atom in the cation, but also those containing the metal atom in the anion, such as $\text{Co}(\text{NO}_2)_6^=$ or $\text{Cr}(\text{CN})_6^=$. The co-ordination number 4 is also encountered, 3 less commonly, 2 is already fairly rare as also is 8, while 5 and 7 hardly occur at all. The co-ordination number thus proves itself to be independent of the nature of the attached groups or ligands. A connection between the co-ordination number and the group valency of the central atom does not exist, since divalent cobalt in hexammine cobaltous chloride

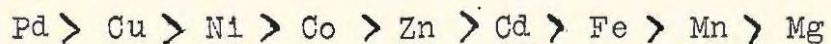


also exhibits the co-ordination number 6. Like cobalt, chromium (III) has the co-ordination number 6.

Quantum mechanical considerations discussed previously give an adequate explanation of these facts, it being now recognised that the co-ordination number is related to the specific electron structure of the element.

For many years progress in co-ordination chemistry was confined almost exclusively to the stereochemistry of complexes and to the preparation of complexes of new types or containing new ligands. The physico-chemical principles involved in complex formation received scant attention, with the result that little quantitative information was available to show the influence of the ligand on the properties of the complexes formed by a

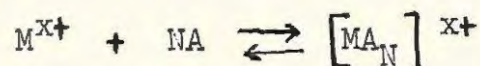
particular metal, or how the properties of complexes containing the same ligand depended on the position of the metal ion in the Periodic Table. In this direction Mellor and Maley (14, 15) have recently pointed out that the stability of complexes of bivalent metal ions follows the order :



irrespective of the nature of the ligands involved, and remark that "although it is not clear what determines the order of the metals in the series, it is worth noting that metals forming $d s p^2$ bonds (Cu^{++} and Pd^{++}) head the list". The theoretical basis for an investigation of the stability of complex ions was laid by Arrhenius' dissociation theory and Werner's co-ordination theory. Abegg and Bodländer (16, 17, 18) initiated the first thorough investigation in this field at the turn of the century.

In any theory intended to explain the phenomena of complex formation the most important measurable quantity is the stability constant of the complex. A metal ion M^{x+} and a monodentate neutral ligand A (i.e., a non-ionic ligand each molecule of which occupies only one co-ordination position around the metal ion) will give as the final complex ion formed $[\text{MA}_6]^{x+}$ when the co-ordination number N is 6 - as is the case with chromium (III). If A were an ion, then the charge on the complex ion would depend on the value of x, the ionic charge on A and the number of A groups attached to M. The overall reaction is reversible and may

be written :



and the overall "complexity" or "stability" constant K_N will be given by

$$K_N = \frac{[MA_N^{x+}]}{[M^{x+}][A]^N}$$

square brackets here representing concentrations. It is assumed that the activities of the reacting groups are equal to concentrations, and the experimental conditions are chosen so that this is approximately the case. N. Bjerrum has shown, however, that the formation of complex ions occurs stepwise, the stability of the various species being characterised by a series of consecutive constants of the form :

$$k_n = \frac{[MA_n]}{[MA_{n-1}][A]} \quad n = 1, 2, \dots$$

In this connection Bjerrum (19) says, "It is pertinent to emphasise the great importance which attaches to all potentiometric methods, which make it possible to determine either the concentration of the free metal ions, or that of the free ligand in the solution under examination. That the concentration of unco-ordinated ligand (provided it is a sufficiently strong base) can always be determined with the aid of a glass or hydrogen electrode has proved to be of the greatest practical importance. It should be noted that in solutions of systematically varied

composition, if only one of the above-mentioned concentration parameters is known, it is relatively easy to carry out a complete calculation of the mass action constants for the whole system." (20, 21, 22, 23).

From the value of K_N found above may be calculated the standard free energy ΔG° and the standard potential E° for the reaction, by means of the usual relationship :

$$\Delta G^\circ = - RT \ln K_N$$

$$E^\circ = \left(\frac{RT}{nF} \right) \ln K_N$$

Bjerrum (19) gives values of the consecutive constants for a number of systems where it has proved possible to carry out a complete investigation. As Bjerrum (24) was among the first to point out, one should expect, on purely statistical grounds, that the first ligands to be taken up would in effect appear to be bound more strongly than the subsequent ones. If the ligand is an electrically charged anion the electrostatic effect, which has the effect of lowering still further the affinity for subsequent ligands, must also be considered. The statistical correction is introduced in such a way that the logarithm of the mean complexity constant defined by

$$\log k = \frac{1}{N} \log K_N = \frac{1}{N} \log k_1, k_2 \dots k_N$$

has the same value when calculated from the statistically corrected constants as from those determined by direct experiment.

Using the glass electrode and the procedure of Bjerrum (20) comparisons of the basic strength of various amines and their complex-forming affinity for silver and mercuric ions have been made by Bjerrum and others (19, 25, 26, 27). Data compiled by Bjerrum (19) show that the tendency of silver and mercuric ions to complex with various ligands increases on the whole in the same relative order. With the ethylenediamine molecule (en) and the silver ion, the molecule of en taken up primarily must be assumed to be bound chelately through both of its amino groups, regardless of the fact that the silver ion has linear valencies and thus cannot enter as a constituent of a five-membered ring without some coercion. When the second molecule of en is co-ordinated it must be assumed that the ring is opened. The mercuric ion, on the other hand, exhibits a marked tendency to change from a linear to a tetrahedral configuration, so that it must be assumed that both en molecules are bound chelately in the mercuric bis-complex.

Not only ethylenediamine but also ligands such as propylenediamine, the oxalate ion and the malonate ion etc., are bound exclusively in the form of chelate rings for those metal ions with co-ordination number 4 or 6. Data on these bidentate ligands show that the five-membered ring as a whole is somewhat more stable than the six-membered ring.

When dealing with bidentate ligands, such as en,

we have $N = 2 Z$. The figures for $\text{Cu}^{++} - \text{en}$ and $\text{Ni}^{++} - \text{en}$ systems (28) show that, as expected, $k_n > k_{n+1}$ except when the normal value of N is exceeded. However, it is important to note that the values of k are very much greater than for the ammonia complexes as is shown by the figures of Burkin (28).

System	log k_1	log k_2	log k_3	log k_4	log k_5	log k_6	log k_{av}
$\text{Cu}^{++} + 5\text{NH}_3$	4.15	3.50	2.89	2.13	-0.52		3.17
$\text{Ni}^{++} + 6\text{NH}_3$	2.80	2.24	1.73	1.19	0.75	0.03	1.46
$\text{Cu}^{++} + 3\text{en}$	10.72	9.31	-1.0				10.02
$\text{Ni}^{++} + 3\text{en}$	7.66	6.40	4.55				6.20

The two stages of the co-ordination of a bidentate ligand must be supposed to be, firstly, the attachment to one co-ordination position, followed by the second co-ordinating group occupying the second co-ordination position. The value of k_1 gives the free energy for the co-ordinating of both groups, so that for a bidentate ligand k_1 must be compared with $(k_1 \times k_2)$ for a monodentate ligand.

Since values of k are measured at equilibrium conditions, consider what happens when a complex dissociates. An ionically neutral monodentate ligand molecule (e.g. NH_3) is free to migrate once it is split from the complex, whereas with a bidentate ligand (e.g. en), even though one end of the ligand molecule may be freed from the

complex the second group holds it in the vicinity of the metal ion, so that it would be more readily re-attached than a monodentate ligand.

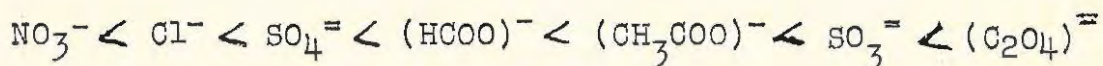
This can also be considered from another point of view. Once the first group of a bidentate molecule is attached in a co-ordinating position the activity of the other group with reference to its reaction with the metal ion is increased. It must also be remembered that at equivalent molar concentrations the bidentate ligand, having two reactive groups, is statistically more liable to co-ordinate than a monodentate ligand.

It is noteworthy that in the series of complexes formed by the aliphatic diamines and dicarboxylic acids the stabilities decrease as the number of CH_2 groups between the two active groups increases. This may be attributed partly to the decrease in effective activity of the second group after the first is bound, owing to its increased distance from the metal atom. The extremely large values of the equilibrium constants found for polyamine-metal complexes (see table above) are of great importance.

Most metals, including those of the alkali and alkaline-earth series, form stable bonds when carboxylic acid groups co-ordinate to them. Extremely stable complexes are formed if amino-polycarboxylic acids such as ethylenediaminetetraacetic acid (enta) or the amino-phosphoric acids are used as co-ordinating agents since these behave in a manner exactly analogous to the polyamines,

with the exception that the carboxyl ions are the effective ligands. So stable is this attachment that it is possible to titrate metal ions with such "complexones" in just the same way as hydrogen ions can be titrated with alkali.

The combination of organic and other acids with chromium (III) has received much attention in recent years in connection with the so-called "masking agents" employed in chrome tanning. Stiasny (136) has arranged the anions in a series of increasing tendency towards complex formation



A systematic study of the relative stabilities of the carboxylic acid chromium complexes has been made by Shuttleworth (56, 57, 58, 59, 60, 61, 62, 63, 64, 65) using conductimetric techniques. He has shown (58, 59), by conductimetric titration at high dilution on chromium oxalate and malonate complexes, that oxalic acid, sodium oxalate and sodium malonate in boiling concentrated solution displaced approximately quantitatively all sulphate groups attached to the anionic complex formed by boiling chrome alum (potassium chromium sulphate) in concentrated solution. He concluded that the chromium oxalate five-membered ring is more stable than the chromium malonate six-membered ring. Extending this work to maleic, fumaric and succinic acids Shuttleworth (61) suggests that maleic acid forms a seven-membered internal ring complex with chromium, the stability

of which is intermediate between that of complexes with monobasic acids and the six-membered ring suggested for the malonic acid complex.

The results for fumaric and succinic acids were similar to those obtained for monobasic acids, but for complexes formed with dibasic acids of more than four carbon atoms conductimetric titration (60) suggests that both acidic groups participate, while the degree of displacement of sulphuric acid by the organic acid group appears to be independent of the dissociation constant.

Shuttleworth's work provides experimental confirmation that the stability of chromium complexes involving chelate structures depends largely on the type of internal ring which the co-ordinating acid groups can form; the general order of stability is $5 > 6 > 7$ or 4 in terms of atoms per ring.

For non-chelated structures such as are involved in chromium complexes with monobasic aliphatic acids there is evidence that the relative stability is inversely related to the dissociation constant of the ligand (65). Bjerrum (19) has demonstrated a similar relationship between dissociation constants and co-ordination tendency for silver and mercury complexes, i.e. $\log K_{Ag+}$ shows a linear relationship when plotted against $\log K_{H+}$ for the ligand. According to Shuttleworth (65), "another way of stating this is that the tendency of an ion to co-ordinate with metal ions is in the same order as its tendency to co-

ordinate with hydrogen ions. In solution the metal and hydrogen ions (H_3O^+) are co-ordinated to water and the ligand can be regarded as competing with water in both cases".

Abegg and Bodländer (16, 17, 18) found that the position of the metal and the ligand in the electromotive series or their relative electronegativity was of the highest significance as regards their tendency towards complex formation. This was, in fact, at its greatest between the most electronegative metals and the least electronegative ligands, which shows directly that there must be an electron displacement from ligand to metal ion whenever a complex is produced.

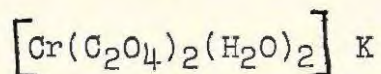
Thus it appears that when due consideration is given to the constitution of the ligand molecules and to steric effects there actually exists in many cases a definite correlation between the electron donating power of the different types of ligands and their affinity for metal ions. This actually tells us nothing of the nature of the forces between ligand and the metal ion in complex compounds.

The Chemistry of Some Typical Co-ordination Compounds of Chromium.

Co-ordination compounds of chromium have been known for a considerable time although it was not until the brilliant researches of Werner at the turn of the century that the constitution of even the simplest was known with certainty. Thus Croft (31) prepared potassium tri-

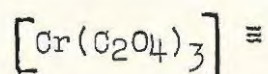
oxalatochromiate more than a century ago but Werner succeeded in resolving this compound into optical isomers thereby establishing the structural formula which followed from spatial considerations resulting from his theory of directional valency forces. His work has since been confirmed by Johnson and others (32, 33) and it is of interest to note that the structure ascribed to this compound by Werner has recently been confirmed from a consideration of X-ray data (132).

Investigations into the mechanism of complex formation with chromium (III) are complicated by the fact that there are six co-ordination positions available for substitution. Burley (29) overcame this by preparing the dioxalatodiaquochromiate salt



which only has two positions available since the bidentate oxalate groups are fairly firmly co-ordinated. Using the method of preparation of Werner (30), Burley was able to prepare the trans-salt but not the cis-isomer. Fortunately it was found that in aqueous solution, the trans-isomer passes over spontaneously to the cis-form in about 3 hours at room temperature for a 0.01M solution. The discovery of this conversion depended upon the fact that the two isomers have different absorption spectra in solution. Burley studied this reaction kinetically and found it to be of the first order. He also carried out a study of the kinetics of the reaction between potassium oxalate and

potassium cis-dioxalatodiaquochromiate in dilute solution to form the trioxalatochromiate ion :



This reaction was found to be of the second order.

Burley also studied the reactions between cis-dioxalatodiaquochromiate and the bidentate acid ligands - malonate, succinate, adipate, fumarate, maleate and phthalate - but the interpretation of the resultant spectrophotometric data proved very difficult.

Later Friend (34), using different colorimetric techniques, confirmed the results found by Burley on the kinetics of the reaction between potassium oxalate and potassium cis-dioxalatodiaquochromiate. He also succeeded in isolating the cis-dioxalatodiaquochromiate salt by Werner's method (30) in a comparatively pure form.

Potassium cis-dioxalatodiaquochromiate reacts with alkali to give successively dioxalatohydroxoquochromiate and dioxalatodihydroxochromiate. Titration curves obtained by Burley on an aged solution of the trans-salt show that the reaction is stepwise and the ion appears to behave as a weak dibasic acid with titration constants :

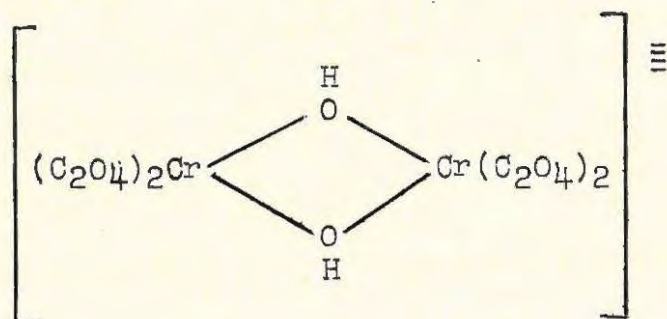
pK_1	7.09
pK_2	9.45

Friend (34) in a later investigation showed that the thermodynamic ionisation constants were identical for the first stage but differed for the second stage. The

figures quoted for the pK values after extrapolation to zero ionic strength are

	<u>cis-salt</u>	<u>trans-salt</u>
pK ₁	7.53	7.54
pK ₂	9.71	10.46

It has long been known that binuclear complexes involving hydroxyl bridges may be formed from chromium compounds through the phenomenon of "olation". Tetraoxalato u dihydroxodichromate (III) was originally described by Werner (30) and represents the typical complex of this kind. Conditions of formation of this compound

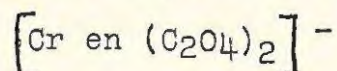


have been investigated by Burley who found that the reaction could proceed to 80% completion in aqueous solution under appropriate conditions.

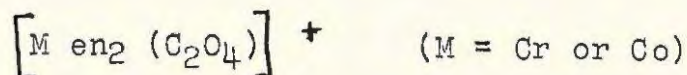
As follows from the fact that the valencies in co-ordination compounds are directional in space many chromium complexes exhibit stereochemical isomerism. The racemisation of potassium trioxalatochromiate may occur either through simple rearrangement of the oxalate groups while still held within the co-ordination complex or by a process of secondary ionisation. Long (45) has shown

from a study of the kinetics of inversion using radioactive carbon in the oxalate molecule that secondary ionisation does not occur.

Johnson (35) has reviewed the racemisation of the trioxalato-compounds of both chromium and cobalt. Continuing in this field of work Bushra and Johnson (33) found, contrary to Werner's observations (37), that in all probability $[\text{Cr en}_2 (\text{C}_2\text{O}_4)]^+$ did not racemise. They succeeded, however, in racemising the compound



Bushra and Johnson (33) postulate that inversion takes place by intramolecular rearrangement without the detachment of oxalate. In their own words : "An octahedral disposition of the six atoms (nitrogen or oxygen) linked to the metal being assumed in all cases, the net result of optical inversion is an interchange of two points of attachment in cis-positions. Evidently this process happens more readily between co-ordinated oxalate than between ethylenediamine radicals. Whether racemisation invariably occurs by intramolecular rearrangement remains to be proved, but the fact that the complex ions



do not racemise is consistent with this view, since a given configuration will persist so long as the two molecules of ethylenediamine remain undisturbed; the detachment and subsequent recombination of the oxalate

ion might be expected to provide opportunities for inversion. The decomposition of $[\text{Cr en}_2 (\text{C}_2\text{O}_4)]^+$ in solution, which appears to involve the displacement of the oxalate ion, is also against the theory of racemisation by secondary ionisation."

In addition Bushra and Johnson found that the magnitude of E (Arrhenius equation) is practically identical for both the di- and the tri-oxalato-ions of chromium, suggesting a common mechanism of inversion. The introduction of a molecule of ethylenediamine seems hardly to affect the characteristics of the two remaining oxalate radicals.

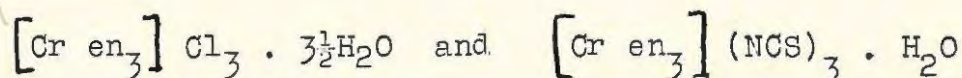
The present investigations, which are concerned with methods of preparation of a number of derivatives involving oxalate, ethylenediamine, propylenediamine etc., and a study of their properties, were undertaken with a view to elucidating some general principles involved in the formation of co-ordination compounds of chromium.

Since it was intended to direct attention specifically towards complexes containing nitrogen bases it is convenient at this stage to review some of the past work in this field.

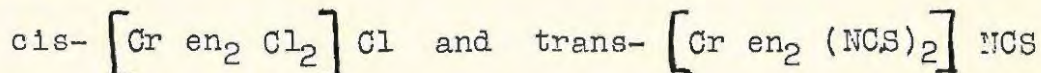
Verner gives methods of preparation of di-oxalatoethylenediaminochromic salts (30) and oxalato-bisethylenediaminochromic salts (38) but Bushra and Johnson (33) have modified these to give better yields. Abegg (39) also gives a preparation of trisethylenediamino-

chromic salts. Trisethylenediaminochromic salts and trispropylenediaminochromic salts can also be prepared by the methods of Rollinson and Bailar (40).

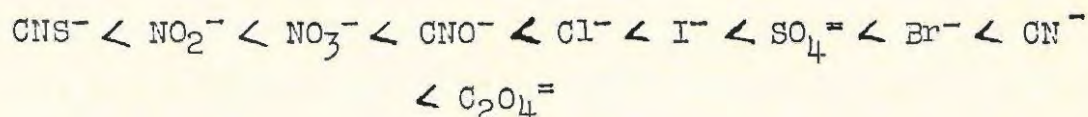
Pfeiffer and co-workers (41) observed that the leuto salts



on heating at 160° and 130° respectively for several days yielded



Continuing this work, O'Brien and Bailar (42) found the decomposition temperatures (relative thermal stability) of various trisethylenediaminochromic salts and trispropylenediaminochromic salts. They found the stabilities of the latter salts to be in the same order as, and in general slightly less than, the corresponding former salts. The order of stability was



In connection with the present work it is of interest to note the relatively high thermal stability of the oxalate salt (280°C . compared with 130°C . for the thiocyanate salt of trisethylenediaminochromiate).

In a series of papers, Balthis, Bailar and co-workers (40, 42, 43, 44) give details of methods of preparation of some chromous and chromic ammines from such

starting materials as chromous acetate, chromous chloride, anhydrous ethylenediamine and its homologues.

It is evident therefore that despite the considerable interest in the derivatives and reactions of oxalato-chromium complexes, there is not an extensive literature on this subject. Accordingly the methods of preparation of a number of such derivatives described by Werner and more recently Bushra and Johnson have been re-investigated with a view to a more detailed study of the properties of these compounds.

CHAPTER II

EXPERIMENTAL TECHNIQUES

A. PHYSICAL METHODS

In dealing with reactions involving the formation of chromium complexes the need was felt for some method of separation and identification of the resultant products. One of the most obvious differences lending itself to qualitative and quantitative estimation is the nett charge on the complex ion. To this end the methods of electrophoresis and ion-exchange resins are available.

Following the excellent results found in many fields of analysis by paper chromatography it was decided to try this method also for the qualitative separation of chromium complexes. This chapter deals mainly with these techniques, followed by a description of the spectrophotometric and potentiometric methods employed in individual studies.

1. Electrochromatography

Electromigration (70, 71, 72, 73) and chromatography (74, 75, 76, 77, 78, 79) have long been employed for the resolution of mixtures of solutes. In 1939, Strain utilised electromigration, without flow of solvents, for the separation of dyes in a column of moist porous

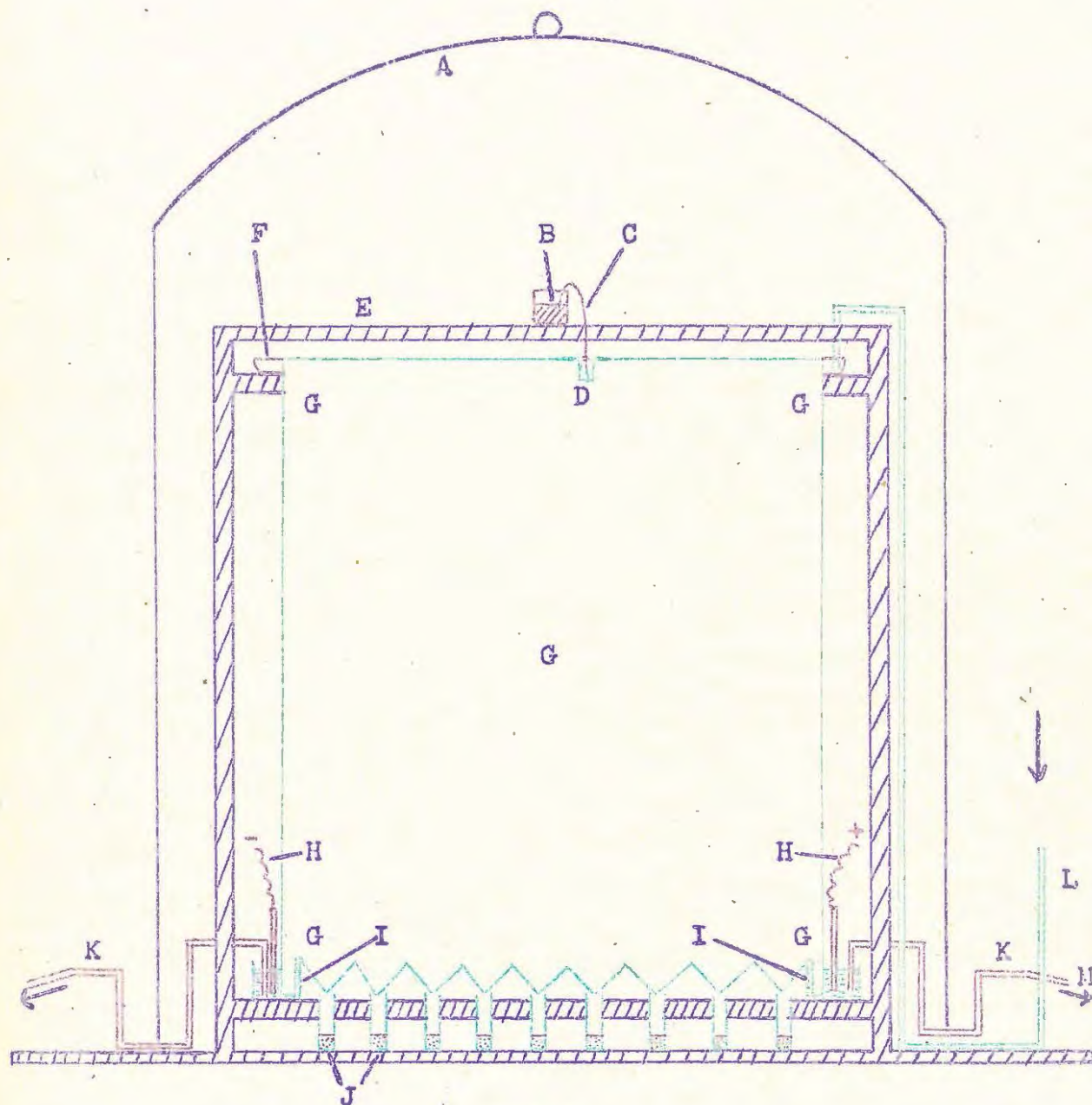


FIG. 4

ELECTROCHROMATOGRAPHIC APPARATUS.

- | | |
|--|--|
| A. Bell Jar. | G. Paper with serrated edges. |
| B. Solution under examination. | H. Platinum electrode. |
| C. Wick. | I. Electrode vessel. |
| D. Point of contact of the wick and the paper. | J. Tubes for collecting the separated fractions. |
| E. Wooden Stand. | K. Constant level tubes for electrode vessels. |
| F. Background electrolyte trough. | L. Background electrolyte feed tube. |
| | M. Waste tube for excess background electrolyte. |

adsorbent (80). This method, under the name of electrochromatography has been widely applied to the resolution of mixtures in columns and in strips of filter paper (74, 75, 81, 82, 84, 85, 86, 87).

The combination of electrical migration plus simultaneous flow of solvent for the discontinuous separation of ionised substances in a sheet of paper, the current flowing at right angles to the flow of solvent, was used by Haugaard and Kroner (88). Svensson and Brattsten (89) utilising electrical migration plus simultaneous flow of solvent, carried out a continuous separation of dyes in a cell filled with powdered glass in which there was no adsorption of ionised solvents.

Following a paper on continuous electrophoresis and ionophoresis on filter paper by Durrum (90) it was decided to build an electrochromatographic apparatus and investigate the possibilities of its use in separating chromium complexes. In the field of inorganic compounds good separations employing these methods were obtained by Strain and others (91, 92, 93).

The final apparatus that was employed is represented diagrammatically in Figs. 4 and 5.

The paper G (Whatman No. 11) was suspended from an earthenware trough F, the side of which had been cut off on a diamond wheel and replaced by a perfectly flat sheet of glass attached with Canada balsam. The reason for this was that the edge of the trough, not being horizontal, resulted in an uneven flow of background

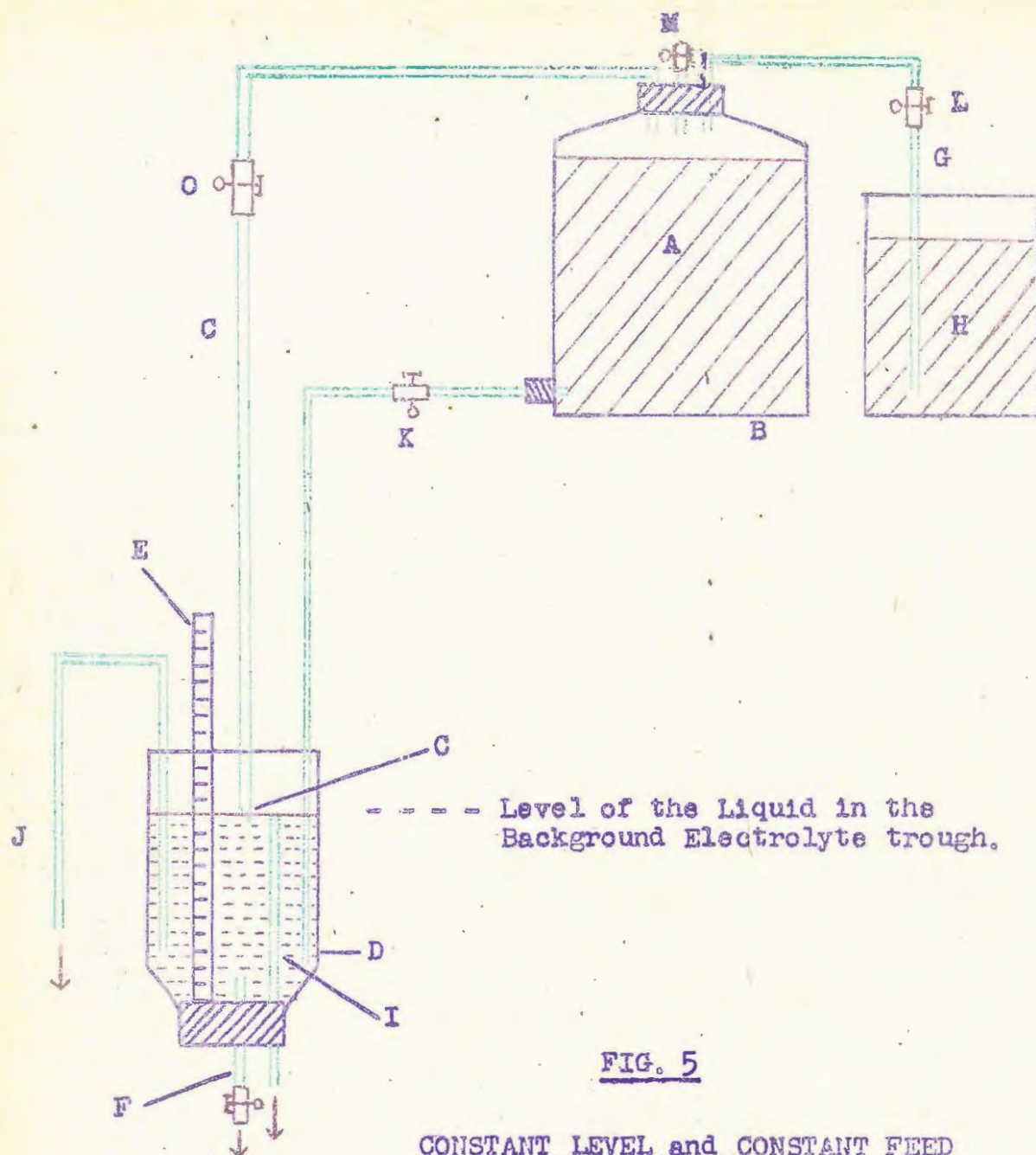


FIG. 5

CONSTANT LEVEL and CONSTANT FEED

APPARATUS.

- A. Background Electrolyte.
- B. Aspirator (4 litres).
- C. Make and break tube to control the flow of electrolyte from the aspirator B.
- D. Constant level control vessel.
- E. Scale to measure variations in the constant level.
- F. Tube for emptying vessel D.
- G. Tube for refilling B while the apparatus is in operation.
- H. Supply of Background Electrolyte.
- I. Overflow tube.
- J. Tube to Electrochromatographic Apparatus.
- K. L. M. O. Pinchcocks.

electrolyte from the trough and down the paper. It was found advisable to fold the vertical edges of the paper to give a 2 cm. flap which added to the strength of the paper. The internal dimensions of the trough employed were 9" long by $4\frac{1}{2}$ " wide with a depth of $\frac{3}{4}$ ". The bottom edge of the paper was serrated for two reasons - to induce a more even flow of electrolyte down the paper and to make the collection of separated fractions in tubes J very easy.

The bottom ends of the paper dipped into two electrode vessels I, which carried the platinum electrodes H. These beakers were also fitted with automatic devices for keeping a constant level (tubes K). A solution containing the solutes to be separated was then placed in beaker B and was slowly added to the paper by means of a cigarette lighter wick C which contacted the paper at D.

The level of the background electrolyte in the trough F was kept at a constant height by means of a continuous feed system, Fig. 5. By means of this constant-level apparatus the height of the background electrolyte in the trough and hence the rate of flow down the paper could be varied by raising or lowering vessel D and the make-and-break tube G.

By consideration of the factors involved in this electrochromatographic apparatus it will be seen that if the rate of flow of electrolyte, and hence the rate of flow of the solution to be separated, is too great then the electrical field will be unable to draw the charged ions of

the solution to be separated towards one electrode or the other, and consequently this solution will flow vertically down the paper. The required rate of flow for any set of conditions of separation depends upon the substances under examination and the potential applied across the paper.

It was found during many runs that the variation in height of the background electrolyte in vessel D was less than 0.1" and usually of the order of 0.05". During some runs it was found that more than 4 litres of background electrolyte was needed, but by adopting the following procedure the vessel A could be refilled without disturbing the separation. The taps O and K were closed and flask H containing more of the background-electrolyte placed with tube G dipping well down into the solution. On opening tap L, solution from flask H was drawn into vessel A by means of the slight back-pressure always present in A. When vessel A was refilled tap L was closed and taps K and O opened, when the system returned to the constant level.

The potential across the paper was maintained by a valve rectifying unit providing a D.C. supply of 360 - 400 volts at 0 - 30 milliamps.

As can be seen from the diagram, most of the apparatus was covered with a bell jar; this and a beaker full of water prevented too much evaporation of solvent from the paper. The apparatus could not be made completely airtight because of the necessary feed tubes and wires which had to enter from the outside.

Fig. 6A

Electrochromatographic patterns for a mixture of potassium dioxalatodiaquochromate and potassium trioxalatochromate at different points of contact on the paper.

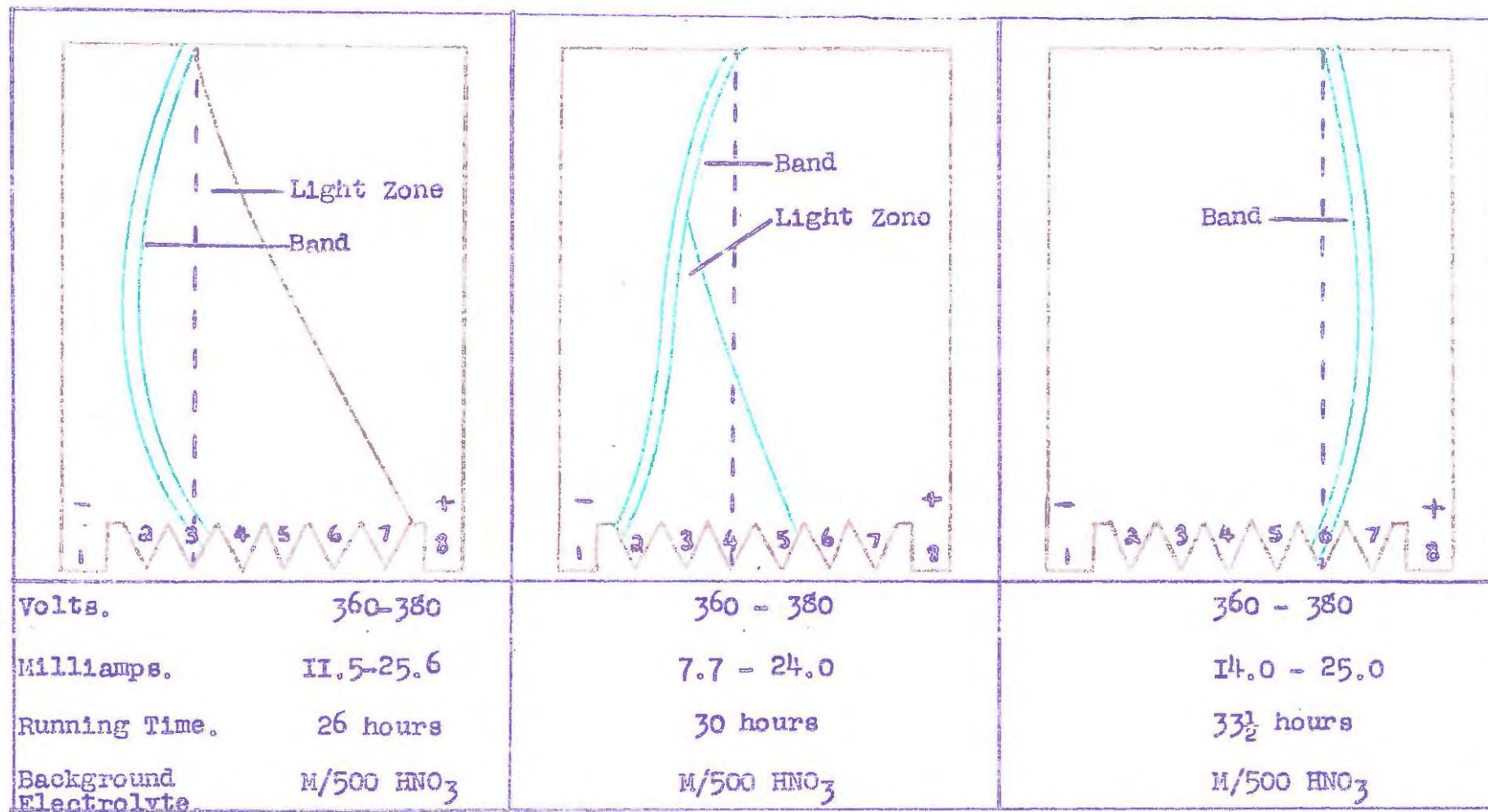


FIG. 6B

Electrochromatographic patterns for potassium trioxalatochromiate at different points of contact on the paper.

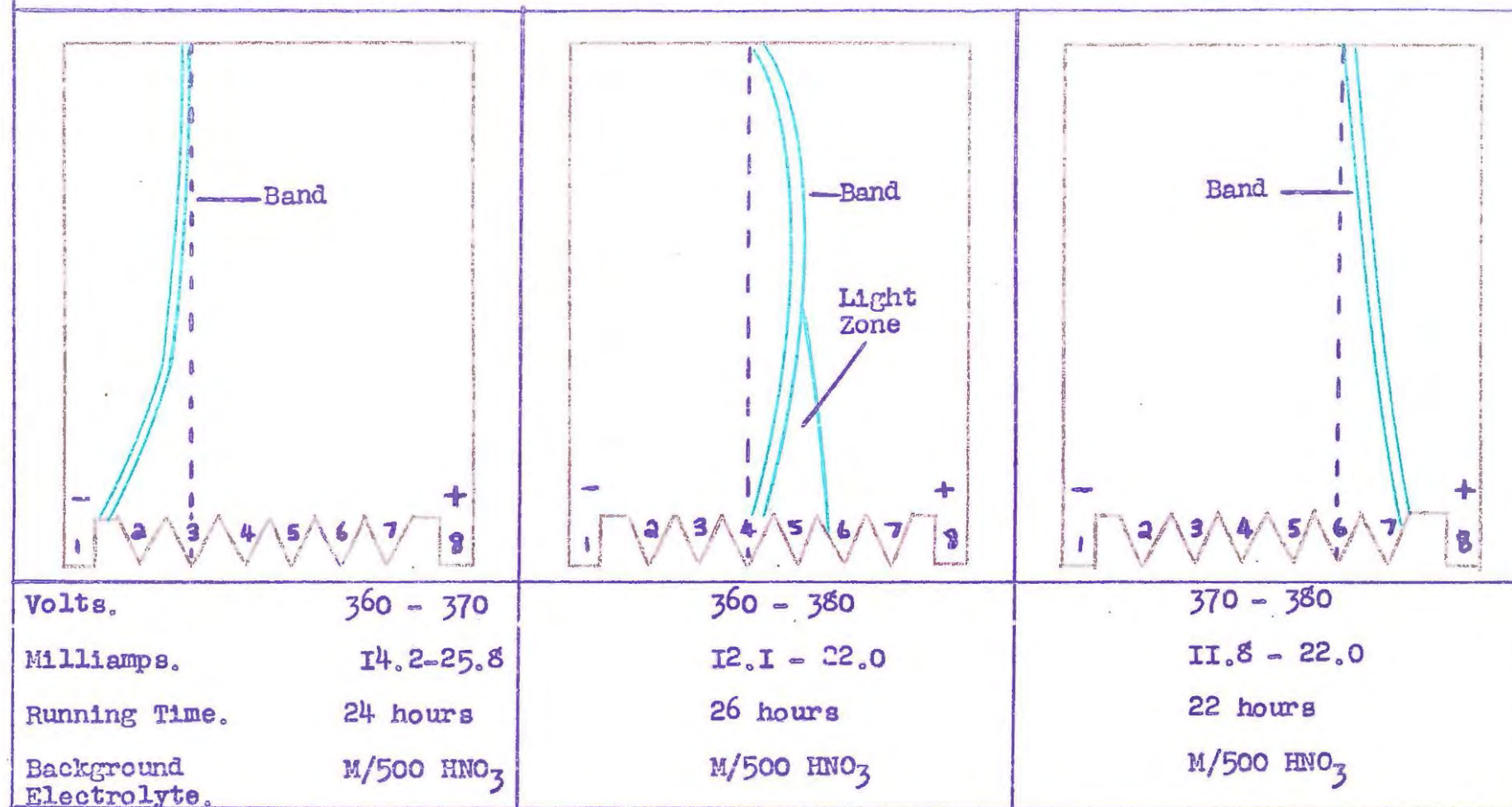
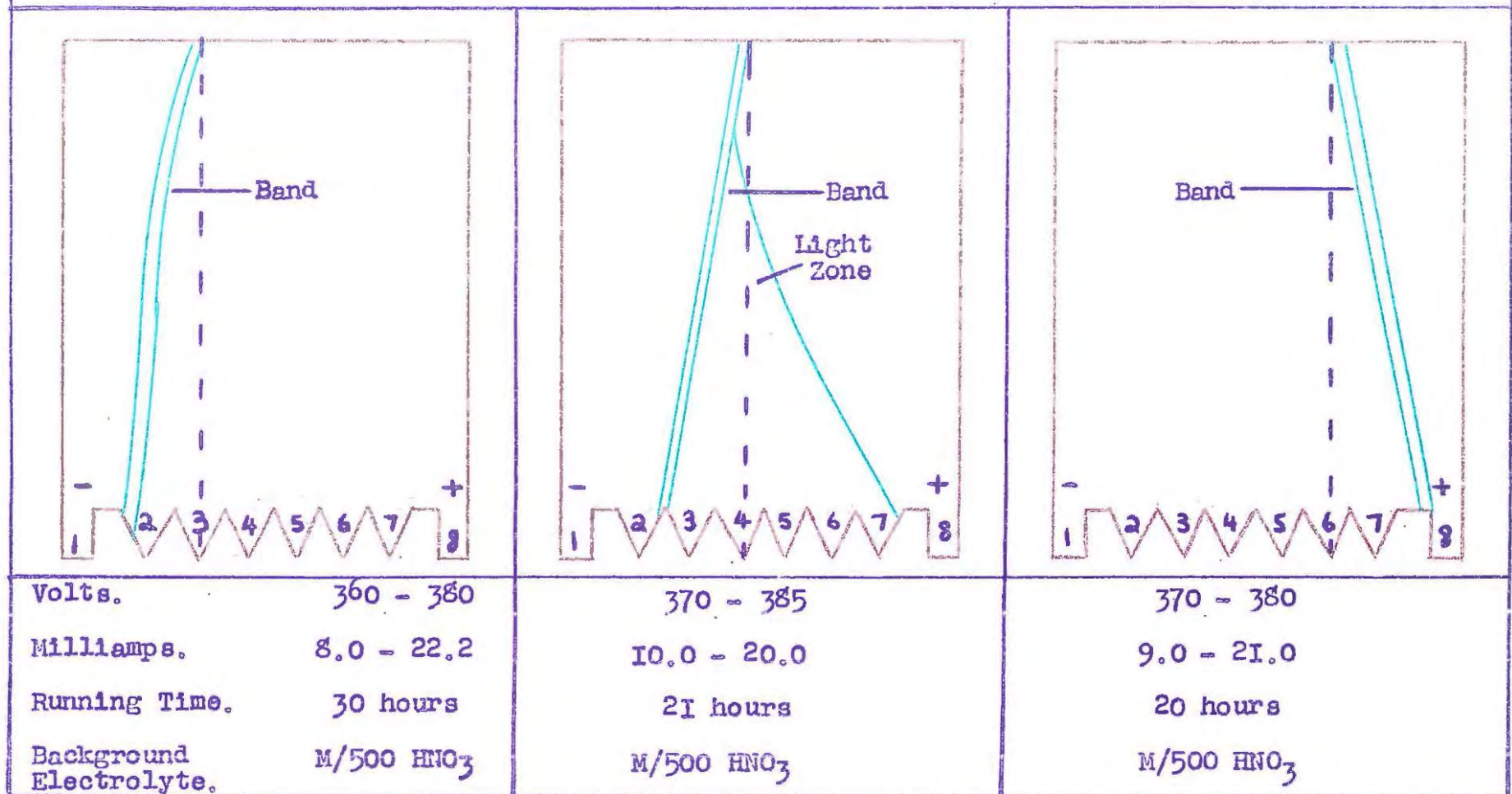


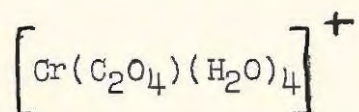
FIG. 6c

Electrochromatographic patterns for potassium dioxalato diaquochromate at different points of contact on the paper.



A summary of the general shape of the patterns obtained with cis-dioxalatodiaquochromiate, trioxalatochromiate and mixtures of these, using M/500 HNO₃ as background electrolyte, is given in Fig. 6.

Consideration of the patterns for the individual substances shows clearly that the shape of the pattern obtained - i.e. the direction of electromigration - depends on the position of the points of contact on the paper relative to the anode and cathode. The reason for this variation probably lies in the fact that basic and acidic regions, which Strain and Sullivan deal with in greater detail (91), are built up on the paper in the vicinity of the electrodes. Thus with trioxalatochromiate and dioxalatodiaquochromiate, when the point of contact is near the cathode (i.e. in the basic zone) the pattern obtained would seem to indicate that a cationic complex is present, whereas both these are known to be anionic. The explanation probably lies in the formation of cationic complexes such as :

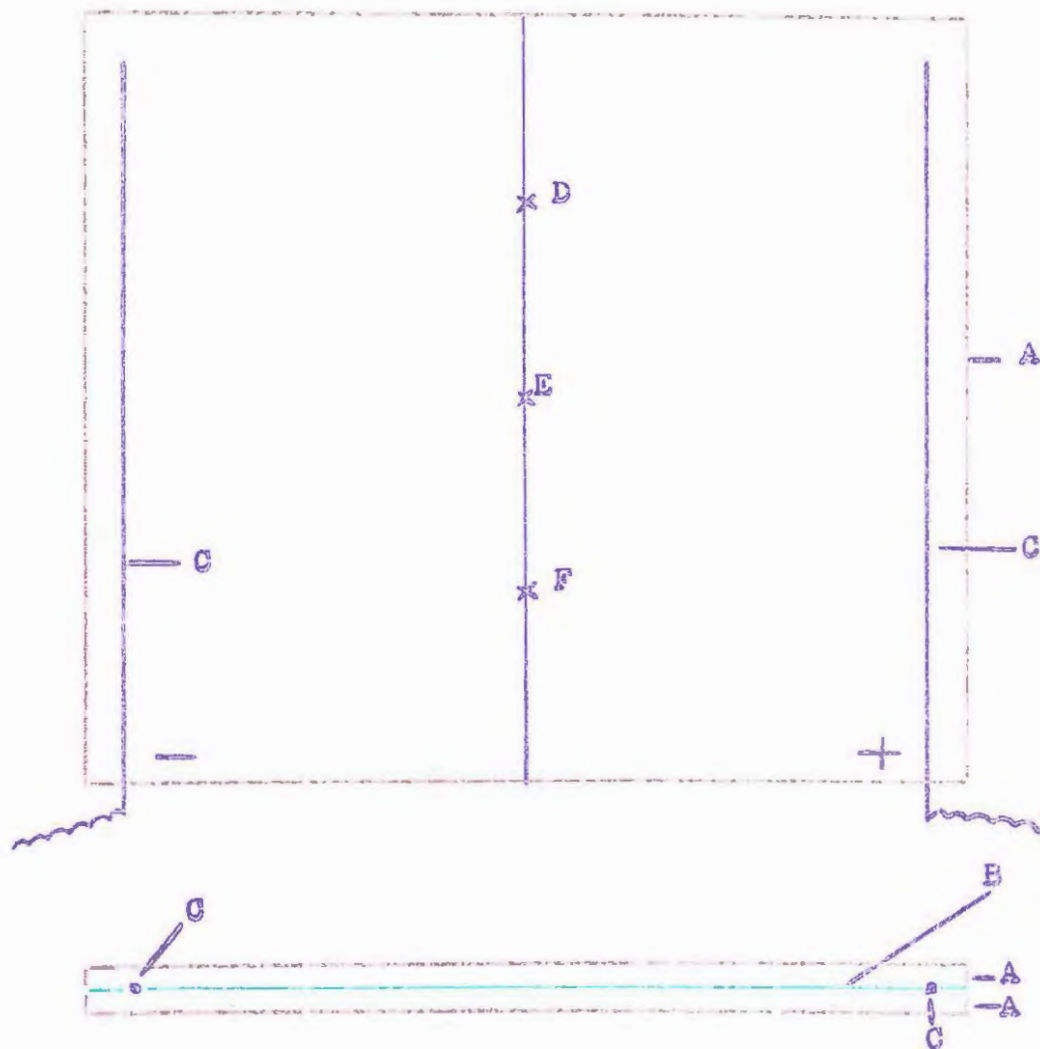


under the influence of pH and the electrical field.

The conclusion drawn from many experiments of this nature is that the technique or apparatus is unsuitable for the separation of chromium complexes, but that better results may be obtained with a similar apparatus designed by Strain and Sullivan (91) and modified by Sato et al (93),

FIG. 7

FILTER PAPER ELECTROPHORESIS APPARATUS.



- A. Glass plate.
- B. Paper.
- C. Platinum electrodes.
- D. E. F. Spots of solutions under examination.

FILTER CIRCUIT.

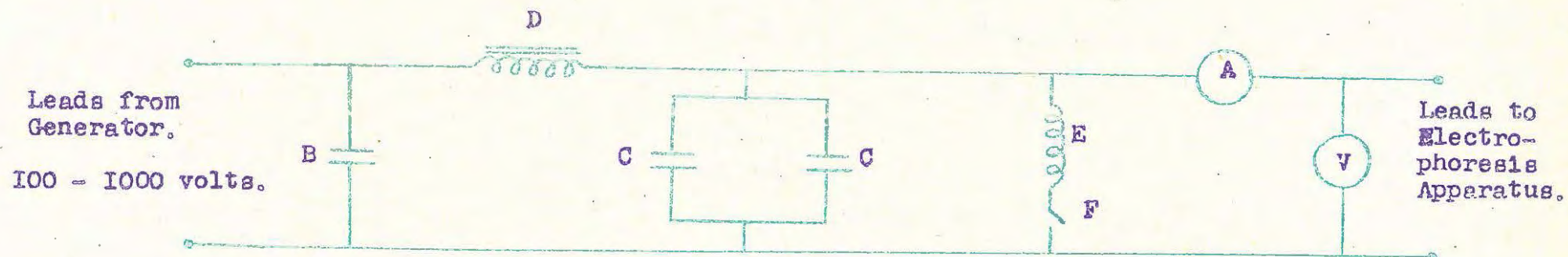


FIG. 8

- B. Condenser 10 mfd. 2000 volts. D.C. Type I3I.
C. Condenser 4 mfd. 1600 volts D.C.
D. L.F. Choke type D/652. 10Hy. 100 ma.
E. Resistance 10,000 ohms.
F. Switch.

in which the paper is suspended between glass plates rather than hung in air.

Eliminating the chromatographic effect and employing electromigration alone, an apparatus was then built along the lines of that employed by Strain (92). This consisted of two glass plates 9" x 10" with two grooves $\frac{1}{4}$ " from the edge down the shorter edge of one of the plates in which platinum wires for electrodes were placed. The paper, Whatman No. 54, was moistened with the appropriate electrolyte, the excess electrolyte being dried off on blotting paper; then spots of the solutions under examination were made in the centre of the paper with a graduated fine capillary tube and a second glass plate placed on top of the paper (Fig. 7). The platinum wires were then connected to a constant D.C. supply of 100 - 1000 volts and 0 - 100 milliamps which consisted of a generator driven by a variable speed motor and a filter circuit (Fig. 8).

Using this apparatus and various background electrolytes, good separations of trioxalatochromiate and dioxalatodiaquochromiate were obtained. (Electrochromatograms 1 - 10 Appendix A). Electrochromatogram 4 reveals that though separation occurred, part of spot 1 and spot 3 moved towards the cathode indicating that the dioxalatodiaquochromiate forms a cationic complex with the background electrolyte of ethylenediamine hydrochloride while the trioxalatochromiate either remains unchanged or forms an anionic complex. Similarly with ethylenediamine as background

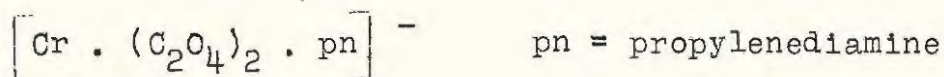
electrolyte, although the spots moved towards the anode, they showed a distinct colour change from the normal blue-violet of the dioxalatodiaquochromiate and trioxalatochromiate to salmon-pink. This probably corresponds to the formation of



(See electrochromatogram 5).

With propylenediamine as background electrolyte, electrochromatogram 6 was obtained, analysis of which reveals :

- (a) A trail probably corresponding to dioxalatodiaquochromiate.
- (b) A distinct pink spot corresponding in all probability to



- (c) A greenish zone changing to pink on standing.
- (d) A distinct pink spot corresponding probably to the complex in (b) above.
- (e) A greenish zone changing to pink on standing.
- (f) A slight trail, probably dioxalatodiaquochromiate.
- (g) A distinct pink spot corresponding probably to the complex in (b) above.

In electrochromatogram 7 there was no evidence of formation of cationic complex between dioxalatodiaquochromiate and propylenediamine hydrochloride as was the case with ethylenediamine hydrochloride in electrochromatogram 4 but the first evidence of an impurity, (spot e) in

the trans-dioxalatodiaquochromiate as prepared by Burley (29) and Friend (34) according to Werner's method (30), appeared. This will be fully investigated later. Once again this impurity is shown up by electrochromatograms 8 and 10. In electrochromatogram 9 all the spots moved towards the cathode where b and d formed spots of light green (a and c) and then moved towards the anode. Spot e did not form a corresponding green spot. This would seem to indicate reaction between the trioxalatochromiate and urea. In addition a continuous yellow spot formed at the anode - on standing this turned green.

As a result of electrochromatograms 7, 8 and 10, in which the dioxalatodiaquochromiate appeared to have an impurity of charge similar to that of the trioxalatochromiate it was decided to investigate the method of preparation. (See Chapter III).

Work on the purity of the various preparations indicated that the technique is extremely useful and convenient, but although good results were obtained, experience showed that there were possible sources of error and inconvenience. The apparatus lacked efficiency in that if the electromigration was carried on too long the paper became dry, resulting in general in an increase in the voltage and a decrease in the amperage. This caused considerable heating, with the result that the glass plates cracked or the paper burned. In addition, with the electrodes in contact with the paper it was possible for



FIG. 9.

FILTER PAPER ELECTROPHORESIS
APPARATUS.

acidic and alkaline zones to build up around the anode and cathode respectively; this, as has been pointed out above, is very undesirable - especially when dealing with substances whose very composition depends upon the prevalent pH (e.g. cis-dioxalatodiaquochromate). A further source of error is due to the presence of background electrolyte between the paper and the glass sheets, thus destroying the whole object of the method which is for the electromigration to take place in the paper.

Kunkel and Tiselius (94) and Gustavson (95) using a modified apparatus designed by Tiselius (96) have overcome most of these difficulties and errors. Along these lines a more efficient filter paper electrophoresis apparatus was built (Fig. 9). Using glass plates of the same size as before the difficulty of air bubbles between the plates was overcome by greasing both glass plates with silicone grease and clamping them tightly between wooden boards held by four thumb screws. Fig. 9 shows the apparatus with the top wooden board removed. The use of large electrode vessels eliminated the possibility of pH changes reaching the paper. In order to eliminate any flow of background electrolyte from one vessel to the other due to differences in levels, these levels were equalised before the start of each experiment. To allow for any imperfections in the smoothness of the glass plates which might cause air bubbles, a thicker paper (Asoka white blotting No. 38) was used.



FIG. 10.

CHROMATOGRAPHIC APPARATUS.

2. Chromatography

Following the success of the filter paper electrophoresis apparatus in separating dioxalatodiaquo-chromiate and trioxalatochromiate it was decided to attempt a separation using filter paper chromatography. The apparatus employed was similar to the one dimensional filter paper chromatographic apparatus employed by Roux (97) in the separation of the constituents of wattle tannins. (Fig. 10). Although 20 different solvent mixtures were employed no good separation was obtained. The solvent mixtures used were :

1. Acetone + 10% v/v HCl.
2. Glacial acetic acid + 25% v/v dry methyl alcohol.
3. n-Butanol saturated with water.
4. 70% v/v Glacial acetic acid + 30% v/v n-butanol.
5. 70% v/v Glacial acetic acid + 30% v/v absolute alcohol.
6. 70% v/v Glacial acetic acid + 20% v/v n-butanol +
10% v/v methanol.
7. n-Butanol + pyridine + 1 N ammonia (2 : 1 : 2)
8. 70% v/v Glacial acetic acid + 30% v/v tert-butanol.
9. 70% v/v Glacial acetic acid + 30% v/v n-propanol.
10. Phenol saturated with water.
11. 75% v/v phenol saturated with water + 25% v/v glacial
acetic acid.
12. 80% v/v water + 20% v/v formic acid.
13. 10% w/v oxalic acid..
14. 80% v/v water + 20% v/v lactic acid (SG 1.21).
15. 60% v/v phenol saturated with water + 40% v/v glacial
acetic acid.

16. 20% v/v water
20% v/v ammonia (SG .880)
60% v/v n-propanol
17. Saturated sodium chloride solution.
18. 90% v/v phenol saturated with water + 10% v/v glacial acetic acid.
19. Saturated potassium nitrate solution.
20. Benzyl alcohol 20% v/v
Acetic acid 20% v/v
Water 60% v/v

Top layer used on the paper and bottom layer used to saturate vapour of vessel.

Most of these solvent mixtures had been used for the separation of inorganic or organic compounds by other workers.

3. Spectrophotometry

General Principles

In the words of Mellon (98) - "Spectrophotometry is a term that by practically universal usage is taken to refer to the relative measurement of radiant energy or radiant flux as a function of wavelength. By strict derivation the term might be restricted to such measurements made visually, but in actual practice the word has long been applied also to photographic and photoelectric methods of measurement in the ultraviolet, visible and more recently in the infrared regions of the spectrum".

In recent years the field of spectrophotometry

has received a great deal of attention, resulting in much literature on the principles of precision colorimetry (98, 99, 100, 101, 102, 103), and even more on the analytical applications. A recent review by Mellon (104) with almost three hundred references, gives a good general picture of the situation.

The instrument employed in the present work was the Beckmann Quartz Spectrophotometer Model DU. The advantage of this instrument over the other types is that a good proportion of the literature on spectrophotometry deals specifically with this model and its applications. The optical arrangement of the instrument and its applicability to various systems are given in more detail by Burley (29) and Friend (34).

In all readings recorded in the present work, a systematic procedure was adopted. One of the Corex cells (1 cm light path), filled with distilled water and placed in the cell holder in the same way every time, was always taken as the standard cell. The other three cells were then filled with distilled water and standardised at every 10 mu in the range 300 to 700 mu against this standard cell. This standardisation was repeated at regular intervals after the cells had been cleaned with fine tissue paper. Suitable marks on the cells enabled them always to be oriented in the same way in the cell holder. In measuring the optical density the sensitivity knob was always turned to the extreme clockwise position (maximum sensitivity) and the

slit width alone adjusted to balance the galvanometer needle at any chosen wavelength. When not in use the cells were stored in a dish of distilled water.

Standardisation and calibration of the instrument was carried out according to the instructions of the manufacturer.

Following a number of careful studies on the instrument (100, 105, 106) it is generally agreed that, although readings on a particular model are almost exactly reproducible, differences of the order of 1% in the optical density reading of a given solution may be expected between different instruments. Hiskey and his co-workers (107) have compared three commercial spectrophotometers, one of which was the Beckman model DU, and have concluded that in practice the best results are obtained at maximum sensitivity and at the highest absorbance values of the reference standard which may be obtained without absorption law deviations.

In the analysis of coloured solutions we are interested in the relation between the incident light entering the solution and the transmitted light for a given solute concentration. The first of these laws, formulated by Bouguer (108) but often attributed to Lambert, expresses the relationship between absorptive capacity and thickness of the absorbing medium. The second law, formulated by Beer, expresses the relationship between absorptive capacity and the concentration of the solute in a solution.

These laws both assume monochromatic light and may best be summarised by the equation :

$$I = I_0 \cdot 10^{-KCl} \quad \dots\dots\dots (2.1)$$

where I_0 is the intensity of the incident light and I the transmitted intensity after passing through a solution of thickness " l " containing the absorbing substance at concentration C . Here K is the extinction coefficient and is constant for a given substance at a given wavelength. The quantity I/I_0 is known as the Transmission of the solution and can be used directly as a measure of the amount of light absorbed. It is often more convenient to use the optical density (D) which is defined as :

$$D = \log_{10} \frac{I_0}{I} \quad \dots\dots\dots (2.2)$$

It follows from (2.1) and (2.2) that

$$D = K.l.C \quad \dots\dots\dots (2.3)$$

Equation (2.2) may be rewritten :

$$D = \log_{10} \frac{1}{T_s} \quad \dots\dots\dots (2.4)$$

$$\text{or} \quad A_s = \log_{10} \frac{1}{T_s} \quad \dots\dots\dots (2.5)$$

where T_s is the transmittancy or the ratio of the transmittance of the solution to that of the solvent in equal

thickness and A_s is the absorbancy.

Now spectrophotometric plots with $\log A_s$ ($\log \log 1/T_s$) and wavelength as co-ordinates may be interpreted graphically with great speed and accuracy. With this plot the curve shape is a qualitative identification and the vertical height of the curve is a quantitative indication of the amount of material present. In logarithmic form equation (2.3) becomes

$$\log D = \log K + \log l + \log C \quad \dots\dots (2.6)$$

The concentration C and the cell thickness l are not functions of wavelength; and the shape of the curve will therefore be determined solely by $\log D$, which is a function of wavelength. Consider two solutions of the same substance in which the solute concentrations are C and $b.C$, where b is a numerical factor.

The optical densities are then given by :

$$\log D_1 = \log K + \log l + \log C \quad \dots\dots (2.7)$$

$$\log D_2 = \log K + \log l + \log C + \log b \quad \dots (2.8)$$

Since the equations apply at any given wavelength the difference between the equations is the term $\log b$, which is a constant term independent of wavelength.

The validity of this theoretical derivation is shown practically by comparison of the $\log D$ values for 0.0092 M and 0.0046 M Potassium cis-dioxalatodiaquo-chromiate which obey the equations 2.7 and 2.8 within

experimental error.

Wavelength mμ	log D ₁ for .009208M cis-diox	log D ₂ for .004604M cis-diox	log D ₂ - log D ₁
340	-1.4685	-1.7696	.3011
350	-1.3279	-1.6383	.3004
360	-1.0410	-1.3372	.2962
370	-0.7696	-1.0809	.3113
380	-0.5544	-0.8477	.2933
390	-0.3893	-0.6840	.2947
400	-0.2832	-0.5751	.2919
410	-0.2204	-0.5129	.2925
			theoretical = .3010

When two absorbing materials a and d are present together and have additive optical densities, it follows that

$$D_{a,d} = \epsilon_a \cdot x + \epsilon_d \cdot (1 - x) \quad \dots\dots (2.9)$$

where ϵ_a = extinction coefficient of component a

ϵ_d = extinction coefficient of component d

x = fraction of component a

(1 - x) = fraction of component d

$D_{a,d}$ = optical density of the mixture.

In qualitative analysis it is frequently desirable to be able to predict the curve of a mixture of two components; equation (2.9) makes this a simple process.

Application to Reacting Systems

In studying reactions between complex forming molecules it is essential to know the number of different complexes formed and their empirical formulae. This information may be obtained from spectrophotometric data under certain prescribed conditions.

The first method tried in the present work was the "molar Ratio method" devised by Yoe and Jones (109) and later modified by Harvey and Manning (110). This method gave unsatisfactory results.

Job's "Continuous variation method" (111) as modified by Vosburgh and Cooper (112) has been used by Foley and Anderson (113) in spectrophotometric studies of complex formation between the uranyl ion and sulphosalicylic acid, by Jonassen and Dexter (114) on copper (II)-ethylenediamine complexes, by Gould and Vosburgh (115) on several complexes of iron, nickel and copper and by Kingery and Hume (116) in studying bismuth thiocyanate complexes. This method proved successful in the present work and is described more fully below.

The mathematical treatment as given by Vosburgh and Cooper (112) is as follows :

Assume substance A and B react according to the following equation :



and that solutions of A and B, both of concentration M moles

per litre, are mixed in varying proportions. Let the mixtures be made by the addition of x litre of B to $(1 - x)$ litre of A ($x < 1$), with no appreciable volume change on mixing. Let c_1 , c_2 and c_3 be the concentrations of A, B and AB_n respectively. For any mixture the following equations apply :

$$c_1 = M(1 - x) - c_3 \quad \dots\dots (2.11)$$

$$c_2 = Mx - nc_3 \quad \dots\dots (2.12)$$

$$c_1 c_2^n = Kc_3 \quad \dots\dots (2.13)$$

Activity coefficients are not needed in equation 2.13 if A and AB_n are ions of the same valence type, and B is a non-electrolyte. The condition for a maximum in the curve of c_3 plotted against x is that

$$\frac{dc_3}{dx} = 0 \quad \dots\dots (2.14)$$

Differentiation of equations (2.11, 2.12 and 2.13) and combination of the three resulting differential equations with equations 2.11 to 2.14 gives

$$n = \frac{x}{1 - x} \quad \dots\dots (2.15)$$

Determination of the value of x for which c_3 is a maximum allows the calculation of n by this equation.

It remains to be shown that a maximum (or minimum) in the absorption of monochromatic light when x is varied coincides with the maximum of c_3 . If ϵ_1, ϵ_2



and ϵ_3 are the extinction coefficients of A, B and AB_n at a given wavelength, the optical density is

$$D = l (\epsilon_1 c_1 + \epsilon_2 c_2 + \epsilon_3 c_3) \quad \dots (2.16)$$

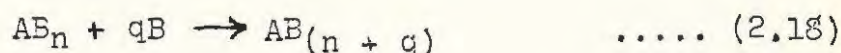
where l is the length of path of the light through the solution.

Let Y be the difference between D and the optical density that the solution would have had if there had been no reaction on mixing the solutions of A and B

$$Y = l [\epsilon_1 c_1 + \epsilon_2 c_2 + \epsilon_3 c_3 - \epsilon_1^M (1-x) - \epsilon_2^M x] \quad \dots (2.17)$$

By differentiating this equation with respect to x it can be shown that Y is a maximum when c_3 is a maximum if $\epsilon_3 > \epsilon_1$, or a minimum when c_3 is a minimum if $\epsilon_1 > \epsilon_3$.

It has been assumed so far that only one complex ion is formed. Let us now suppose that a second complex ion is formed according to the equation



Let the concentration of the second complex ion be c_4 .

A c_4 term must be added to equation 2.11, another to equation 2.12, and another equation added, namely

$$c_3 c_3^q = K^1 c_4 \quad \dots (2.19)$$

The condition for a maximum in c_3 can be shown to be

$$n = \frac{x}{1-x} + \frac{q(q+n)c_4}{M(1-x)} \quad \dots (2.20)$$

If the stability of the two complex ions is such that when c_3 is a maximum c_4 is small, n can be calculated, provided that the maximum in c_3 can be found experimentally. Similarly it can be shown that $(n + q)$ can be determined from the composition corresponding to a maximum in c_4 , provided that at the maximum c_3 is small.

If three complex ions can be formed from the same two components, and if they are rather stable, the situation should not be much different than when only two are formed. When an appreciable amount of the third ion is present, the amount of the first should be small, and it is necessary to consider only two complex ions at a time.

The use of the optical density for the determination of the composition values corresponding to the concentration maxima is not as simple when two or more compounds are possible as when only a single compound is formed. If the extinction coefficient of compound B is assumed to be zero, which is often true in complex ion formation, the optical density of any of the solutions is given by

$$D = l(\epsilon_1 c_1 + \epsilon_3 c_3 + \epsilon_4 c_4) \quad \dots (2.21)$$

The difference Y , defined as for equation 2.17 is

$$Y = l[\epsilon_1 c_1 + \epsilon_3 c_3 + \epsilon_4 c_4 - \epsilon_1 M(1-x)] \quad \dots (2.22)$$

Differentiation of equation 2.22 and combination with

$$\frac{dc_1}{dx} = -M - \frac{dc_3}{dx} - \frac{dc_4}{dx} \quad \dots (2.23)$$

gives

$$\frac{dY}{dx} = 1 \left[(\epsilon_3 - \epsilon_1) \frac{dc_3}{dx} + (\epsilon_4 - \epsilon_1) \frac{dc_4}{dx} \right] \dots (2.24)$$

In general the maximum (or minimum) value of Y will not coincide with the maximum in either c_3 or c_4 since it is not necessary for either dc_3/dx or dc_4/dx to be zero when dY/dx is zero. Furthermore, the value of x at which dY/dx is zero should vary with the values of the extinction coefficients and so with the wavelength used.

However there are some useful special cases in the application of equation 2.24. If the wavelength can be chosen so that $\epsilon_4 = \epsilon_1$ and $\epsilon_3 \neq \epsilon_1$, the maximum in Y corresponds to the maximum in c_3 . Also, if the wavelength is such that $\epsilon_3 = \epsilon_4$ the same is approximately true, provided that the complex ions are highly stable. The condition for maximum Y is then

$$\frac{dc_3}{dx} + \frac{dc_4}{dx} = 0 \dots\dots (2.25)$$

When c_4 and dc_4/dx are small, as they must be when c_3 is a maximum (if compound AB_n is highly stable), the maximum in Y corresponds approximately to the maximum in c_3 .

It can be shown similarly that a slightly different Y -function is a maximum when c_4 is a maximum, provided that ϵ_4 is considerably larger than ϵ_3 . Beyond the point of maximum AB_n concentration, as more B is added, $AB_{(n+q)}$ is formed from AB_n . If $\epsilon_4 = \epsilon_3$, this reaction causes no change in light absorption, but if ϵ_4 is enough

larger than ϵ_3 , the optical density of the solution will continue to increase after c_3 is a maximum in spite of the continuous dilution of the solution as B is added. Let us define Y^1 as the difference between the actual optical density and the density calculated on the assumption that all of the A has been converted to AB_n , but the latter does not react further with B. Let us assume further that the complex ions are so stable that when considerable $A(n + q)$ is present, there is no appreciable A left uncombined. The condition for maximum Y^1 can then be shown to be

$$(\epsilon_4 - \epsilon_3) \frac{dc_4}{dx} = 0 \quad \dots\dots (2.26)$$

and since $(\epsilon_4 - \epsilon_3)$ is finite, dc_4/dx must be zero and c_4 is either a maximum or a minimum.

Thus the method of continuous variation as given by Job (111) has been extended to cases in which more than one compound is formed from a given pair of components. When only a single compound is formed, the results are independent of the wavelength of the light used, but when more than one compound is formed, the results obtained depend on the wavelength of the light, and for useful conclusions the wavelength must be carefully selected.

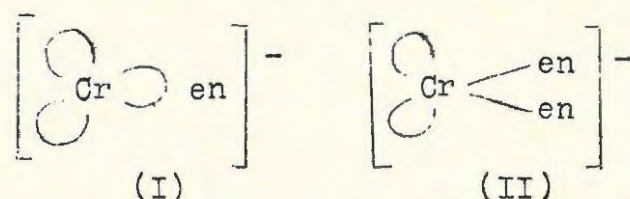
Various other spectrophotometric methods have been used by other workers (117, 118, 119, 120, 121, 122, 123, 124, 125, 126) to determine chelate stability, stability

constants, number of complexes formed between two substances and geometrical configuration of complexes.

4. Potentiometry

Introduction

Potentiometric titrations provide important evidence concerning the nature of acidic and basic groups present in the complex ions. This is of particular importance in the case of water molecules which are in the complex and in deciding whether certain groups, such as the amines, are present as rings or straight chains. Consider the following two complexes as typical examples :



(Here the unmarked rings are oxalate and en is the standard abbreviation for ethylenediamine).

Charge determination by electrophoresis will not differentiate between the two ions but analysis and potentiometry will. Compound (I) will have the normal titration curve of a neutral salt (e.g. KNO_3) while compound (II) will show the titration of two basic groups. These examples serve to illustrate the value of potentiometry.

Potentiometric studies on chrome complexes have been carried out by several workers. Stiasny (127) observed the changes in electrode potentials and pH induced

by varying the ionic environment of chromium chloride and sulphate solutions. He also used this method to study the hydrolysis and ageing of chromium salts. Britton (128) studied the chromium dioxalato complex and Atkin and Chollet (129) the hydrolysis of chrome alum by potentiometry. Work by Burley (29) and Friend (34) on the titration curves of the cis- and trans-dioxalatodiaquochromiates and the trioxalatochromiate yielded useful information.

Apparatus and materials.

The instrument employed was the "Cambridge Bench Type" pH meter with the dip-type glass-calomel electrode system. The instrument was standardised using the following buffer solutions :

- (i) M/20 Potassium hydrogen phthalate (130).

The variation of the pH with temperature (t) between 0°C and 60°C for this buffer is negligible and given by

$$\text{pH} = 4.000 \text{ at } 15^{\circ}\text{C}.$$

$$\text{pH}_t = 4.000 + \frac{1}{2} \left(\frac{t - 15}{100} \right)^2$$

$$\text{i.e. } 3.97 \text{ at } 20^{\circ}\text{C}.$$

- (ii) M/20 Sodium Borate (130).

The variation of the pH with temperature (t) between 0°C and 60°C is high and given by

$$\text{pH} = 9.27 \text{ at } 15^{\circ}\text{C}$$

$$\text{pH}_t = 9.27 - 0.008 (t - 15)$$

$$\text{i.e. } 9.18 \text{ at } 20^{\circ}\text{C}.$$

pH Meter - Electrode assembly.

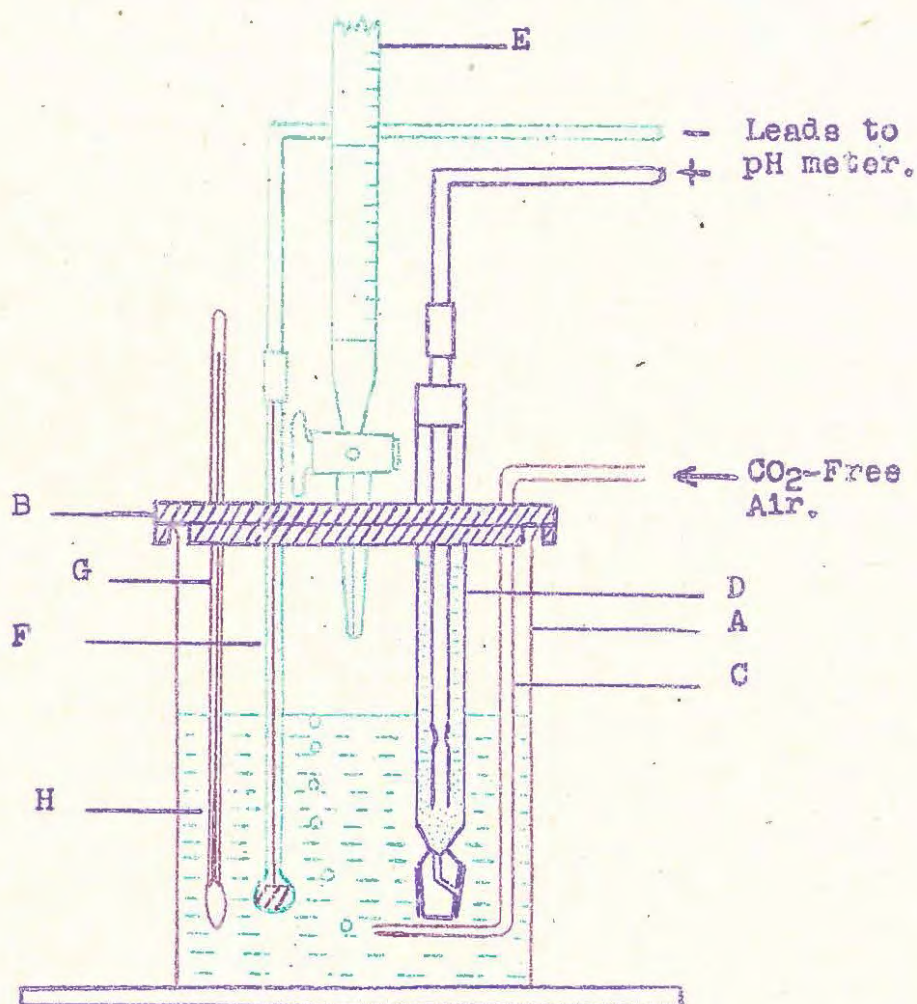


FIG. II

- | | |
|-------------------------|------------------------|
| A. 250 ml. Pyrex Beaker | E. Micro - Burette. |
| B. Wooden Cover. | F. Glass Electrode. |
| C. Bubbler. | G. Thermometer. |
| D. Calomel Electrode. | H. Titration Solution. |

The instrument is provided with a special "Alki" electrode for pH values above 9 but, as shown by Friend (34), for potassium salts, better results were obtained using the normal glass electrode; the "Alki" electrode being too sluggish.

The apparatus used is given diagrammatically in Fig. 11. All titrations were performed in a 250 ml. Pyrex glass beaker which was boiled several times with distilled water prior to using.

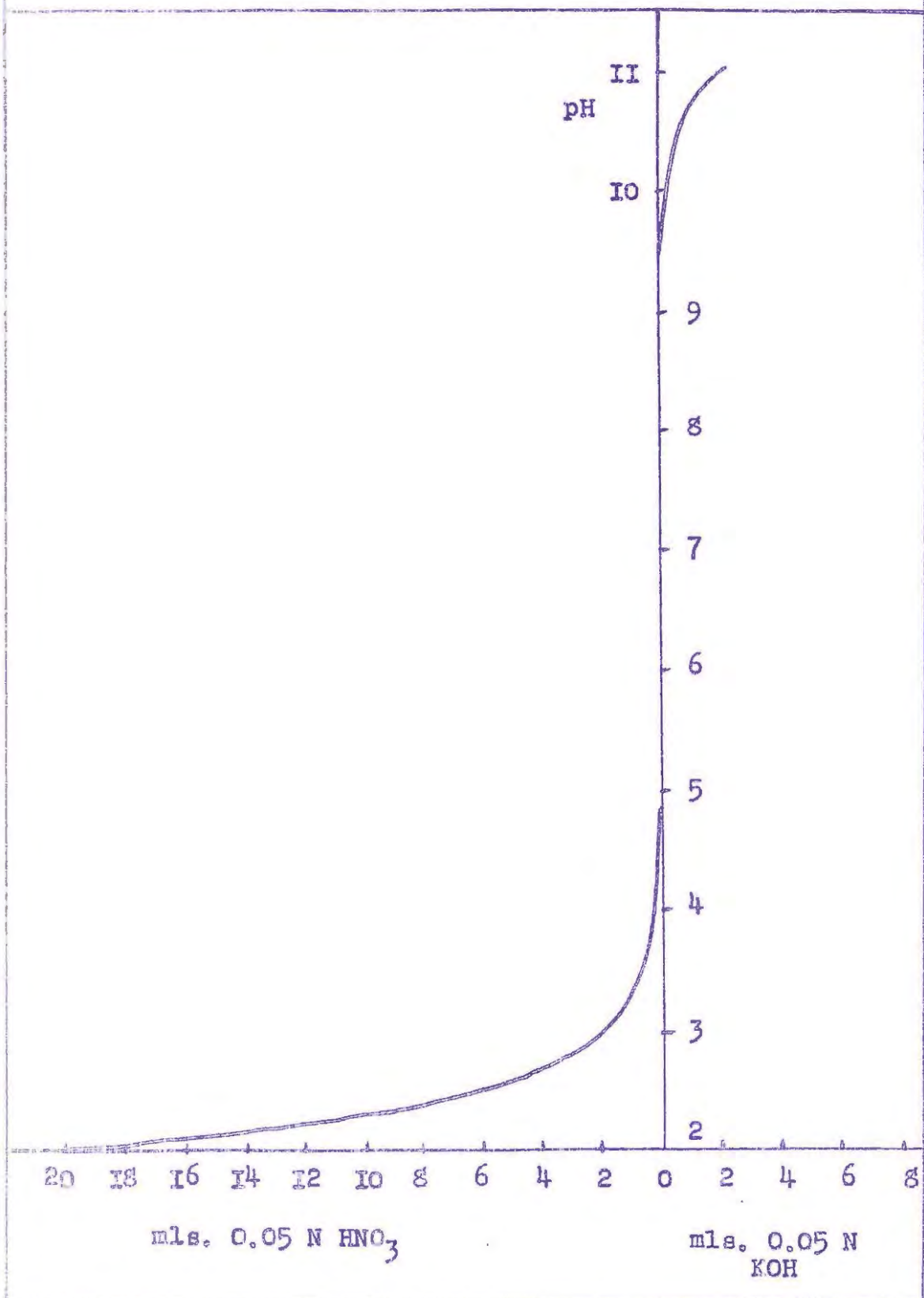
The beaker A was fitted with a grooved wooden cover B, so that the reaction mixture was kept out of contact of air to prevent solution of carbon dioxide. Through this wood cover passed the glass electrode F, the calomel electrode D, a thermometer G, the burette end E, and the CO₂-free air bubbler C. This bubbler was bifunctional in keeping the solution CO₂-free and in stirring after each addition of acid or alkali from the burette. Both the bubbler and burette, which was a 10 ml. microburette Grade A.NPL., were fitted with soda-lime tubes.

For all solutions used in the titrations, freshly prepared CO₂-free water was employed. This was made by redistilling ordinary distilled water from a pyrex still and collecting while still warm. Immediately before use CO₂-free air was bubbled through this bi-distilled water for at least 12 hours to remove the last traces of dissolved carbon dioxide.

The alkali solution used was approximately 0.05N

FIG. 12

Blank titration on Potassium Nitrate (0.00092 M).



KOH (A.R.) made up with CO_2 -free water and kept in a bottle lined with paraffin wax. This solution was standardised against potassium hydrogen phthalate dried over concentrated sulphuric acid just after each series of titrations.

The acid solution was nitric acid (C.P.) 0.05N made up with CO_2 -free water and standardised against sodium borate, kept over sucrose solution, after each series of titrations.

The general maintenance of the instrument was carried out according to the manufacturers' instruction sheet.

Procedure

The required amount of pure chromium salt to give a 0.00092 M solution with respect to chromium was weighed directly into the beaker and dissolved in 100 ml CO_2 -free water or 100 ml. of a 0.00092 M solution in CO_2 -free water was pipetted out using NPL pipettes. The electrodes were immersed in this solution, the beaker covered and the titration carried out as rapidly as possible after the pH meter had been allowed to warm up.

A preliminary blank was performed on a neutral salt by the titration of 0.00092 M KNO_3 at 20°C . (Fig. 12). All titrations on chromium salts were corrected according to this blank at the appropriate temperature.

B. ANALYTICAL METHODS

1. Nitrogen.

According to Keller and Edwards (66) the usual Kjeldahl method for the determination of nitrogen requires modification if the sample contains large amounts of cobalt or other strong complex-forming metal ions. In the method recommended by these workers, digestion is carried out with sulphuric acid in the presence of potassium sulphate and copper sulphate in the ordinary way, but in the subsequent distillation, a solution saturated with both sodium sulphide and sodium hydroxide is used in order to prevent any complex formation between the metal ions present and the liberated ammonia.

In the present work, attempts to standardise this method against known mixtures of ethylenediamine, purified by fractional distillation, and chrome alum (A.R.) led to completely unreliable results. When 40% sodium hydroxide saturated with sodium sulphide was used the distillate became cloudy, due to colloidal sulphur. As it was impossible to titrate this distillate directly, it was redistilled using 40% sodium hydroxide alone as no metal ions were now present. The second distillate contained no ammonia at all.

When a solution of sodium hydroxide not completely saturated with sodium sulphide was used, the distillate was fairly clear, but the methylene blue of the

mixed indicator (methyl red - methylene blue) was de-colourised by the sulphide evolved in the distillation. This made the titration with acid to a clear end-point very difficult. Redistillation of this distillate with sodium hydroxide alone gave a second distillate which on titration with acid resulted in good end-points but bad precision.

On distilling acid-digested samples with sodium hydroxide only, the distillate was clear, resulting in good end-points but poor precision on titration.

In all the above methods the precision and accuracy were poor as the results were around 50% low.

After using various catalysts in place of copper sulphate (e.g. Hg) and varying the digestion time it was found that the best results were obtained with a digestion mixture of :

100 mls of a solution containing 3 l. water

1 l. conc. H_2SO_4

240 gms. sodium sulphate

24 gms. copper sulphate

+ 10 mls phosphoric acid (A.R.) for 1 hours digestion.

The method was standardised by using the above digestion mixture on 20 mls of ethylenediamine (.3847% w/v), estimated by titration following Jonassen and Dexter (114), and 10 mls of a 3% w/v chrome alum (A.R.) solution. The results are given in Table I below.

TABLE I.

% N by Titration	% N by Kjeldahl
.4125	.3999
	.3871
	.3954
	.3969
	.3962
	.3958
	Mean : .3952

Standard error of the mean (estimated from the range) = ± 0.002 .

2. Chromium.

The method employed was similar to that of Smith and Sullivan (67) as modified by Davies and Innes (68) whereby perchloric acid is used to oxidise the chromium and all organic matter present in chrome-tanned leather.

By systematic standardisation, Friend (34) has shown that the method gives results consistently 1% low in chromium.

The method was as follows :

About 0.2 gms of the chromium compound was accurately weighed into a 300 ml. Kjeldahl flask and about 5 ml. water + 5 ml. oxidising mixture added. This consisted of 60%

perchloric acid and 80% sulphuric acid in the volume ratio of 2 : 1. For compounds containing reactive organic groups, 10 ml. of strong nitric acid was also added.

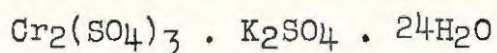
The mixture was heated, gently at first and then more strongly, until the solution turned from green to yellow. The heating was continued for a further two minutes to complete the oxidation. The flask was then removed from the flame, tilted and a thistle funnel placed in the neck. From a wash bottle 10 ml of distilled water was carefully added in one lot. A further 40 ml. of water was added and the mixture boiled for ten minutes to expel the chlorine. After cooling, the contents of the flask were titrated against standard N/20 ferrous ammonium sulphate using n-phenylanthranilic acid as indicator.

An alternative oxidant is ammonium persulphate (69).

The perchloric acid method was standardised on potassium chrome alum (A.R.) in the presence of ethylenediamine. From the table below it will be seen that the mean result is 1% low.

TABLE II

Potassium chromium sulphate



Theoretical % Cr	% Cr Found
10.41	10.28
	10.28
	10.30
	10.34
Mean :	10.30

3. Ethylenediamine and Propylenediamine

These amines were purified by dehydration and distillation according to the method of Rollinson and Bailar (146). The boiling points were :

Ethylenediamine 114 - 115°C at 71.6 cms and 18°C.

Propylenediamine 117 - 119°C at 71.6 cms and 18°C.

Dilute solutions of these anhydrous amines were estimated by titration with hydrochloric acid using bromophenol blue indicator (114).

CHAPTER III.

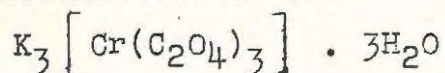
PREPARATION AND PROPERTIES OF SOME

CHROMIUM (III) COMPLEXES

In the light of the success of the new technique of filter paper electrophoresis in separating dioxalatodiaquochromiate and trioxalatochromiate, and in detecting the formation of new complexes (as found in the previous chapter), the methods of preparation of several chromium complexes were re-investigated. The outcome of these researches showed that the products of some of the preparative methods, which had previously been assumed to be pure, were in some cases contaminated, and in another the method produced a complex completely different to that anticipated.

Apart from the academic interest, these complexes were prepared as standards for the spectrophotometric and potentiometric investigation of the reactions of dioxalatodiaquochromiate and trioxalatochromiate with amino-bases and their derivatives. This section of the work is discussed in succeeding chapters.

(A) Potassium Trioxalatochromiate



Preparation.

The usual method of preparation of this salt is



FIG. 13.

POTASSIUM TRIOXALATOCHROMIATE.

(magnification 75)

that due to Croft (31, 131). The procedure employed was as follows :

To a solution of 19 gms of potassium dichromate dissolved in about 50 ml. of water were added 23 gms of potassium oxalate and 55 gms of oxalic acid in 100 ml. water. Effervescence occurred, and when this subsided the solution was boiled down to a small volume and allowed to crystallise.

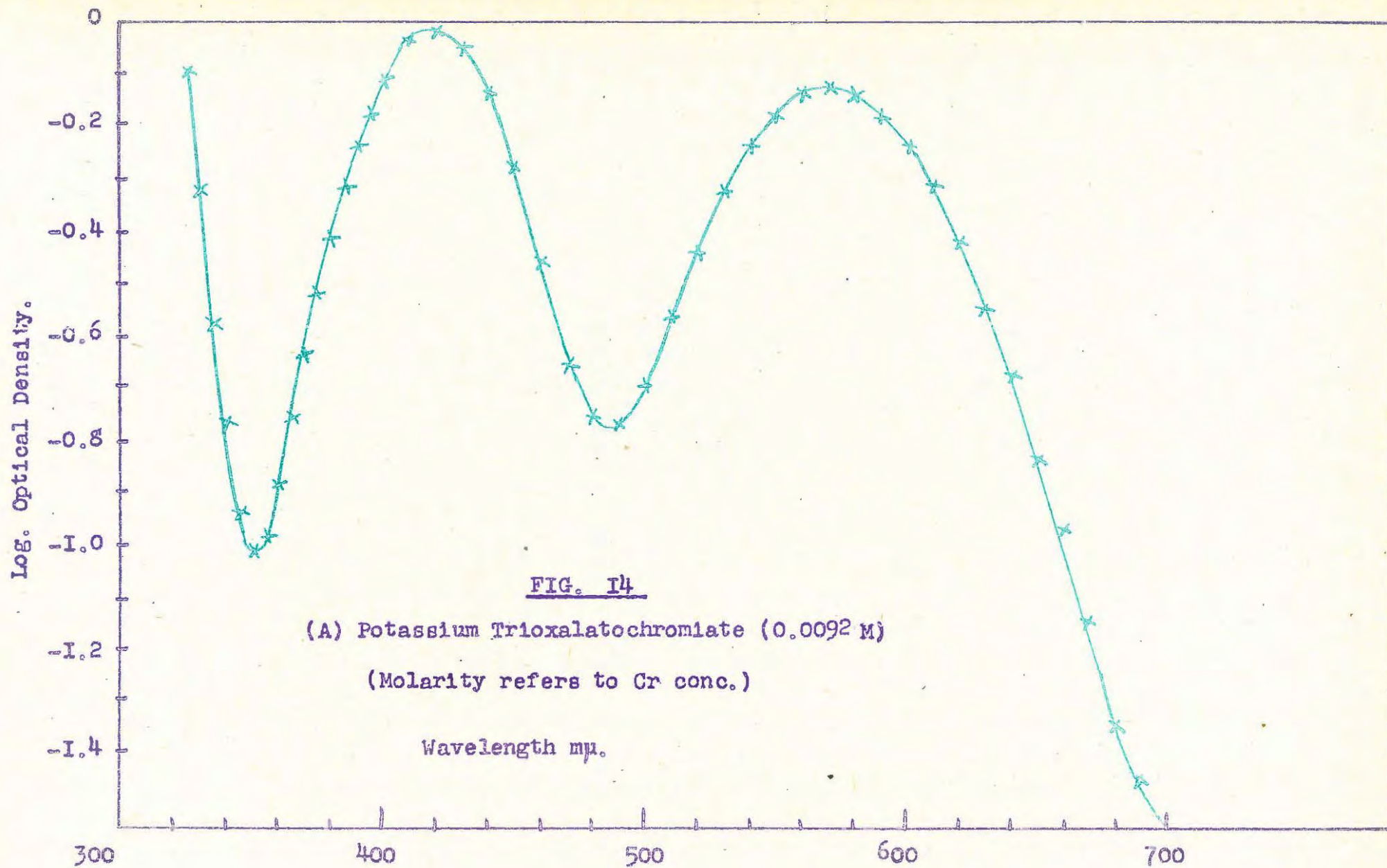
The blue-green crystalline mass was filtered off, recrystallised from hot water and dried over fused calcium chloride.

Properties

Potassium trioxalatochromate exists in two optically active forms. Racemisation studies on the salt by Werner (135), Long (45), Bushra and Johnson (33) and Schweitzer and Rose (137) lead to the conclusion that the mechanism of racemisation does not involve an ionisation step, but some sort of intramolecular rearrangement. Werner's explanation (135) that the racemisation might involve the breaking of only one of the bonds with one of the oxalate ions seems the most likely. Accordingly when prepared as above a racemic mixture is obtained.

The product obtained consisted of blue-green needle-like crystals, a photomicrograph of which is given in Fig. 13.

The purity was checked by filter-paper electro-

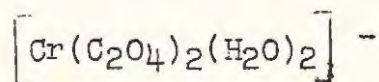


phoresis and spectrophotometry. The spectrophotometric curve (Fig. 14) of the present preparation of potassium trioxalatochromiate shows maxima at 420 and 570 mμ in good agreement with the values of Burley (29), Friend (34), Theis (133) and Meade (134).

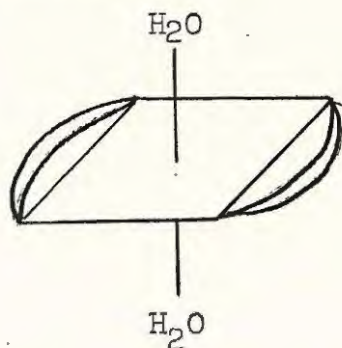
That the salt is neutral has been confirmed by Burley's titration curve (29).

(B) The Potassium dioxalatodiaquochromiates

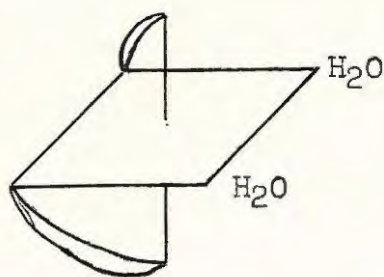
Compounds containing two oxalate molecules per chromium atom were first prepared in 1842 (138) but there was some doubt as to their constitution. In terms of the Co-ordination Theory, Werner (139) and others (140) clarified the position and postulated the formula



Werner et al (30) prepared the two isomeric forms of the dioxalatodiaquochromic ion and suggested the formula



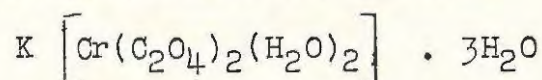
trans-



cis-

Preparations

Potassium trans-dioxalatodiaquochromiate

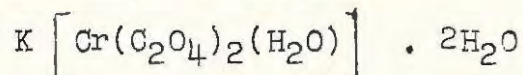


The following method of preparation is due to Werner (30).

450 gms of oxalic acid hydrate is added to about 2000 ml. of water and heated to boiling. Then 150 gms of powdered potassium dichromate are added continuously in small portions. Violent effervescence occurs, and when this has subsided, the solution is boiled gently for half an hour and then set aside to crystallise at room temperature. After several days, a small reddish crystalline deposit settles at the bottom of the beaker and small particles were observed floating on the surface of the liquid. The solid is filtered off each day and washed with small quantities of water.

The separate portions of solid were combined and the salt purified by dissolving in water containing about 1% nitric acid (29), boiling for half an hour, and allowing to crystallise as before. A second recrystallisation was carried out from boiling 1 : 1 alcohol-water resulting in a product found to be pure by filter paper electrophoresis and spectrophotometry (See below).

Potassium cis-dioxalatodiaquochromiate



Werner (30) gives two methods of preparation of

this salt :

- (a) from reacting potassium dichromate and oxalic acid.
- (b) from the trans-salt by allowing a concentrated solution to cool slowly.

Friend (34) found it necessary to modify the latter method as on slow cooling both the cis- and trans-isomers were formed. He reports better yields of the cis-salt on rapid cooling in dry ice and acetone. As will be shown later this modified method was found not to give a satisfactory product.

The first method, which is described below, gave a product shown to be pure by filter-paper electrophoresis and spectrophotometry.

450 gms of crystalline oxalic acid and 150 gms potassium dichromate were pulverised and well mixed. The whole mass was moistened evenly with a very small amount of water and left. After about 15 minutes a very vigorous reaction occurred resulting in a dark syrup which solidified on cooling. This mass was stirred up with water and suction filtered. The residue was stirred up with two lots of alcohol then sucked dry in a buchner funnel. The resultant solid was dried over concentrated sulphuric acid and the purity checked by electrogram.

Properties of the Dioxalatodiaquochromiates

van Niekerk and Schoening (141) from X-ray diffraction data have worked out the structure of the trans-

salt. This salt exists as pinkish crystals which are stable at room temperature. It does not readily dissolve in cold water but is very soluble in boiling water owing to its conversion to the highly soluble cis-isomer. On long standing this solution deposits crystals of the trans-salt.

The blue-pink cis-salt is very soluble in cold water, consequently it is difficult to recrystallise. It may be obtained in a somewhat impure form by rapid cooling of a hot concentrated solution of the trans-salt.

Purification of the Dioxalatodiaquochromiates

On dissolving in cold water samples of both Burley's and Friend's preparations of Potassium trans-dioxalatodiaquochromiate (twice recrystallised from 1% nitric acid in accordance with the finding of Burley (29) that nitric acid destroys trioxalatochromiate) and then ageing overnight to the cis-salt, it was found (electrochromatogram 11) that both contained an impurity, probably trioxalatochromiate.

Electrochromatogram 12 which refers to the first, second and third crops of the first recrystallisation from this solution indicates that the impurity is still present in all samples. These three crops were then combined and recrystallised once more from 1% nitric acid. The three successive crops from this recrystallisation were also found to be contaminated (electrochromatogram 13). It appears most probable that the impurity is trioxalatochromiate.

It is evident therefore that Burley's claim that digestion in 1% nitric acid destroys all the trioxalatochromate ion is not substantiated despite his evidence that the optical density falls to the correct value (29). Consequently it was decided to investigate the effect of heating dioxalatodiaquochromate solutions as it seemed likely that the impurities arose from this source. Moreover an investigation into the method of preparation of the pure cis-salt (see below) suggested that recrystallisation from a 1: 1 alcohol-water mixture might lead to a purer product in the purification of the trans-isomer.

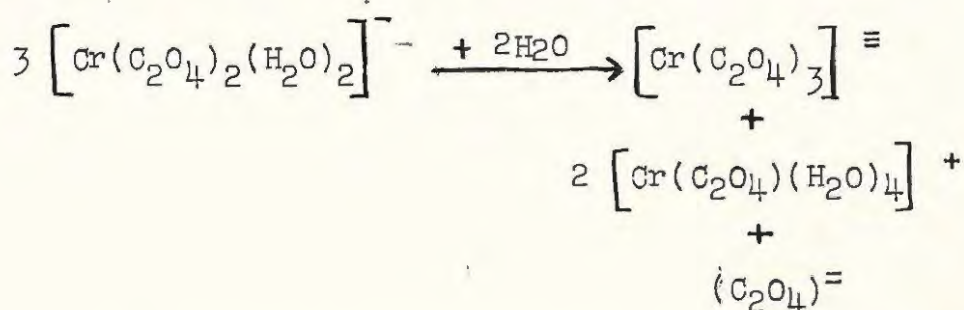
Accordingly some potassium trans-dioxalatodiaquochromate was recrystallised by this method, resulting in very good crystals. Approximately 10% solutions of these crystals were prepared in the cold and treated as follows :

(1) Boiled for about 10 minutes and then allowed to stand overnight.

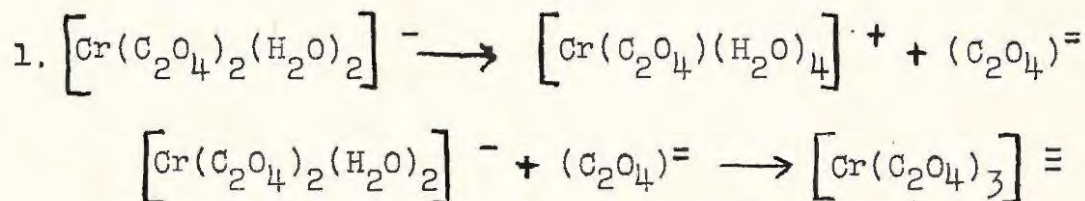
(2) Allowed to stand overnight without previous boiling.

The results obtained (electrochromatogram 15) were very interesting in that the unheated solution showed no impurities whereas the heated solution gave a spot corresponding to dioxalatodiaquochromate (spot b); one corresponding to trioxalatochromate (spot c); and a vague spot, the result of a cationic complex (spot a). These results can be explained as due to the occurrence of

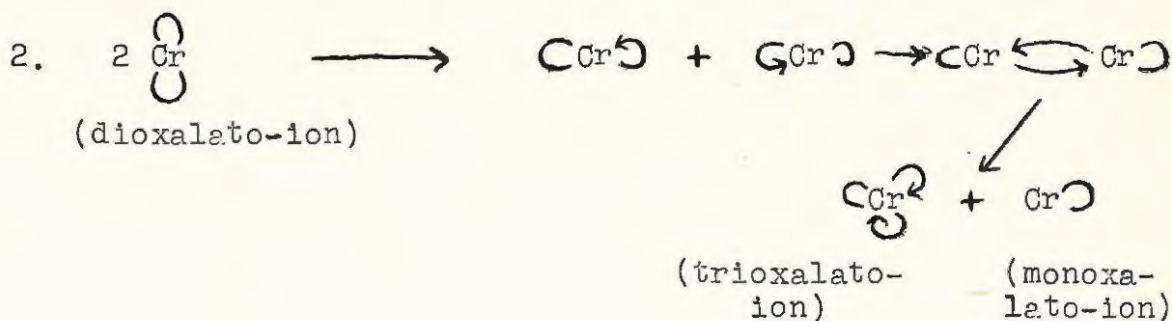
disproportionation on heating :



Two possible mechanisms for this disproportionation reaction suggested are :

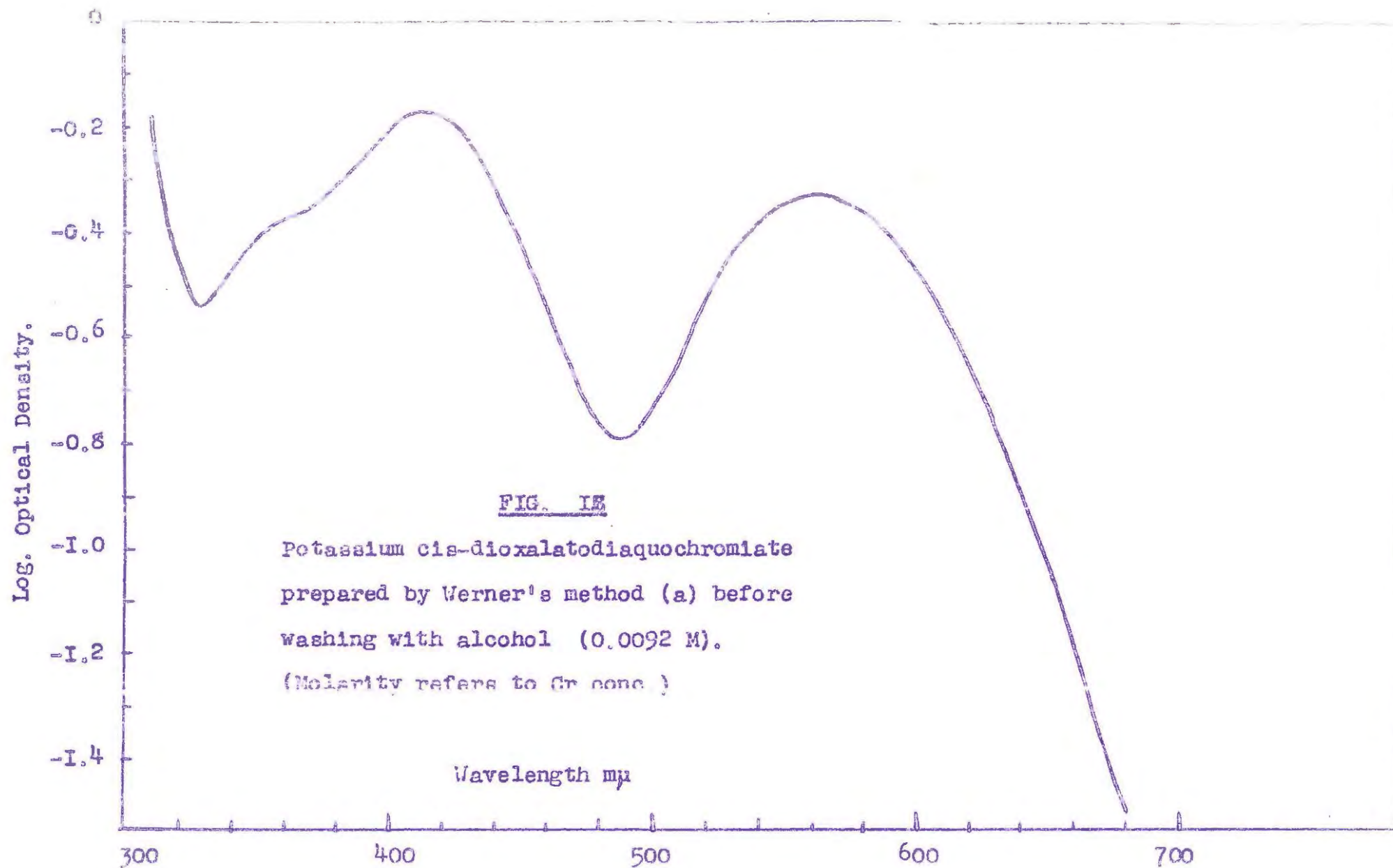


Here the products are mixed as the potassium and monoxalato-tetraaquochromiate ions are the cations of the trioxalatochromiate ion.



Here the rings represent the oxalate groups (bidentate chelating) and the other co-ordinating groups (e.g. H_2O) are excluded.

On Burley's findings of the mechanism of oxalate reactions (29) and on the evidence from the racemisation studies of the trioxalatochromiate presented above, it



seems likely that the reaction follows the course outlined in 2.

Werner (30) gives two methods for the direct preparation of cis-dioxalatodiaquochromiate. Electrochromatograms were run on products prepared by each of these methods by Friend (34) to determine whether they also contained trioxalatochromiate. Thus electrochromatogram 14 reveals that :

(1) Potassium cis-dioxalatodiaquochromiate, prepared by Werner's method (a), washed with alcohol and dissolved in cold water and used immediately, contains no visible impurity.

(2) Potassium cis-dioxalatodiaquochromiate; prepared by Werner's method (a) dissolved in cold water (without previously washing with alcohol) and used immediately, shows the absence of trioxalatochromiate but the presence of dichromate (yellow spot moving ahead of dioxalatodiaquochromiate spot).

(3) The solution of Potassium cis-dioxalatodiaquochromiate; prepared by Werner's method (b) dissolved in cold water and used immediately shows the absence of trioxalatochromiate.

The presence of dichromate as an impurity was also suspected by Friend (34) while carrying out spectrophotometric studies of the above salts. His curve (Fig. 15) for the cis-dioxalatodiaquochromiate does not agree with the curve for the cis-salt prepared by aging the

Log. Optical Density.

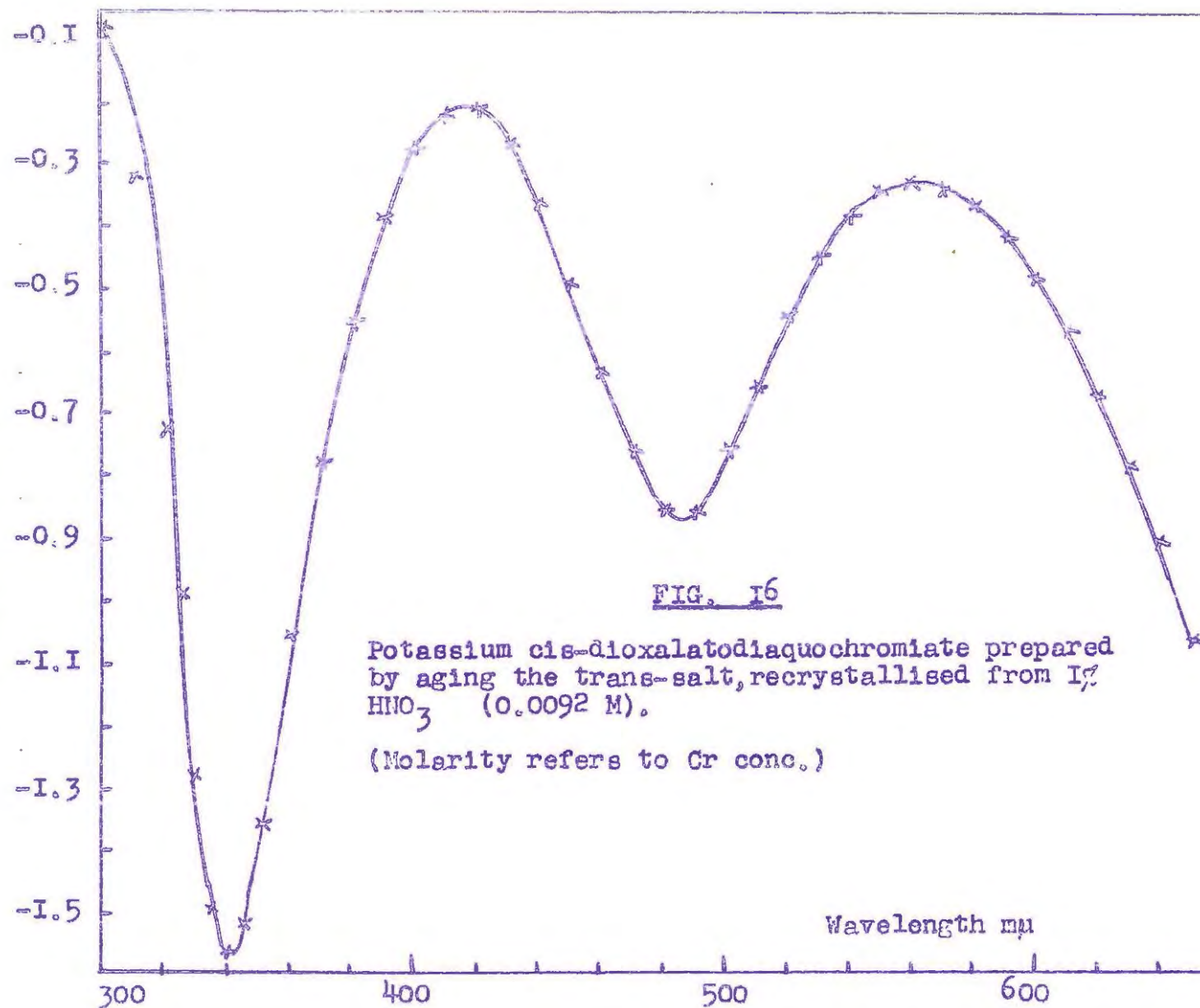


FIG. 16

Potassium cis-dioxalatodiaquochromate prepared
by aging the trans-salt, recrystallised from HNO_3 (0.0092 M).

(Molarity refers to Cr conc.)

Wavelength mμ

trans-salt (Fig. 16). The main difference is around 340 mu, in which region dichromate has a peak in the absorption curve. Thus the higher value of the minimum at 340 mu in Fig. 15 over that in Fig. 16 may be attributed to the superimposition of the dichromate peak on that of the cis-dioxalatodiaquochromiate in the former.

In confirmation of the findings of a disproportionation reaction electrochromatogram 16 was obtained on the following solutions :

(1) A sample of Friend's cis-salt washed with alcohol was dissolved in water, boiled for about 10 minutes and then allowed to stand for 4 days.

(2) A similar solution prepared from a sample of the trans-salt made by Burley and twice recrystallised from 1% nitric acid.

(3) A solution identical with that described under (2) except that the boiling was omitted.

Now (1) and (2) show the presence of trioxalatochromiate (spots c and f) and spots possibly corresponding to mono-oxalatotetraaquochromiate (spots a and d) while (3) only shows the presence of trioxalatochromiate (spot h). This indicates that (1), (2) and (3) originally contained trioxalatochromiate, but (1) and (2) also produce it presumably by disproportionation. This follows from the development of the spots a and d, representing a cationic component not present in the unheated solution. Here is further evidence that Burley's nitric acid re-

crystallisation of the trans-dioxalatodiaquochromiate yields an impure product. It must be admitted, however, that the amount of impurity is probably small.

According to electrochromatogram 14, the alcohol-washed cis-dioxalatodiaquochromiate as prepared by Friend (34), when used in cold water shows the absence of trioxalatochromiate; whereas the same salt when used in boiling water (electrochromatogram 16) shows the presence of trioxalatochromiate. This is positive evidence for the disproportionation reaction.

Although the evidence above points to the impurity in the product obtained by recrystallisation of trans-dioxalatochromiate from 1% nitric acid, and by heating a solution of pure cis-dioxalatodiaquochromiate, as being trioxalatochromiate; the possibility of the "olated" complex must not be overlooked.

Hence an experiment was designed in order to ascertain whether "olation" could possibly account for the results. As "olation" cannot occur in acid medium, the spectrophotometric curve for a solution of the cis-salt heated in 1% nitric acid was compared with that for the cis-salt heated under the same conditions in water.

Burley has shown that the spectrophotometric curve for the "olated" complex differs from that of cis-dioxalatodiaquochromiate. Accordingly the spectrophotometric curves of the following solutions were obtained :

- (1) 0.0092 M Potassium cis-dioxalatodiaquochromiate

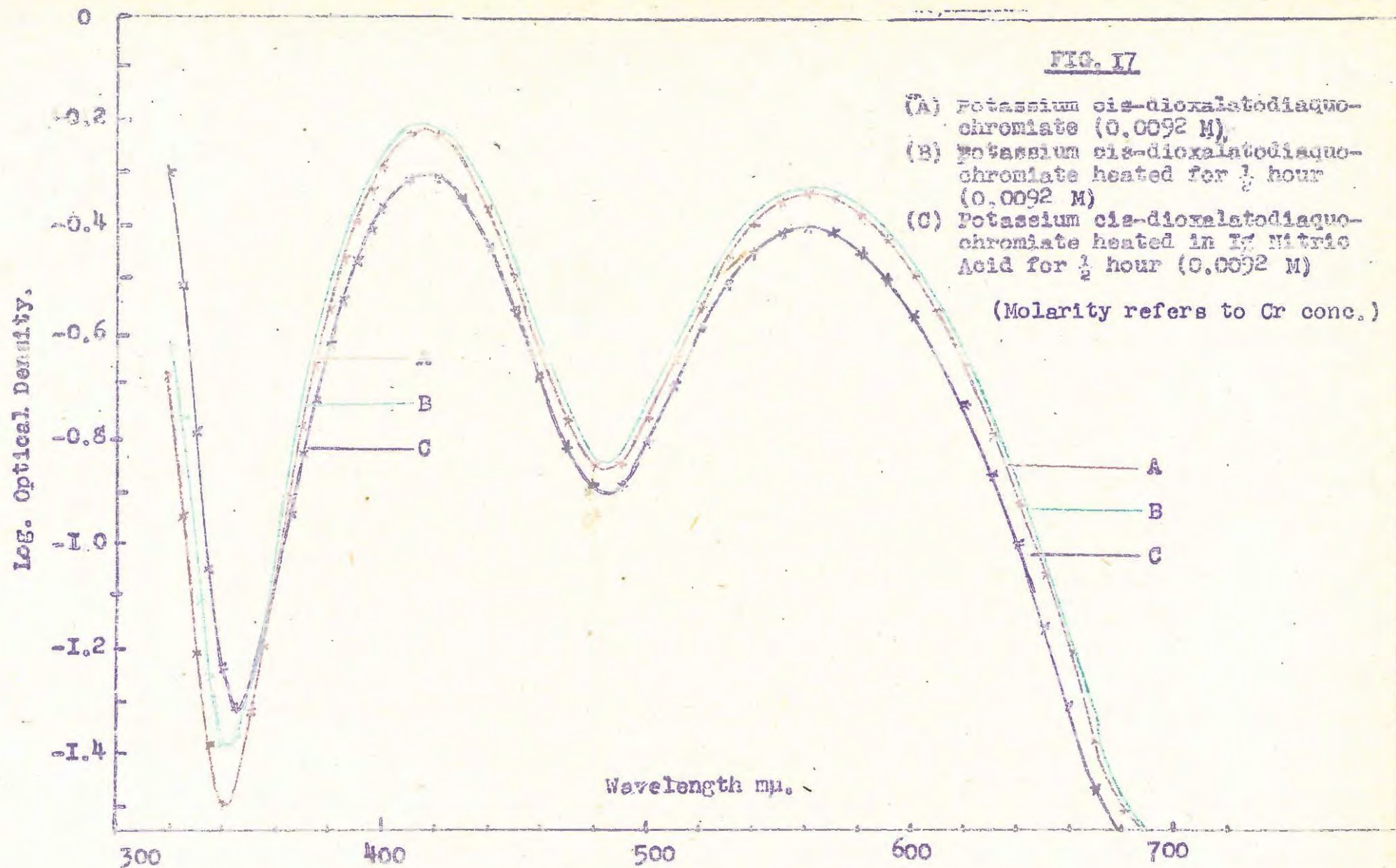
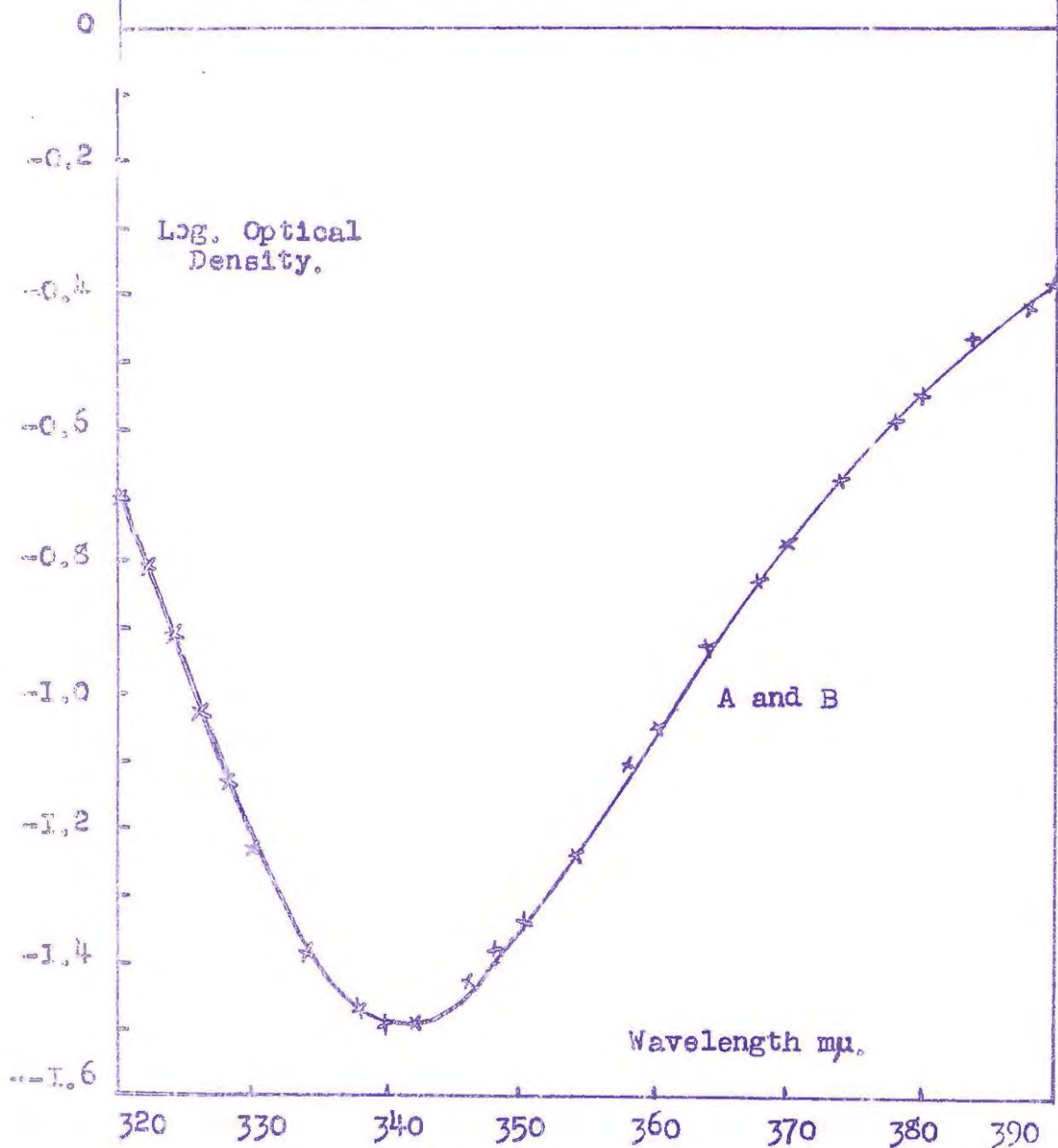


FIG. 18

(A) Potassium cis-dioxalatodiaquochromiate prepared from the trans-salt, once recrystallised from 1% HNO_3 and once recrystallised from 1:1 alcohol-water. (0.0092 M).

(B) Potassium cis-dioxalatodiaquochromiate made from the cis-salt, prepared by Werner's method (a) then washed with alcohol. (0.0092 M).

(Molarity refers to Cr conc.)



prepared from Friend's cis-salt washed with alcohol and dried over concentrated sulphuric acid.

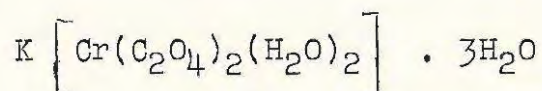
(2) 50 ml of the above solution boiled for 30 minutes, cooled and made up to volume (0.0092 M).

(3) 50 ml of the solution from (1) to which concentrated nitric acid (solution then contained 1% nitric acid) was added, was boiled for 30 minutes, cooled and made up to volume (0.0092 M).

The evidence from these curves (Fig. 17) proves the impurity to be the result of disproportionation rather than olation. Since the degree of olation is increased by boiling it would be expected that if the results obtained had been due to this cause, the optical density of the boiled solutions would in both cases be generally greater than that of the unboiled solution. Moreover the solution boiled in the absence of nitric acid should show evidence of a greater degree of olation than that to which nitric acid had been added. Actually since Fig. 17 shows only a slight difference over the whole range between solutions (1) and (2) while solution (3) - containing nitric acid - has a lower optical density than the control it is evident that "olation" is not the operating factor.

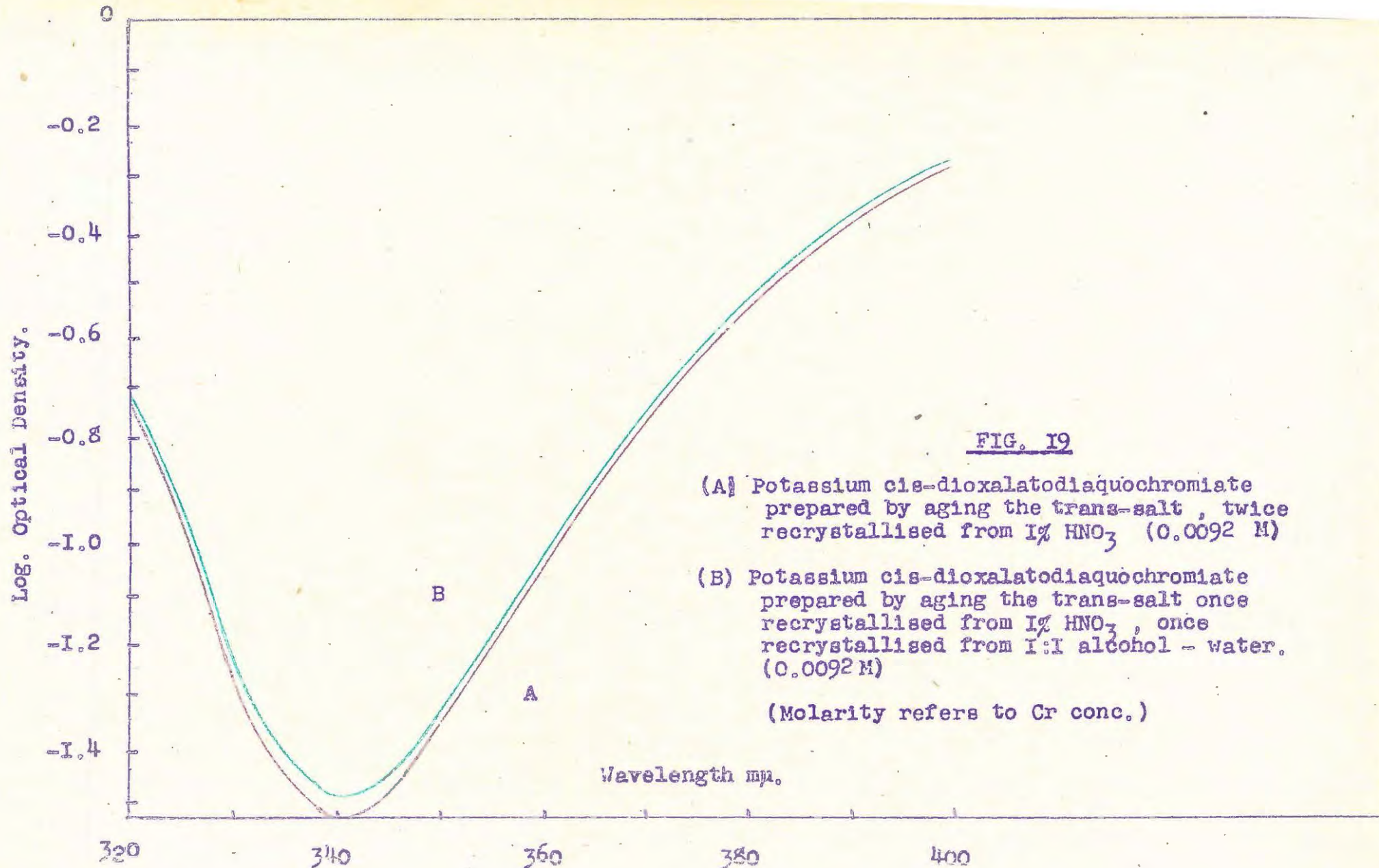
Electrochromatogram 14 reveals that Friend's preparation of cis-dioxalatodiaquochromiate by Werner's method (a) with subsequent washing with alcohol, yields a pure product as shown by electrochromatogram. In Fig. 18 are given the spectrophotometric curves of a solution of

this salt and a solution of cis-dioxalatodiaquochromiate prepared by aging the trans-salt recrystallised once from 1% nitric acid and once from 1 : 1 alcohol-water. These curves agree within experimental error, confirming that the trans-salt recrystallised from alcohol is pure. The possibility that recrystallisation from alcohol may lead to alcohol of crystallisation may be excluded on the following grounds. In preparing the 0.0092 M solution of the alcohol-recrystallised trans-dioxalatodiaquochromiate for Fig. 13 the following formula was used :



The spectrophotometric curve of this aged solution was then found to coincide with that for the cis-salt solution prepared from Friend's cis-salt (pure by electrochromatogram); this could only occur if the chromium concentrations were the same, whence the formula assumed above must be correct and it may be concluded that no alcohol of recrystallisation can be present.

Comparison of Burley's, Friend's and the present author's optical density figures for cis-dioxalatodiaquochromiate prepared by aging the trans-salt, as recrystallised by Burley's method, shows that Burley's figures are much higher around the minimum at 340 mμ. This is probably due to the trioxalatochromiate impurity now known to be present. On the other hand the low values obtained for the trans-salt aged to the cis-isomer as

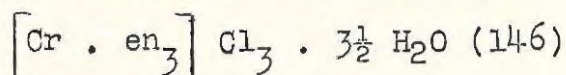


found in preparations (2) and (3) (see table below) relative to the pure cis-salt (preparations 4 and 5) are probably due to unchanged trans-salt which, according to Friend, has a low optical density (0.025) at 340 mμ (Fig.19).

Preparation	Method of re-crystallisation	330 mμ	340 mμ	Electrochromatographic evidence.
(1) trans-aged to cis Burley	1% nitric acid	0.089	0.047	trioxalato-chromiate impurity
(2) trans-aged to cis Friend	1% nitric acid	0.053	0.027	trioxalato-chromiate impurity
(3) trans-aged to cis Cooper	1% nitric acid	0.052	0.029	trioxalato-chromiate impurity
(4) cis-by Werner's method (a) Friend	alcohol-water	0.059	0.031	pure
(5) cis-by Werner's method (a) Cooper	alcohol-water	0.062 0.057	0.034 0.032	pure
(6) trans-aged to cis Cooper	alcohol-water	0.058	0.032	pure
(7) cis-by Werner's method (b) Friend	alcohol-water	0.102	0.091	pure
(8) trans-salt Friend	1% nitric acid	0.040	0.025	-

It is noteworthy that Friend's preparation of the cis-salt, by Werner's second method, although it has been shown to contain no impurities which are visible on electrochromatogram 14, yields a product with high optical density around 340 mu (preparation 7). Although the conditions of the preparation are favourable for the formation of the isolated complex as a side reaction, and this would account for the anomalously high optical densities, the presence of isolated complexes does not appear to be confirmed by the electrochromatographic evidence.

(C) Trisethylenediaminochromic Chloride



Preparation

Several methods are available for the preparation of this salt. Rollinson and Bailar (40) give several methods of preparation involving the use of anhydrous ethylenediamine, anhydrous chrome alum etc. Pfeiffer (142, 144) and Pfeiffer and Haimann (143) have described methods using aqueous ethylenediamine and trichloropyridine chromium. Balthis and Bailar (145) reacted ethylenediamine and its homologues with chromous chloride or chromous acetate.

The method found to be most convenient was that of Rollinson and Bailar (146) as described below.

Anhydrous $\text{Cr}_2(\text{SO}_4)_3$ is prepared by heating the hydrate for 2 - 3 days in an oven at 100 - 110°C, grinding,

and reheating.

875 mls of 70% ethylenediamine and 500 g NaOH are digested on a steam bath overnight. The upper layer is decanted and redigested with 150 g NaOH, decanted again and distilled (116° - 117° at 760 mm).

49 gms $\text{Cr}_2(\text{SO}_4)_3$ and 50 ml ethylenediamine are heated with occasional shaking on a steam bath in a 300 ml flask fitted with an air condenser until a brown mass with no liquid is formed, and then left on a steam bath overnight. The orange yellow mass of $[\text{Cr en}_3]_2(\text{SO}_4)_3$ (I) is powdered, washed with alcohol and dried in air (yield 95%).

32 gms of (I) is dissolved in a mixture of 30 ml water and 5 ml concentrated hydrochloric acid at $60 - 65^{\circ}$. The solution is filtered rapidly, treated with 27 mls concentrated hydrochloric acid and 42 mls alcohol and cooled. Yield of yellow $[\text{Cr en}_3] \text{Cl}_3 \cdot 3\frac{1}{2} \text{H}_2\text{O}$ is 60%.

To purify dissolve 20 gms in 20 ml water at 65° and cool (yield 60%).

The bromide, iodide and thiocyanate can also be prepared in this way.

The analytical figures for the trisethylene-diaminochromic chloride, prepared as described above, are given below.

From these data it would appear most probable that the salt obtained contains only one molecule of water of crystallisation and not $3\frac{1}{2}$ as found by Rollinson and Bailar (145). Also since the ratio of N/Cr is also some-



FIG. 20.

TRISETHYLENEDIAMINOCHROMIC

CHLORIDE

(magnification 75).

what low it is possible that the analytical figure for the nitrogen content is low.

Compound	% Cr	% N	N/Cr
$[\text{Cr en}_3] \text{Cl}_3 \cdot 3\frac{1}{2} \text{H}_2\text{O}$	12.97	20.94	1.61
$[\text{Cr en}_3] \text{Cl}_3 \cdot 2 \text{H}_2\text{O}$	13.88	22.44	1.62
$[\text{Cr en}_3] \text{Cl}_3 \cdot \text{H}_2\text{O}$	14.58	23.57	1.62
Found	14.79	22.88	1.55

Properties

A photomicrograph of the orange-yellow crystals is given in Fig. 20.

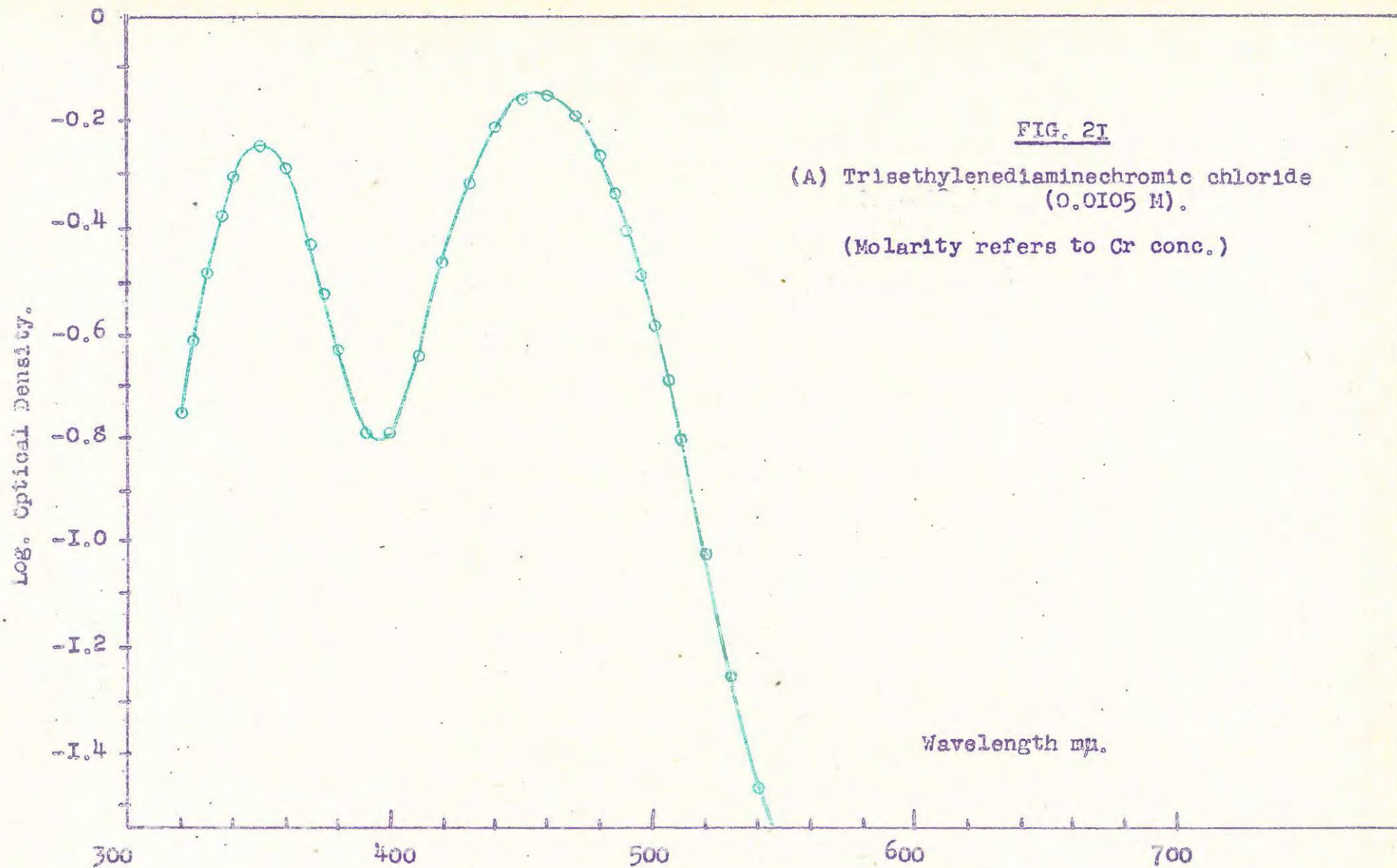
It has been observed that $[\text{Cr en}_3] \text{Cl}_3 \cdot 3\frac{1}{2} \text{H}_2\text{O}$ and $[\text{Cr en}_3] (\text{SCN})_3 \cdot \text{H}_2\text{O}$ lose one-third of their ethylenediamine (and all their water of crystallisation) when heated for several days, the former at 160°C , and the latter at 130°C . These facts have been utilised (41, 144, 147, 148, 149) in the preparation of cis- $[\text{Cr en}_2 \text{Cl}_2] \text{Cl} \cdot \text{H}_2\text{O}$ and trans- $[\text{Cr en}_2 (\text{SCN})_2] \text{SCN} \cdot \text{H}_2\text{O}$

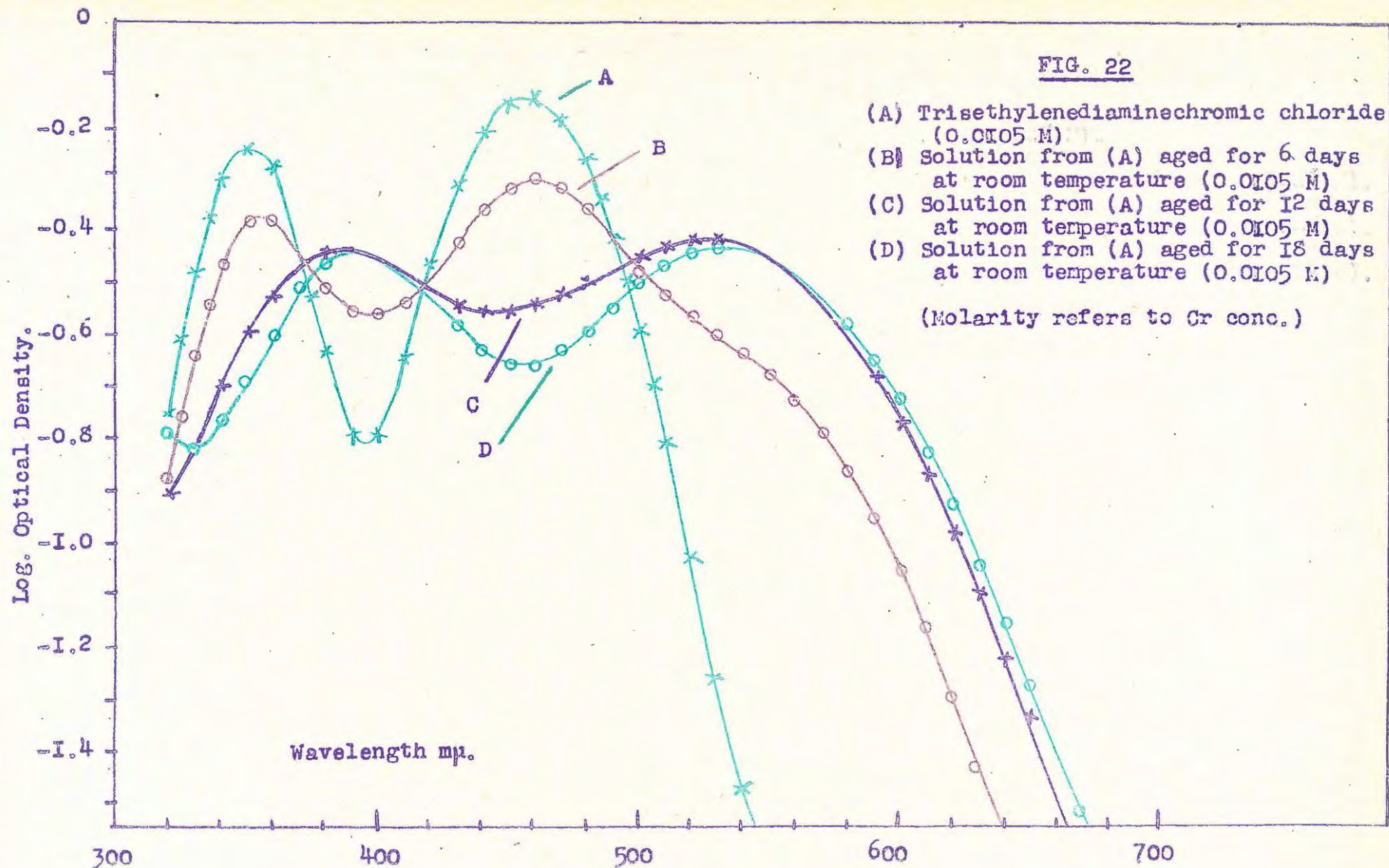
Thermal decomposition studies have also been carried out by Rollinson and Bailar (44) who note that there is a significant influence of the anion on the configuration of the product. This fact has been confirmed by O'Brien and Bailar (42) who have studied the relative thermal stabilities of a number of triethylene- and tri-

propylenediamine chromic salts and have drawn up a table of decomposition temperatures of these salts.

Linhard (150) has carried out light absorption studies on trisethylenediaminochromic salts in 0.01M to 0.001M solutions in the range 220 - 560 mu. Extinction coefficients derived from absorption spectra in aqueous solution of some co-ordination compounds of chromium have been obtained by Mead (134). In the table below their values are compared with those found in the present work. These optical densities were obtained for a 0.0092. M solution, assuming the formula of Rollinson and Bailar (146), viz. $[\text{Cr en}_3] \text{Cl}_3 \cdot 3\frac{1}{2} \text{H}_2\text{O}$. As this formula was found later not to agree with the analytical figures, the optical density values recorded in the last line of the table below are corrected for the chromium concentration, as found by analysis, taking into account that the method of analysis for chromium gives results 1% low (found experimentally).

Salt	Molar Extinction Coefficient		Wavelength		Author
	log k_1	log k_2	1	2	
$[\text{Cr en}_3]^{+++}$	1.90	1.84	457	351	Linhard (150)
$[\text{Cr en}_3] \text{Br}_3$	0.75	0.34	(467)	(347)	Lifschitz and Rosenbohm (152)
$[\text{Cr en}_3] \text{Cl}_3$	1.78	1.75	455	351	Kuroya and Tsuchida (151)
$[\text{Cr en}_3] \text{Cl}_3$	1.84	1.72	457.5	350	Mead (134)
$[\text{Cr en}_3] \text{Cl}_3$	1.83	1.73	456	350	Cooper





It is evident from the good agreement between the molar extinction coefficients recorded in the table above that the compound prepared must have been $[\text{Cr en}_3] \text{Cl}_3$; any divergences in the analytical figures being due to differences in the water of crystallisation.

The spectrophotometric curve for trisethylene-diaminochromic chloride is shown in Fig. 21. The curve was obtained on a 0.0105M solution as calculated from the chrome content found by analysis.

Effect of Aging.

On allowing this yellow solution to stand at room temperature for several days it was noticed that the colour changed through orange to red. It was therefore decided to obtain spectrophotometric readings on the solution after standing for 6, 12 & 18 days. These curves are given in Fig. 22.

From the relative differences in optical density of these four curves it may be deduced that a fundamental change occurs in the structure of the trisethylenediaminochromic ion on aging an aqueous solution of trisethylene-diaminochromic chloride. Where the spectrophotometric curve for the freshly prepared aqueous solution shows maxima (350 and 456 mμ) the corresponding curve for this solution aged for 18 days gives minima, and vice versa.

Confirmation of the fact that trisethylenediaminochromic chloride is unstable in solution, as indicated above, is supplied by the following electrophoretic investigation into the change in charge on the complex with aging. Electrochromatogram 35 shows that, in contrast to

FIG. 23

- (A) Freshly prepared solution of triethylenediamino-
chromic chloride. (0.00092 M)
(B) Solution of triethylenediaminochromic chloride aged
for 6 days at 20°C. (0.00092 M)
(C) Solution of triethylenediaminochromic chloride aged
for 18 days at 20°C (0.00092 M)

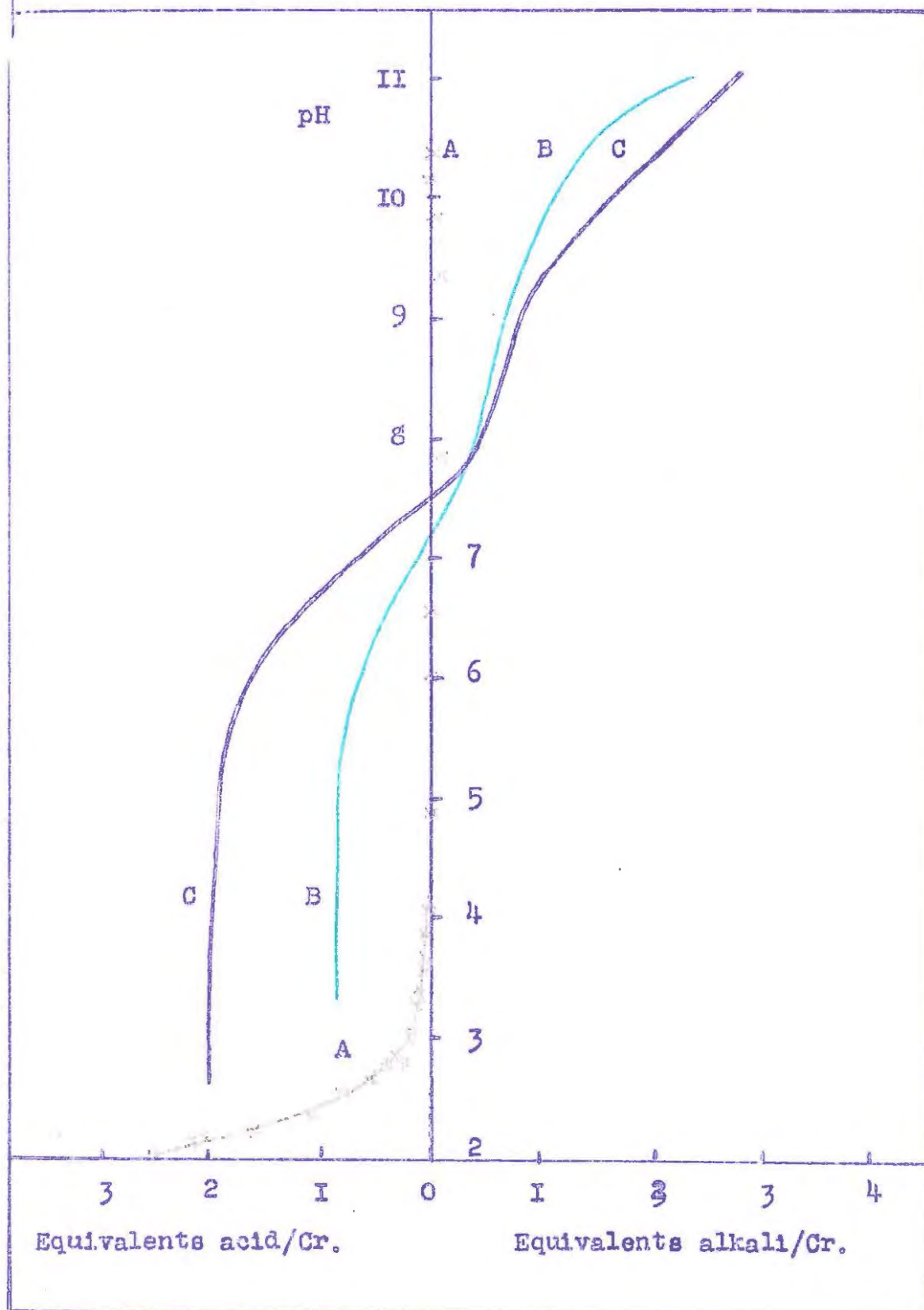
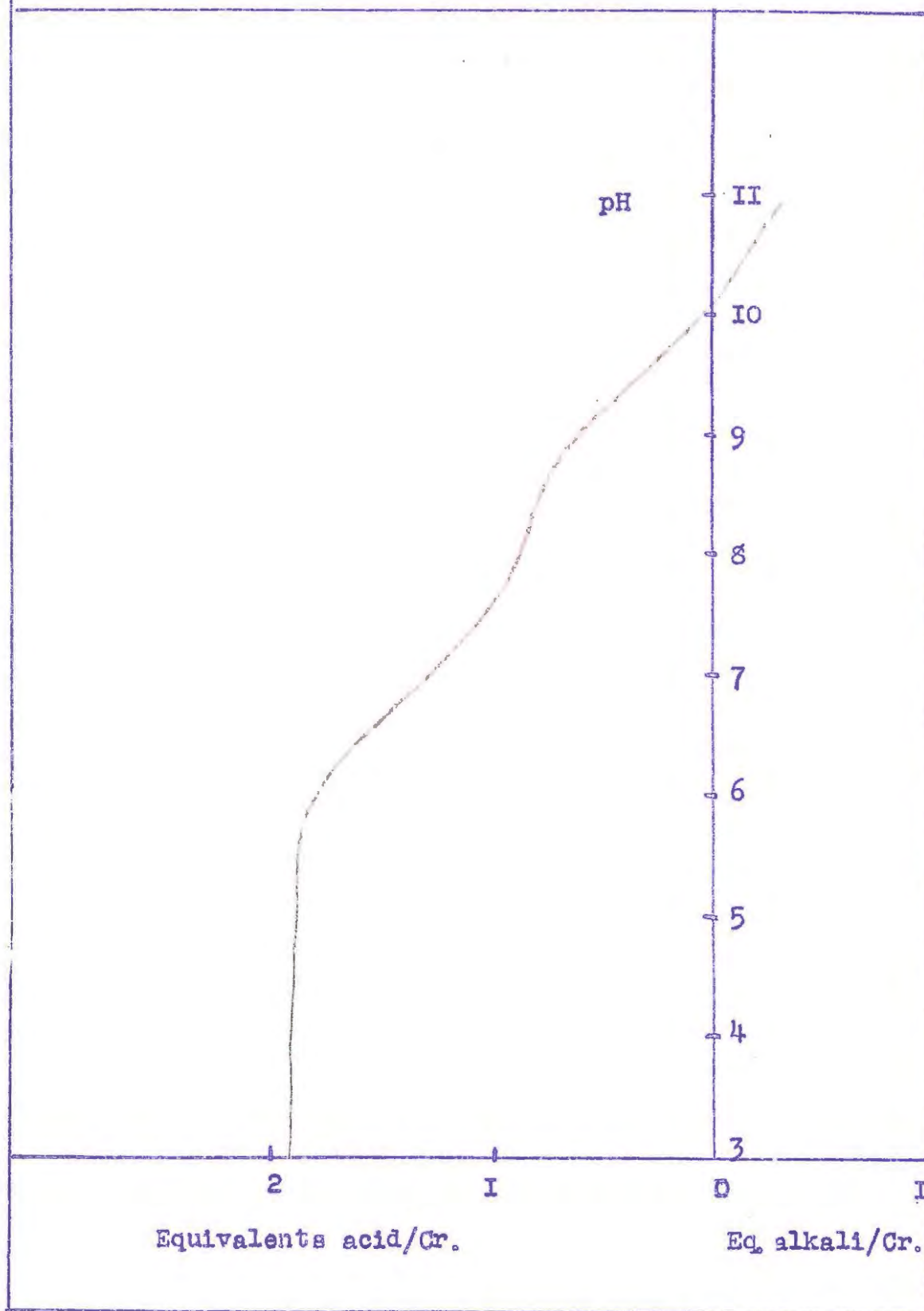


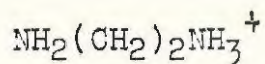
FIG. 24

Ethylenediamine purified by dehydration and
distillation (0.00092 M).



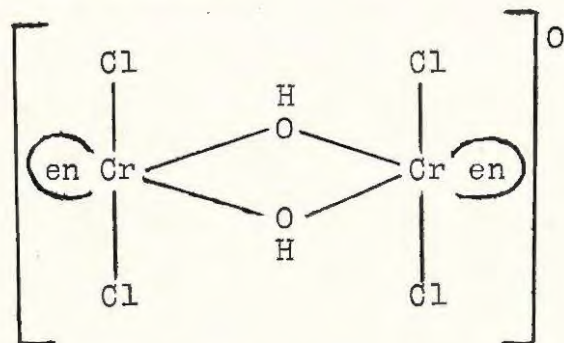
the freshly prepared solution which consists of one cationic complex, the 6 day aged solution (pH 7.44) consisted of two cationic complexes of different charge; while the solution aged for 12 days (pH 7.60) showed the presence of only one cationic complex (charge probably one positive - electrochromatogram 36). After 18 days the solution (pH 7.74) contained a neutral complex only (electrochromatogram 37). The pH of the original solution was 5.5.

The titration curves corresponding to these four solutions are shown in Fig. 23. It is obvious from the titration of freshly dissolved triethylenediaminochromic chloride that it is a neutral salt. Consideration of the titration of the 18 day old solution in the light of that of pure ethylenediamine (Fig. 24) suggests that in the former two moles of free ethylenediamine per mole of chromium are being titrated. The pH of the 18 day aged solution corresponds to half-neutralised ethylenediamine :

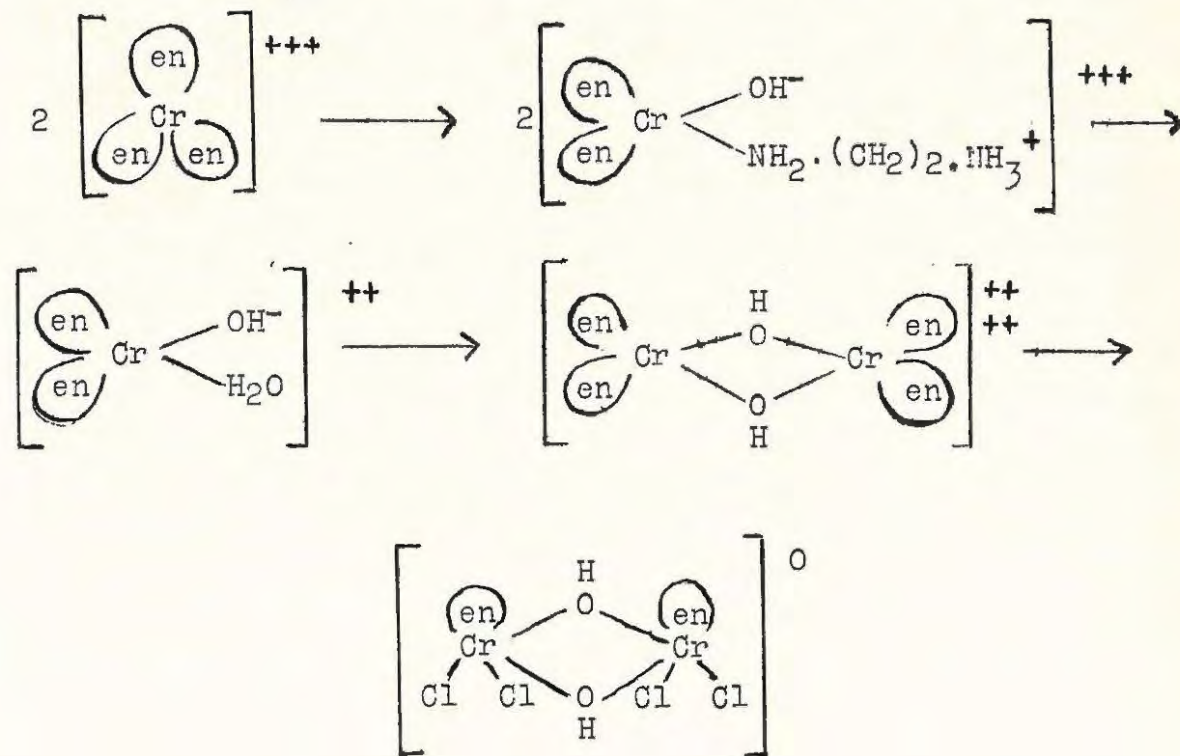


Electrochromatogram 38 on the aged solution adjusted to pH values of 4.50, 7.74 and 12 shows that the charge on the complex is zero in all cases and is thus independent of pH. This eliminates the possibility of co-ordinated water molecules (or hydroxyl ions, depending on the prevalent pH of the solution) because, if these were present, the charge on the complex would vary with pH (cf. dioxalatodiaquochromiates).

As a result of this evidence the following formula is tentatively suggested for the complex present in the solution of trisethylenediaminochromic, aged for 18 days at room temperature.



Here the rings represent bidentate chelating ethylenediamine. It is assumed that this complex does not react instantaneously with acid or alkali on titration. The stages of the reaction are probably as follows :



A binuclear compound of the type indicated can exist in

three possible geometrical isomers (cis-cis-, cis-trans- or trans-trans-).

If the above formula is correct, then one-third of the total chlorine originally present in the trisethylenediaminochromic chloride should be unco-ordinated and present in the solution as chloride ions. Attempts to estimate this free chlorine directly by gravimetric precipitation as silver chloride, resulted in all the chlorine, including that in the complex, being precipitated. The free chlorine could probably be estimated by electrometric methods using silver chloride electrodes and further experiments of this nature would be required before the formula could be established with any degree of certainty.

Comparison with corresponding sulphate.

It was of interest to compare the reaction of trisethylenediaminochromic chloride with that of the corresponding sulphate under similar conditions, and an attempt to prepare an analogous compound from the sulphate salt is described below.

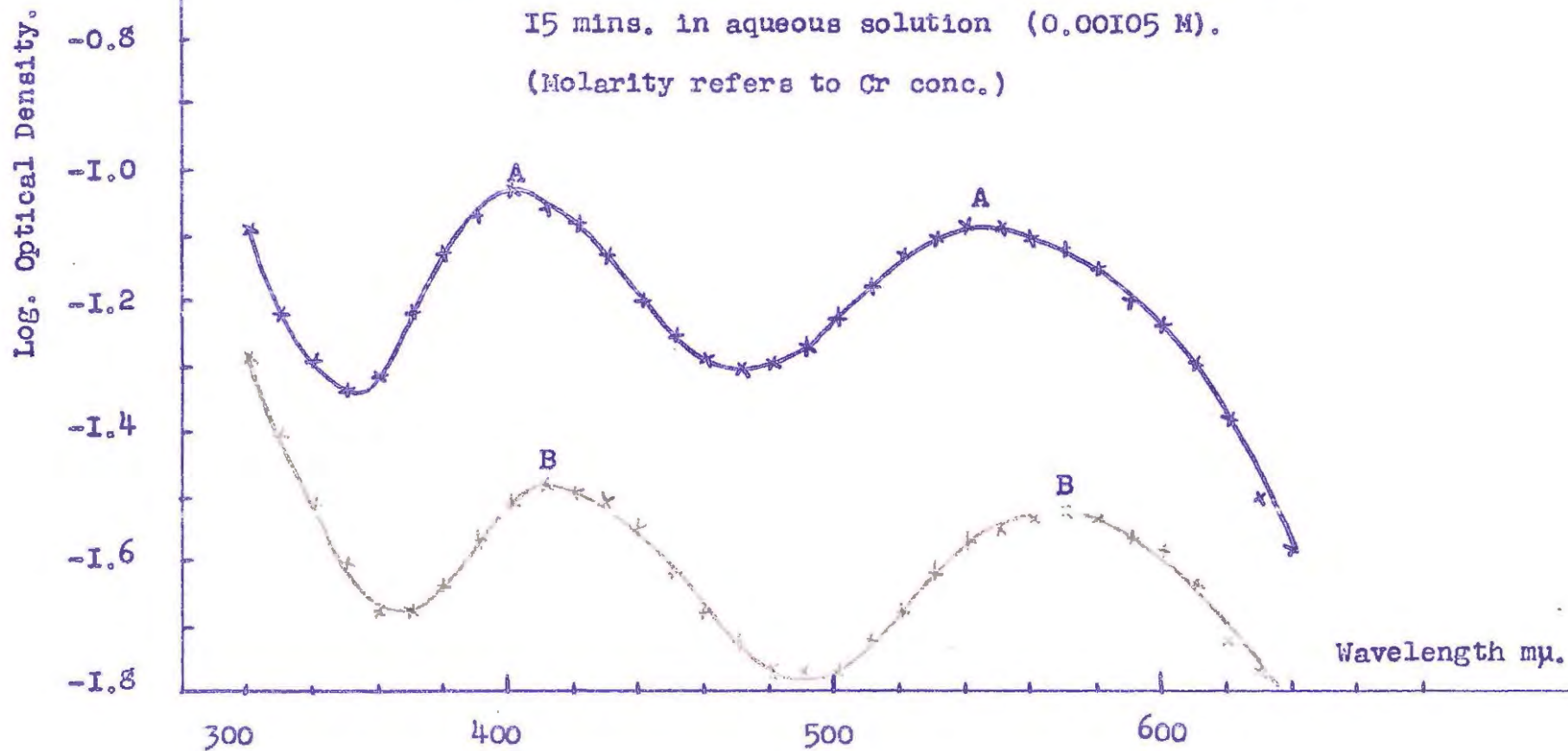
In attempting to prepare a dilute solution (0.0092M) of $[\text{Cr en}_3]_2(\text{SO}_4)_3$ it was found that the salt, unlike the corresponding chloride, was very insoluble (indeed hydrophobic) and on continuous boiling (20 minutes) a precipitate settled out. This resembled normal chromium sulphate in appearance (greyish-purple) but was only slightly soluble.

Eventually an extremely dilute solution (0.00092M) was successfully prepared by gentle boiling of the sulphate

FIG. 25

(A) Trisethylenediaminochromic sulphate boiled for
15 mins. in aqueous solution (0.00092 M).

(B) Trisethylenediaminochromic chloride boiled for
15 mins. in aqueous solution (0.00105 M).
(Molarity refers to Cr conc.)



salt (10 minutes), but from a comparison of the spectrophotometric curve obtained for this solution with that for freshly prepared triethylenediaminochromic chloride it appeared that the complex had changed in constitution. This follows from the fact that the spectrophotometric curve for triethylenediaminochromic sulphate should have been identical with that for the corresponding chloride (Fig. 21) but in fact showed certain significant differences.

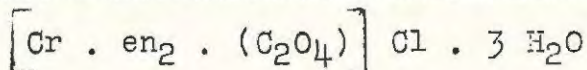
Since it appeared likely that the change in composition of the complex ion derived from the sulphate was a result of the heating required to effect solution,, the influence of heat on the corresponding product from the chloride was studied. Thus the spectrophotometric curves of the products after boiling triethylenediaminochromic chloride and sulphate at the same concentration (0.001M) for 15 minutes are shown in Fig. 25. These curves have in general the same shape but the chloride complex has lower optical densities than the sulphate at corresponding wavelengths. In addition there is a slight difference in the wavelengths of the maxima and minima.

It would appear, therefore, although this cannot be stated with certainty, that the products obtained on heating either the chloride or the sulphate are of the same general type. The differences observed in the absorption spectra could be accounted for by the fact that in one case the complex bound ion would be chloride ion whereas in the other it would be the sulphate ion.

An electrochromatogram on the heated sulphate salt solution (pH 7.5) shows the complex formed to be neutral; this is in accord with the above hypothesis.

As in the case of the chloride salt, it is evident that a more exhaustive inquiry is needed before the constitution of the product derived from heating the sulphate salt can be established.

(D) Oxalatobisethylenediaminochromic Chloride



Preparation

Bushra and Johnson (33) claim a simplified preparation over that reported by Werner (38). The preparation is as follows.

A solution containing potassium trioxalatochromiate (100 gms) and ethylenediamine hydrate (25 gms) is gently heated until the deep red-pink complex begins to form, and is then allowed to cool; yield 35 - 45 gms. The whole is ground to a thin paste with concentrated hydrochloric acid (40 mls) and mechanically stirred for 10 minutes, absolute alcohol (20 mls) then being gradually added, and a similar addition made again after a further 5 hours stirring. The residue is filtered off, washed with absolute alcohol, and finally purified by recrystallisation from hot water (60°C) - yield 10 gms.

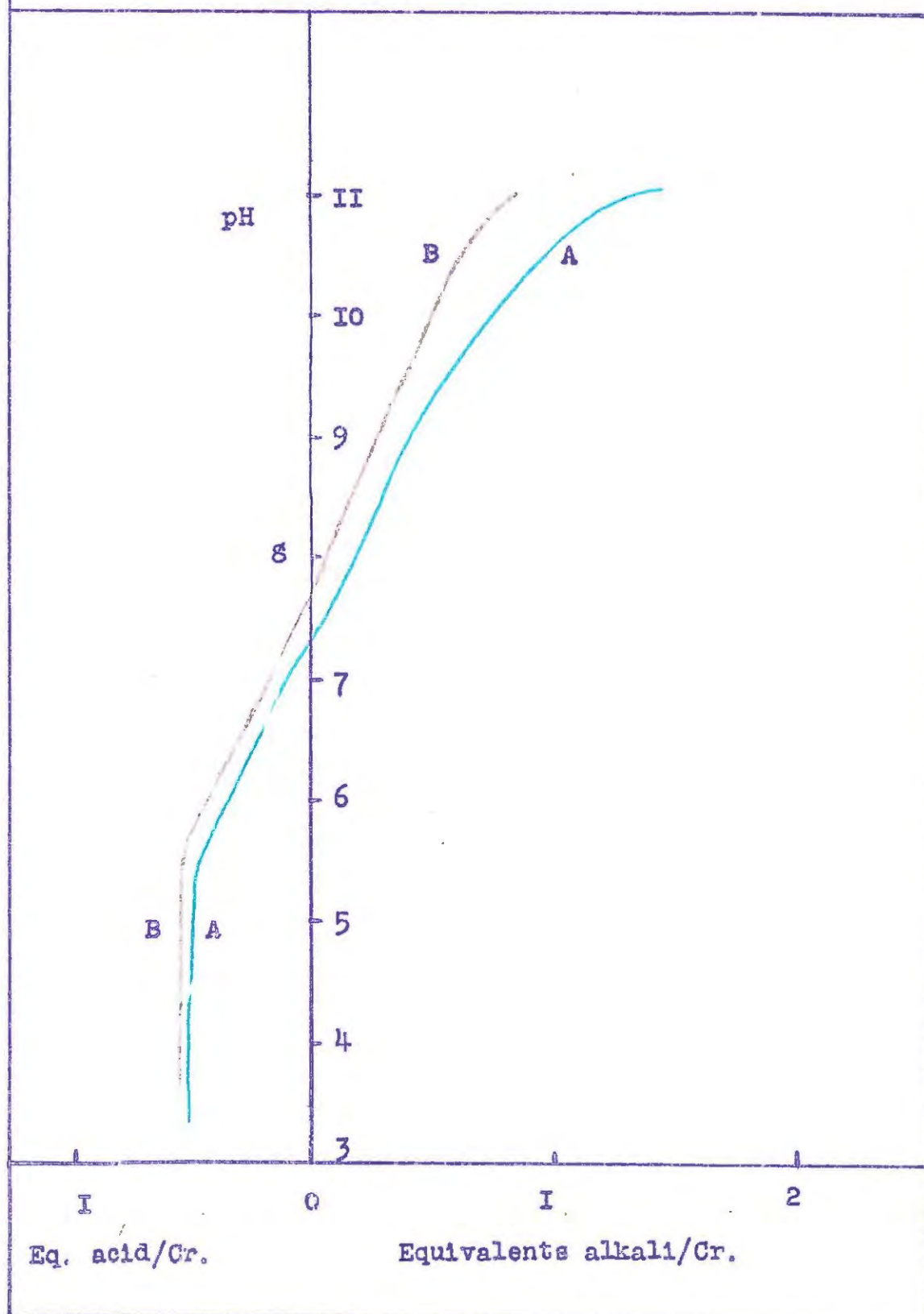
Properties

This preparation was carried out twice, yielding

FIG. 26

(A) Preparation I of $[\text{Cr en}_2(\text{C}_2\text{O}_4)] \text{Cl}$
(0.001 M)

(B) Preparation II of $[\text{Cr en}_2(\text{C}_2\text{O}_4)] \text{Cl}$
(0.001 M)



two different products, one being orange and the other a deep wine-red in colour (preparations 1 and 2 respectively). The products should have been cationic but were found by electrochromatogram 17 to be anionic. Preparation 2 was also found to contain a trace of trioxalatochromiate.

On these grounds it was decided to wash the two products with 1 : 1 alcohol-water and dry over concentrated sulphuric acid. Electrochromatogram 18 on these products showed them to be anionic but pure.

The analytical figures obtained for the two apparently homogeneous preparations (as indicated by electrochromatography) are given below :

Compound	% Cr	% N	N/Cr	moles "en" moles Cr
<u>Theoretical :</u> [Cr en ₂ (C ₂ O ₄)] Cl.3H ₂ O	14.90	16.00	1.073	2
<u>Found :</u> Preparation 1. (orange powder)	16.0	15.49	0.970	1.81
Preparation 2 (wine-red crystals)	17.41	13.55	0.778	1.45

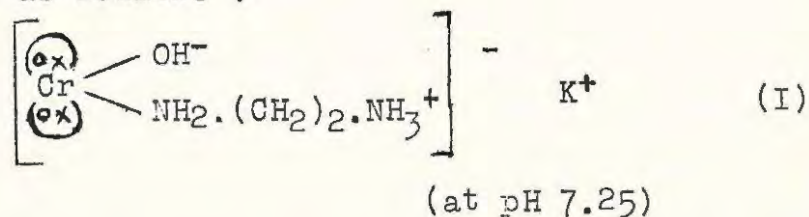
The titration curves of these two products are given in Fig. 26. Analysis of these shows that in preparation 1 about 0.75 equivalents of alkali per mole of Cr are required to raise the pH to 10, while 0.5 equivalents of acid are required to lower the pH to 5. Now the only

possible groups capable of titrating with alkali are :

- (a) water molecules co-ordinated to the chromium.
- (b) unionised carboxyl groups of oxalic acid which co-ordinated to chromium through the other carboxyl group.
- (c) $R.NH_3^+$ groups from either co-ordinated or unco-ordinated ethylenediamine molecules.
- (d) the grouping $Cr-H_2N.R$ if this is unstable to alkali, one equivalent of alkali being consumed for every such group opened.

Since the complex is anionic there must be at least four negatively charged ligand groups in the complex. The simplest assumption is that these are provided by the four carboxyl groups of two moles of oxalic acid, whence (b) can be excluded. (N.B. even if co-ordination of the carboxyl groups were incomplete it is evident that at the pH of the solution, viz. 7.25, no unionised carboxyl groups could be present).

Assuming therefore that at least four co-ordination positions are occupied by carboxyl groups and for the moment that only one ethylenediamine molecule is co-ordinated, the total number of titratable groups available between pH 7.25 and 10 would be one equivalent per mole of chrome. In order to account for the anionic character of the complex the configuration (adopting the assumptions made above) could be as follows :

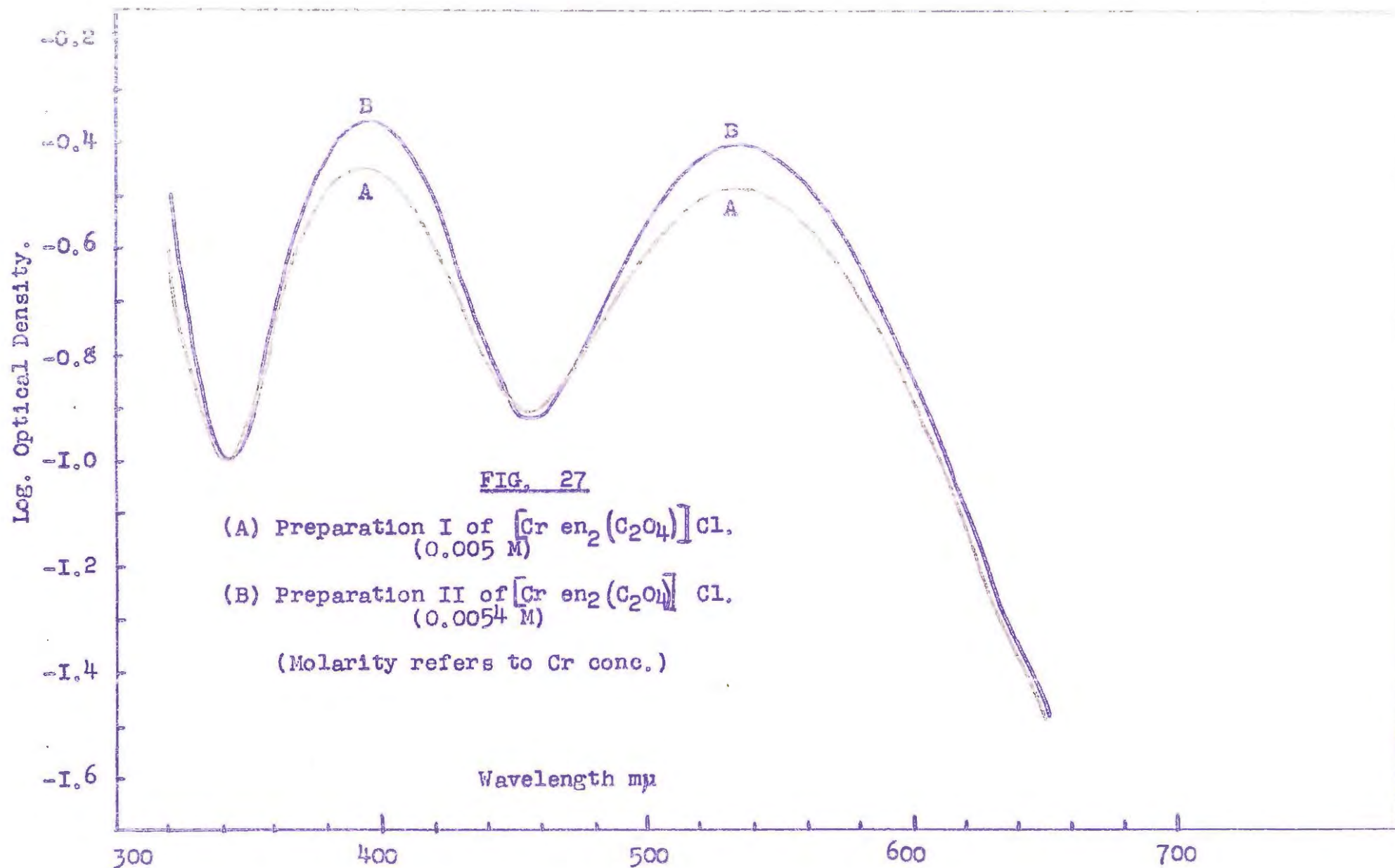


This should require one equivalent of alkali in the alkaline titration and one equivalent of acid in the acidic titration and the calculated ratio of nitrogen to chromium would be 0.54. Since the titration figures observed are 0.75 and 0.5 equivalents respectively, the titration curve could be accounted for adequately by structure I in conjunction with structure II as shown below :



While these assumptions are perfectly consistent with the titration data and the electrophoretic evidence (where heterogeneity would not be detected since both complexes have the same charge) the hypothesis must be abandoned because the ratio of nitrogen to chromium is only 50% of that calculated from the actual analytical data. Moreover the analytical composition as regards the nitrogen and chromium content is not in accord with the above postulates.

Nevertheless in view of the difficulty of reconciling the homogeneity of the charge and the titration data with the analytical composition on other postulates it seems reasonable to conclude that the salt corresponds to a mixed potassium and ethylenediamine salt of the dioxalatoethylenediamine ion in which the ethylenediamine may be functioning partly as a bidentate ligand and partly as a monodentate ligand (ring closed or opened). This

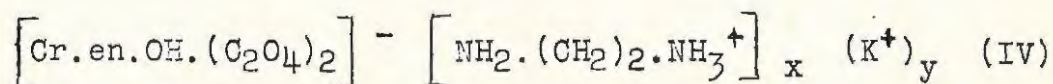
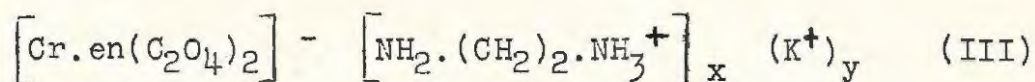


would account for the fact that different products can be obtained from the same preparative technique.

It can be shown that a similar explanation can be applied to the titration data of preparation 2. From the potentiometric curves it appears that preparation 2 has more complex bound ligands than 1 and that more free ethylenediamine titrates in preparation 1 than in 2.

The spectrophotometric curves for the solutions of the above two preparations are given in Fig. 27. It may be concluded from the differences in optical densities that two different products resulted from the same method of preparation. Moreover from these data there is reason to believe that preparation 2 has more complex bound ethylenediamine than preparation 1; in agreement with the conclusions drawn from the potentiometric data.

On these grounds it is tentatively suggested that complexes formed in this preparation are mixtures of the two types :



(where $x + y = 1$)

where the proportions of III and IV and the ratio of x and y may vary from preparation to preparation.

In conclusion it may be mentioned that Mead (134) reports the spectrophotometric curve for :



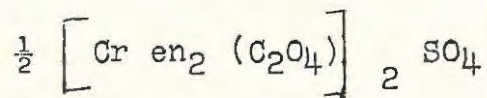
FIG. 28.

OXALATOBISETHYLENEDIAMINOCHROMIC

CHLORIDE

Preparation II.

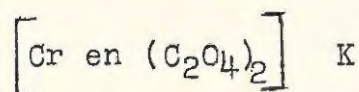
(magnification 75).



with maxima at 495 and 370 mμ. Both the present preparations show maxima at 534 and 393 mμ.

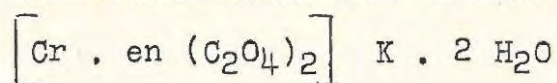
A photomicrograph of the deep wine-red crystals, recrystallised from an alcohol-water mixture is shown in Fig. 28. It will be observed that there is no evidence of heterogeneity among these crystals as might have been expected according to the hypothesis presented above.

Obviously further evidence is necessary before a definite formula can be established but it seemed worth while to attempt the preparation of :



This is described in the next section.

(E) Potassium dioxalatoethylenediaminochromiate



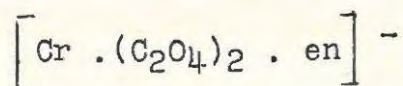
Preparation

The methods of Werner (30), from potassium dioxalatodiaquochromiate via the potassium iodide addition compound, and Bushra and Johnson (33), from potassium trioxalatochromiate, were tried but both gave poor yields.

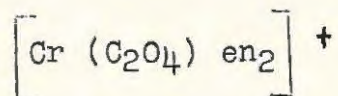
Properties

The products from both these preparations were combined and recrystallised from warm water (50°C). Elec-

trochromatogram 19 was run on a heated solution of this recrystallised salt and showed the presence of an anionic complex, presumably :



However, evidence for the presence of a cationic complex was also apparent and it is assumed that this compound is :



In view of the evident difficulty in preparing mixed chromium complexes of ethylenediamine and oxalic acid of unambiguous composition it was decided to return to the main theme of the present investigation which is an attempt to elicit information on the principles underlying the reactions between chromium complexes and basic compounds.

CHAPTER IV.

REACTIONS BETWEEN POTASSIUM CIS-DIOXALATODIAQUOCHROMIATE AND AMINO BASES.

For a quantitative study, by spectrophotometric means, of the formation of complexes between a metal ion and a ligand, a number of methods described in Chapter II, are available. Before the quantitative aspect can be studied, however, it is necessary to know the wavelengths at which the differences in extinction coefficients of the reactants and products attain maxima. Accordingly the following preliminary experiments were performed.

The potassium cis-dioxalatodiaquochromiate used in all these experiments was prepared by Werner's first method, as described in Chapter III, and shown to be pure by electrophoresis and spectrophotometry.

Reactions with propylenediamine

The first series of experiments consisted of mixing cis-dioxalatodiaquochromiate (0.0092M) with propylenediamine in the ratio of 1 mole to 1 mole, 1 mole to 2 moles and 1 mole to 3 moles respectively. These three solutions were then heated in an air oven operating at 101 - 108°C for 4 hours, cooled and made up to be 0.0092M again. The optical densities were measured over the range 320 - 700 mμ and the resultant spectrophotometric curves

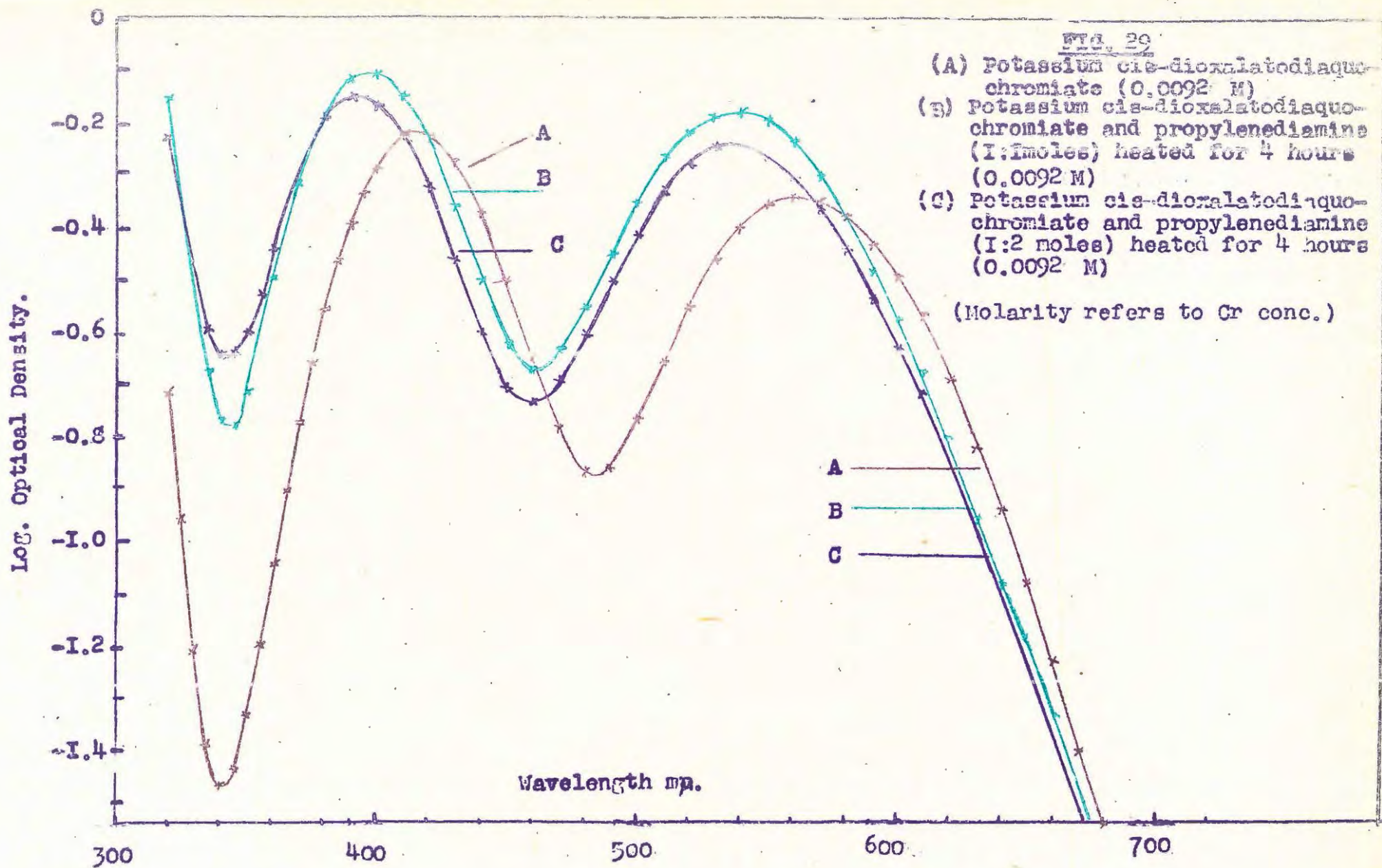


Fig. 30

(A) Potassium *cis*-dioxalatodiamino-
chromate and propylenediamine
(1:3 moles) heated for 4 hours
(0.0092 M)

(Molarity refers to Cr conc.)

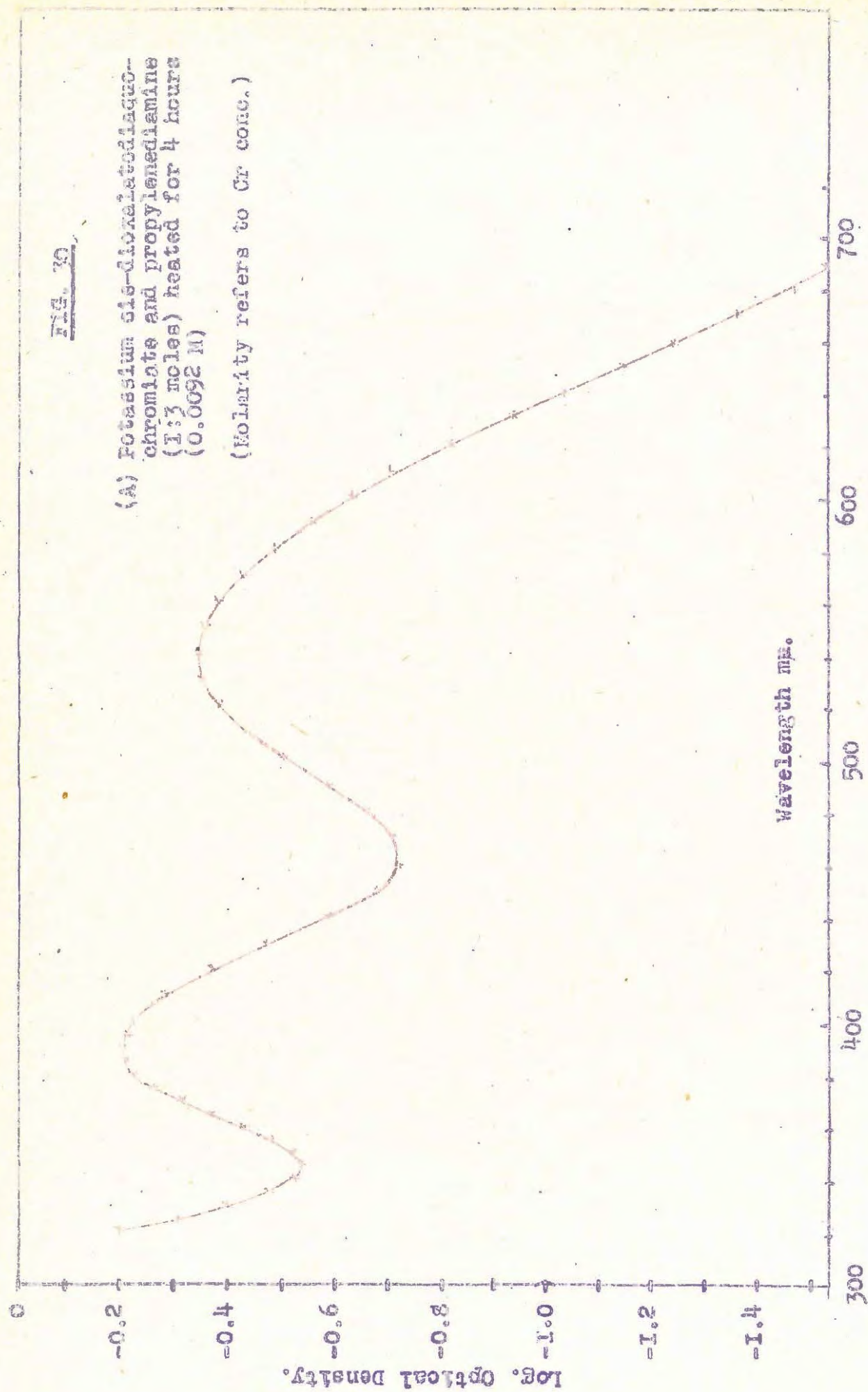


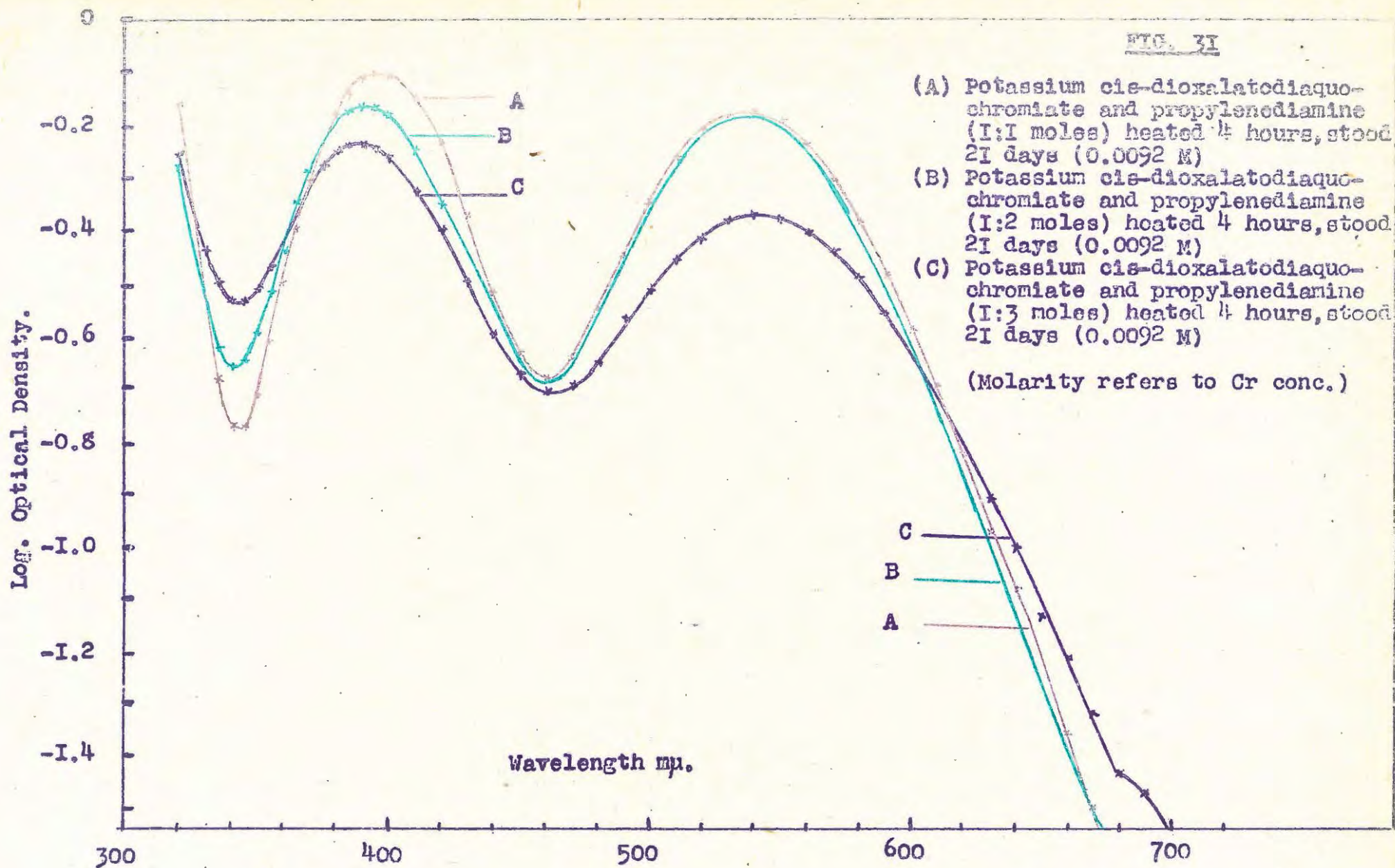
FIG. 31

Log. Optical Density.

- (A) Potassium cis-dioxalatodiaquo-chromate and propylenediamine (1:1 moles) heated 4 hours, stood 21 days (0.0092 M)
(B) Potassium cis-dioxalatodiaquo-chromate and propylenediamine (1:2 moles) heated 4 hours, stood 21 days (0.0092 M)
(C) Potassium cis-dioxalatodiaquo-chromate and propylenediamine (1:3 moles) heated 4 hours, stood 21 days (0.0092 M)

(Molarity refers to Cr conc.)

Wavelength mμ.



obtained are shown in Figs. 29 and 30. From the change in wavelength of the maxima and minima and the log. D values at these points, as compared at the same chrome concentration with the curve for potassium cis-dioxalatodiaquochromiate, it seems obvious that reaction has occurred between the cis-dioxalatodiaquochromiate ion and propylenediamine at this pH; more correctly, since the pH of the system is around 7 the reaction is between dioxalato-hydroxo-aquochromiate and propylenediamine. It was shown that propylenediamine has a low optical density in the range under consideration.

During the initial mixing of the two solutions the colour of the cis-dioxalatodiaquochromiate changed to green, as is characteristic of the behaviour of this compound on raising the pH above 7. After heating the solution was a red colour.

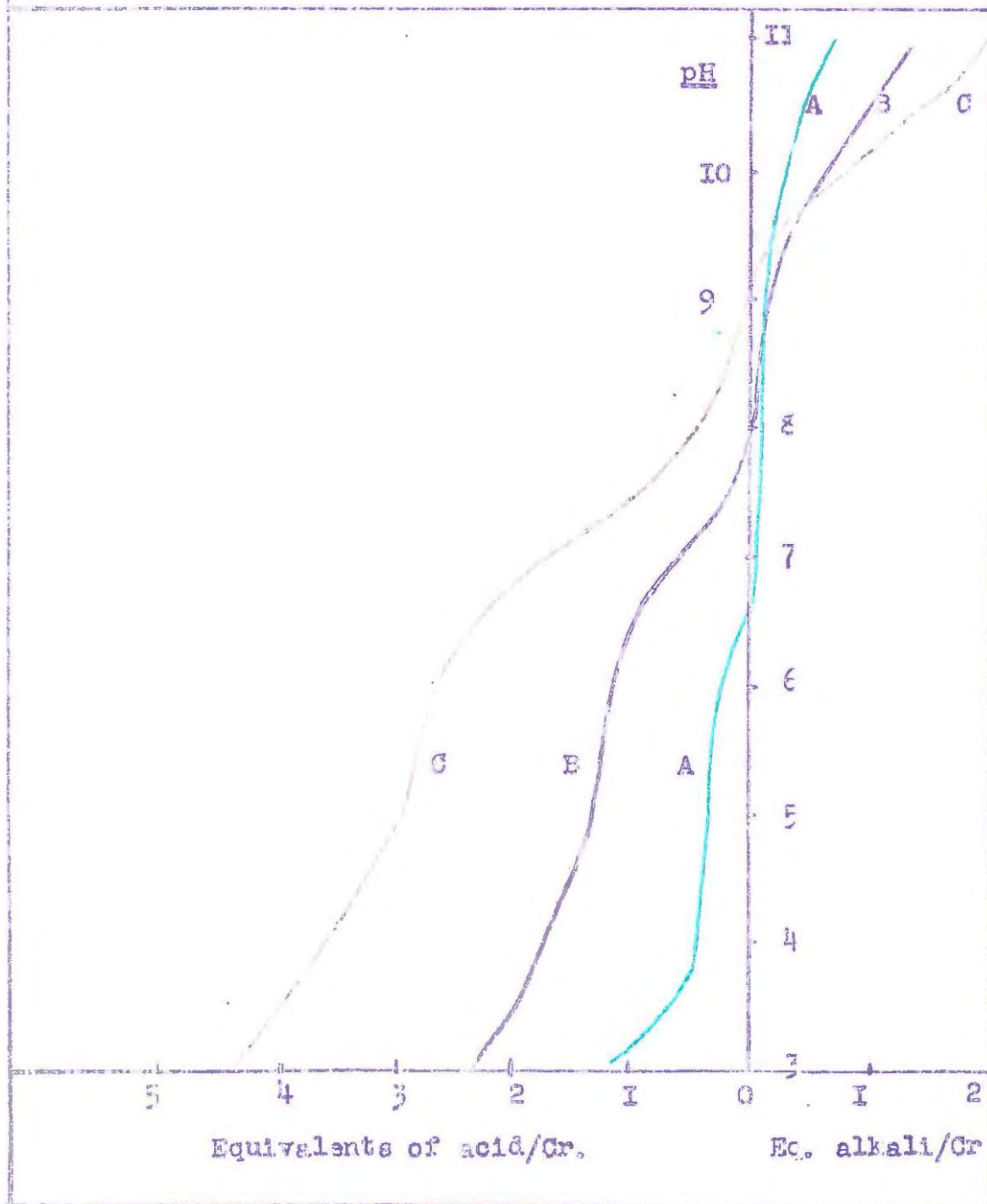
The above three solutions were then aged for 21 days at room temperature (20°C) and the optical densities measured over the same range. These are shown in Fig. 31. Comparison of the corresponding spectrophotometric curves in Figs. 29, 30 and 31 shows that, within experimental error, there is very little difference between the curve for the heated solutions and the same solutions on aging.

Electrochromatogram 20 on these aged solutions shows that :

(1) Potassium cis-dioxalatodiaquochromiate + propylenediamine (1 : 1 moles) on heating and aging produced an anionic complex.

FIG. 32

- (A) Potassium cis-dioxalatodиаquochromiate and propylene-diamine (1:1 moles) heated for 4 hours at 100°C then aged for 21 days. (0.00092 M)
- (B) Potassium cis-dioxalatodиаquochromiate and propylene-diamine (1:2 moles) heated for 4 hours at 100°C then aged for 21 days. (0.00092 M)
- (C) Potassium cis-dioxalatodиаquochromiate and propylene-diamine (1:3 moles) heated for 4 hours at 100°C then aged for 21 days. (0.00092 M)



(2) Potassium cis-dioxalatodiaquochromiate + propylenediamine (1 : 2 moles) on heating and aging produced an anionic complex.

(3) Potassium cis-dioxalatodiaquochromiate + propylenediamine (1 : 3 moles) on heating and aging produced a cationic complex.

The titration curves of these three solutions are given in Fig. 32. The curves have been corrected as described in the section on potentiometry.

Interpretation of these curves is facilitated by making the following general assumptions :

(1) that the carboxyl groups are completely titrated between pH 3 and 5 except in the case of free oxalic acid in solution, when the proportion titrating is calculated from the second dissociation constant ($pK_2 = 3.8$).

(2) that between pH 5 and 10 all co-ordinated water molecules and amine groups not directly involved in a co-ordinate bond are completely titrated.

Consider first curve A, for the solution of cis-dioxalatodiaquochromiate and propylenediamine (1 : 1 moles). From this curve the following titration values are obtained :

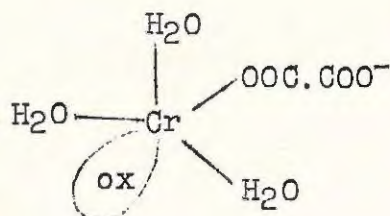
pH 3.0 - 5.0	0.82 equivalents of reagent per Cr.
pH 5.0 - 10.0	0.70 equivalents of reagent per Cr.

Now, if the titration below pH 5 were due only to free oxalic acid in solution (i.e. not complex bound), the number of moles of oxalic acid would be given by

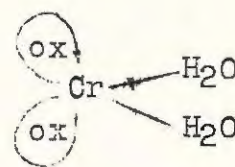
0.82/0.88 . This follows from the fact that between pH 3 and 5 it can be shown that only 0.88 equivalents are required for each mole of oxalic acid, taking the second dissociation constant to be pK_2 3.8.

In actual fact the presence of free oxalic acid in solution can in the present case be excluded because the product was found to have a negative charge by the electrophoretic method. Since the pH of the solution employed for this determination was ca. 6.5 the presence of complex bound hydroxyl groups, due to ionisation of co-ordinated water molecules, may be safely excluded (the pK values of the two co-ordinated water molecules in cis-dioxalatodiaquochromate are ca. 7 and 9 respectively). Accordingly, since no free oxalic acid may be present in the solution, the titration between pH 3 and 5 may be ascribed to carboxyl groups belonging to oxalic acid molecules functioning as monodendate ligands.

For example consider the following two structures present in the proportions indicated :



82%



18%

Such a mixture would correspond to a titration between pH 3 and 5 of 0.82 equivalents, as found experimentally.

Fig. 33

Group	Cr	oxalate chelated	oxalate unchelated	oxalate free in solution	pn chelated	pn unchelated	pn free in solution	co-ordinated water molecules
pH titration range	-	-	3 - 5	3 - 5	-	5 - 10	5 - 10	5 - 10
Average Composition mole ratio (1 : 1)	1	1.18	0.82	-	1	0.06	-	0.76
Average Composition mole ratio (1 : 2)	1	1	1	-	1	0.5	0.5	0.5
Average Composition mole ratio (1 : 3)	1	0.42	0.58	1.0	1.0	1.36	0.64	1.22

If for the moment, we accept the above proportions and structures on the grounds that titration between pH 3 and 5 is thereby accounted for, we may calculate the expected titration over the range pH 5 - 10, bearing in mind that the propylenediamine is also available for titration unless chelated.

In the range pH 5 - 10 :

from the Cr atoms : $(3 \times .82) + (2 \times .18) = 2.82 \text{ eq/Cr.}$

from the pn (2 moles/2 Cr) :	2.00 "
Total :	4.82 "

Found by titration : 0.70 "

To be accounted for : 4.12 "

Let x = proportion of chelated pn

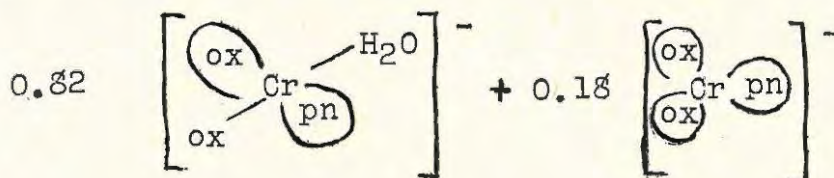
and y = proportion of unchelated pn

and since each chelated pn loses 4 eq/Cr and each unchelated pn 2 eq/Cr in replacing H_2O groups.

$$4x + 2y = 4.12$$

If the number of chelated pn groups per Cr atom is taken to be unity, then $y = 0.06$, that is, negligible. Therefore the average composition of the reaction product is given in Fig. 33.

A mixture which fits this average composition as well as the potentiometric and electrophoretic evidence is



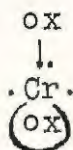
for each mole of chromium salt.

This mixture contains a small amount of the complex in which propylenediamine has replaced the coordinated water molecules and a larger amount of a similar complex where one of the chelated oxalate groups has opened up.

Consider now the second titration curve for cis-dioxalatodiaquochromiate and propylenediamine (1 : 2 moles). The titration data from this curve are :

pH 3.0 - 5.0	1.0 equivalent of reagent per Cr.
pH 5.0 - 10.0	2.04 equivalents of reagent per Cr.

As the titration between pH 3 and 5 requires 1 eq/Cr consider the structure :



where "-ox" represents oxalic acid functioning as a monodentate ligand.

In the range pH 5 - 10	
from the Cr atoms :	3 eq/Cr
from the pn (2 moles/Cr) :	4 "
Total :	7 "
Found by titration :	2 "
To be accounted for :	5 "

As before, chelated pn loses 4 eq/Cr (4x) and unchelated pn 2 eq/Cr (2y)

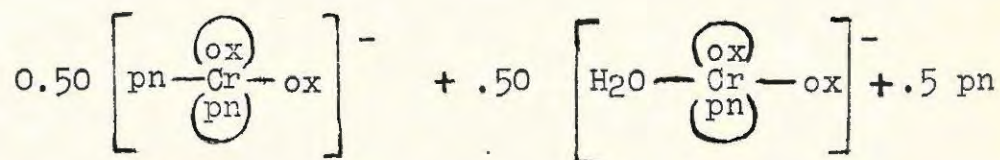
$$4x + 2y = 5$$

$$\text{when } x = 1, \quad 2y = 1$$

$$y = \frac{1}{2}$$

Therefore the average composition of the reaction product is given in Fig. 33.

A mixture which fits this average composition as well as the potentiometric and electrophoretic evidence is :



for each mole of chromium salt.

This mixture contains one constituent with chelated oxalate and propylenediamine molecules and an oxalate molecule functioning as a monodendate ligand (i.e. one of the oxalate rings of the original cis-salt employed in the reaction has opened up). The second constituent is the same as above but contains a propylene-diamine molecule present as a monodendate ligand in place of the co-ordinated water molecule. These products are consistent with a step-wise reaction taking place.

The third curve represents the reaction between cis-dioxalatodiaquochromiate and propylenediamine (1 : 3 moles). The titration data from this curve is :

pH 3.0 - 5.0	1.4 equivalents of reagent per Cr.
pH 5.0 - 10.0	3.85 equivalents of reagent per Cr.

It can be shown that for oxalic acid ($\text{pK}_2 = 3.8$) titration in the range pH 3 - 5 requires 0.88 eq/mole. As in the curve under consideration free oxalic acid must

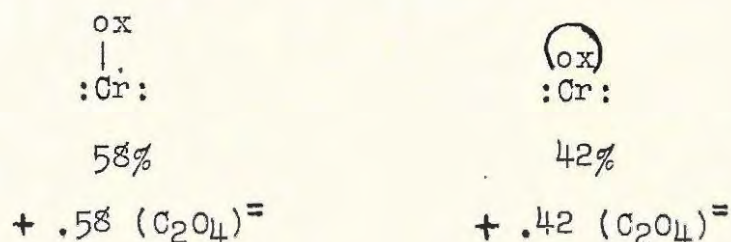
be present in solution (electrophoretic evidence shows complex to be cationic), the titration value in this range must be multiplied by the factor $\frac{1}{0.88}$.

Therefore titration in the range pH 3.- 5

$$= 1.40 \text{ eq/Cr} = \frac{1.4}{0.88} \text{ -COO- gps/Cr}$$

$$= 1.58 \text{ -COO- gps/Cr}$$

Consider the structures :



where the fractions represent the amount of oxalate per Cr free in solution.

In the range pH 5 - 10 :

From the Cr atoms: $(0.58 \times 5) + (0.42 \times 4) = 4.58 \text{ eq/Cr}$

From the pn (6 moles/2 Cr) : 6.00 "

Total : 10.58 "

Found by titration : 3.85 "

6.73 "

As before, chelated pn loses 4 eq/Cr (4x) and unchelated pn 2 eq/Cr (2y).

$$4x + 2y = 6.73$$

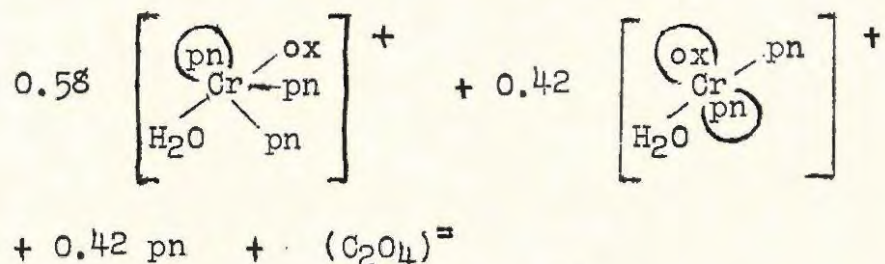
$$\text{when } x = 1$$

$$2y = 2.73$$

$$y = 1.36$$

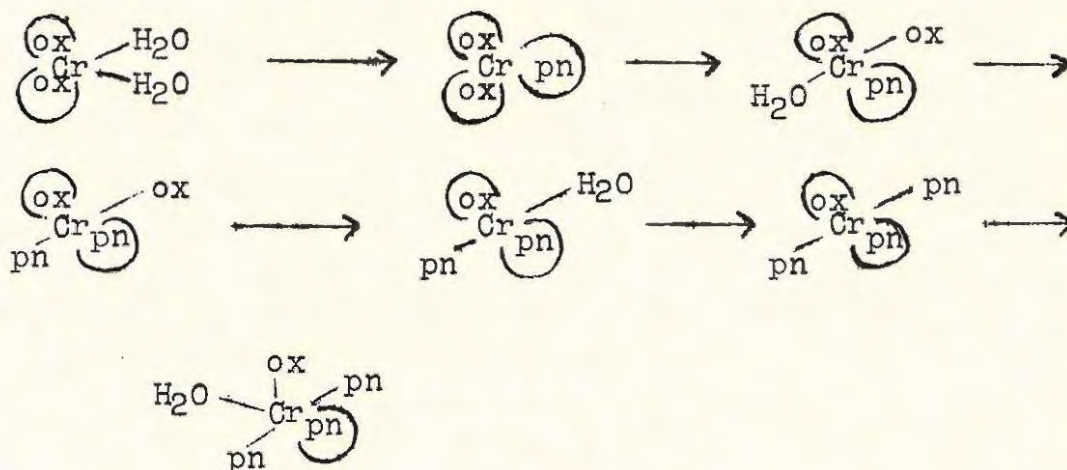
therefore the average composition of the reaction product is given in Fig. 33.

A mixture which corresponds to this average composition as well as the potentiometric and electrophoretic evidence is :

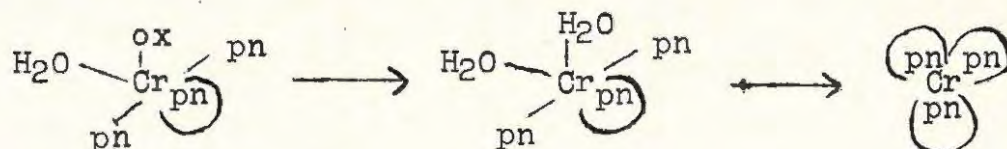


for each mole of chromium salt.

Consideration of these reaction products shows that they fall into a general sequence of reactions as more propylenediamine is added :



with possible further reactions, not encountered under the present experimental conditions, of the type :



The successive replacement of the oxalate ions by propylenediamine suggests that chelated structures

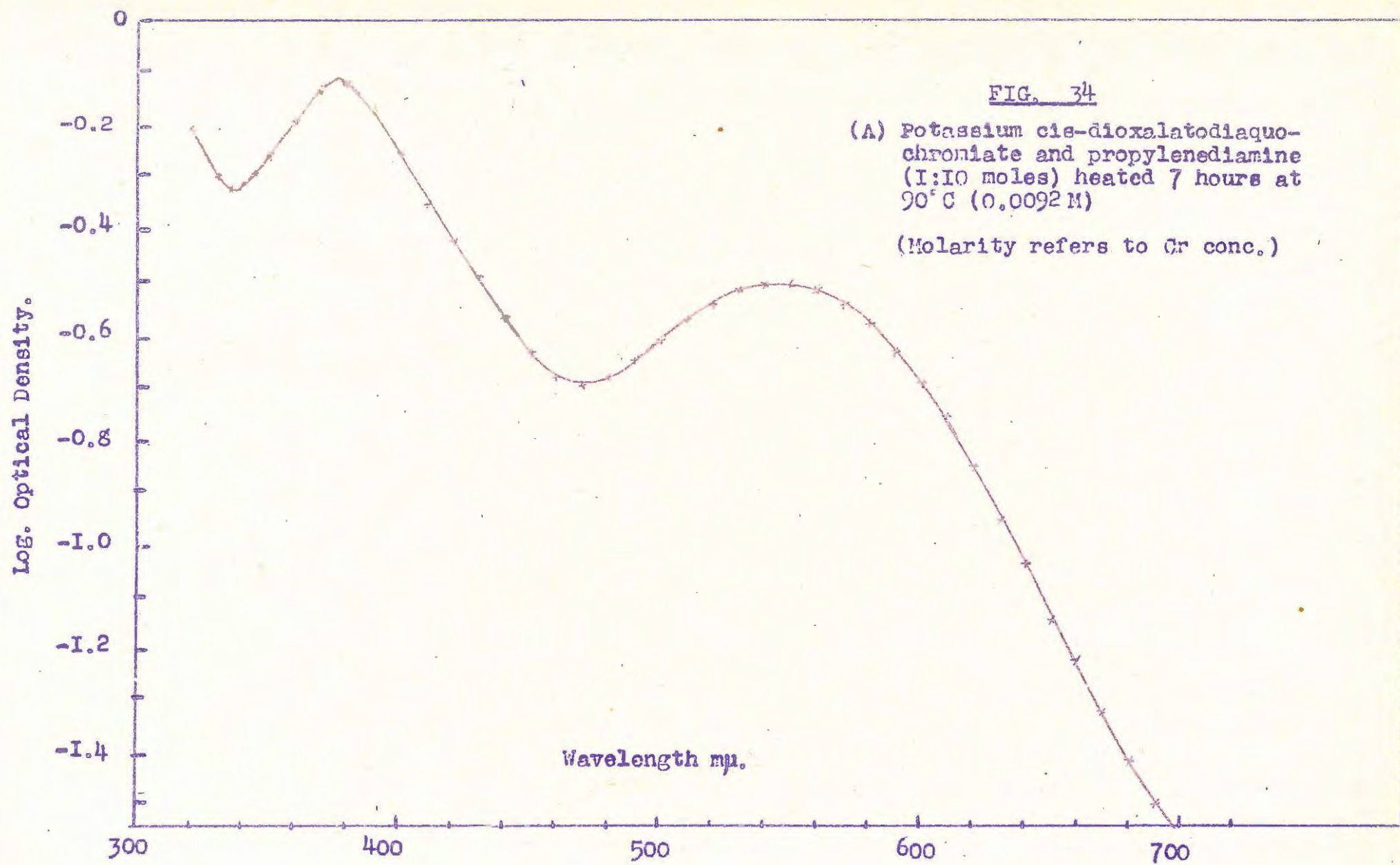


FIG. 34

(A) Potassium cis-dioxalatodiaquo-chromate and propylenediamine (1:10 moles) heated 7 hours at 90°C (0.0092 M)

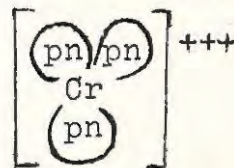
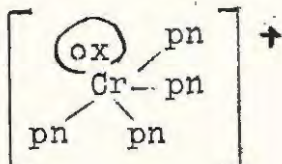
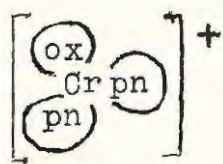
(Molarity refers to Cr conc.)

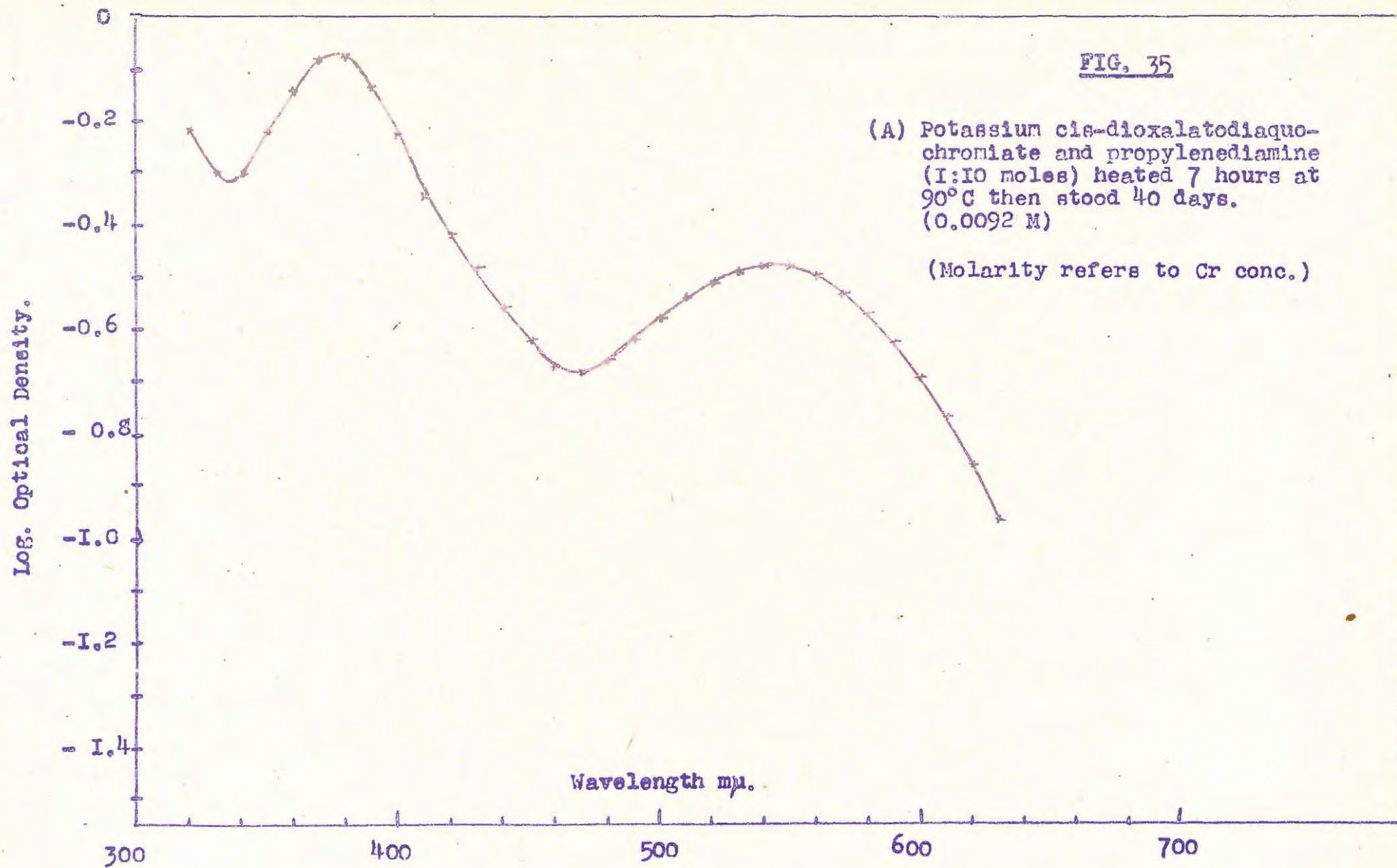
involving the latter are more stable than the corresponding oxalate systems. However, the oxalato-complexes are known to decompose at high pH due to the stepwise displacement of oxalate groups by hydroxyl ions. Since in the case of the amino compounds an increase in pH will (within limits) favour complex formation owing to the removal of protons from the amino group, the above considerations do not necessarily apply to the same extent to the latter compounds. The relative stabilities are therefore a direct function of the pH of the system.

Reaction with excess propylenediamine.

The effect of reacting cis-dioxalatodiaquochromiate with excess propylenediamine in alkaline medium was studied in the following experiments.

A solution of cis-dioxalatodiaquochromiate (0.0092M) and propylenediamine (1 : 10 moles) was heated for 7 hours at 85 - 95°C, cooled and made up to be 0.0092M. The spectrophotometric curve for this solution, aged for 4 days, is shown in Fig. 34. The initial pH values were 4.55 for the cis-dioxalatodiaquochromiate, 11.85 for the propylenediamine and the final pH of the mixture was 10.27. Electrochromatogram 21 shows that a similar cationic complex is formed as that between cis-dioxalatodiaquochromiate and ethylenediamine (which will be discussed later). Possible products of this reaction are of the types :





where the fully chelated complexes are considered more probable.

As shown by Fig. 35 very little change occurs in the spectrophotometric curve on aging the above solution for 40 days.

Potentiometric data were not obtained in this case as interpretation of the curves would have been rendered difficult by the relatively large excess of propylenediamine in the solutions.

From most of the spectrophotometric studies carried out in this work it is evident that the absorption curves for ethylenediamine complexes are very similar to those for the same propylenediamine complexes. Bearing this in mind and comparing Fig. 34 with the curve for trisethylenediaminochromic chloride (Fig. 21) it seems unlikely that they represent analogous complexes. It would appear therefore that among the possibilities quoted above the trispropylenediaminochromic ion, in the fully chelated form might reasonably be excluded.

In an attempt to follow the course of the above reactions a similar solution (containing 1 mole of cis-dioxalatodiaquochromate to 10 moles of propylenediamine, 0.0092M in chromium) was stored in ice immediately after preparation in order to slow down the reaction rate. The spectrophotometric curve was then measured on this ice-cooled solution, the solution in the optical cells being replaced by fresh ice-cooled solution after every four or five readings. The rest of the solution was then placed

FIG. 36

Log. Optical Density.

(A) Potassium cis-dioxalatodiaquo-
chromiate and propylenediamine
(1:10 moles) immediately after

mixing (0.0092 M)

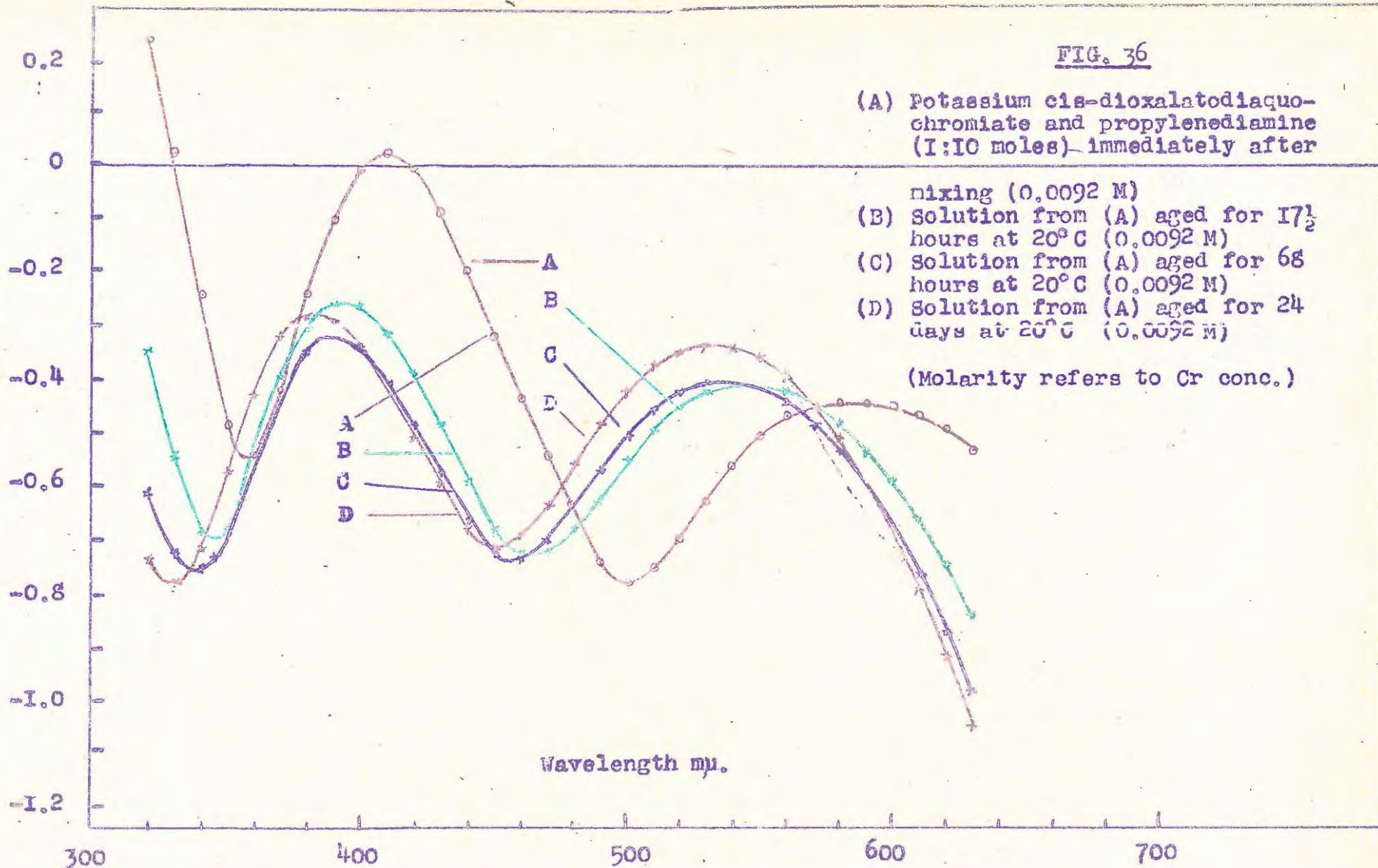
(B) Solution from (A) aged for 17½
hours at 20°C (0.0092 M)

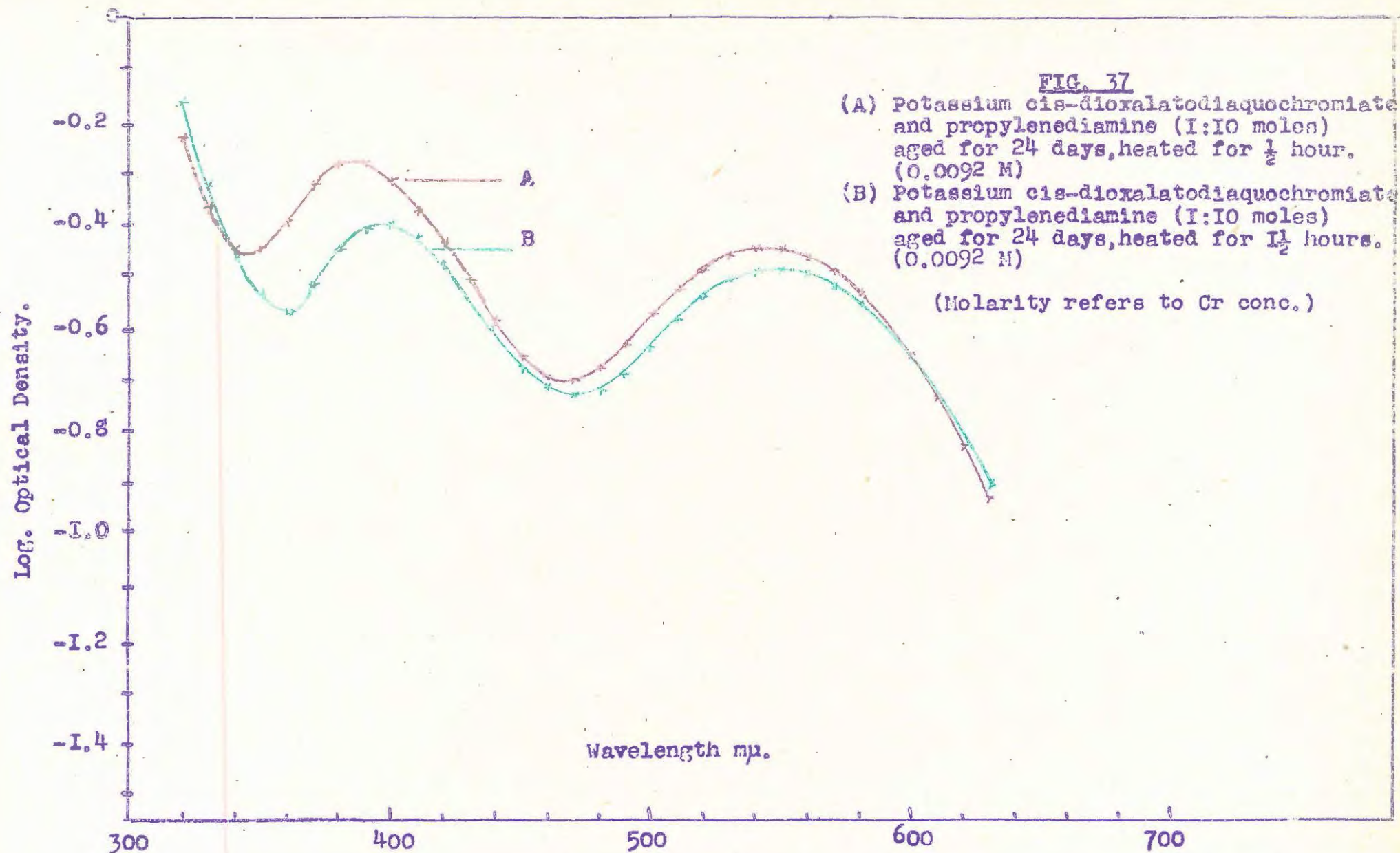
(C) Solution from (A) aged for 68
hours at 20°C (0.0092 M)

(D) Solution from (A) aged for 24
days at 20°C (0.0092 M)

(Molarity refers to Cr conc.)

Wavelength mμ.





in a well stoppered flask immersed in a thermostatically controlled water bath at 20°C . The optical density readings were then obtained after $17\frac{1}{2}$ hours, 68 hours and 24 days. These curves are shown in Fig. 36. The charge on the complex in each of the last three solutions is shown in electrochromatograms 22, 23, 24, along with similar solutions prepared with ethylenediamine, (which will be discussed later) to be positive. The pH values of the four solutions under consideration were respectively 12.8, 11.42, 10.52 and 10.42 while the colour, initially green after mixing, became a red-violet.

After the solution had stood for 24 days two aliquots were heated for $\frac{1}{2}$ hour and $1\frac{1}{2}$ hours respectively, cooled and made up to the same concentration as before. The resultant curves are shown in Fig. 37. The general shape of these curves is very similar to those of Fig. 34 indicating possibly different extents of the same reaction.

It was then decided to find the effect on cis-dioxalatodiaquochromiate of altering the pH to about the same value as that produced when propylenediamine is added to the cis-dioxalatodiaquochromiate. To this end 2 equivalents of KOH per mole of chromium were added to the cis-dioxalatodiaquochromiate and the solution diluted to be 0.0092M, cooled in ice, and spectrophotometric measurements made as before. The mixture was then placed in a well-stoppered flask immersed in a water-bath thermostatically controlled at 20°C , and optical density readings noted after $17\frac{1}{2}$ hours, 68 hours and 20 days. The results

FIG. 38

(A) Potassium cis-dioxalatediaquochromate and 2 equivalents of KOH per mole of chromium, immediately after mixing. (0.0092 M)

(B) Solution from (A) aged for 17½ hours at 20°C. (0.0092 M)

(C) Solution from (A) aged for 68 hours at 20°C. (0.0092 M)

(D) Solution from (A) aged for 20 days at 20°C. (0.0092 M)

(Molarity refers to Cr conc.)

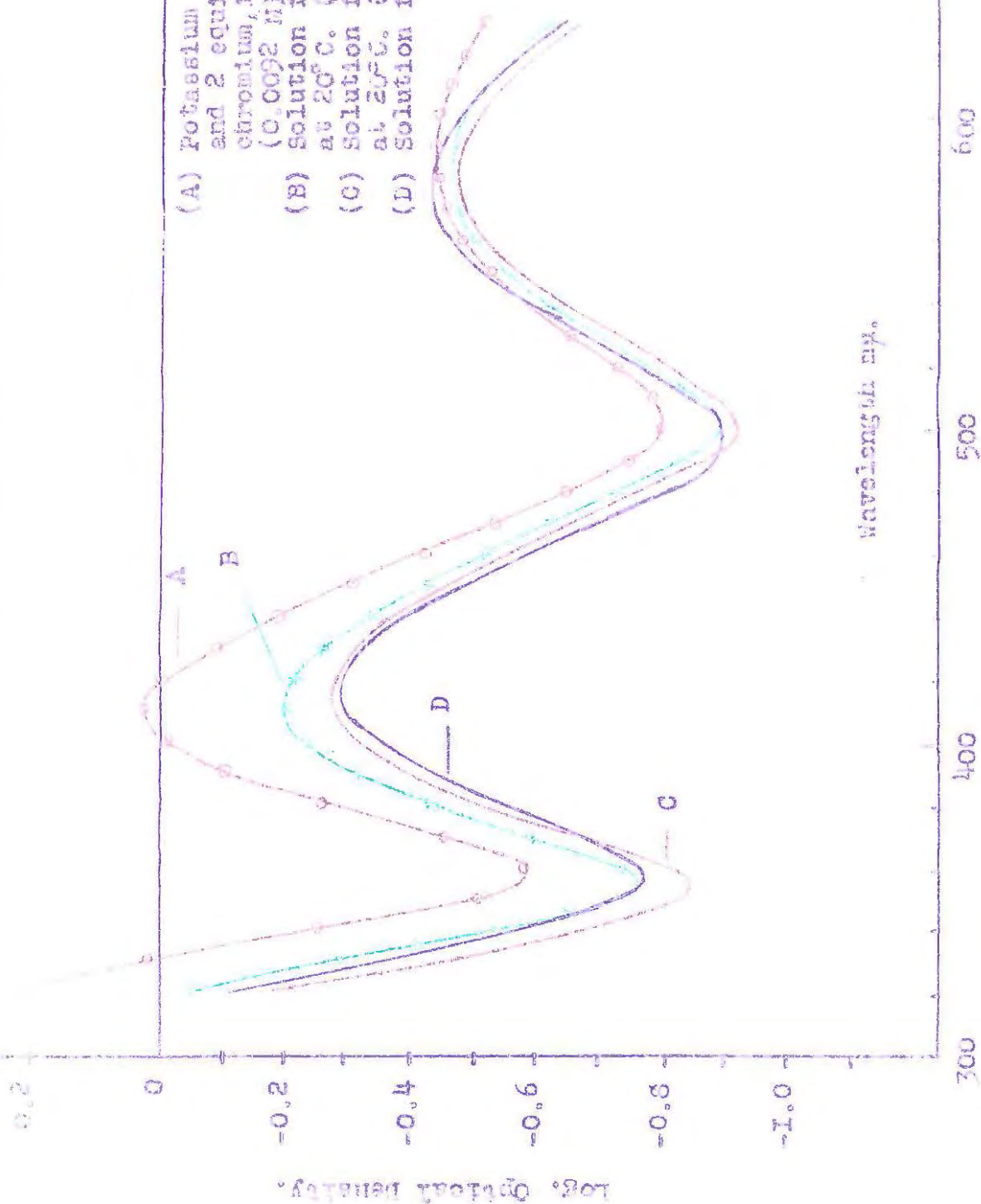


FIG. 39

(A) Potassium cis-dioxalatodihydroxochromate

(0.0092 M)

(B) Potassium cis-dioxalatodiaquochromate and
propylenediamine (1:10 moles) immediately
after mixing (0.0092 M).

(Molarity refers to Cr conc.)

Log. Optical Density.

A and B

A and B

Wavelength $m\mu$.

-1.2

300

400

500

600

-1.0

-0.8

-0.6

-0.4

-0.2

0

0.2

are shown in Fig. 38. The corresponding pH values of the solutions were 10.44, 9.40, 8.80 and 7.92.

The filter-paper electrophoresis diagrams of the aged solutions reveal the charge on the complex ion to be negative in all three cases (Electrochromatogram 25, 26, 24).

The initial product in this reaction, corresponding to Fig. 38A must be cis-dioxalatodihydroxochromiate

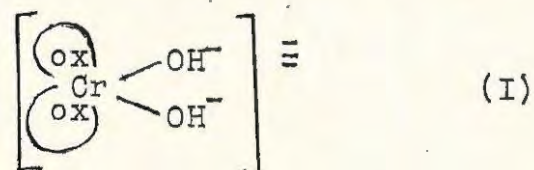
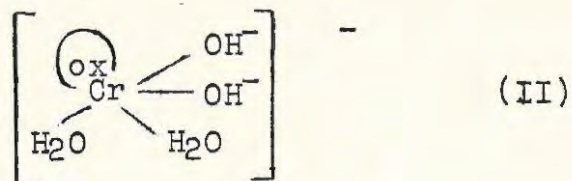
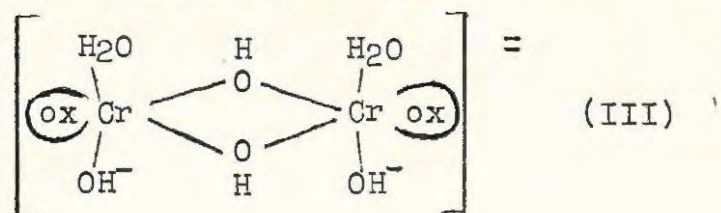


Fig. 39 shows that the initial product on mixing cis-dioxalatodiaquochromiate and propylenediamine, is also cis-dioxalatodihydroxochromiate.

This compound is known to be unstable and loses oxalate to give :



which can olate, due to the co-ordinated water molecules produced by the decomposition, to form :

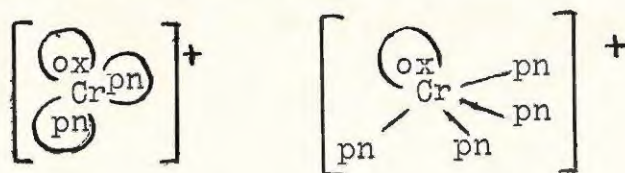


Consequently the products on aging cis-dioxalatodiaquochromiate and 2 equivalents of potassium hydroxide will

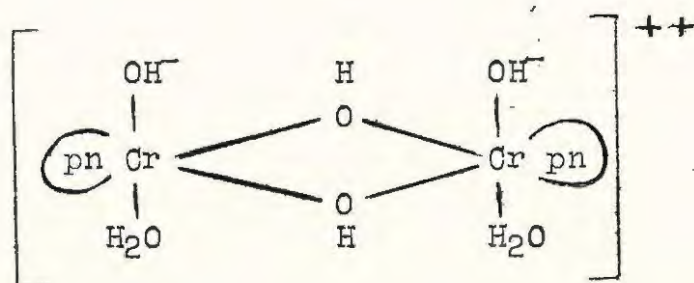
consist of one or more of compounds I, II and III or products exhibiting an even higher degree of olation.

Since the initial product is the same whether propylenediamine or potassium hydroxide is added to cis-dioxalato δ iaquochromiate, it is reasonable to suppose that, if complex formation between propylenediamine and the cis-dioxalato δ ihydroxochromiate so formed did not occur, the same end products (presumably olated compounds) would ultimately be attained on aging. If this were so the spectrophotometric curves for the two mixtures would be of the same general shape when aged for similar periods.

Comparison of Figs. 36 and 38 shows that these spectrophotometric curves, apart from those corresponding to the solutions immediately after mixing in each case, do not coincide at all as the maxima and the minima of corresponding solutions in the two series of curves and the log D values at these wavelengths are not the same. This indicates that reaction occurs between cis-dioxalato δ iaquochromiate and propylenediamine (ca. pH 11) on mixing and aging. Since the product is cationic (see Electrochromatograms 22, 23, 24) the possibilities are limited to complexes of the type :



and possibly also olated structures such as :



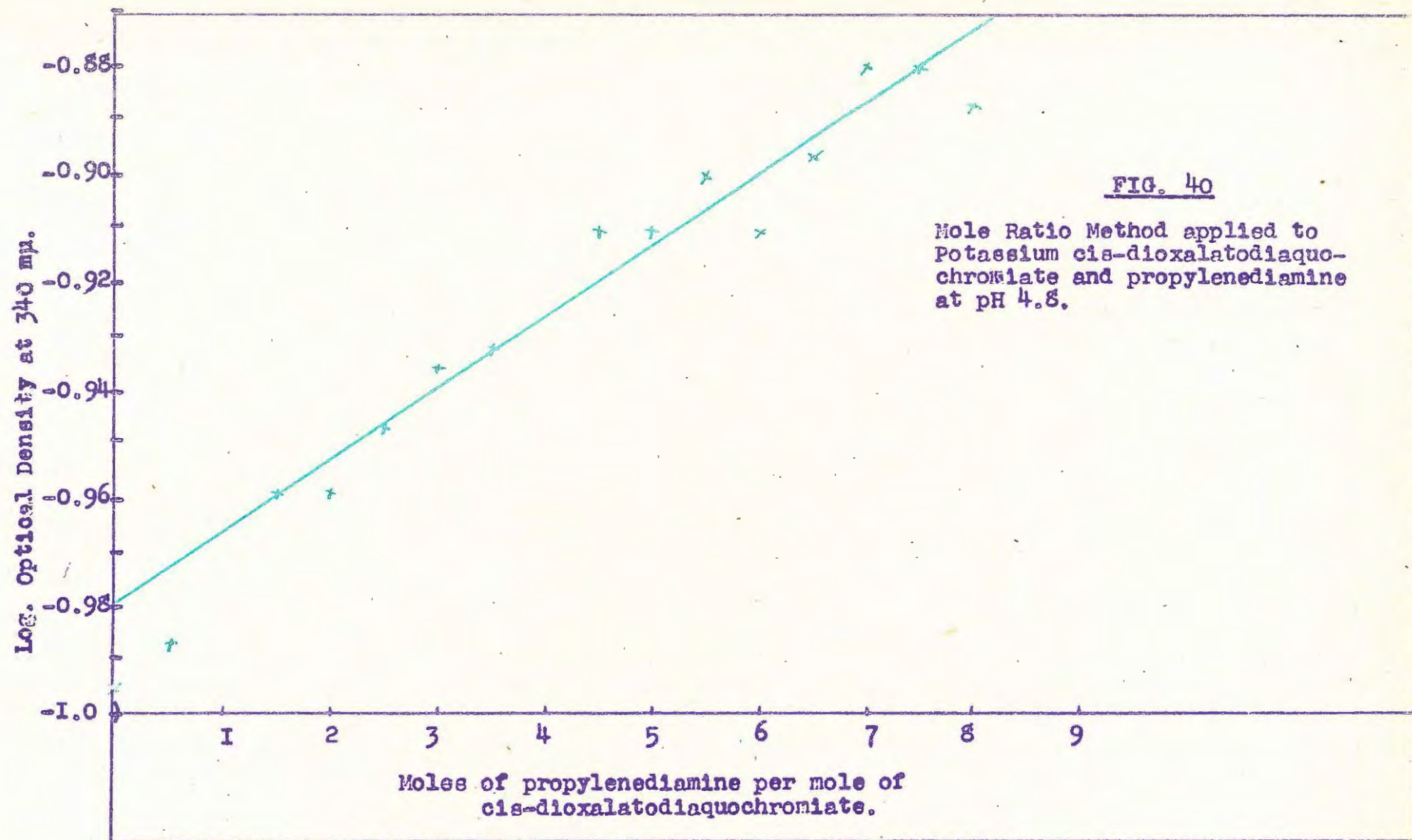
Once again the trispropylenediaminochromic ion can be excluded as none of the spectrophotometric curves of the products of the reactions described above show any resemblance to the curve for the trisethylenediaminochromic ion (Fig. 21).

Further evidence for the view that the products of the reaction on aging cis-dioxalatodiaquochromate and potassium hydroxide (1 : 2 moles) are not the same as those produced by cis-dioxalatodiaquochromate and propylenediamine (1 : 10 moles) is given by the electrophoretic data. Here, the products of the former mixture are shown to be anionic while those of the latter are cationic.

Reaction at pH 4.8.

Having definitely established that cis-dioxalatodiaquochromate reacts with propylenediamine at high pH values it was decided to find the number of moles combining at any given pH by use of the "Molar Ratio Method" (109) and "Continuous Variation Method" (111, 112).

In the "Molar Ratio method" potassium cis-dioxalatodiaquochromate (0.0092 M - pH 4.8) was mixed



Log. Optical Density.

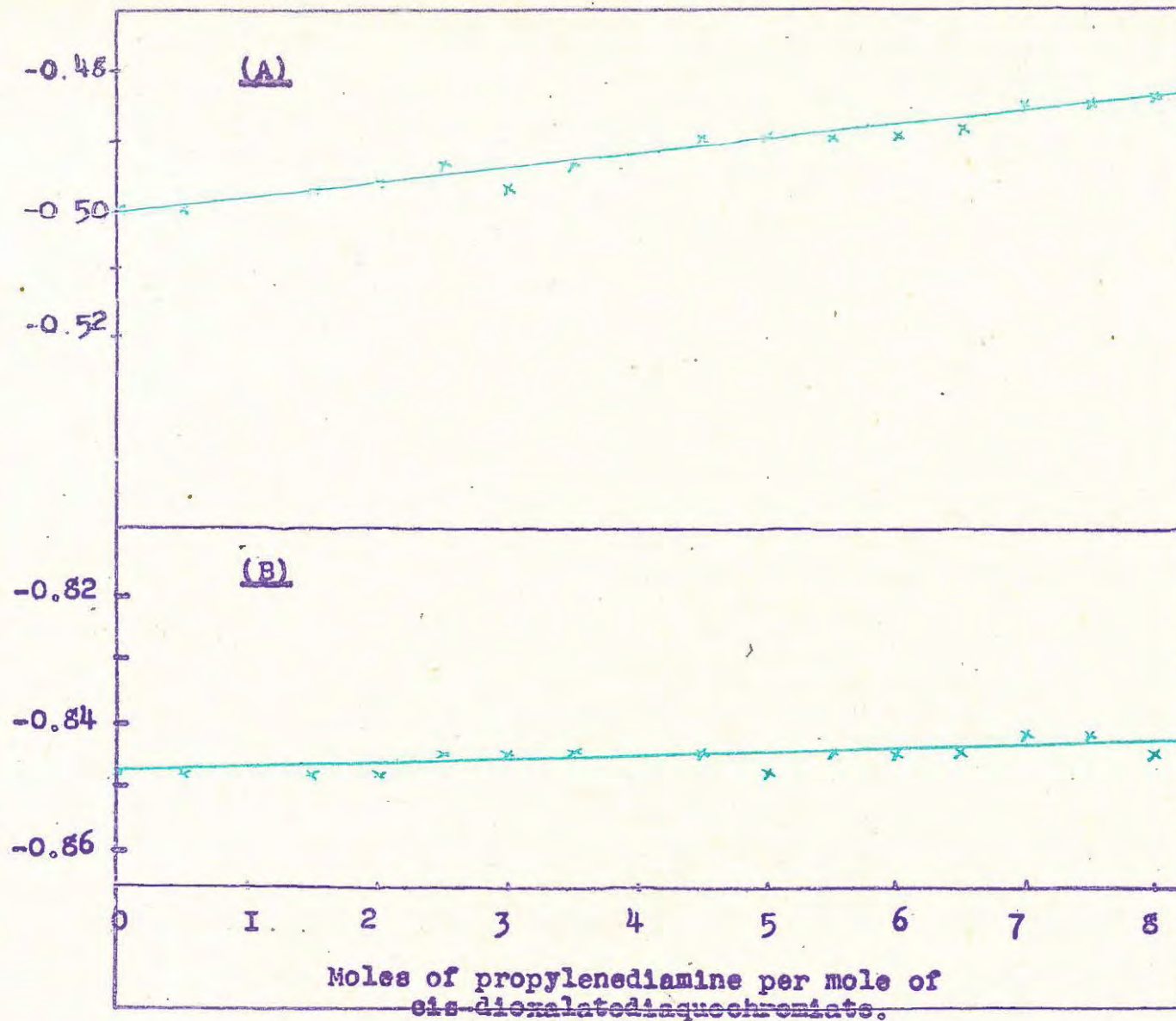


FIG. 4I.

Mole Ratio Method applied to Potassium cis-dioxalatediaquechromate and propylenediamine at pH 4.8.

(A) At 380 mμ.

(B) At 480 mμ.

with propylenediamine (brought to pH 4.8 with nitric acid) in molar ratios from 1 : 1 to 1 : 8. The resultant solutions were boiled for 25 minutes, cooled and made up to be 0.0092M. (It may be noted that the conditions of this reaction are here milder than were employed in earlier experiments). The optical densities were recorded at 340, 380 and 480 mμ and the pH of each solution noted. The log of the optical densities were then plotted against the number of moles of propylenediamine per mole of cis-dioxalatodiaquochromiate (Figs. 40, 41). The results indicate that, even though the optical density has changed, especially at 340 mμ, there is no stepwise change - which in this method is characteristic of reaction between the substances under examination.

Final confirmation of the very important fact that no reaction occurs between cis-dioxalatodiaquochromiate and propylenediamine at pH 4.8 was obtained by application of the "Continuous variation method".

Here 50(1 - x) mls of 0.0092M cis-dioxalato-diaquochromiate (pH 4.8) was mixed with 50x mls of 0.0092M propylenediamine (brought to pH 4.8 with nitric acid) where $x < 1$. The resultant solutions were heated for 25 mins, cooled and made up to volume (0.0092M). The optical densities were then read for each solution at 360, 380, 400, 420 and 560 mμ. (see Appendix for readings). From these readings it was found that the quantity Y, defined by:

$$Y = D_2 - D_3$$

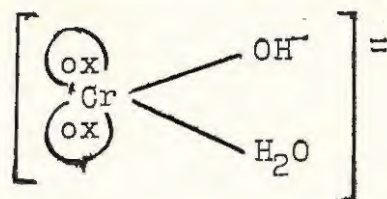
where D_2 = optical density of heated solutions as found experimentally.

D_3 = optical density of heated cis-dioxalatodiaquochromate at dilutions used in the experiment (calculated values),

was negligible, indicating no reaction between the metal ion and the ligand had occurred under the conditions employed.

Reaction at pH 8.0.

Carrying this investigation further, the "Continuous Variation method" was applied to the reaction between cis-dioxalatodiaquochromate and propylenediamine at pH 8.0. Virtually, this is the reaction between propylenediamine and cis-dioxalatohydroxo-aquochromate.



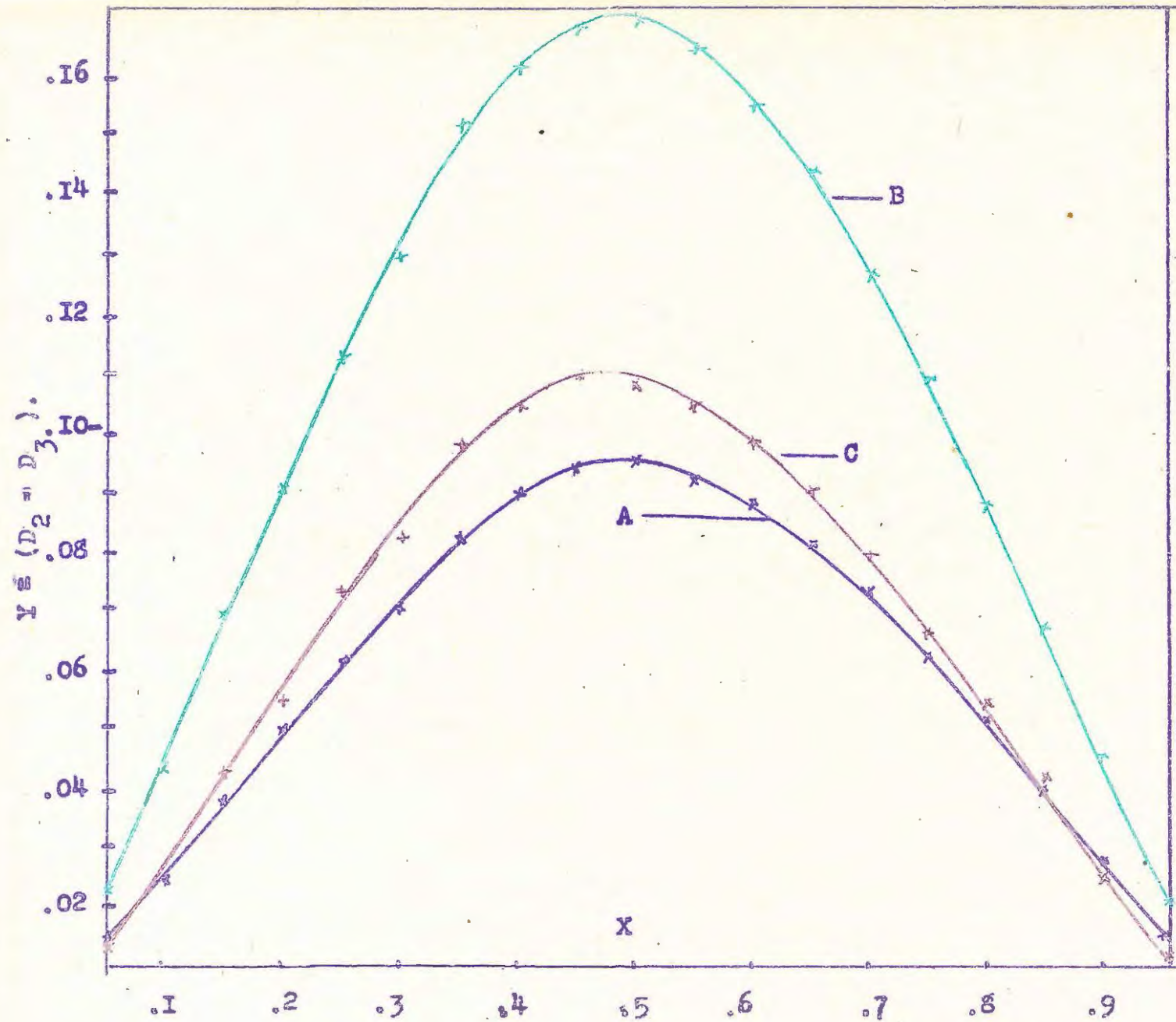
Now on heating the latter substance in solution a change occurs with a resultant change in the spectrophotometric curve (29). These facts were borne in mind when choosing the wavelengths at which the optical densities of the reacted solutions were to be measured. Thus at 400 and 440 mμ both the "isolated complex" and the cis-dioxalatohydroxo-aquochromate have the same optical densities.

In this experiment 50(1 - x) mls. of 0.0092 M potassium cis-dioxalatohydroxo-aquochromate (pH 8.01) were mixed with 50x mls of 0.0092 M propylenediamine (pH 8.02), where $x < 1$, and the solutions boiled for 30

FIG. 42

Continuous Variation Method
applied to Potassium cis-
dioxalatodiaquochromate and
propylenediamine at pH 8.0

- (A) At 360 mμ.
(B) At 380 mμ.
(C) At 400 mμ.



mins. On cooling, these were made up to volume (0.0092M) and the optical densities measured at 360, 380, 400, 440 and 460 mμ. These optical densities minus the calculated optical densities for heated cis-dioxalatohydroxoquo-chromiate at the same dilutions as those used in the experiment, were plotted against x. From the graph (Fig. 42) it is seen that $x = .5$

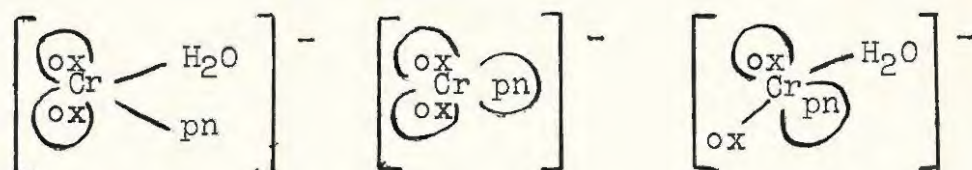
n = no. of moles of ligand combining
with 1 mole of metal ion

$$= \frac{1}{1 - x}$$

$$= \frac{.5}{.5}$$

$$= 1$$

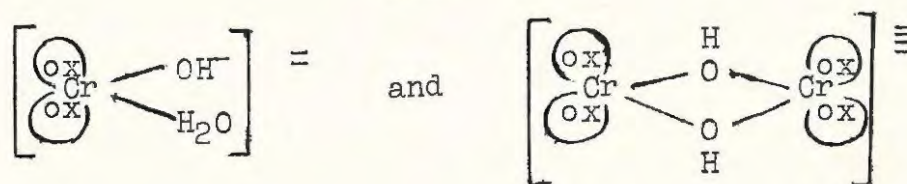
Therefore the complex formed must be one of the following types :



Electrochromatograms 27 and 28 were then run on the solutions for which

$$x = 0, .1, .2, .3, .4, .5.$$

In electrochromatogram 27 spot (a) ($x = 0$) corresponds to the cis-dioxalatohydroxoquo-chromiate or the related complex; owing to the diffuse nature of the spot, probably both

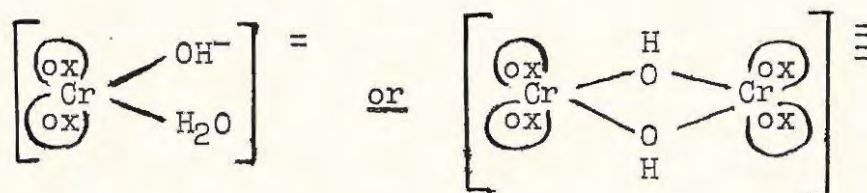


are present.

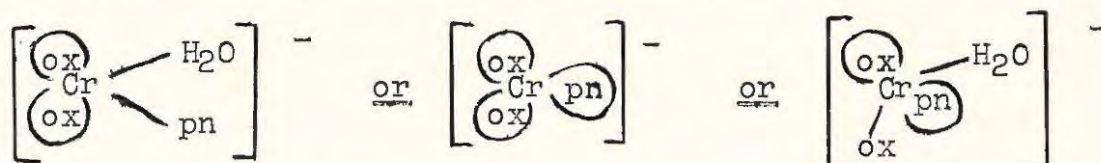
Spots (b) and (c) ($x = .1$) correspond to a reaction product consisting either of



and an unreacted product, either



respectively. The same reasoning may be applied to spots (d) and (e) ($x = .2$) of Electrochromatogram 27 and to spots (a) and (b) ($x = .3$) and (c) and (d) ($x = .4$) of Electrochromatogram 28. Spot (e) ($x = .5$) of Electrochromatogram 28 corresponds to the product of the complete reaction in the formation of one or more of the following :



Following the potentiometric evidence discussed earlier in this chapter, relevant to the reaction between cis-dioxalatodiaquochromiate and propylenediamine (1 : 1, 1 : 2 and 1 : 3 moles), it must be concluded that the product is probably the fully chelated complex :

Log. Optical Density.

-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4

Wavelength $m\mu$.

FIG. 43

(A) Potassium cis-dioxalatodiaquochromate
and ethylenediamine heated for 7
hours at 90° C (0.0092 M)

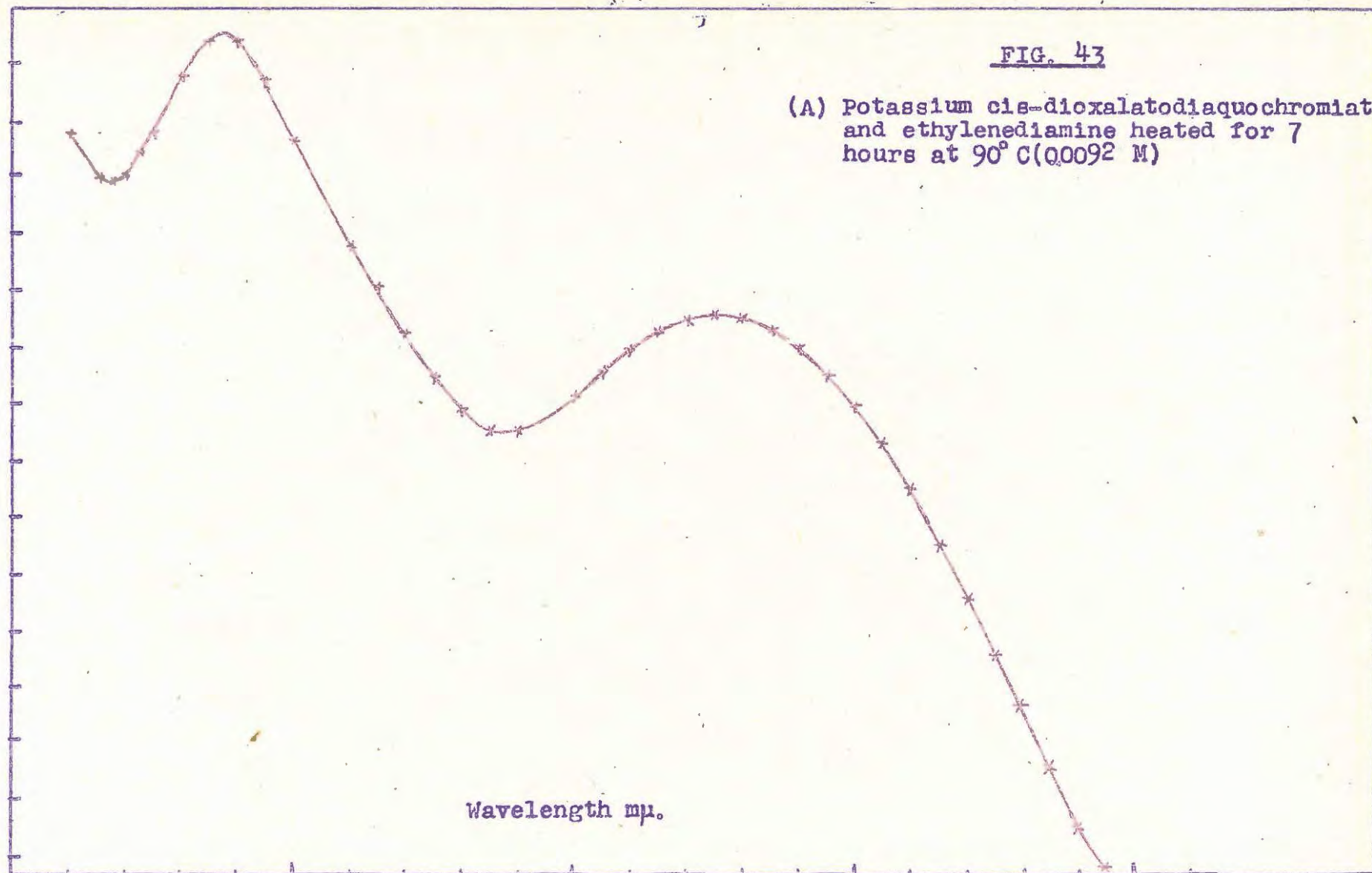
300

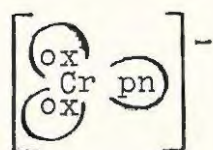
400

500

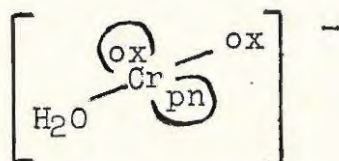
600

700





or, if the reaction has proceeded further according to the reaction course outlined above, the first oxalate ring will have opened up :



B. Reactions with ethylenediamine

Preliminary experiments were carried out with ethylenediamine similar to those with propylenediamine. In all cases the spectrophotometric curves for these two, under similar conditions of reaction, were of the same general shape, although not generally having identical optical densities at any particular wavelength. This is to be expected as they are closely related members of the homologous series of aliphatic amines :



In the first experiment cis-dioxalatodiaquo-chromiate (pH 4.6) was mixed with ethylenediamine (pH 12.0) in the mole ratio of 1 : 9. The solution was heated for 7 hours at 85 - 95°C, cooled, made up to volume (0.0092M) and then aged for 4 days. The spectrophotometric curve of this solution (pH 10.33) is given in Fig. 43. Com-

parison of this curve and that of Fig. 34 shows the close similarity of the spectrophotometric curves of the reaction products of propylenediamine and ethylenediamine. Electrochromatogram 21 reveals that the complex is cationic and probably has a structure corresponding to the type :



It will be recalled that potentiometric data for the reaction between cis-dioxalatodiaquochromiate and propylenediamine (1 : 1, 1 : 2, and 1 : 3 moles) indicated that the products were mixed and fitted a general systematic scheme of successive reactions. There is no reason to doubt that analagous reactions with ethylenediamine will follow a similar course. No potentiometric data were obtained in the present case owing to the difficulties likely to be encountered in interpreting the titration curve in the presence of a large excess of ethylenediamine, but in view of the above considerations it is assumed that the reaction product is a mixture as before. This mixture will consist of closely related complexes with successively displaced oxalate molecules.

In an attempt to follow the course of the above reactions a similar solution (containing 1 mole of cis-dioxalatodiaquochromiate to 9 moles of ethylenediamine, 0.0092M in Cr.) was stored in ice immediately after mixing in order to slow down the reaction rate. As before the

FIG. 44

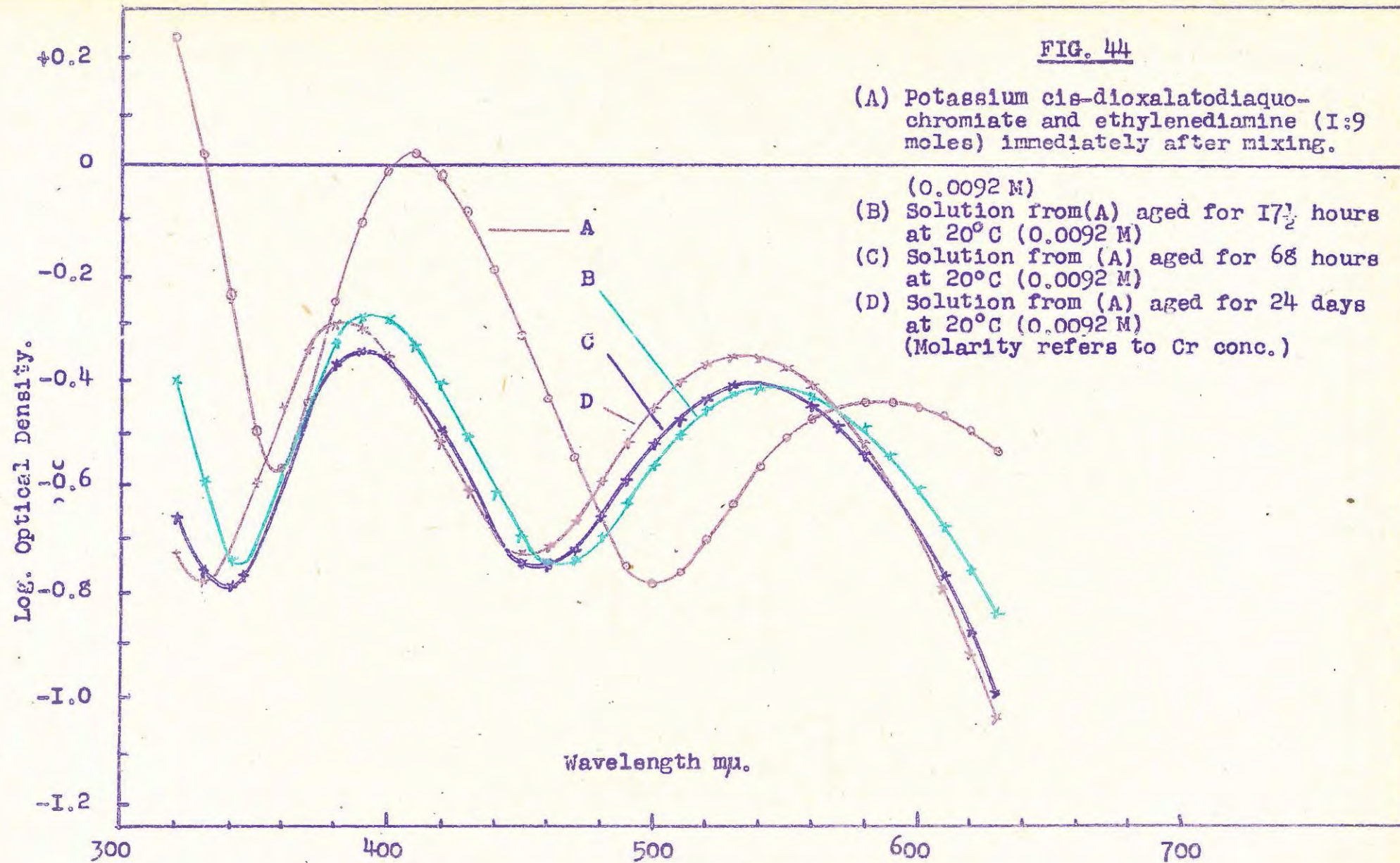
(A) Potassium cis-dioxalatodiaquo-chromate and ethylenediamine (1:9 moles) immediately after mixing.

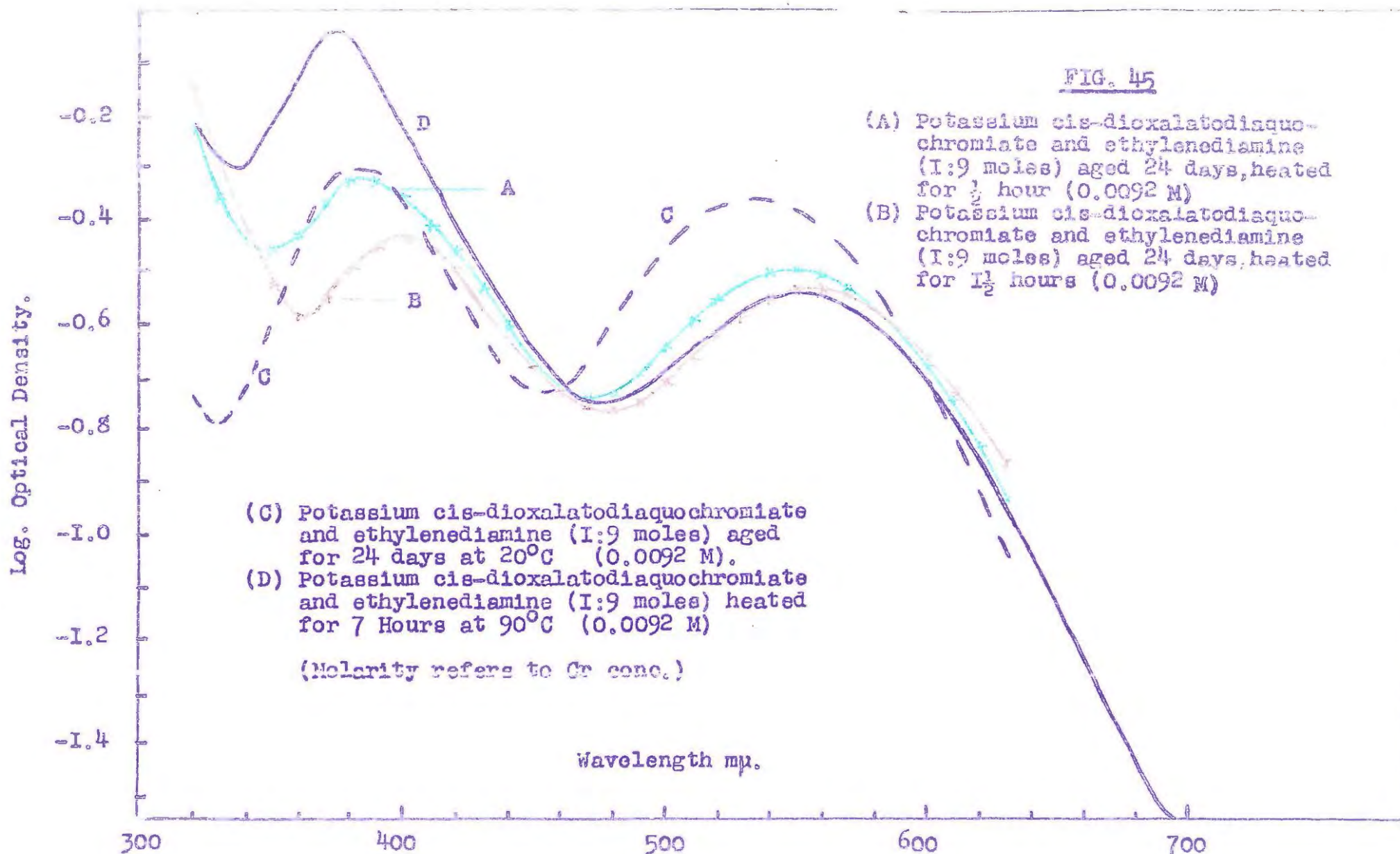
(0.0092 M)

(B) Solution from (A) aged for 17½ hours at 20°C (0.0092 M)

(C) Solution from (A) aged for 68 hours at 20°C (0.0092 M)

(D) Solution from (A) aged for 24 days at 20°C (0.0092 M)
(Molarity refers to Cr conc.)





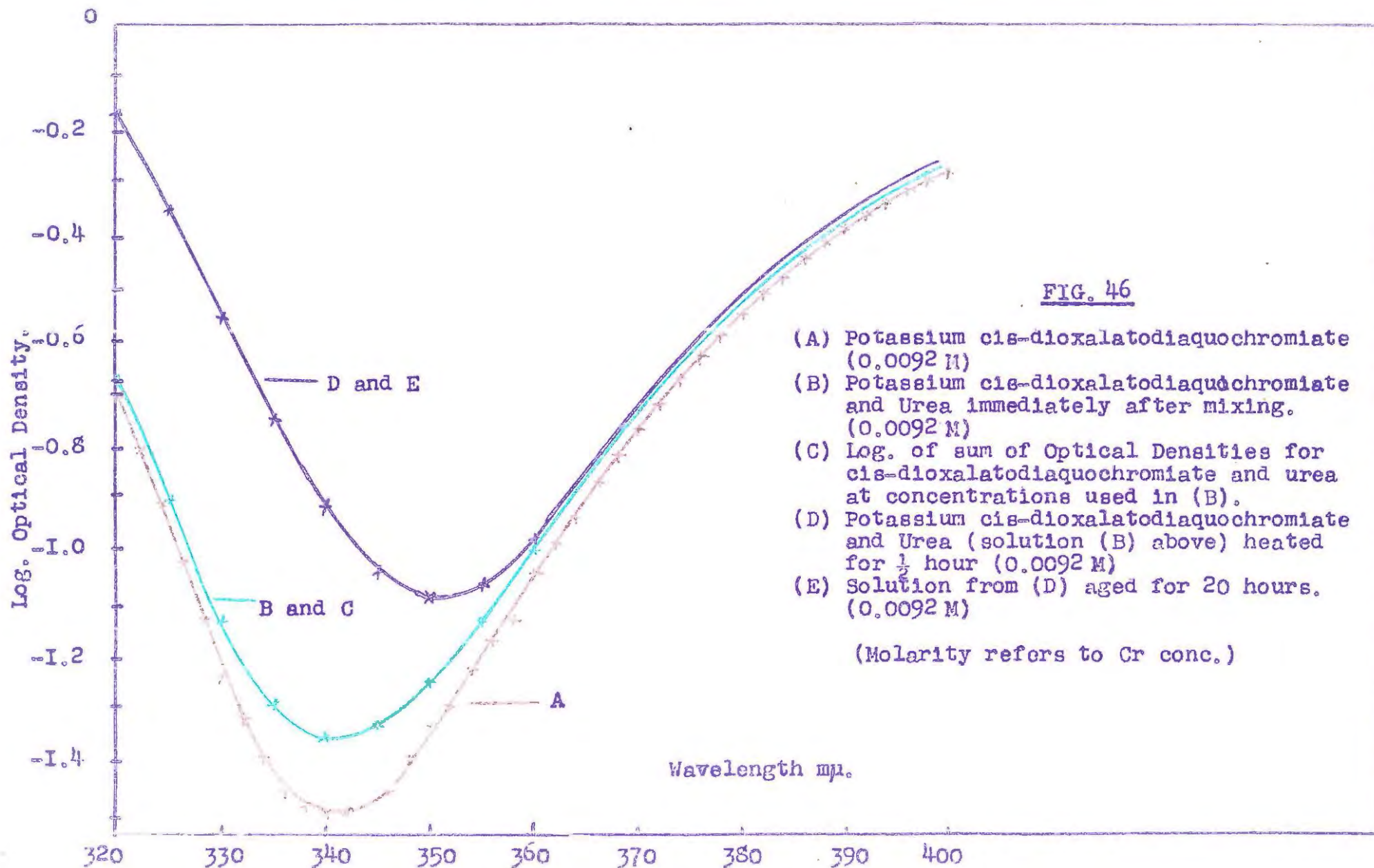
optical densities of this ice-cooled solution were measured in the range 320 - 630 mμ. The rest of the solution was then placed in a well-stoppered flask in a water bath thermostatically controlled at 20°C and the spectrophotometric curves obtained after 17½ hours, 68 hours and 24 days (Fig. 44, Curves A, B, C, D). The pH values of the four solutions were 12.2, 10.7, 10.59 and 10.34 respectively. The complexes in the last three solutions are shown by electrochromatograms 22, 23, 24 to be cationic.

After standing for 24 days aliquots of the solution (corresponding to Fig. 44, Curve D) were boiled for ½ hour and 1½ hours, cooled, and made up to volume (0.0092M).

The effects of aging at 20°C, of heating alone and of aging for 24 days followed by heating are shown in Fig. 45 where the curve of Fig. 43 and curve D of Fig. 44 have been reproduced for comparison with the two solutions boiled for varying periods after 24 days aging at 20°C.

The similarity in shape of the latter two curves (Fig. 45 A and B) to that of the heated solution (Fig. 45 D) subsequently aged for only four days indicates that the final products are the same. On the other hand aging alone (Fig. 45 C) appears to give rise to a different product.

Thus it would appear that the products of the reaction from aging cis-dioxalatodiaquochromiate and ethylenediamine (1 : 9 moles) at 20°C are intermediate to the products produced by heating cis-dioxalatodiaquochromiate



and ethylenediamine (1 : 9 moles). In the absence of titration and other data it is not possible at this stage to ascribe a definite structure to this intermediate product, but in view of the fact that the mixture has been shown to contain complexes homogeneous as regards electrical charge, and that this charge is positive it is evident that more or less oxalate has been displaced from the original cis-dioxalato compound. The alternative structures indicated above represent two possible configurations although there is no doubt that other structures may fit the facts equally well.

C. Reaction with Urea

When cis-dioxalatodiaquochromiate and urea (mole ration 1 : 6) were mixed the solution boiled for $\frac{1}{2}$ hour, cooled, and made up to volume (0.0092M), the spectrophotometric curve of this solution (Fig. 46) showed large changes in optical density in the range 320 - 350 m μ with a shift in the minimum from 341 to 351 m μ . On these grounds it would appear that the urea has formed a complex with the chromium ion. But before such a conclusion can be drawn several factors must be taken into account.

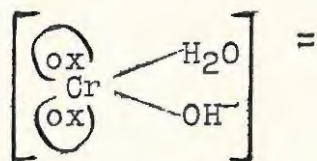
Attempts were made to prepare such a complex on a larger scale by mixing the appropriate amounts of cis-dioxalatodiaquochromiate and urea. This mixture was then heated for $\frac{1}{2}$ hour (pH 4.35). No crystals separated out on allowing this solution to stand and cool hence it was decided to evaporate down the solution to crystallisa-

tion. The result of this treatment was to produce chromium hydroxide.

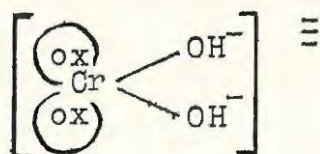
This can be explained on the grounds that urea, when heated in solution, decomposes to give ammonia with a consequent rise in the pH. At high pH values several things may occur to cis-dioxalatodiaquochromiate especially with the application of heat.

(i) dioxalatodiaquochromiate decomposes to give chromium hydroxide.

(ii) cis-dioxalatohydroxo-aquochromiate

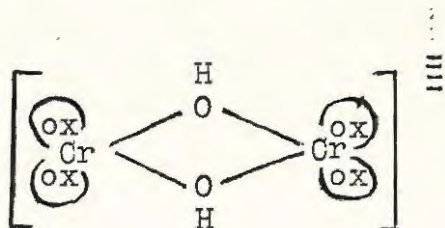


or, if the pH is around 10, cis-dioxalatodihydroxo-chromiate



may be formed.

(iii) cis-dioxalatohydroxo-aquochromiate may form the related complex



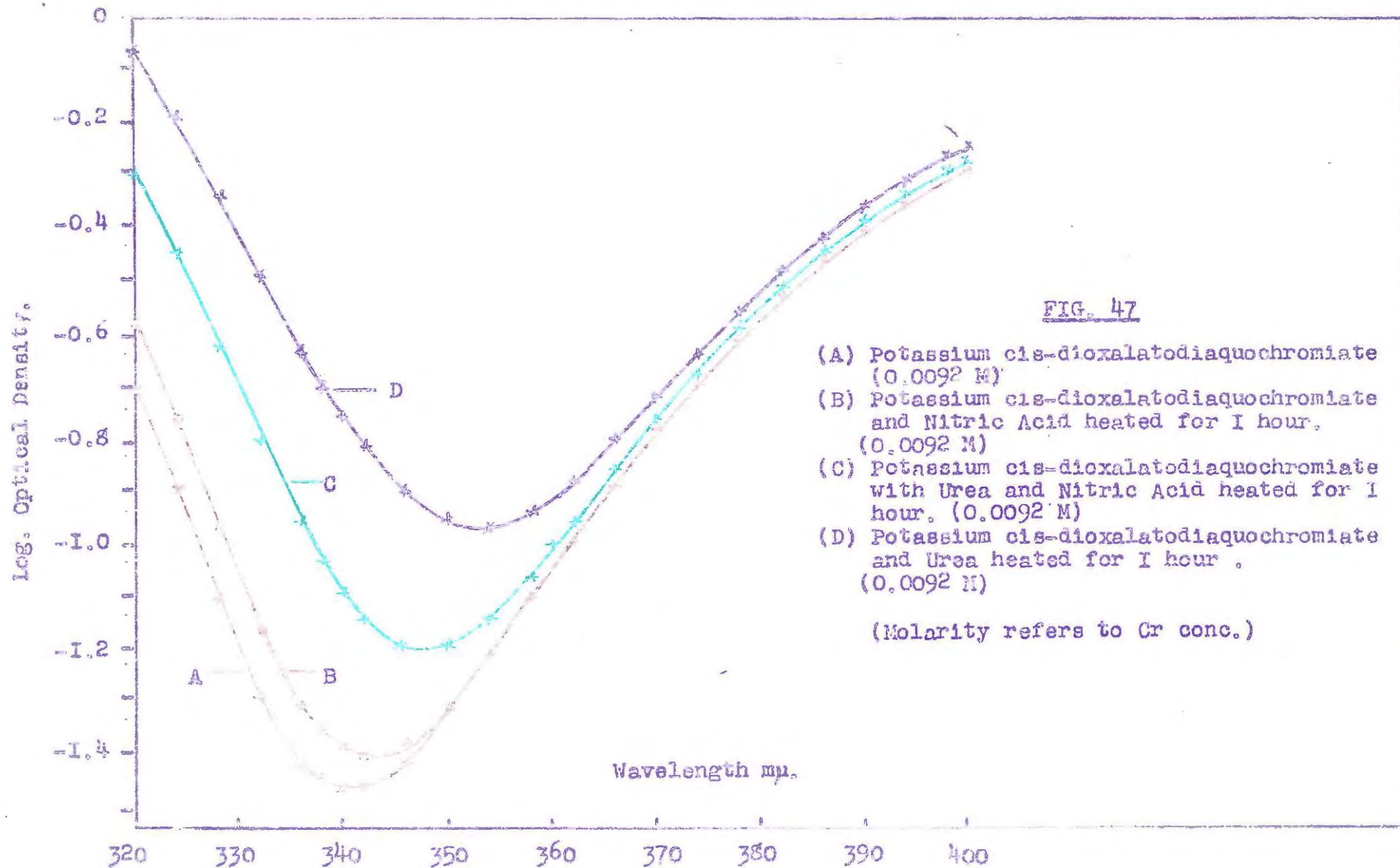
One of these factors, or a combination of more than one, may account for the differences between the graphs of Fig. 46 D and Fig. 46 A and C. Hence it was

decided to carry out the reaction at controlled pH.

A preliminary blank was performed to find out the best method of controlling the pH by the addition of nitric acid. Nitric acid was chosen, as the nitrate ion, which does not readily co-ordinate, would not complicate the issue.

A solution of 100 ml. cis-dioxalatodiaquochromiate (0.0092M) and 0.3360 gms urea C.P. (1 : 6 moles) was treated according to the following table. The purpose of this treatment was to maintain the pH of the solution below 4 by suitable additions of nitric acid. Hence the above solution was boiled for short periods, made up to volume and the pH noted; if this had risen above 4 then nitric acid was added and the pH measured again. This process was repeated for a total of 2 hours boiling with appropriate additions of nitric acid.

Solution	Treatment	Boiling time (mins)	Volume of N/5 HNO ₃ added (mls)	pH after making up to 100 mls
<u>cis</u> -dioxalatodiaquochromiate + urea	1	-	-	4.89
	2	-	5	2.34
	3	15	-	2.50
	4	15	-	2.82
	5	30	-	5.60
	6	-	5	2.38
	7	30	-	5.10
	8	-	4	2.41
	9	30	-	4.70



As the pH recorded in the table above remained fairly constant it was decided to carry out the reaction between cis-dioxalatodiaquochromiate and urea (1 : 6 moles) by controlling the pH to be ca. 4 with suitable additions of nitric acid. In addition, as blank corrections, the reaction was carried out without adding nitric acid to control the pH and the effect of nitric on cis-dioxalatodiaquochromiate alone was investigated also. Finally, by means of a fourth experiment, the pH changes occurring on each addition of nitric acid to the cis-dioxalatodiaquochromiate and urea after boiling were obtained. Accordingly the following solutions were prepared :

(1) 50 mls of cis-dioxalatodiaquochromiate (0.0092M) and 0.168 gms urea (1 : 6 moles). Heated for 1 hour, cooled and made up to 50 mls.

pH before heating = 4.80

pH after heating = 6.75

(2) 50 mls of cis-dioxalatodiaquochromiate (0.0092M) and 0.168 gms urea (1 : 6 moles).

Added 0.5 mls $N/5$ HNO_3 pH = 2.91
then boiled for 30 mins. and added 0.5 mls $N/5$ HNO_3
boiled for further 15 mins. and added 1.0 mls $N/5$ HNO_3
boiled for further 15 mins. and added 1.0 mls $N/5$ HNO_3
then made up to 50 mls pH = 2.75

(3) 50 mls. of cis-dioxalatodiaquochromiate (0.0092M).

Added 0.5 mls $N/5$ HNO_3 pH = 2.90
Boiled for 30 mins. then added 0.5 mls $N/5$ HNO_3

then boiled for 15 mins. and added 1.0 mls $N/5$ HNO_3
then boiled for 15 mins. and added 1.0 mls $N/5$ HNO_3
and made up to 50 mls. pH = 2.28

(4) 100 mls. of cis-dioxalatodiaquochromiate
(0.0092M) and 0.3360 gms urea (1 : 6 moles) treated as
follows :

Added 1.0 mls $N/5$ HNO_3 pH = 3.19
Boiled for 30 mins., cooled, made up to 100 ml.

pH = 5.90

Added 1.0 mls $N/5$ HNO_3 pH = 3.10
Boiled for 15 mins, cooled, made up to 100 ml.

pH = 6.25

Added 2.0 mls. $N/5$ HNO_3 pH = 2.76
Boiled for 15 mins, cooled, made up to 100 ml.

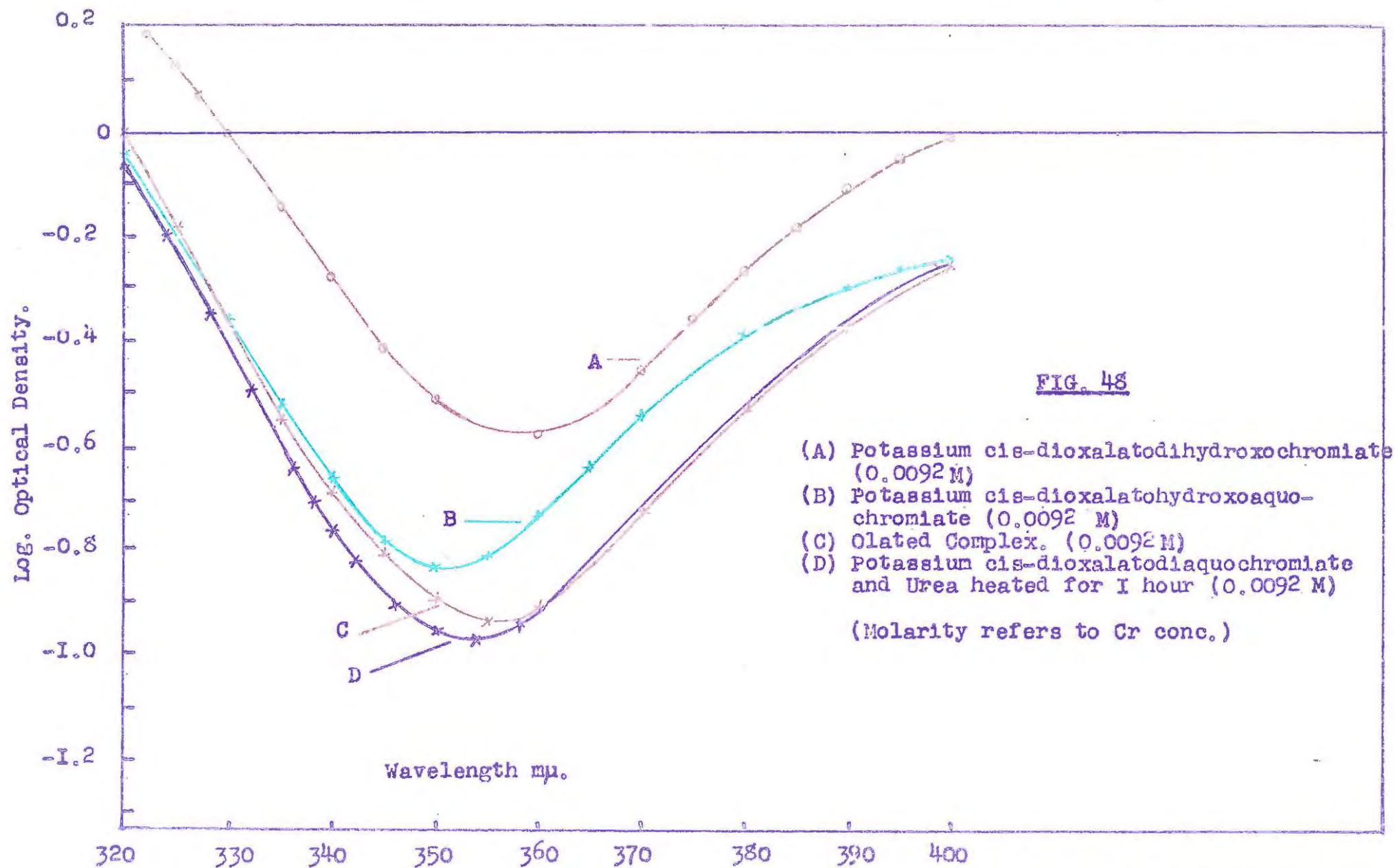
pH = 6.09

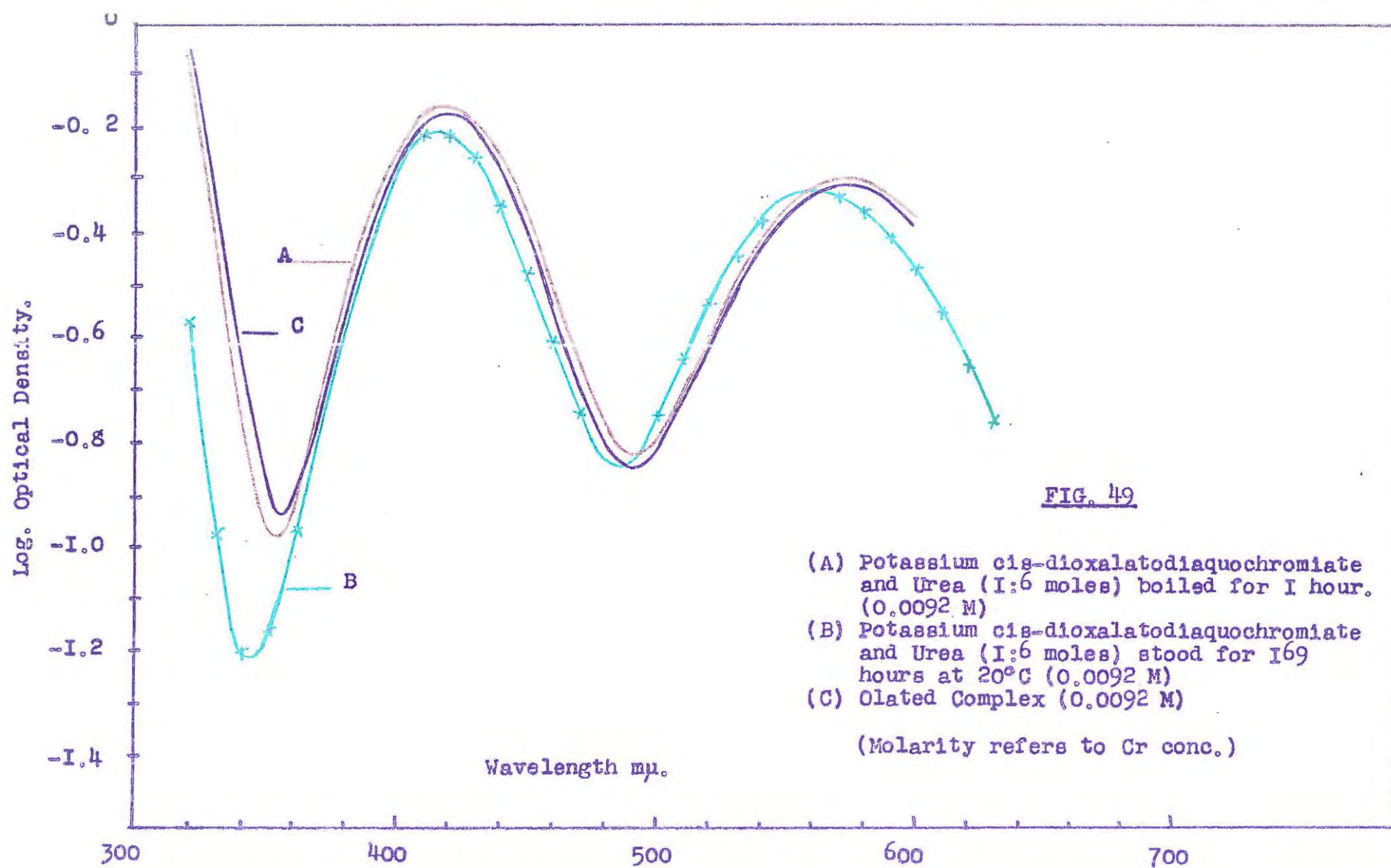
Added 2.0 mls. $N/5$ HNO_3 pH = 2.70

Solution (1) shows that the pH variation on
heating cis-dioxalatodiaquochromiate and urea alone is
quite considerable (4.8 - 6.75). But the pH control
blank (solution 4) shows the variations in pH to be even
more considerable when nitric acid is added.

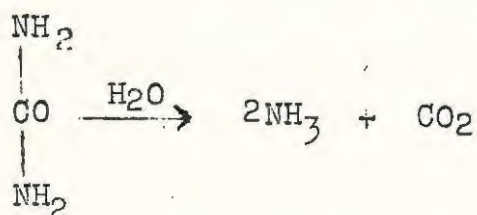
pH 3.19 - 5.9
3.10 - 6.25
2.76 - 6.09

Although this defeats the whole purpose of pH
control between 3.5 and 4.5, it does reveal the fact that
the addition of nitric acid swings the following reaction





to the right



by removing the ammonia. This loss of nitric acid causes a rise in pH.

It is still not quite certain whether a complex has been formed with urea. The possibility seems even more remote when the spectrophotometric curve for cis-dioxalatodiaquochromate + urea (1 : 6 moles) heated together for 1 hour and made up to be 0.0092M, is compared with the curve for the isolated complex as obtained by Burley (Fig. 48). These two curves are practically identical over the range 320 - 400 mμ.

Carrying the investigation a step further, the following reactions were studied spectrophotometrically. Using 0.0092M cis-dioxalatodiaquochromate

(1) 50 mls + 0.1680 gms urea (1 : 6 moles).

Heated for 1 hour, cooled and made up to 50 ml.

pH before heating = 4.48

pH after heating = 6.36

(2) 50 mls + 0.1680 gms urea (1 : 6 moles).

Stood at 20°C. for 169 hours

pH before heating = 4.80

pH after heating = 5.70

The resultant curves are shown in Fig. 49.

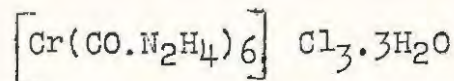
The curve for solution (1) coincides well with that for the related complex and fairly well with that for cis-dioxalatodiaquochromiate except in the region of the minimum 320 - 360 mμ.

The charge on the complex in both the above solutions is shown by electrochromatogram 29 to be negative.

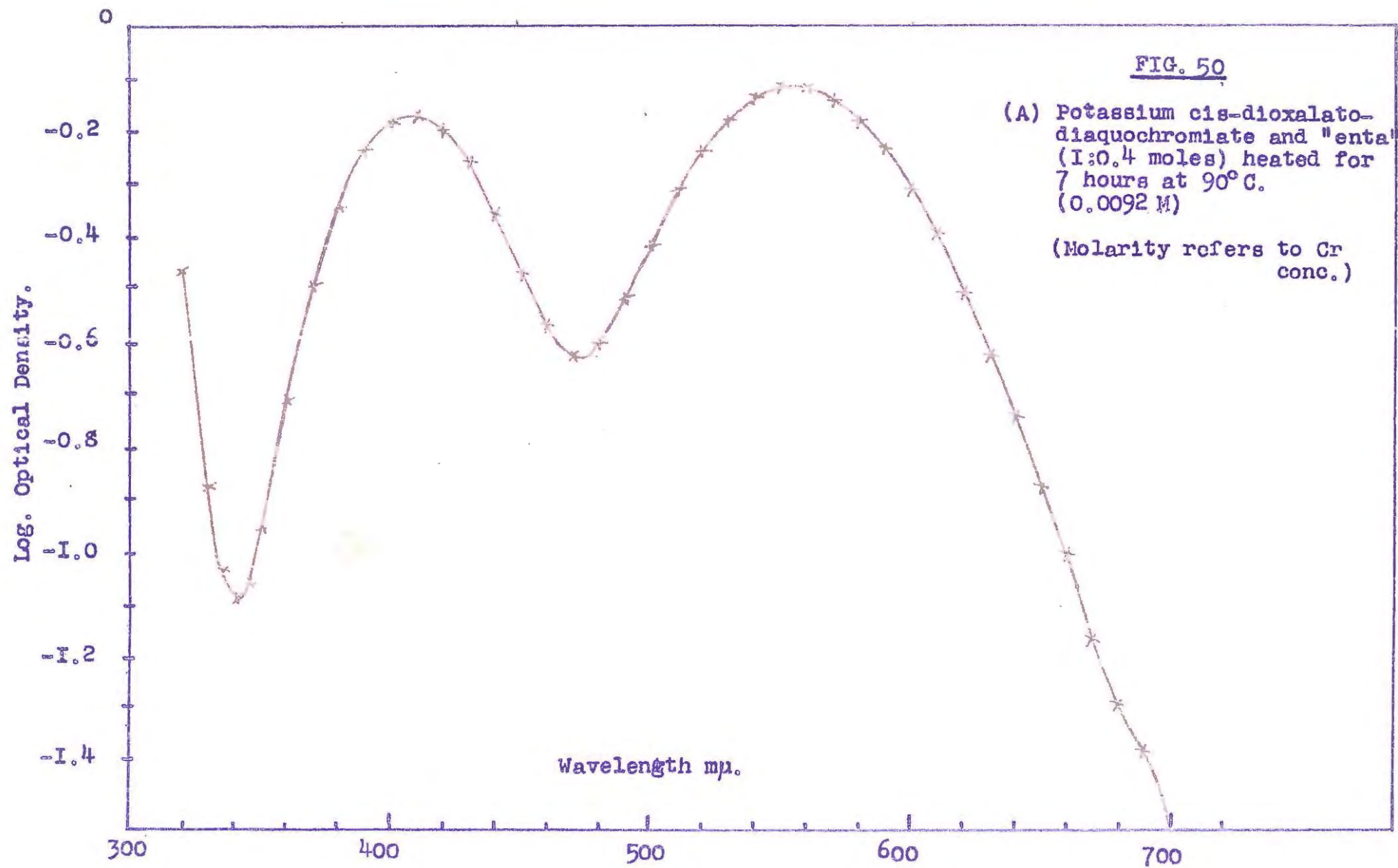
As revealed above the addition of nitric acid at various stages during the boiling of cis-dioxalatodiaquochromiate and urea (1 : 6 moles) does not maintain the pH at a constant value but instead causes further decomposition of the urea to give ammonia which raises the pH. Nevertheless it is possible that boiling cis-dioxalatodiaquochromiate and urea may be a good method for preparing the related complex as under these conditions urea does not co-ordinate with cis-dioxalatodiaquochromiate.

The conclusion which can be drawn from this evidence is that no reaction occurs between cis-dioxalatodiaquochromiate and urea under the conditions of the experiment.

Nevertheless it is possible to prepare chromium complexes containing urea. Werner and Kalkmann (54) prepared the compound



by treating the product of the action of chromyl chloride on carbamide with moist lead chloride. Pfeiffer (55) obtained a similar compound by the direct action of car-



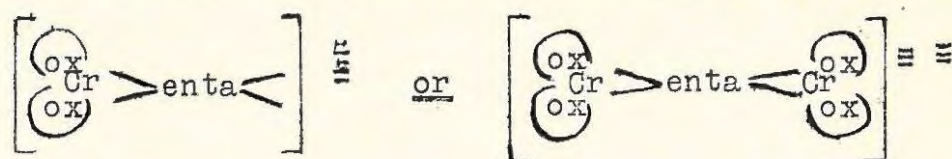
bamide on hydrated chromic salts when the solution is evaporated to a small volume on a water bath.

It would appear that in aqueous systems under dilute conditions urea shows no tendency to enter the chromium complex.

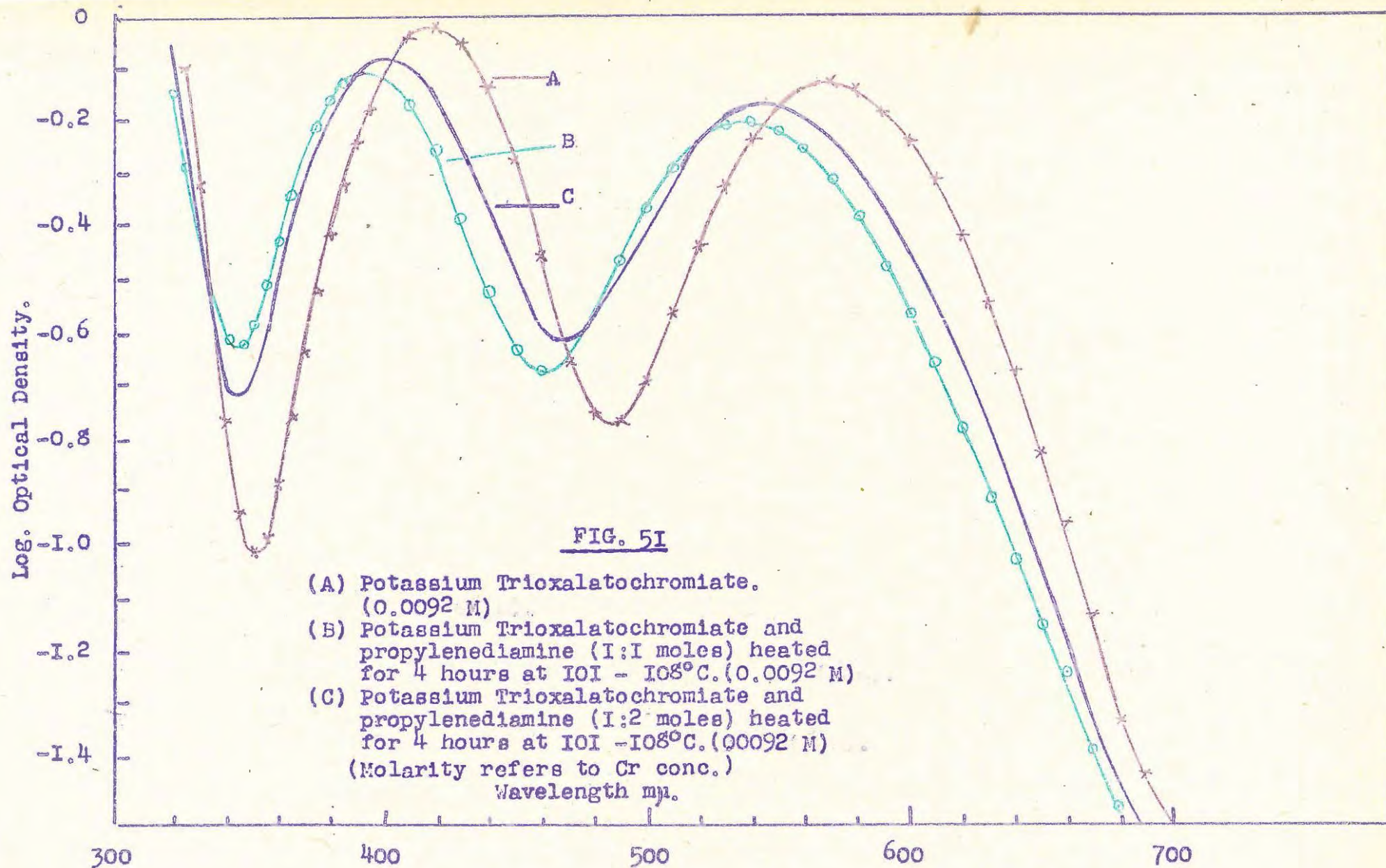
D. Reaction with ethylenediamine tetraacetic acid ("enta")

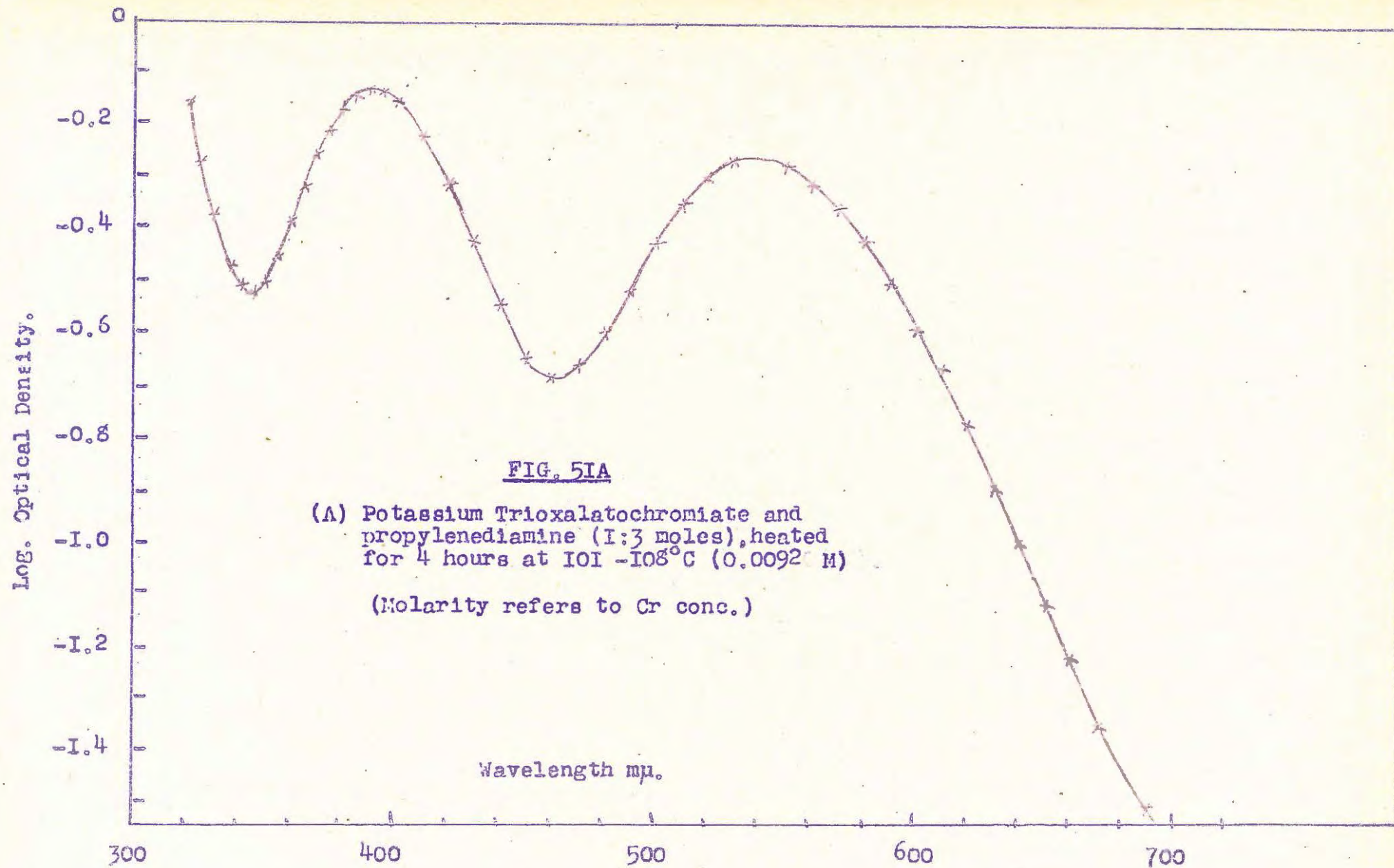
Some preliminary spectrophotometric investigations were carried out on the reaction of this compound with cis-dioxalatodiaquochromiate.

A solution of cis-dioxalatodiaquochromiate (0.0092M) and enta (mole ratio 1 : 0.4) was prepared. This was heated for 7 hours at 85 - 95°C, cooled and made up to volume (0.0092M) then aged for four days (pH = 2.60) and the spectrophotometric curve obtained (Fig. 50). This curve shows a considerable change in general shape from the curve of cis-dioxalatodiaquochromiate and is probably due to the formation of a compound of the type



Further investigation into the reactions between enta and chromium complexes is undertaken in the next chapter.





CHAPTER V.

REACTIONS BETWEEN POTASSIUM TRIOXALATOCHROMIATE
AND AMINO-BASES

In this chapter data dealing with reactions between trioxalatochromiate and amino-bases, similar to those dealt with for cis-dioxalatodiaquochromiate are studied. The object of these researches was to ascertain whether the products of these reactions were the same under similar experimental conditions, and to find the relative stability of the chelated oxalate and amine rings. From a consideration of these two factors it might be possible to formulate a scheme for the course of the reactions involved.

Reactions with propylenediamine.

In the first experiment three solutions of trioxalatochromiate (0.0092M) and propylenediamine were prepared in the mole ratios of 1 : 1, 1 : 2, and 1 : 3. The resultant spectrophotometric curves for these solutions, after heating in an air oven operating at 101 - 108°C for 4 hours, cooling and making up to volume (0.0092M) are given in Fig. 51, with the curve of trioxalatochromiate (0.0092M) for comparison.

These curves are very similar to those obtained by reacting on cis-dioxalatodiaquochromiate under

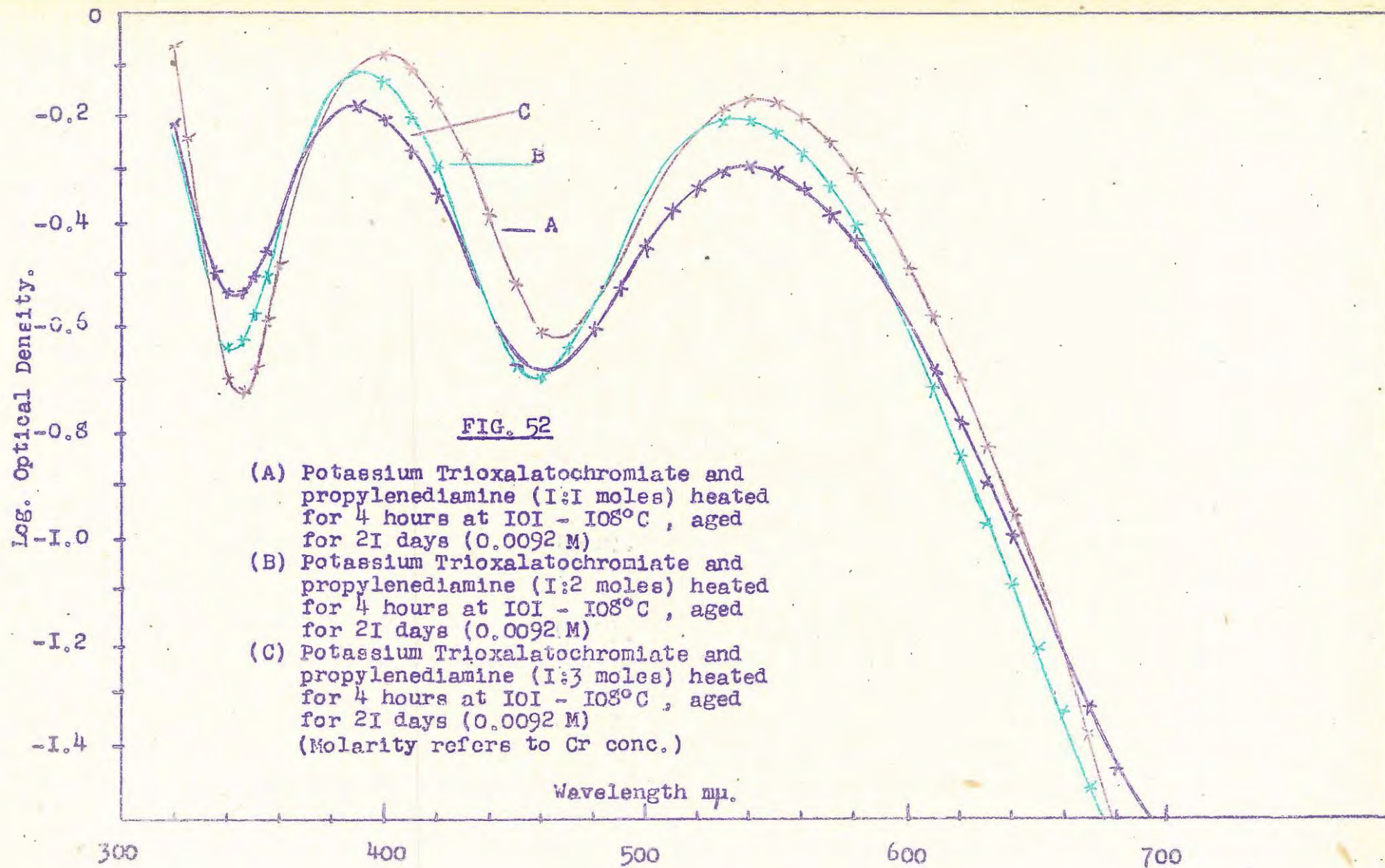
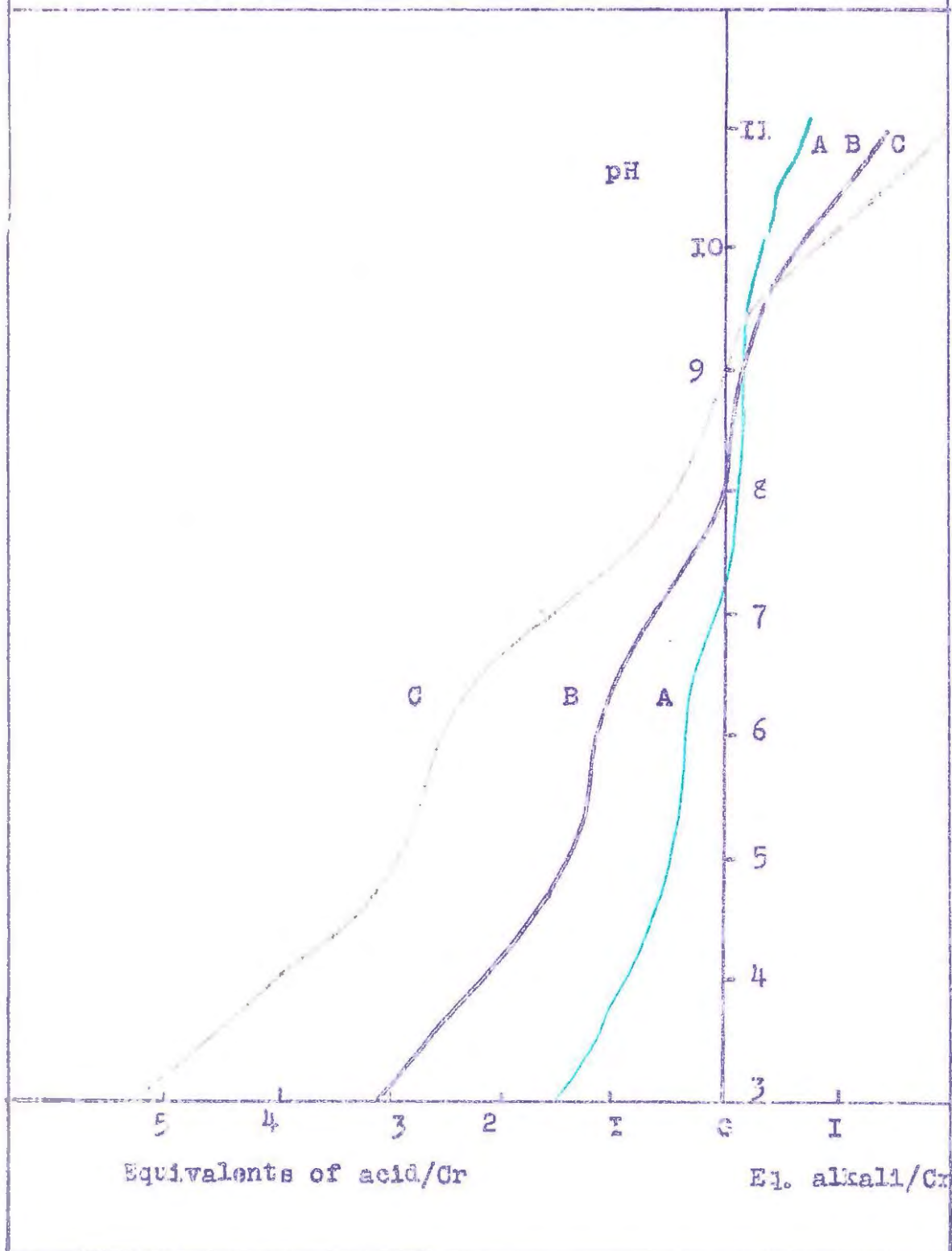


FIG. 53

- (A) Potassium trioxalatochromate and propylenediamine (1:1 moles) heated for 4 hours at 100°C then aged for 21 days. (0.00092 M)
- (B) Potassium trioxalatochromate and propylenediamine (1:2 moles) heated for 4 hours at 100°C then aged for 21 days. (0.00092 M)
- (C) Potassium trioxalatochromate and propylenediamine (1:3 moles) heated for 4 hours at 100°C then aged for 21 days. (0.00092 M)



the same conditions, thus indicating the probability of the formation of the same compounds in the parallel cases.

The three solutions were aged for 21 days and the spectrophotometric curves replotted. (Fig. 52). Once again the curves are very similar to those obtained with the cis-dioxalatodiaquochromiate reactions.

Electrochromatogram 30 revealed that :

(1) trioxalatochromiate and propylenediamine (1 : 1 moles) on heating and aging produced an anionic complex.

(2) trioxalatochromiate and propylenediamine (1 : 2 moles) on heating and aging produced an anionic complex.

(3) trioxalatochromiate and propylenediamine (1 : 3 moles) on heating and aging produced a cationic complex.

(compare with electrochromatogram 20)

The titration curves of these three solutions are recorded in Fig. 53. The curves can be resolved by making the same general assumptions as those used to interpret the titration data of the products of the reaction between cis-dioxalatodiaquochromiate and propylenediamine in Chapter IV.

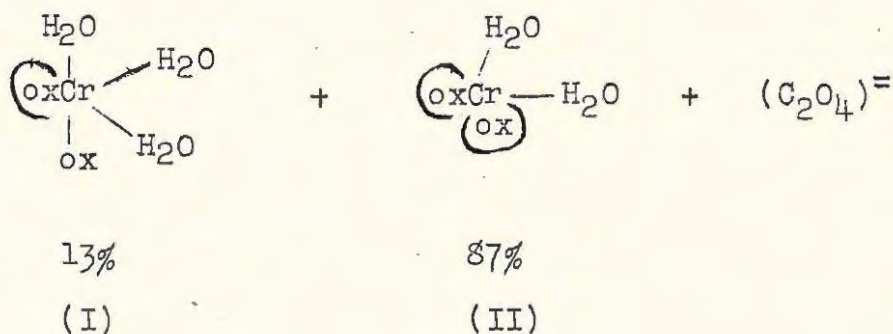
Consider first curve A, for the solution of trioxalatochromiate and propylenediamine (1 : 1 moles). From this curve the following titration values are obtained :

pH 3.0 - 5.0 1.0 equivalents of reagent per Cr.

pH 5.0 - 10.0 0.84 equivalents of reagent per Cr.

The electrophoretic evidence shows the complex to be anionic and accordingly the titration between pH 3 and 5 can be ascribed either to 1 mole per Cr of oxalic acid free in solution or to 1 mole per Cr of oxalic acid functioning as a monodentate ligand.

As an example of the first alternative consider the following structures present in the proportions indicated :



Accepting the above structure on the grounds that it accounts for the titration between pH 3 and 5, corrected as described below, we may calculate the expected titration over the range pH 5 - 10. As described in the previous chapter this titration figure for the range pH 3 - 5 must be corrected for by the factor $\frac{1}{.88}$ when the oxalic acid is free in solution (i.e. unco-ordinated). The corrected value is in the present case 1.13 equivalents/Cr.

In the range pH 5 - 10 :

from Cr atoms :	(2 x .87) + (3 x 13)	= 2.13 eq/Cr
from pn	(2 eq/Cr) :	<u>2.00 "</u>
	Total :	4.13 "
	Found by titration :	<u>0.84 "</u>
	To be accounted for :	3.29 "

Let x = proportion of chelated pn

and y = proportion of unchelated pn.

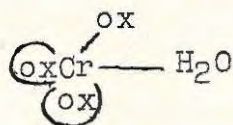
Since each chelated pn loses 4 eq/Cr and each unchelated pn 2 eq/Cr in replacing H₂O groups :

$$4x + 2y = 3.29$$

Thus when x = 0, y = 1.65.

Now this would require a structure with 1.65 moles of unchelated propylenediamine per mole of Cr. Since the solution under consideration has the mole ratio of 1 : 1 this possibility can be excluded.

For the case where there is no free oxalic acid in solution the titration between pH 3 and 5 is due to oxalic acid present as a monodendate ligand (no correction necessary).



(III)

In the range pH 5 - 10 :

Fig. 54.

Group	Cr	oxalate chelated	oxalate unchelated	oxalate free in solution	pn chelated	pn unchelated	pn free in solution	co-ordinated water molecules
pH titration range	-	-	3 - 5	3 - 5	-	5 - 10	5 - 10	5 - 10
Average Composition III	1	2	1	-	-	1.08	-	-

from Cr atoms :	1 eq/Cr.
from pn (2 eq/Cr) :	<u>2 "</u>
Total :	3 "
Found by titration :	<u>0.84"</u>
To be accounted for :	2.16"

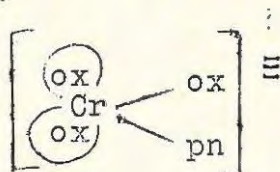
As before, chelated pn loses 4 eq/Cr (4x)
and unchelated pn 2 eq/Cr (2y)

$$4x + 2y = 2.16$$

$$\text{when } x = 0 \qquad y = 1.08$$

Therefore the average composition of the reaction product is given in Fig. 54.

A complex which fits this average composition in addition to the electrophoretic and potentiometric data is given below :



(IIIa)

This complex, which is the product of the reaction between trioxalatochromate and propylenediamine, is a result of the opening of one of the oxalate rings followed by replacement with a monodendate propylenediamine molecule.

The titration data obtained from the second curve, representing the reaction between trioxalatochromate and propylenediamine (1 : 2 moles), are :

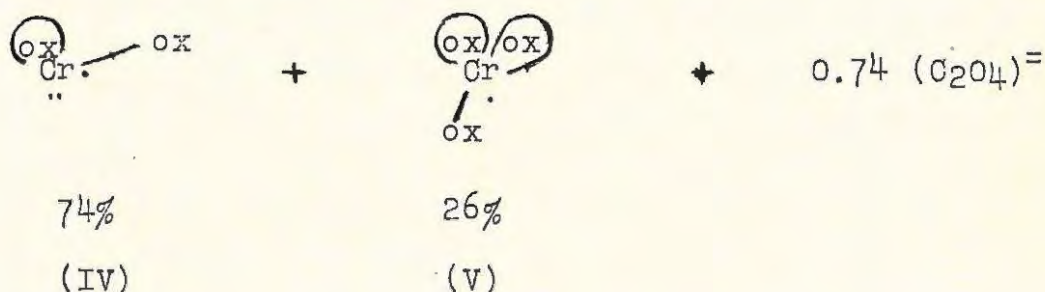
Fig. 55

Group	Cr	oxalate chelated	oxalate unchelated	oxalate free in solution	pn chelated	pn unchelated	pn free in solution	co-ordinated water molecules
pH titration range	-	-	3 - 5	3 - 5	-	5 - 10	5 - 10	5 - 10
74% IV plus 26% V	1.00	1.26	1.00	0.74	1.00	0.22	0.78	0.26
98% IV plus 2% V	1.00	1.02	1.00	0.98	1.00	0.50	0.50	0.50

pH 3 - 5 1.74 equivalents of reagent per Cr.

pH 5 - 10 2.04 equivalents of reagent per Cr.

Consider the structures and their relative proportions as shown below, in which for the moment the co-ordinated propylenediamine is ignored :



The titration of this mixture between pH 3 and 5 requires 1.74 equivalents per Cr. Here no correction has been applied to the titration value obtained from the curve in the pH range 3 - 5.

If the correction is applied to the titration between pH 3 and 5 (although it is realised that not all the oxalate titrating is free in solution) the value becomes 1.98 eq per Cr, which corresponds to structures IV and V, in the proportions 98% and 2% respectively.

The amount of co-ordinated propylenediamine for each of these two cases has been calculated by the same technique as used previously and the average composition is given in Fig. 55.

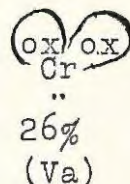
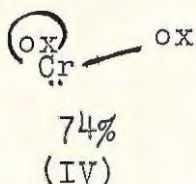
It is not profitable at this stage to indicate in detail the structures of the various components giving rise to the average composition drawn up in the table, but it can be shown that no more than four components are

required in each case.

Although there is some uncertainty as to the exact correction to be applied it is of interest to note that the titration data can be adequately explained on the basis of the structures shown (IV and V), the actual correction employed merely altering the relative proportions of the two components.

Since for each mole of oxalic acid free in solution 0.88 equivalents of reagent are required between pH 3 and 5 it is obviously impossible to differentiate between free oxalic acid in solution and oxalic acid functioning as a monodentate ligand, which would require about 1 equivalent per Cr over the same titration range. For this reason alternative solutions might be expected, but owing to the restrictions imposed by the electrophoretic data the possibilities are limited to the following, in addition to that already discussed. As before the relative proportions of the components appears to depend on the actual correction applied to the titration between pH 3 and 5.

Uncorrected :
(for free oxalic acid)
Found 1.74 eq/Cr.



Corrected :
(for free oxalic acid)
Calculated 1.98 eq/Cr.

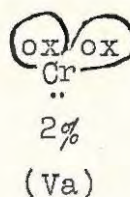
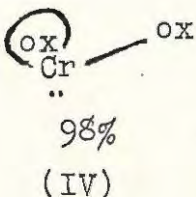


Fig. 56

Group	Cr	oxalate chelated	oxalate unchelated	oxalate free in solution	pn chelated	pn unchelated	pn free in solution	co-ordinated water molecules
pH titration range	-	-	3 - 5	3 - 5	-	5 - 10	5 - 10	5 - 10
74% IV plus 26% Va	1	1.26	0.74	1.00	1	0.35	.65	0.39
98% IV plus 2% Va	1	1.02	0.98	1.00	1.00	0.50	0.50	0.48

The calculated average compositions from these assumptions are given in Fig. 56.

Uncertainty as regards the proportion of free oxalic acid in solution thus renders it impossible to specify the exact composition of the solution with any degree of confidence. Nevertheless the possibilities are definitely restricted and it is sufficient for our purposes to note that the end-products appear to be related in a relatively simple manner. Any differences among them can be accounted for simply in terms of the proportion of displaced oxalate and co-ordinated ethylenediamine (chelated or unchelated).

The two main constituents of the reaction between trioxalatochromate and propylenediamine (1 : 2 moles) appear therefore to be :



The remainder of the titration curve is accounted for by small percentages of complexes which are preceding members to the above two in the reaction series, namely :



All these complexes are consistent with the electrophoretic evidence that an anionic product or

Fig. 57

Group	Cr	oxalate chelated	oxalate unchelated	oxalate free in solution	pn chelated	pn unchelated	pn free in solution	co-ordinated water molecules
pH titration range	-	-	3 - 5	3 - 5	-	5 - 10	5 - 10	5 - 10
66% X plus 34% XI	1	0.66	0.34	2.00	1.00	1.30	1.70	1.04
34% X plus 66% XI	1	0.34	0.66	2.00	1.00	1.50	1.50	1.16

products of the same charge are obtained.

From the third potentiometric titration for the reaction between trioxalatochromiate and propylenediamine (1 : 3 moles) the following data are obtained :

pH 3 - 5	2.34 equivalents of reagent per Cr.
pH 5 - 10	3.75 equivalents of reagent per Cr.

When no correction is applied to the titration between pH 3 - 5 the following structures and proportions fit the potentiometric data in this range :



(X)

66%



(XI)

34%

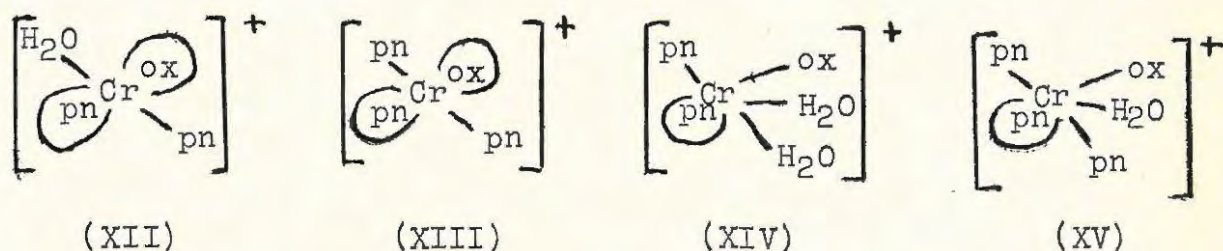
As the electrophoretic evidence on the mixture titrated shows the product or products to be cationic there cannot be more than one mole of oxalate co-ordinated per mole of chromium.

When the correction is applied the titration in the range pH 3 - 5 became 2.66 eq/cr which corresponds to 34% of structure X plus 66% of structure XI.

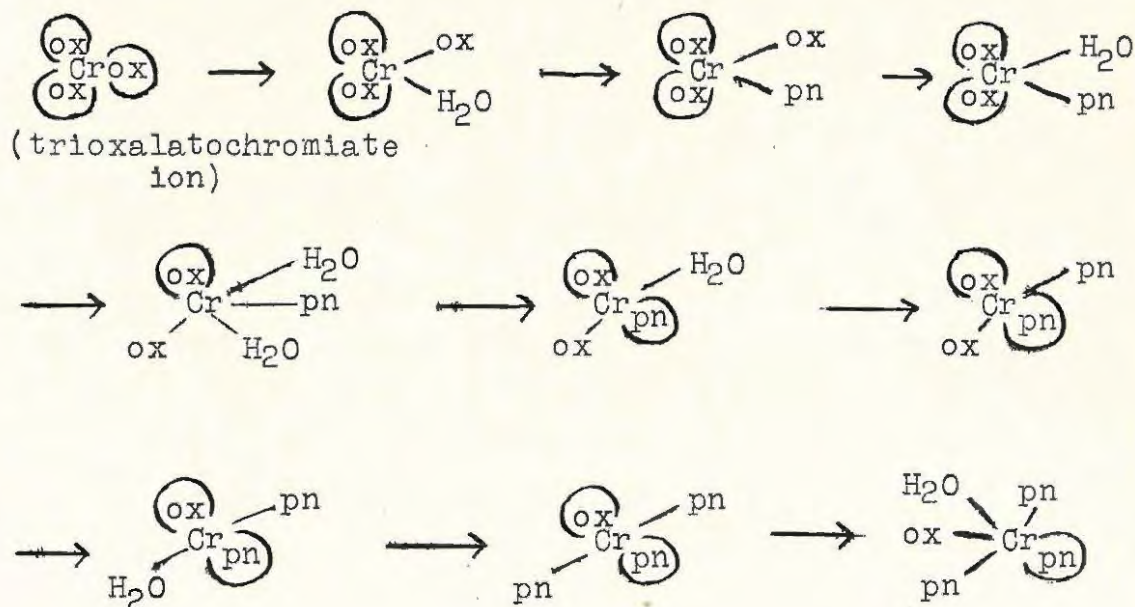
For the two cases (i.e. corrected and uncorrected) the extent of co-ordination with propylenediamine may be calculated, as before, from the titration data. The average compositions calculated for these two cases are given in Fig. 57.

Thus by both interpretations the titration of the reaction product of trioxalatochromiate and propylene-

diamine (1 : 3 moles) is accounted for by different relative proportions of the following four compounds which agree with the electrophoretic evidence :

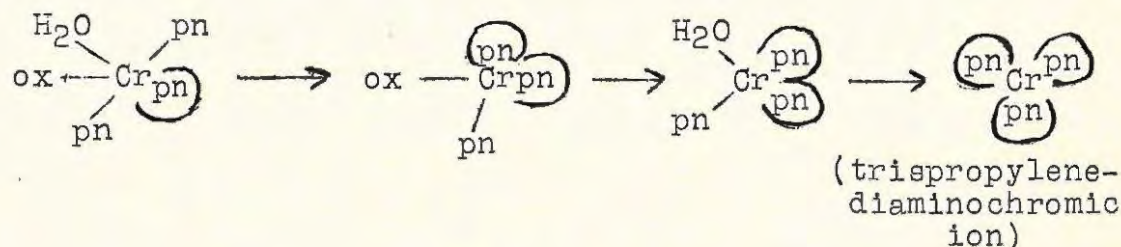


These four compounds, along with those postulated as reaction products in interpreting the previous two titration curves, are all members of a consecutive series of reactions. This series of reactions is analogous to that found in the previous chapter for the reaction between cis-dioxalatodiaquochromate and propylenediamine in various mole ratios, and may be formulated as follows :



According to the above principles further reactions, not encountered under the present experimental

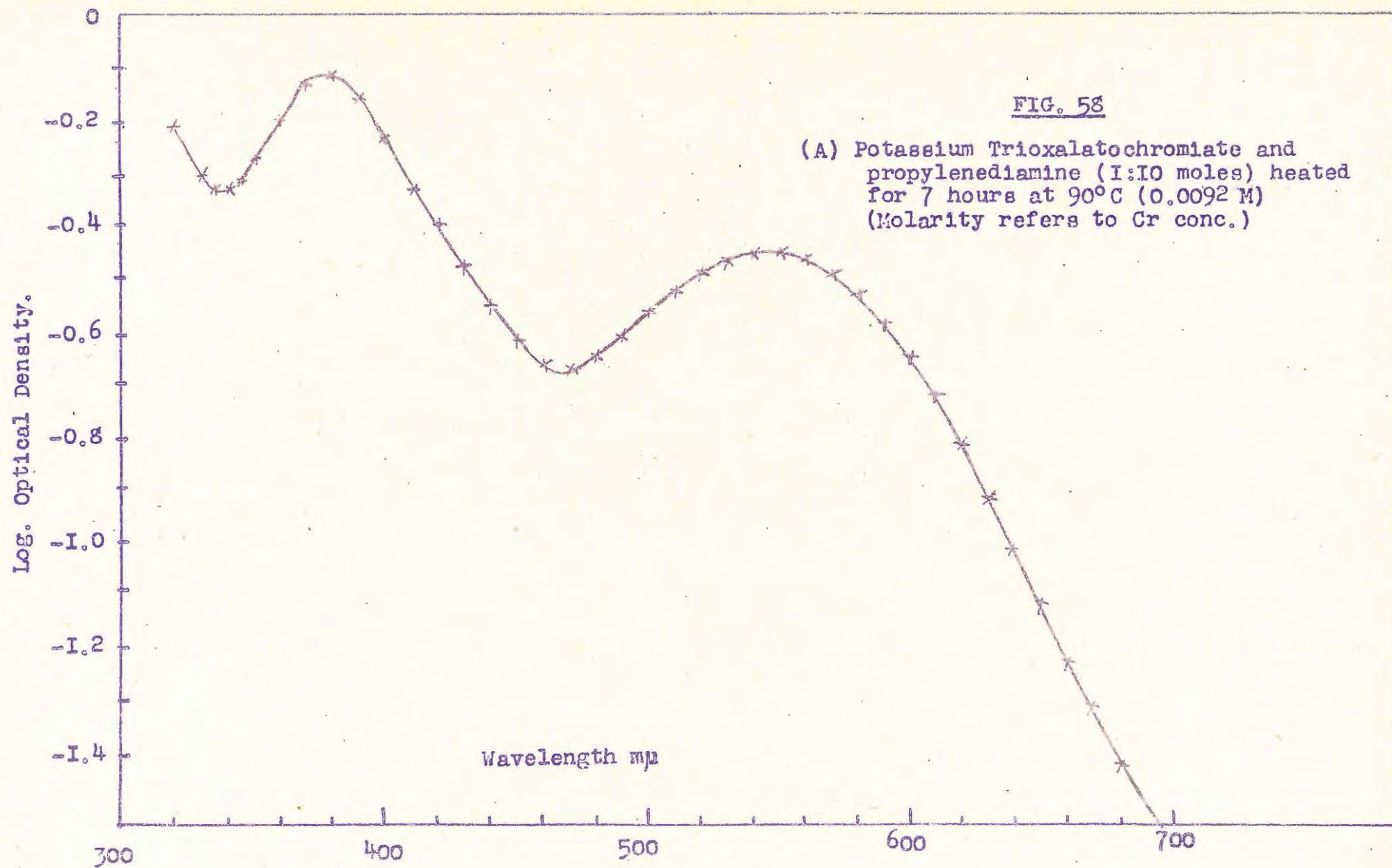
conditions, may be possible, namely :



The actual path of the reactions might be different from that shown above according to the extent to which the experimental conditions favour the cis- or trans- configuration for any given step in the consecutive series of reactions, but the final products may well be the same. Although in the scheme formulated above the reactions are shown as proceeding from left to right it should be borne in mind that at the temperature of the reaction each component may be regarded as being in equilibrium with the preceeding and succeeding member of the series. On this view it is not surprising to find that under the arbitrarily chosen conditions of the experiments several closely related compounds are found to coexist.

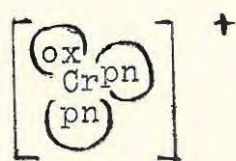
In order to ascertain whether the trispropylene-diaminochromic ion can be obtained according to the scheme outlined above the effect of reacting on trioxalatochromiate with a relatively large proportion of propylenediamine was investigated.

A solution of trioxalatochromiate (0.0092M - pH 5.80) and propylenediamine (pH 11.85) was prepared (mole ratio 1 : 10) and heated at 85 - 95°C for 7 hours. This

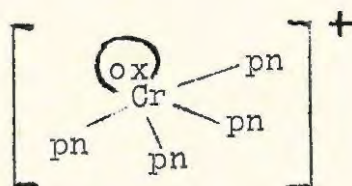


was cooled, made up to volume (0.0092M) and after aging for 4 days (pH 10.32) the spectrophotometric measurements were taken. (Fig. 58). Electrochromatogram 31 shows that a similar cationic complex is formed to that between trioxalatochromate and ethylenediamine which will be discussed later.

Once again this spectrophotometric curve is very similar to that recorded for the reaction with cis-dioxalatodiaquochromate and hence similar reaction products can be assumed :



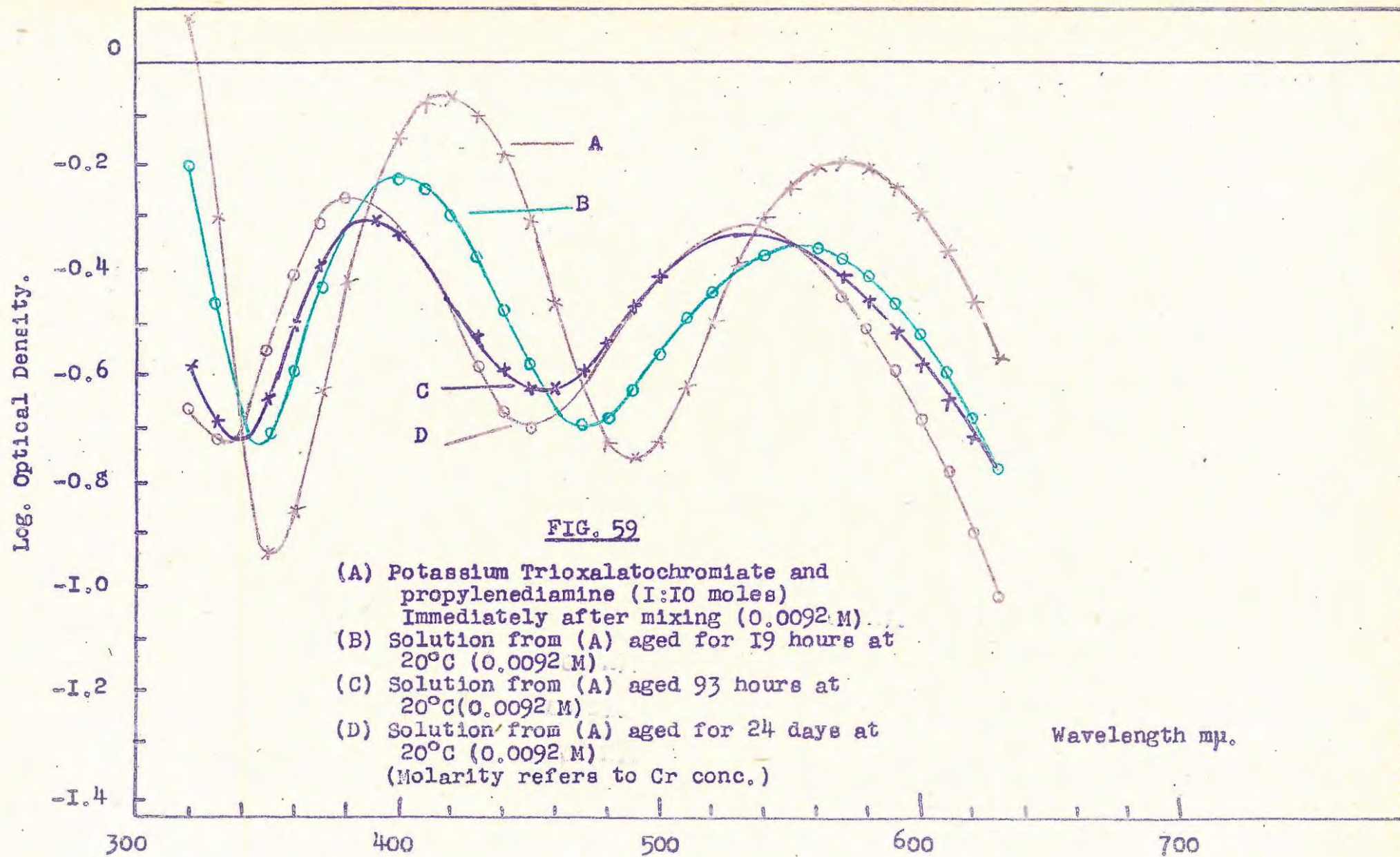
(XVI)



(XVII)

It does not appear therefore that the trispropylene-diaminochromic ion can be prepared simply by direct replacement in the presence of excess propylenediamine since other reaction products appear possible. In an attempt to obtain further information on the reaction it was repeated at a lower temperature.

Thus, as with cis-dioxalatodiaquochromate, a similar reaction to that described above was then carried out at 20°C. A solution of trioxalatochromate and propylenediamine (mole ratio 1 : 10) was prepared and immediately made up to volume (0.0092M). This solution was placed in ice and the spectrophotometer readings recorded on this ice-cooled solution by the same procedure



as already described. The rest of the solution was placed in a well-stoppered flask in a water-bath thermostatically controlled at 20°C. Optical density readings on this solution were obtained after 19 hours, 93 hours and 24 days. The resultant spectrophotometric curves are shown in Fig. 59. The pH values of the four solutions were respectively 11.44, 10.75, 10.45 and 10.52.

The charge on the complex in each of the last three solutions is shown by electrochromatograms 32, 33, and 34 to be positive, a conclusion which also applies to similar complexes prepared with ethylenediamine (which will be discussed later).

A blank carried out on trioxalatochromate without propylenediamine but with the appropriate amount of KOH to bring the solution to the same pH value, precipitated chromium hydroxide after the first 19 hours.

No definite conclusions can be drawn as to the actual structure of the complexes formed in the above reactions as further evidence, such as potentiometric titration, is necessary. Such titrations are complicated by the presence of the large excess of amine in the solutions. Nevertheless it can be stated with certainty that the trispropylenediaminochromic complex has not been formed as none of the spectrophotometric curves obtained show any resemblance to the curve for the trisethylenediaminochromic complex (Fig. 21). The validity of this statement lies in the fact which has been noted several times that the spectrophotometric curves for ethylenediamine complexes

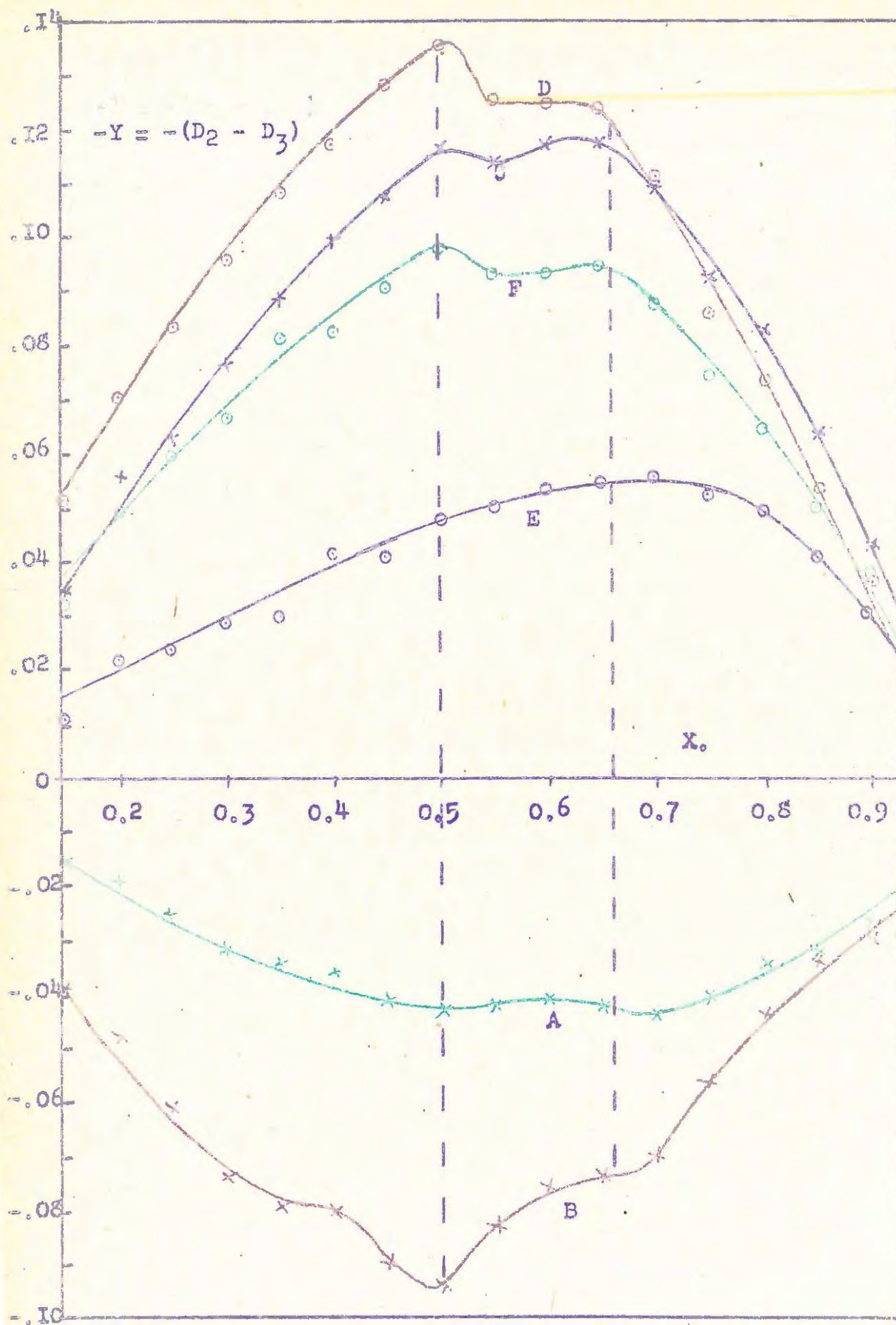


FIG. 60

Continuous Variation Method applied to Potassium Trioxalatochromate and propylenediamine at their natural pH values.

(A) 350 mμ (B) 370 mμ. (C) 420 mμ (D) 440 mμ (E) 560 mμ (F) 530 mμ.

with chromium closely resemble those for analogous propylenediamine complexes.

Having established the conditions necessary for reaction between trioxalatochromiate and propylenediamine and obtained the corresponding spectrophotometric curves for the products, it is now possible to carry out a quantitative estimation of the number of moles of each combining under a given set of conditions.

The "continuous variation method" was applied to trioxalatochromiate and propylenediamine where the solutions were mixed and allowed to react at their natural pH values but, before taking spectrophotometer readings, the pH was brought back to the natural pH of trioxalatochromiate. Mixed 50 (1-x) mls. of 0.0092M trioxalatochromiate (pH=6.1) and 50x mls. of 0.0092M propylenediamine (pH = 10.85) (where $x < 1$) and boiled for 30 mins. The pH of the solutions were recorded and nitric acid added to bring this back to 6.1. The solutions were then diluted to 50 mls. and the optical densities measured at 350, 370, 420, 440, 560 and 580 mμ. These optical densities minus the calculated optical densities of heated trioxalatochromiate solution at the same dilutions as those used in the experiment were plotted against x (Fig. 60) (i.e. the graph of $Y = D_2 - D_3$ against x).

From the graph it is seen that $x = .5$ and $.66$

$$n = \frac{x}{x - 1}$$

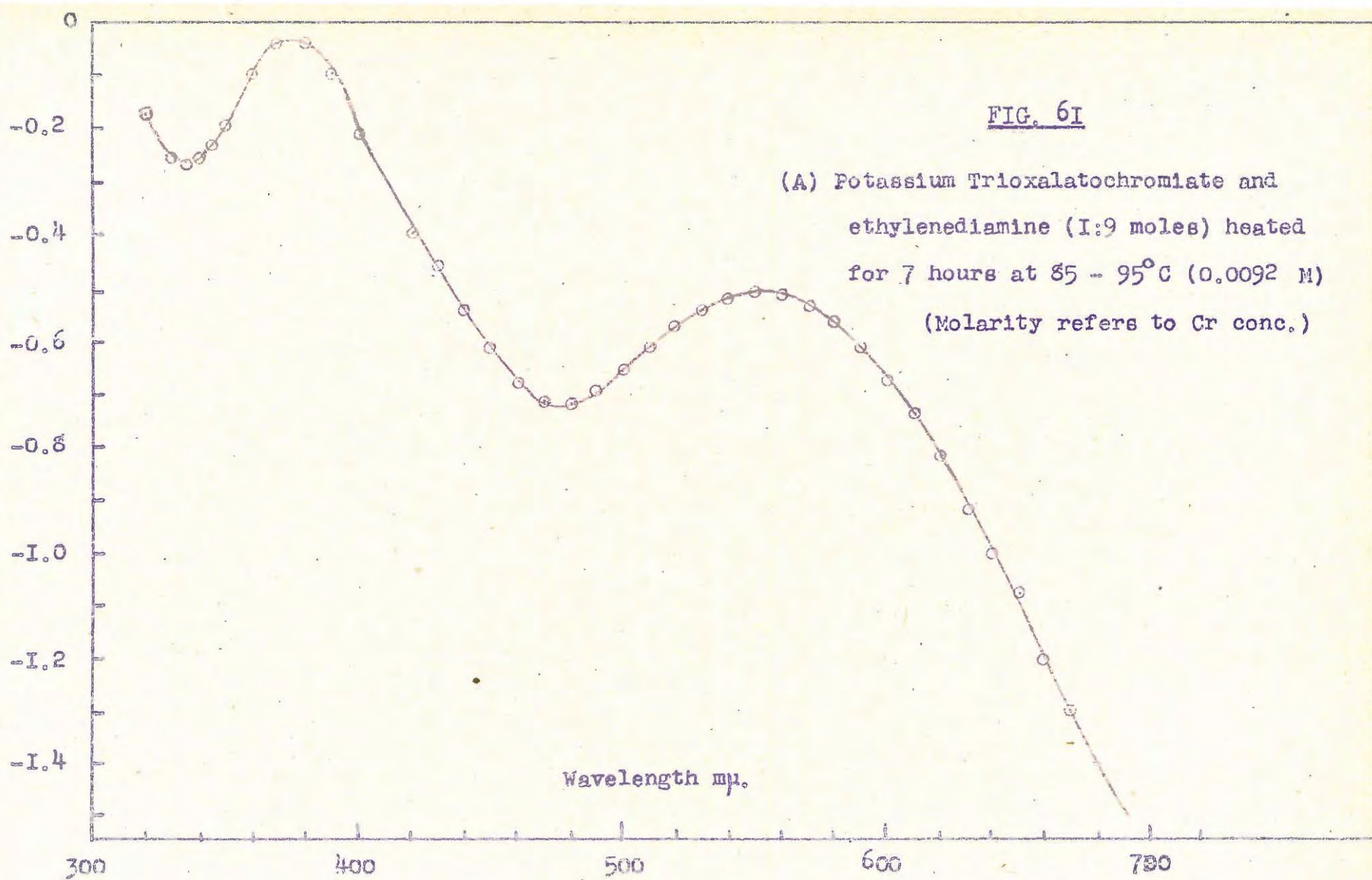
gives $n = 1$ and 2

FIG. 6I

(A) Potassium Trioxalatochromate and
ethylenediamine (1:9 moles) heated
for 7 hours at 85 - 95°C (0.0092 M)
(Molarity refers to Cr conc.)

Log. Optical Density.

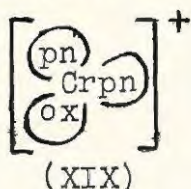
Wavelength mμ.



When $n = 1$ the complex probably is :



while $n = 2$ gives the complex :

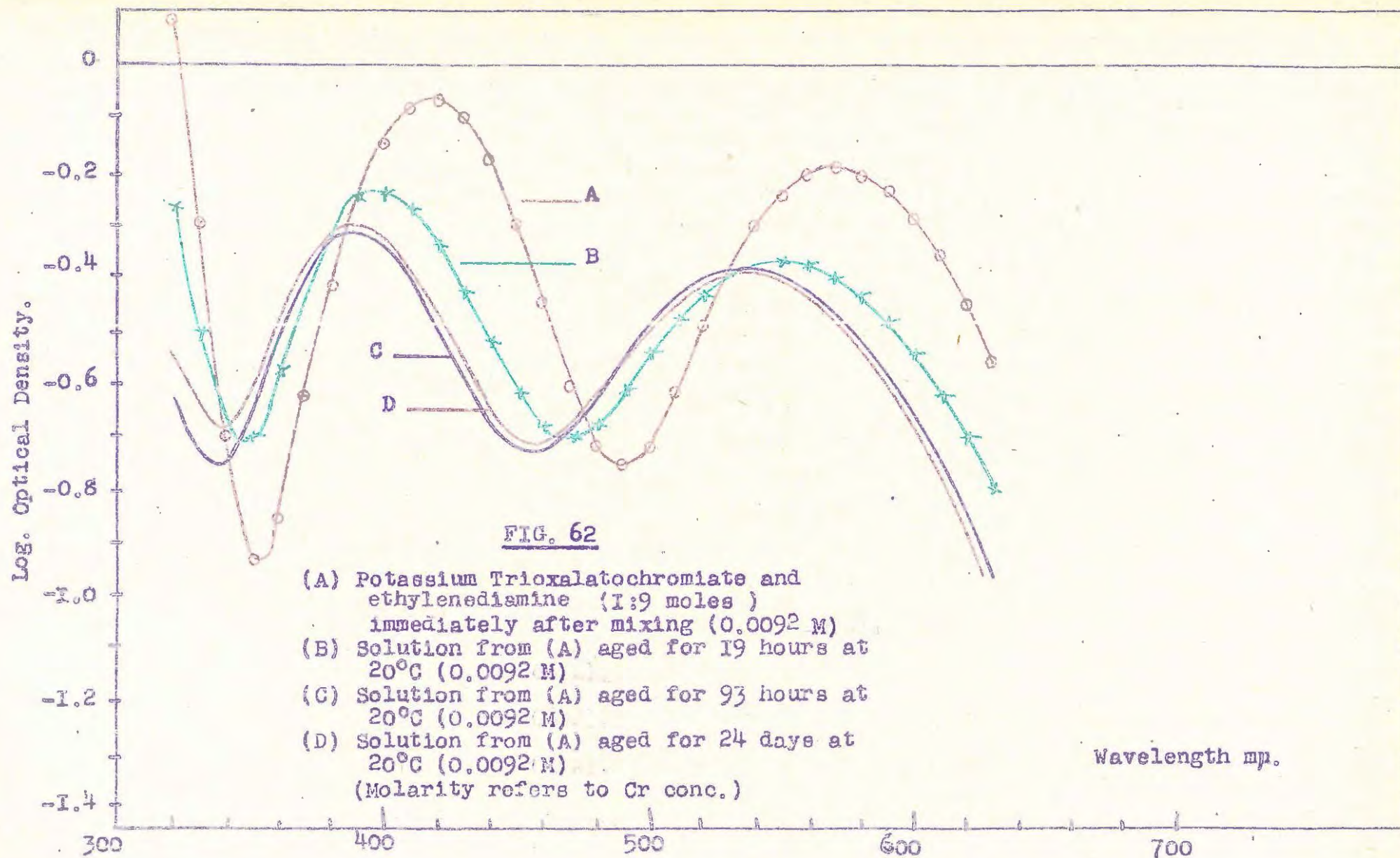


These results are in accord with the conclusions drawn from the potentiometric data for the titration of trioxalatochromate and propylenediamine in various mole ratios.

B. Reaction with ethylenediamine

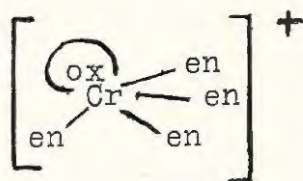
As observed with cis-dioxalatodiaquochromate, the spectrophotometric curves for the reaction products with ethylenediamine are very similar to those with propylenediamine.

In the first experiment trioxalatochromate (0.0092M - pH 5.8) was mixed with ethylenediamine (pH 12.0) in the mole ratio 1 : 9 and the solution heated for 7 hours at 85 - 95°C. This solution was then cooled, made up to volume (0.0092M), and after aging for 4 days the spectrophotometric readings recorded in Fig. 61 (final pH 10.35). The complex formed is shown by electrochromatogram 31 to be cationic and probably has one of the following structures :





(XX)

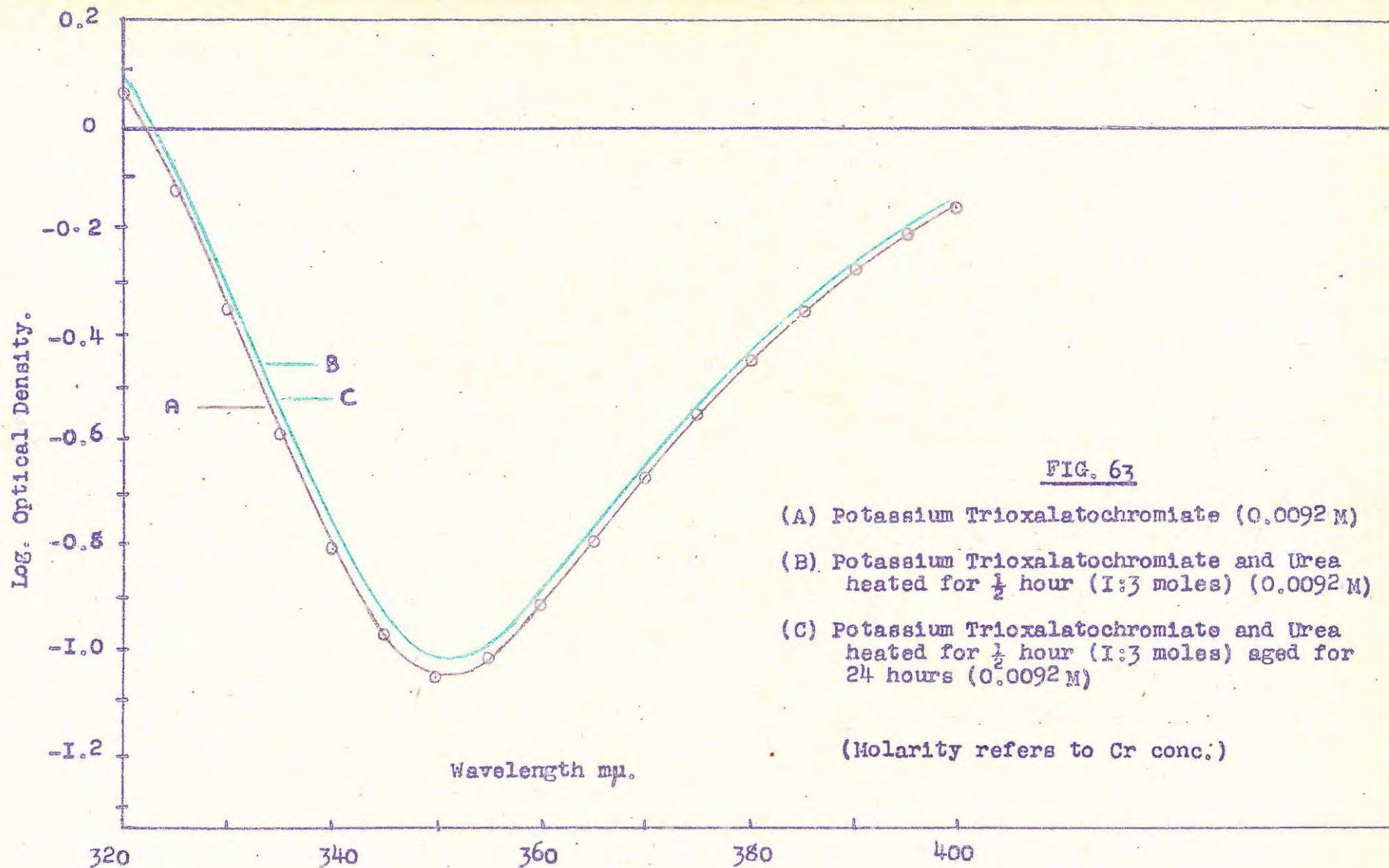


(XXI)

These are similar to the products already described for the reactions with cis-dioxalatodiaquochromiate (cf. XVI and XVII).

A similar reaction to that above was carried out at 20°C. A solution of trioxalatochromiate and ethylenediamine in the mole ratio of 1 : 9 was prepared and made up to volume (0.0092M). This solution was immediately placed in ice and the spectrophotometric readings obtained for this ice-cooled solution by the method already described. The rest of the solution in a well-stoppered flask was placed in a water bath thermostatically controlled at 20°C and the spectrophotometric readings obtained after 19 hours, 93 hours and 24 days. (Fig. 62). The pH values of these four solutions were respectively 11.52, 10.76, 10.6 and 10.59. The charges on the complexes formed in the last three solutions are shown by electrochromatograms 32, 33 and 34 to be positive.

From the spectrophotometric and electrophoretic data it is obvious that on aging solutions of cis-dioxalatodiaquochromiate on the one hand and trioxalatochromiate on the other with ethylenediamine or propylenediamine analogous complexes are obtained. In the previous chapter it was shown that these products in the case of



the cis-salt are intermediate between those formed by heating the cis-salt and the amine.

However, before any definite structures can be assigned to these aged products it is necessary to obtain more evidence, preferably by potentiometry. The latter method has the disadvantage that, as the solutions under consideration have a large excess of the amine present, interpretation of the curves would be difficult. It is suggested that the quantitative removal of free amine from the reaction mixture, e.g. by solvent extraction technique, might prove profitable in further studies along these lines.

C. Reaction with Urea.

As a result of the experiments to be described below there seems little doubt that urea does not react with trioxalatochromiate under the conditions employed.

A solution of trioxalatochromiate (0.0092M) and urea (1 : 3 moles) was boiled for $\frac{1}{2}$ hour, cooled and made up to volume (0.0092M). The resultant spectrophotometric curve is given in Fig. 63. The curve was unchanged after aging this boiled solution for 24 hours.

The close similarity of these curves with that of trioxalatochromiate at the same concentration of chromium indicates that no reaction has occurred between trioxalatochromiate and urea. Since no reaction was obtained with urea and cis-dioxalatociaquochromiate either (see Chapter IV), it may be concluded that neither

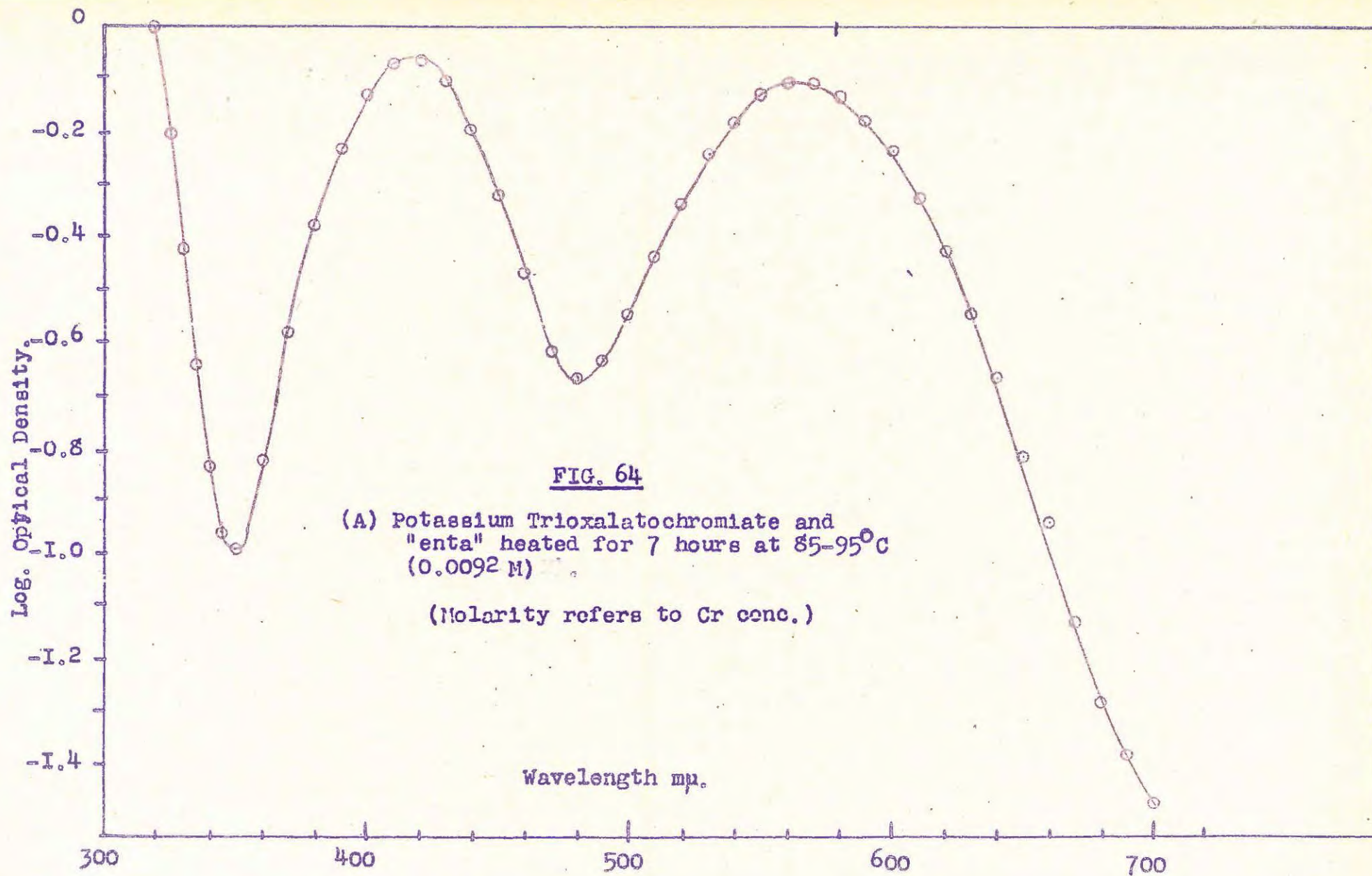
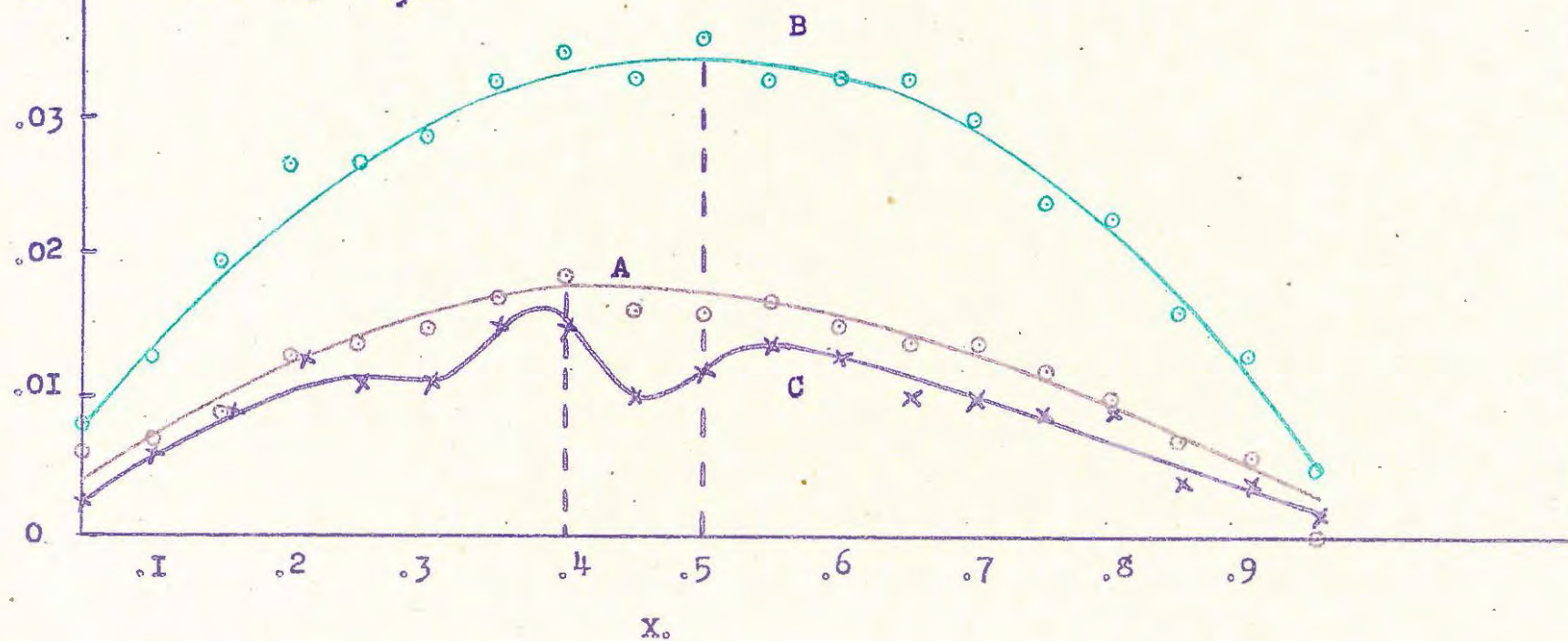


FIG. 65

Continuous Variation Method applied to Potassium Trioxalatochromiate
and "enta"

- (A) 400 m μ .
- (B) 420 m μ .
- (C) 560 m μ .

$$-Y \approx -(D_2 - D_3).$$



the $-NH_2$ groups nor the $-CO$ group of the acid amide show any marked co-ordination affinity for the chromium atom. This fact may have an important bearing on theories of chrome tannage involving the assumption that coordination occurs between the protein peptide groups of collagen and chromium atoms. (see Ch. VI).

D. Reaction with Ethylenediamine tetraacetic acid ("enta").

The preliminary experiment leading up to the application of the "continuous variation method" was as follows. A solution of trioxalatochromiate (0.0092 M) and enta (1 : 0.4) was heated for 7 hours at $85 - 95^\circ C$, cooled, made up to volume (0.0092 M) and after aging for 4 days the spectrophotometer readings recorded (fig. 64). This curve is very similar to that obtained with cis-dioxalatodiaquochromiate under similar experimental conditions and shows the best wavelengths at which to take optical density readings for the continuous variation method.

Now 50 (1-X) mls. of 0.0046 M trioxalatochromiate (pH 6.02) and 50X mls of 0.0046 M enta (pH 2.62), where $X \leq 1$, were mixed and the resultant solutions boiled for 30 minutes, stood overnight and then made up to volume (0.0046 M). The optical densities were measured at 340, 400, 420, 480, 540 and 560 m μ . The difference between these readings and the calculated optical densities for heated trioxalatochromiate at the same chromium concentration as those used in the experiment, were plotted against X (fig. 65).

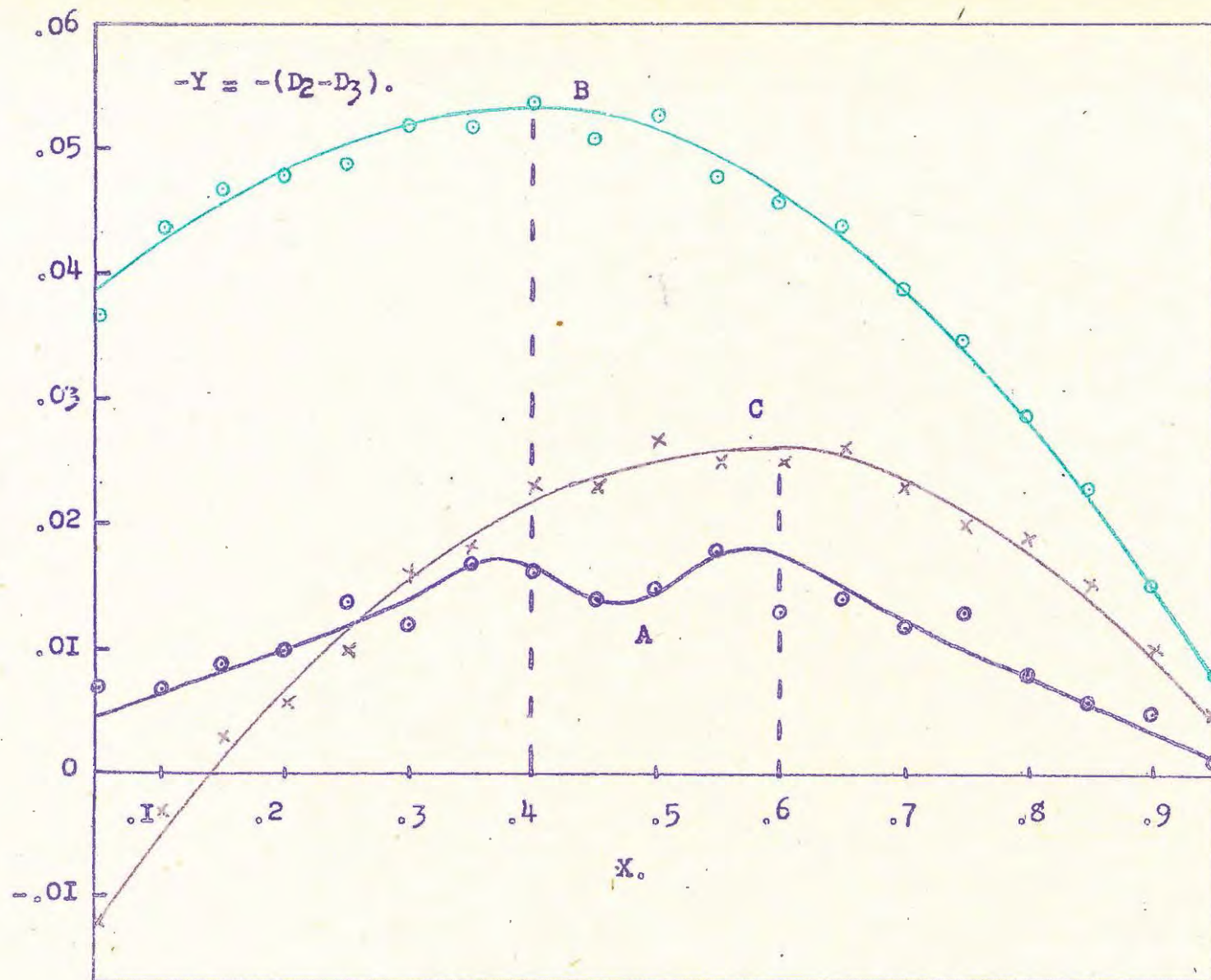


FIG. 66

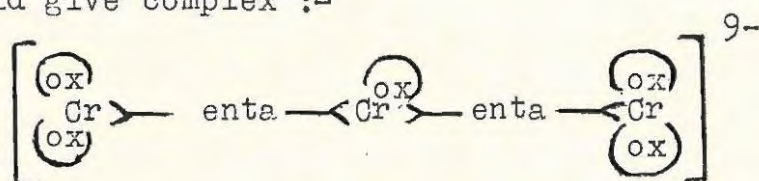
Continuous Variation
Method applied to Pot.
Trioxalatochromate and
"enta" heated then aged
for 4 days.

- (A) 400 mμ.
(B) 420 mμ.
(C) 430 mμ.

From the graphs it is seen that $X = .4$ and $.5$ indicating that the product of the reaction is heterogeneous.

When $X = .4$ $n = \frac{X}{1-X}$
 i.e. $n = \frac{2}{3}$

This would give complex :-



When $X = .5$, $n = 1$,

giving the complex :-

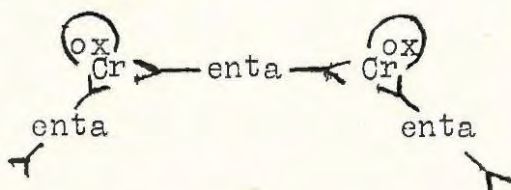


Here the charge will depend on whether the remaining two carboxyl groups of enta are ionised or not.

These solutions were then aged for 4 days and the optical densities measured again and the curves replotted (fig. 66). From the graphs it is seen that $X = .4$ and $.6$.

When $X = .4$, $n = \frac{2}{3}$

giving the same complex as shown above, while $X = .6$ gives $n = \frac{3}{2}$ and a complex :



Once again the charge on the complex will depend

on whether the unco-ordinated carboxyl groups are ionised or not.

The importance of these results lies in the fact that the product, even after aging, was heterogeneous.

CHAPTER VI

THEORETICAL DISCUSSION

The relative stability under identical conditions of groups attached to the central atom of a complex appears to depend on three factors :

- (1) the "inherent co-ordinative power" of the group due to its electronic configuration.
- (2) spatial considerations, such as steric effects and the ability to form chelate rings.
- (3) the environment of the complex, including solvent and pH effects.

According to Fyfe (154) the factors that would be expected to exert the greatest influence on bonding are :

- (1) the electronegativity of the atoms involved in the bond.
- (2) the type of hybrid orbitals available for covalent-bond formation.
- (3) size of the central atom.

The electronegativity which is related to the ionisation potential of the atoms, should play a major role in determining the degree of covalent bonding. The size of the central ion will determine the ease with which the necessary number of ligands can be packed round the ion and will control steric factors and repulsion between ligands.

It is evident that Fyfe, and most other authors

on this subject, do not consider the environmental factor which has been found in the present work to be of great significance.

Consider the so-called "inherent co-ordinative power", which is dependent on the electronic configurations of both the metal ion and the ligand. The electronic arrangement determines both the type of hybrid bond that the central atom can form (d^2sp^3 in the case of chromium) and the electronegativity of this atom or ion. This in turn governs the degree of covalency and ionic character of the co-ordinate bond with any particular ligand.

An important distinction must be made between the "degree of ionic character" in a given compound and the degree of ionisation (i.e. electrolytic dissociation) in solution. According to Pauling (7) the ionic character of the bond is determined by the importance of the ionic structure (A^+B^-) when the nuclei are at their equilibrium distance, whereas the tendency to ionise in solution is determined by the relative stability of the actual molecules in the solution and the separated ions in solution.

In general, however, the tendency towards ionisation in solution accompanies large ionic character of bonds, since both result from great differences in electronegativity of bonded atoms.

For covalent bonds Gordy (156) and Walsh (157) have suggested that the bond-force constant may be expressed as a function of the product of the electronegativities of the bonded atoms, and may be taken as a measure of bond

strength. Gordy (loc.cit.) has introduced a relation between the force constant (k), bond order (N), bond length (R_e) and the electronegativities (x_A and x_B) of the bonded atoms. The relation is of the form :

$$k = a N (x_A \cdot x_B / R_e^2)^{\frac{3}{4}} + b.$$

where a and b are constants. This may be applied widely to bonds in diatomic and polyatomic molecules when the bond is not distorted by forces between non-bonded atoms.

According to Linnett (153) it appears that three factors affect the bond force constant, namely :

- (1) the nature of the orbital (whether sp , sp^2 or sp^3 hybridised etc.)
- (2) the electrostatic state of the bond, this being affected by neighbouring groups.
- (3) resonance with various ionic structures.

Kabesh and Nyholm (155) state that an extension of the idea put forward by Gordy and Walsh, regarding the correlation between bond-force constant and the product of the electronegativities of the bonded atoms, to the co-ordinate link seems reasonable. Once formed, there is really no difference between the two types of bond except that the charges on the atoms will be different. This would presumably alter the effective electronegativities of the two atoms as compared with a covalent bond.

It must be emphasised that the strength of a bond, as reflected by the appropriate force constant, is

not necessarily a measure of the stability of a complex in a given solvent.

In the present work attempts were made to determine the relative stabilities in aqueous solution of oxalate, propylenediamine and ethylenediamine chelated to the chromium atom. The results indicate that the stabilities are a function of the environment of the complex. However, if for the moment these effects are ignored, the relative strength of the co-ordinate bonds between chromium and nitrogen on the one hand and chromium and oxygen on the other may be calculated by Gordy's rule (156).

Pauling (7) gives the electronegativities as 3.0 for N and 3.5 for O. The complexes under consideration involve co-ordinate bonds with N^+ and O^- . The consequent changes in electronegativities can be calculated from Pauling's "screening constant" (7). Here, if x^+ represents the electronegativity of an element with a +1 charge, then approximately :

$$x^+ = x + \frac{2}{3} (x_r - x)$$

where x is the value for the neutral atom and x_r is the value for the atom immediately to the right of it in the periodic table. Similarly, for a negative unit charge,

$$x^- = x - \frac{2}{3} (x - x_l)$$

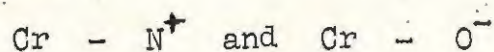
where x_l is the electronegativity of the element immediately to the left in the Periodic Table.

The values for N^+ and O^- calculated from these equations are 3.3 and 3.2 respectively.

Applying Gordy's rule it will be seen that the respective products of these electronegativities and that of chromium (not given by Pauling but estimated as ca 2.7) are very nearly the same :

Cr - O	9.45	Cr - O ⁻	8.64
Cr - N [†]	8.91	Cr - N	8.10

and hence, to a first approximation, the strengths of the co-ordinate bonds :



are of the same order.

These calculations are subject to several refinements arising from the occurrence of resonance in the compounds containing the N and O atoms. In addition no account can be taken of the resultant nett charge on the chromium atom as it has not as yet been assigned a place in the electronegativity scale, owing to the fact that the requisite thermochemical data are not available.

If we assign an extrapolated value of 2.7 to chromium, it can be shown that the differences in electronegativity correspond to about 10% ionic character in the co-ordinate bonds of chromium with nitrogen and oxygen.

In a discussion on the factors influencing the stability of metal ammines and complex ions Fyfe (154) points out that, "when an ammonia molecule approaches a hydrated metal ion, displacement of the water should occur because nitrogen, being less electronegative than oxygen, should form a more covalent bond with the metal". The

FIG. 67

Cr⁺⁺⁺

4p ○ ○ ○

For pure ionic or d^2sp^3
bonds.

3d ○ ○ ○ ○ ○

4s ○

Fe⁺⁺⁺

3d ○ ○ ○ ○ ○

For pure ionic bonds.

3p ○ ○ ○

3s ○

Fe⁺⁺⁺

3d ○ ○ ○ ○ ○

For d bonds.

3p ○ ○ ○

3s ○

Fe⁺⁺⁺

4p ○ ○ ○

For d^2sp^3 bonds.

4s ○

3d ○ ○ ○ ○ ○

implication of this statement is that the more covalent character the co-ordinate bond possesses, the stronger it is in aqueous solution.

It is known that in aqueous solution Ag^+ , Hg and Cu form complexes with ammonia, in agreement with the above discussion of Fyfe. But chromium does not form ammine complexes by the action of ammonia on the chromium ion in solution except under special conditions. The reason for this may lie in the type of hybrid bond used for complex formation (Copper dsp^2 , Silver sp and Chromium d^2sp^3).

In this connection Fyfe (loc. cit.) suggests that "in the paramagnetic complexes of ammonia and water with bivalent transition-metal ions, insufficient bond energy is available to supply the necessary energy to pair off the electrons in the d level and supply the six d^2sp^3 hybrid orbitals. The remaining s and three p orbitals must thus be used for bonding".

Using magnetic moments of the octahedral complexes of the transition elements, Pauling (7) shows that complexes with relatively large magnetic moments (e.g. $[CoF_6] \equiv \mu = 5.3$ Bohr magnetons) are essentially ionic complexes while those with small magnetic moments (e.g. $[Co(NH_3)_6]^{+++} \mu = .00$) are essentially covalent complexes. This magnetic moment results from unpaired electrons,

Thus the ferric complex FeX_6 , which may have in its normal state a structure of ionic type (Fig. 67), with five unpaired electrons, or a structure of the d^2sp^3 covalent type,

with one unpaired electron, cannot have an intermediate structure corresponding to resonance between these two, since the conditions for resonance require that the resonating structures have the same number of unpaired electrons. It is accordingly possible by measuring the magnetic moment of an octahedral ferric complex to determine which of the two types it represents.

The magnetic moment method cannot be applied to chromium (III), the structures of the two extreme types having the same number of unpaired electrons and entering into resonance with each other.

From fig. 67 it will be seen that for the chromic ion no change is necessary in the 3d orbital electrons for either a pure ionic or d^2sp^3 hybrid bond to be formed. However, for the formation of d^2sp^3 or d hybrid bonds in the case of the ferric ion, pairing off four of the five unpaired 3d orbital electrons is necessary.

For these reasons the bonds of chromium (fig. 67) may be taken to be very similar to those formed by protons. This fact has been made use of in a general rule (to be discussed later) relating the dissociation constants of organic acids and the ability to co-ordinate with chromium.

Recently Pauling (159) has introduced a new concept, account of which must be taken in considering co-ordinate bonds. According to Pauling, "it seems likely that in general all of the atoms in the complexes that constitute stable chemical substances have resultant electrical charges smaller than those shown by these most electroposi-

tive and electronegative atoms in their compounds with one another". In consequence of which he introduces "the postulate of the essential electrical neutrality of atoms : namely, that the electronic structure of substances is such as to cause each atom to have essentially zero resultant electrical charge, the amount of leeway being not greater than about $\pm \frac{1}{2}$, and these resultant charges are possessed mainly by the most electropositive and electronegative atoms, and are distributed in such a way as to correspond to electrostatic stability".

In this connection it may be noted that the covalent bond is more capable of distributing the charge on a cation than an electrovalent bond.

Stabilities of complexes should only be compared in isoelectronic series of metals where the type of hybrid orbitals available for covalent bond formation can be kept constant. According to Fyfe (154), if this is done, it is found that the free energy of complex formation approximates closely to a linear function of the ionisation potential and thus, presumably, to the electronegativity of the metal atom. Calvin and Melchoir (160) have come to a similar conclusion, but it must be emphasised that electronegativity values would be only approximate, since the electron affinity and ionisation potential of a metal atom are seldom known with accuracy.

The second factor governing the stability of groups attached to the central atom of a complex depends on spatial considerations such as steric effects and the ability

to form rings.

In this connection Shuttleworth (65) reports that "the bidendate ligands such as polybasic organic acids or α -hydroxy acids can be divided into two categories :-

(a) Bidendate ligands forming 5, 6 or 7 membered rings, giving no increment in the number of chromium atoms per mole, and occupying available co-ordination positions with stability enhanced by the additional states of resonance provided by the ring structure. The damping effect on this resonance caused by interposing CH_2 groups in the ring, plus additional strain, appears to be the reason for decreasing stability with increasing size of ring.

(b) Long chain polydendate ligands which enhance the size of the chromium complex and increase chrome fixation in leather by linking chromium atoms together. It is suggested that these non-ring forming polydendate ligands can be regarded, from a stability viewpoint, as fitting into the series of monodendate ligands, with stabilities inversely proportional to their dissociation constants".

Since both propylenediamine and ethylenediamine form five-membered rings they should, other factors being disregarded, form stable chelated structures with the chromium atom.

The number of ligands bound by an ion appears to depend largely on the number of orbitals available for bond formation and on the number of linkages that will be required to reduce the charge on the central ion to a minimum (154,

159). Size is not entirely a controlling factor, for the large silver ion takes two ligands (sp and possibly sp^3 hybrid bonds) and mercuric ion four, while the smaller ions of the transition elements take six.

The third factor (i.e. the environment of the complex) affecting the stability seems to have received little attention by most workers in the field of co-ordination chemistry. Yet is it this factor which, after a complex has been formed to satisfy the previous two factors, determines whether the complex so formed remains stable or not under given conditions.

As an example consider the trioxalatochromiate ion which in the crystalline form as the potassium salt and in aqueous solution at its natural pH (ca 6.0) is a stable complex.

In alkaline solution, on aging alone, the trioxalatochromiate ion precipitates chromium hydroxide. The chelated oxalate rings of the trioxalatochromiate are considered to be continually opening and closing (i.e. the co-ordinate bonds are in dynamic equilibrium or the molecule possesses mesomeric structures). When the pH of the solution is ca 10, as one end of a co-ordinated oxalate ring opens, it is replaced by a hydroxyl ion which cannot then be displaced by the oxalate. Thus in a series of step-wise reactions the oxalate becomes completely displaced from co-ordination with chromium by hydroxyl ions. In this way chromium hydroxide is precipitated.

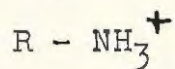
In strong acid solution the trioxalatochromiate ion

is also unstable for the following reason. As one end of the oxalate ring opens it is replaced by a water molecule and the ionised carboxyl group is titrated and becomes an unionised carboxyl group which cannot reform a co-ordinate bond as it is unable to donate an electron. The same set of conditions is operative for the other carboxyl group, resulting ultimately in free oxalic acid in solution.

If, as postulated above, there is a dynamic equilibrium in the co-ordination bonds of the chelated oxalate ion, then there must be a relevant equilibrium constant. The constant is either the stability constant of the complex bound ligand or is related to it.

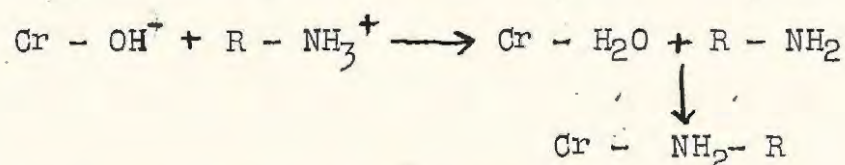
The most important point to emerge from the present research is concerned with the interaction of chromium oxalato-complexes and amino-bases at various pH levels. The results from reacting cis-dioxalatodiaquochromiate or trioxalatochromiate with amino bases indicate that at low pH values compounds containing amino-groups will not co-ordinate with metal ions through this group.

In acid solution amines exist in the ionised form:



and just as H^+ will not co-ordinate with metal ions so the ionised amino-group will not. Consider the actual reaction necessary for an amine to become co-ordinated to the chromium atom. This amine molecule ($R.NH_3^+$) must in the first instance approach sufficiently close to the chromium atom of the dioxalatodiaquochromiate or trioxalatochromiate ion to enable a bond to be formed. On electrostatic grounds this

is possible as the cationic amine group will be attracted to the anionic complex (i.e. the complex ion is surrounded by excess electrons) but on approaching sufficiently close to form a bond with the chromium atom the amine must replace either a water molecule (or hydroxy group, depending on the prevalent pH of the reaction mixture) or one end of the oxalate ion by donating electrons to form a bond. It is possible, however, for the above to take place through a reaction of the following type :



where the other groups co-ordinated to the chromium have been omitted.

From the above equation it is seen that the hydroxyl ion is titrated by the ionised amino group forming a co-ordinated water molecule and an unionised amine free in solution. The amino-group in the unionised form can then replace the co-ordinated water molecule from its position on the chromium atom; the important point being that the amine in the ionised form does not directly co-ordinate with the chromium atom.

It is of interest to apply the above considerations to the question of chrome-tanning which is generally carried out with cationic chromium salts, usually chromium sulphate or chloride. It follows from the work of Shuttleworth (65) and Burley (29) that in the range of pH at which carboxyl groups are ionised, co-ordination may be expected between these groups and the chromium atom regard-

less of the formal charge on the latter provided it contains water molecules capable of replacement.

Similarly, as indicated above, it would seem at least theoretically possible for the charged amino group ($R-NH_3^+$) to displace a hydroxyl group through the indirect elimination of a water molecule. In chrome-tanning which is usually conducted in the pH range 3 - 4, the collagen of the hide exists largely in the zwitterionic condition while chromium sulphate would be partially basic. Thus it would seem probable that the function of the chromium in converting pelt into leather is to sequester both carboxyl and amino groups of the protein, accompanied presumably by more or less cross-linking of the molecular chain.

The above theory has been accepted by a number of authorities, notably Gustavson, until comparatively recently when it has been recognised that co-ordination of the amino groups does not occur as readily as might be anticipated from the reaction shown above.

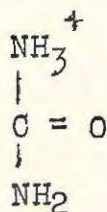
Shuttleworth (153) has consistently put forward the view that the chromium atom in chrome-tanning co-ordinates directly onto the ionised carboxyl groups of the protein side chains, and has adduced evidence "that amino groups of the types found in collagen do not co-ordinate appreciably with basic chromium complexes in dilute aqueous solution under the conditions of chrome-tannage".

This latter view has recently been accepted by Gustavson.

Plant (36) has shown that the free or non-zwitterion carboxyl groups of collagen are blocked by chrome-tanning.

acid medium (pH ca 4) urea does not co-ordinate with chromium on reacting it with cis-dioxalatodioquochromiate or trioxalatochromiate. The theoretical discussion above supplies a ready explanation for this important fact.

Urea is a weak base but the ionised form :



is a very strong acid ($\text{pK}_1 = 0.18$); therefore by the above rule urea, in the unionised form, will not readily co-ordinate with metal ions.

Further confirmation of the applicability of the rule is obtained from the fact that the hydroxyl ion, which may be regarded as an extremely weak acid (i.e. high affinity for hydrogen ions), forms one of the strongest co-ordinate bonds.

Several workers have made comparisons of the basic strengths of various amines and their complex-forming affinity for silver and other ions. Bjerrum (19) records these data for the silver ion, from several sources, as shown in the following table :

However, the results did not make it possible to determine to what extent the zwitterion carboxyl groups are also involved.

There is now a considerable body of evidence in support of Shuttleworth's (65) view that "the chief mechanism of chrome-tannage is co-ordination of chromium to the carboxyl groups of protein side chains. This reaction is not determined by the charge on the complex, but by the number and stability of the groups occupying the available co-ordination positions on the chromium atom. The charge is one of several factors influencing ligand stability."

These views are supported to some extent in the present work, particularly as regards the non-reactivity of primary amino groups at pH 5 or less.

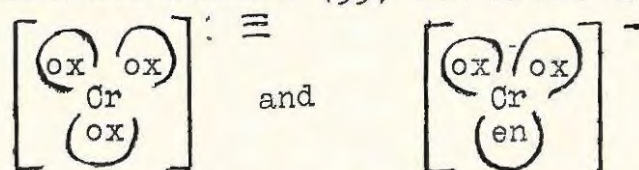
Despite this it was found that on raising the pH above 7 the oxalate ion could be replaced from its co-ordination position on the chromium atom by ethylenediamine or propylenediamine. Since the oxalate ion is present as a bidentate chelating ligand the reaction is probably step-wise. The fact that propylenediamine displaces co-ordinated oxalate from the trioxalatochromate ion when the pH is ca 8 probably results from the situation where the reactive ends of the oxalate ion (which form the co-ordinate bonds with the chromium atom) are in a dynamic equilibrium (i.e. the oxalate rings are continuously opening and closing). As one end of a chelated oxalate ring opens it is replaced by a hydroxyl ion. It is not possible for the oxalate ion to replace the hydroxyl ion but, as shown above, the ionised amino-group can. By such a series of step-wise reactions it is possible for the propylenediamine to displace the

co-ordinated oxalate.

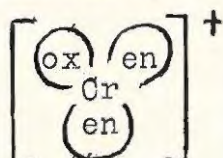
The trioxalatochromate ion can be considered as having several canonical forms. The proportion of each form will depend on the pH of the solution.

Thus it is statistically possible that, when one end of the oxalate ion co-ordinated to the chromium atom opens up, a monodentate ligand or one end of a bidentate ligand may take up this momentarily unused co-ordinate valence of the chromium atom. If this attachment is not in a dynamic equilibrium, possibly due to the inherent electronic configuration of the ligand, then the bond formed will be stable. Further the other end of the partially displaced oxalate ion can break its bond and become an unco-ordinated ion. The co-ordinate valence thereby set momentarily free can be taken up by another monodentate ligand or by the other end of the bidentate ligand having one group already co-ordinated. In the latter case steric effects must also be expected.

Confirmation of this postulate may be found in the work of Bushra and Johnson (33) who found that :



could be racemised, whereas :

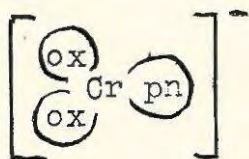


could not. This is because the process of racemisation is considered to depend on the opening and closing of the ring

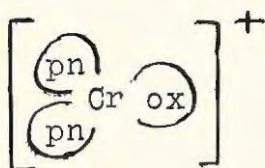
rather than on a secondary ionisation reaction. That the latter compound does not racemise may be due to the fact that the ethylenediamine chelated rings do not open and close continuously.

The "continuous variation method" applied to potassium trioxalatochromiate and propylenediamine in alkaline solution indicates that either one or two, but not three molecules of the amine can displace the equivalent number of oxalate molecules from the chromium complex. Assuming that the propylenediamine molecules which displace the oxalate ions from rings, then a plausible explanation for the fact that three molecules of propylenediamine do not go into the chromium complex can be given on the basis of the theory postulated above.

When one ion of oxalic acid is displaced by one molecule of propylenediamine and no dimer is formed, then the product is :



This complex ion still possesses two oxalate rings and the bonds of these with chromium will be in dynamic equilibrium and thus permit further substitution as the bonds open and close. But when two oxalate rings are displaced, the complex becomes :



Due possibly to the influence on the oxalate ion of the

addition of two neutral groups co-ordinated to the chromium atom, some change in electronic configuration prevents the remaining oxalate ion from opening and closing. In any case it is highly probable that electrostatic effects resulting from the change in charge on the complex inhibit the opening and closing of the rings. This makes it more difficult for the last remaining oxalate ion to be displaced by propylenediamine.

In spite of the ability of propylenediamine and ethylenediamine to displace oxalate ions from the trioxalatochromiate ion in alkaline solution it is evident from the present work that the latter ion is inherently more stable than the trisethylenediaminochromic ion (cf. the decomposition of trisethylenediaminochromic chloride in solution).

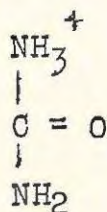
The author is indebted to Dr. Cunningham for the idea that as a general rule the affinity of an ion (e.g. oxalate) or a molecule (e.g. ethylenediamine, propylenediamine or urea) for hydrogen ions can be taken as a direct measure of the "co-ordinative power" of the ligand for a cation. Shuttleworth (65) records this in the statement "that the ability of protein carboxyl groups to displace other ligands from chromium complexes is shown to be inversely related to the dissociation constants of the ligand".

Extending this to bases, the greater the tendency for a base to exist in the ionised form ($R - NH_3^+$) the greater is the "co-ordinative power" of the base in the unionised form ($R - NH_2$) for metal ions.

In the present work it has been shown that in

acid medium (pH ca 4) urea does not co-ordinate with chromium on reacting it with cis-dioxalatodioquochromiate or trioxalatochromiate. The theoretical discussion above supplies a ready explanation for this important fact.

Urea is a weak base but the ionised form :



is a very strong acid ($\text{pK}_1 = 0.18$); therefore by the above rule urea, in the unionised form, will not readily co-ordinate with metal ions.

Further confirmation of the applicability of the rule is obtained from the fact that the hydroxyl ion, which may be regarded as an extremely weak acid (i.e. high affinity for hydrogen ions), forms one of the strongest co-ordinate bonds.

Several workers have made comparisons of the basic strengths of various amines and their complex-forming affinity for silver and other ions. Bjerrum (19) records these data for the silver ion, from several sources, as shown in the following table :

Ligand	$\log k_{H^+}$	$\log k_{Ag^+}$	$t^{\circ}C$	Medium
Ammonia	9.28	3.60	25	0.5 M NH_4NO_3
Ethylenediamine	10.18	3.70	25	1.0 M KNO_3
Methylamine	10.72	3.34	25	0.5 M NRH_3NO_3
Ethylamine	10.81	3.65	25	0.5 M KNO_3
n-Butylamine	10.71	3.74	25	0.5 M NRH_3NO_3
Triethylamine	10.77	2.40	25	0.4 M NR_3HNO_3
Diethylamine	10.96	3.10	30	0.5 M KNO_3

Where k_{H^+} as a measure of the basic strength denotes the reciprocal of the acid dissociation constant of the base cation AH^+ :

$$k_{H^+} = \frac{[AH^+]}{[A][H^+]}$$

while k_{Ag^+} denotes the mean complexity constant of the complexes formed in the corresponding metal-amine system.

Thus the silver-amine complexes increase in stability in the order methylamine < ethylamine < n-butylamine and primary > secondary > tertiary. Fyfe (154) considers two factors, both becoming more marked as the amine becomes more complex, which appear to contribute to these orders. They are primarily a steric effect due to the crowding of groupings around the central ion, and, secondly, the repulsion of the cation by the polar groupings of the amine. The stability is also reduced by the addition of electron-

attractive groups, as shown in the table by the ethylamines.

If the rule relating the degree of dissociation of acids in aqueous solution to the affinity for complex formation is extended to include inorganic acids, it would have to be concluded that hydrochloric acid and nitric acid (pK values < 2.0) should not readily co-ordinate. This is true for nitric acid, but it has been found that the chloride ion of hydrochloric acid co-ordinates fairly readily with chromium. This apparent exception to the rule is readily accounted for by the electronic configuration of the chloride and nitrate ions.

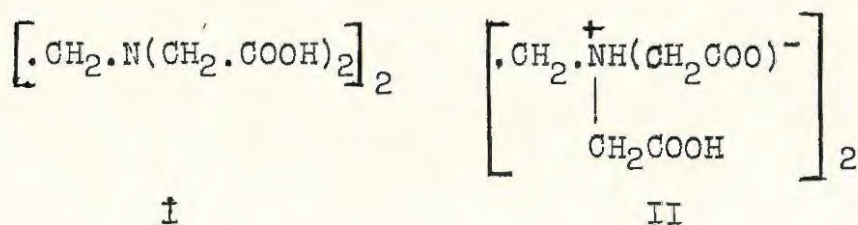
In the modern concepts of valency, discussed in the introduction, it is generally accepted that no compound has perfect covalent or electrovalent bonds but that all chemical bonds fall onto a scale the one extreme of which is a pure covalent bond while the other is a pure electrovalent bond. Therefore electrovalency and covalency are not considered as different kinds of bonds but as different degrees of the two perfect extremes of electronic configurations.

Applying these facts to nitric acid it is found, that the hydrogen ion is bound almost exclusively by electrovalent forces. Consideration of the electronic configuration of the nitrate ion shows that the stability of the ion depends on almost complete possession of the electron donated by the hydrogen atom; if the bond were covalent the nitrate ion itself would be unstable. On the other hand, the hydrochloric acid molecule is known to possess a

relatively large degree of covalency. A similar electro-
nic state exists in organic acids and hence it may be ten-
tatively suggested that acids which form largely electro-
valent bonds with the ionisable hydrogen atom will not
readily co-ordinate with metal ions. Alternatively it may
be said that acids with a large dissociation constant (i.e.
with a small affinity for hydrogen ions due to the pre-
dominance of electrovalency) will not co-ordinate readily.

In the above considerations, account has not been
taken of steric effects such as chelation. Hence the
relative stabilities of complexes formed with monobasic
acids cannot be compared with those formed by dibasic acids
as the latter are capable of forming chelate rings.

As an example of a chelating compound, consider
ethylenediamine tetraacetic acid which is finding increas-
ing application as a complexing substance (46,47,48,53).
Zwitterion characteristics have been attributed to this
compound, for Long et al (49) and Schwarzenbach (50) re-
presents the two forms as :



Vickery (52) has commented that the zwitterion would not
be expected to promote complex formation through the nitro-
gen atom because of the positive charge on the latter.
According to Vickery, since an equilibrium would exist be-
ween the zwitterionic and non zwitterionic forms of "enta",

the effect of zwitterion formation would be to reduce the rate of complex formation. It is difficult to see why this need be so if the step determining reaction is that involving only the ionised carboxyl groups.

Schwarzenbach (50,51) claims that, since "enta" may be titrated as a tetrabasic acid, the zwitterion effect may be disregarded in calculations of stability constants.

The discussion above has been concerned with only one of the environmental factors, namely, the effect of pH on the complex stability. No consideration has been given to ionic strength in aqueous solution, the nature of the solvent or the effect of the electrostatic field produced by the dielectric of a particular solvent.

Werner (135) first directed attention to the marked retarding influence of acetone upon the rate of racemisation of chromioxalate. Bushra and Johnson (33) found that acetone depressed the rate of racemisation of $[\text{Cr en}(\text{C}_2\text{O}_4)_2]^-$ rather less than that of chromioxalate. This is probably due to the influence of the chelated ethylenediamine.

In studying the kinetics of the formation of the trioxalatochromate ion by the reaction between the cis-dioxalatodiaquochromate and oxalate ions in aqueous solution, Friend (34) found that the ionic strength of the solution affected the rate of reaction. Friend (loc. cit.) also found that an almost saturated solution of potassium nitrate decreased the decomposition rate of the potassium dioxalatosulphatoaquochromate complex.

Atkin (161) reports that a commercial chrome liquor, containing excess sodium sulphate, and which yielded a heavy precipitate of benzidine sulphate when treated with benzidine hydrochloride, was diluted with saturated potassium chloride, and it was found that no precipitate was produced on adding benzidine hydrochloride.

According to Barnes et al (162) insufficient attention has been paid hitherto to the possibility of the modification of the intra-ionic relationships, such as the nature of the ligand bonds or the charge distribution throughout the complex ion as a consequence of inter-ionic forces. Accepting Paulings postulate (159) of the essential electrical neutrality of atoms, it follows that the capacity of the ligands to distribute or "drain-off" the central metallic charge in a complex is probably related intimately to such phenomena as valency stabilisation. In addition the "draining off" effect must be connected with the complementary ionic atmosphere.

As this atmosphere is withdrawn by progressive dilution of concentrated solutions, the peripheral charge must decrease with consequent increase in the residual charge on the central metallic atom, and probably some modification in the nature of the metal-ligand bonds. The addition of electrolytes to the solutions must also lead to similar effects. At low ionic strengths it is probable that the effect of dilution becomes negligibly small with further dilution, until at zero ionic strength, the complex

ion is completely abstracted from its complementary atmosphere, and the peripheral charge is at the minimum.

Barnes et al (loc. cit.) suggest that different species of oxidant and reductant exist in various ionic environments, and since their energy relationships are different, the potential is different. These potential changes are superimposed upon the normal charge potential arising from purely interionic interaction, and lead to deviations from the Debye-Huckel theory.

Dwyer (163) found that the dissociation constant of the tris (1 : 10-phenanthroline) ferric ion is not constant but varies with the acidic strength of the solution. Tentatively it was suggested that the decrease in the value of the constant with increased acidic strength of the solution, which implies an increase in the stability of the complex ion, was due to proton addition to some of the nitrogen atoms.

These phenomena are consistent with the view that the nature of complex ions in solution can be changed by alterations of the ionic environment.

CONCLUSION.

Consideration of the above discussion reveals that the stability of a complex ion depends on three factors.

The first of these concerns the "inherent co-ordinative power" of the ligand and is governed by the type of bond available for co-ordination. In addition, the type of bond (i.e. sp^3 , d^2sp^3 etc.) predicts the spatial distribution of the complex (i.e. planar, tetrahedral etc.) and hence the possibility of the occurrence of geometrical or optical isomers.

The second factor is mainly concerned with bidentate ligands and their ability to form chelate structures. Assuming no distortion in bond angles or bond lengths it is possible for chelate ring structures to be stabilised by resonance. Other steric effects such as steric hindrance, which would be operative when the ligands are large organic molecules, must also be taken into account.

Finally, the stability of a complex depends on its environment, which includes :

- (a) solvent effects.
- (b) electrostatic effects resulting from the dielectric of the solvent and the charge on the complex ion.
- (c) the ionic strength of the solution.
- (d) the pH of the solution.

This environmental factor has only recently received attention and still has to be placed on a quanti-

tative basis.

Up to now no systematic quantitative study has been carried out on the conditions of formation of mixed oxalato and amino chromium complexes and the present work has been of necessity on a semi-quantative basis. Nevertheless, if due consideration is given to the above factors, such an approach should now be possible.

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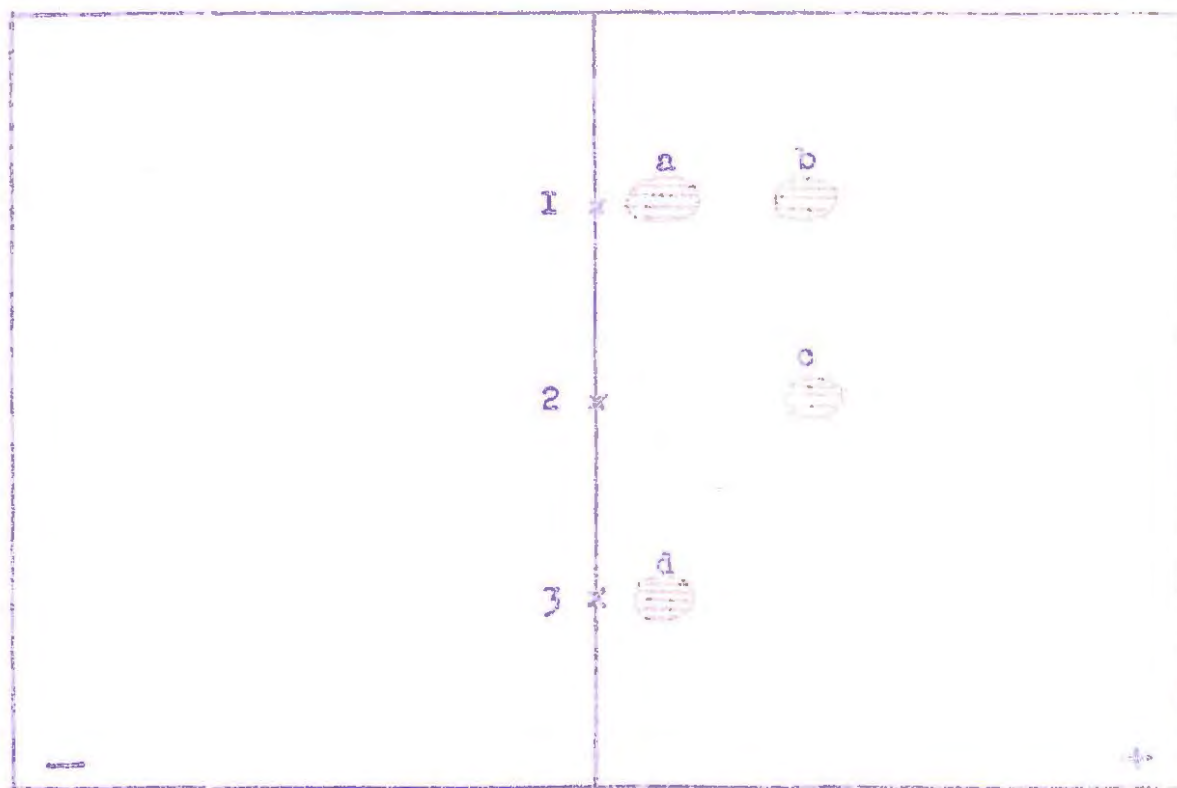
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APPENDIX A

ELECTROCHROMATOGRAPHIC

DATA

ELECTROCHROMATOGRAM I



1. Mixture of 2 and 3 below.

2. 20 % Recrystallised Potassium Trioxalatochromate.

3. 10 % Potassium cis-dioxalatoaquochromate prepared by aging the recrystallised trans-salt.

EXPERIMENTAL CONDITIONS.

120 - 145 volts.

7.5 milliamperes.

Background Electrolyte 10 % Lactic Acid

Running Time 110 mins.

Paper Whatman 54.

Distances of Migration:

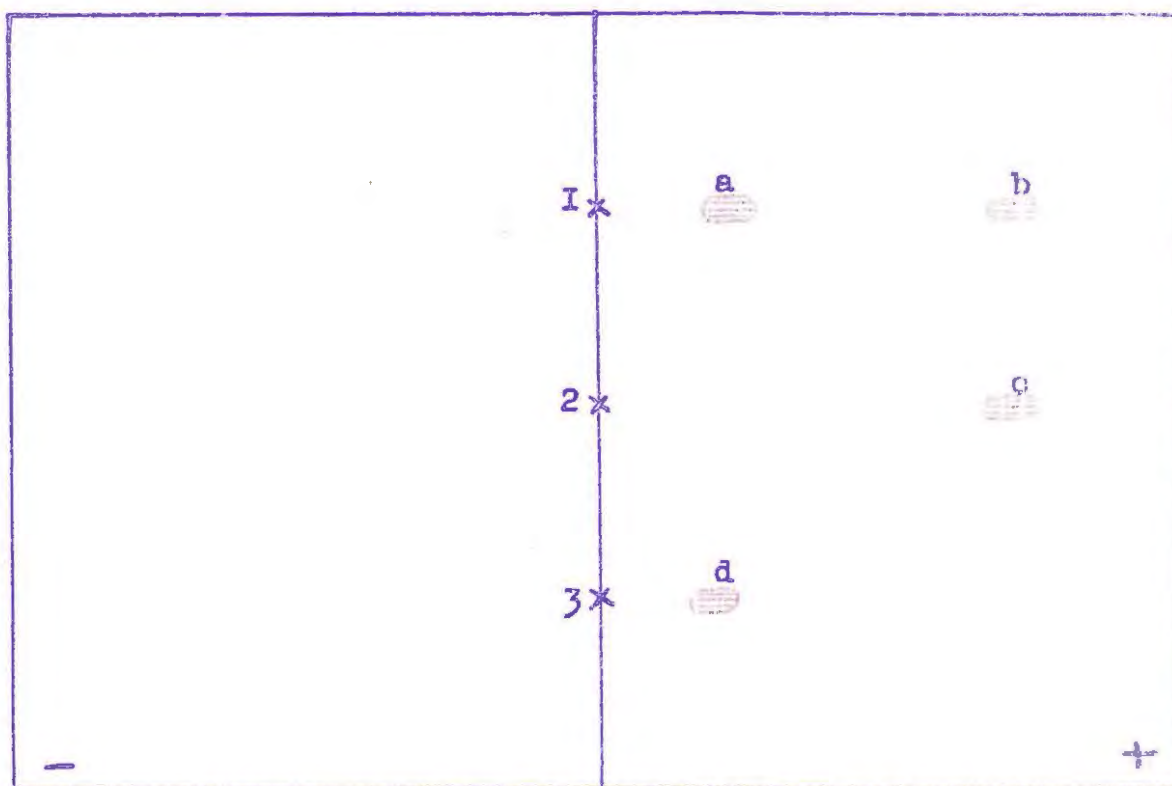
(a) 0.3 cms. - 1.5 cms.

(b) 3.7 cms. - 4.4 cms.

(c) 3.3 cms. - 4.7 cms.

(d) 0.5 cms. - 1.8 cms.

ELECTROCHROMATOGRAM 2



1. Mixture of 2 and 3 below.
2. 20 % Recrystallised Potassium Trioxalatochromiate.
3. 10 % Potassium cis-dioxalatodiaquochromiate prepared by aging the recrystallised trans-salt.

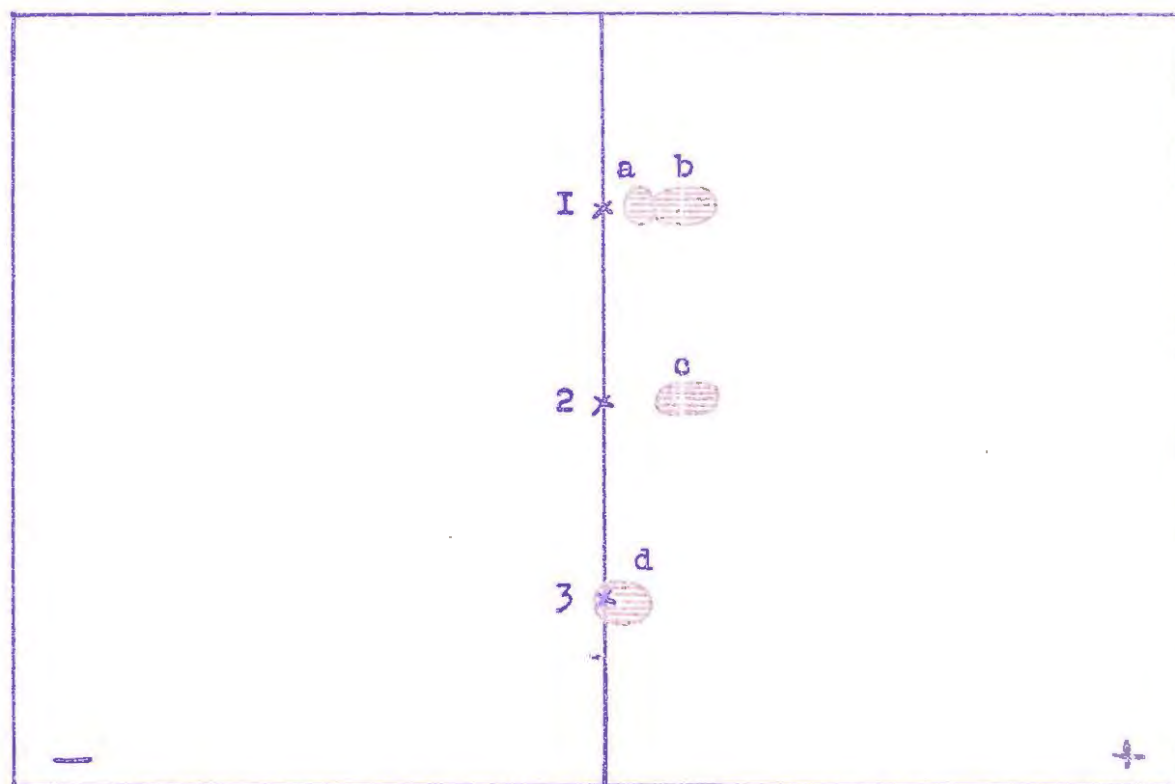
EXPERIMENTAL CONDITIONS.

400 - 510 volts 11.0 - 22.5 milliamps
 Background Electrolyte 10 % Lactic Acid.
 Running Time 75 mins. Paper: Whatman 54.

Distances of Migration:

- (a) 1.4 cms. - 4.2 cms.
- (b) 7.0 cms. -
- (c) 6.0 cms.
- (d) 1.4 cms.

ELECTROCHROMATOGRAM 3.



1. Mixture of 2 and 3 below.

2. 20 % Recrystallised Potassium Trioxalatochromiate.

3. 10 % Potassium cis-dioxalatodiaquochromiate prepared by aging the recrystallised trans-salt.

EXPERIMENTAL CONDITIONS.

90 - 120 volts

72.5 - 80.0 milliamps.

Background Electrolyte 1 M Oxalic Acid

Running Time 85 mins.

Paper: Whatman 54.

Distances of Migration:

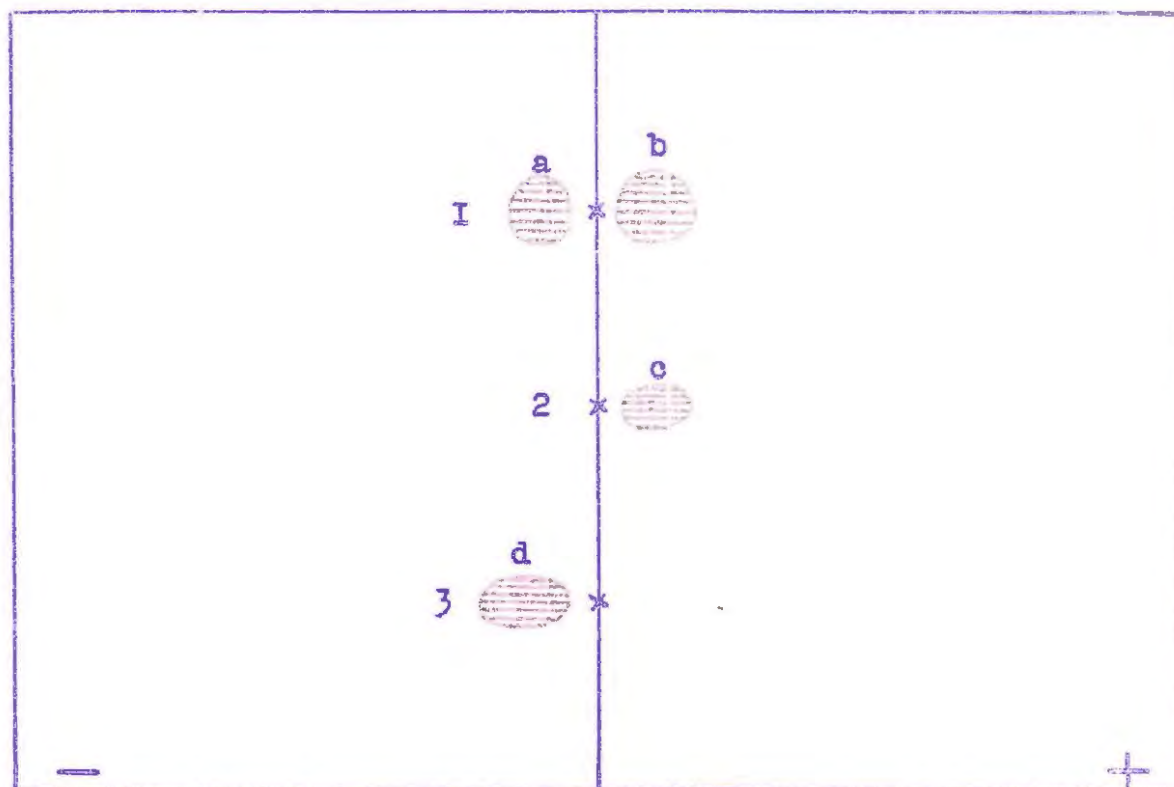
(a) 0.1 cms. - 1.3 cms.

(b) 1.3 cms. - 3.9 cms.

(c) 1.0 cms. - 3.0 cms.

(d) 1.3 cms.

ELECTROCHROMATOGRAM 4.



1. Mixture of 2 and 3 below.

2. 20 % Recrystallised Potassium Trioxalatochromiate.

3. 10 % Potassium cis-dioxalatodiaquo-chromiate prepared by aging the recrystallised trans-salt.

EXPERIMENTAL CONDITIONS.

100 - 180 volts

9.5 - 27.2 milliamps.

Background Electrolyte: 2 % Ethylenediamine hydrochloride.

Running Time: 180 mins.

Paper: Whatman 54.

Distances of Migration:

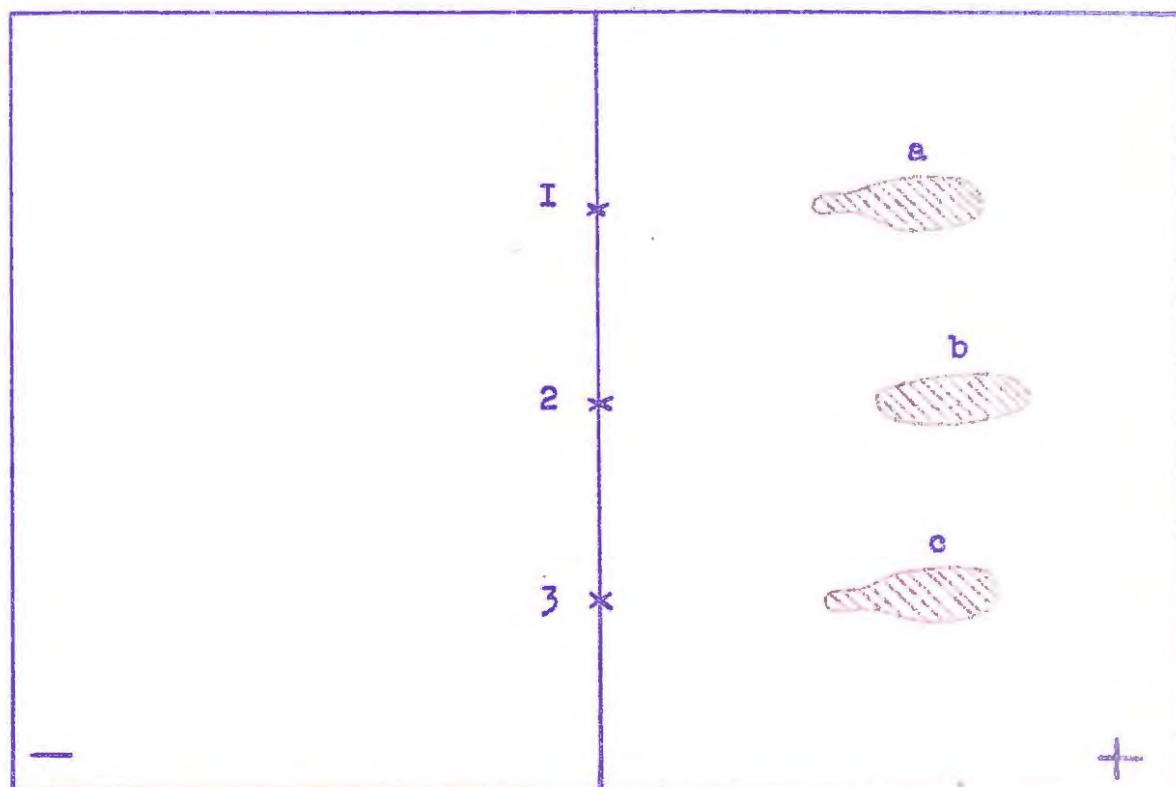
(a) 0.1 cms. - 2.0 cms.

(b) 0.2 cms. - 2.5 cms.

(c) 0.3 cms. - 2.1 cms.

(d) 0.4 cms. - 3.6 cms.

ELECTROCHROMATOGRAM 5.



1. Mixture of 2 and 3 below.

2. 20 % Recrystallised Potassium Trioxalatochromiate.

3. 10 % Potassium cis-dioxalatodiaquochromiate prepared by aging the recrystallised trans-salt.

EXPERIMENTAL CONDITIONS.

360 volts.

27.6 - 32.1 milliamps.

Background Electrolyte: 5 % Ethylenediamine.

Running Time: 35 mins.

Paper: Whatman 54.

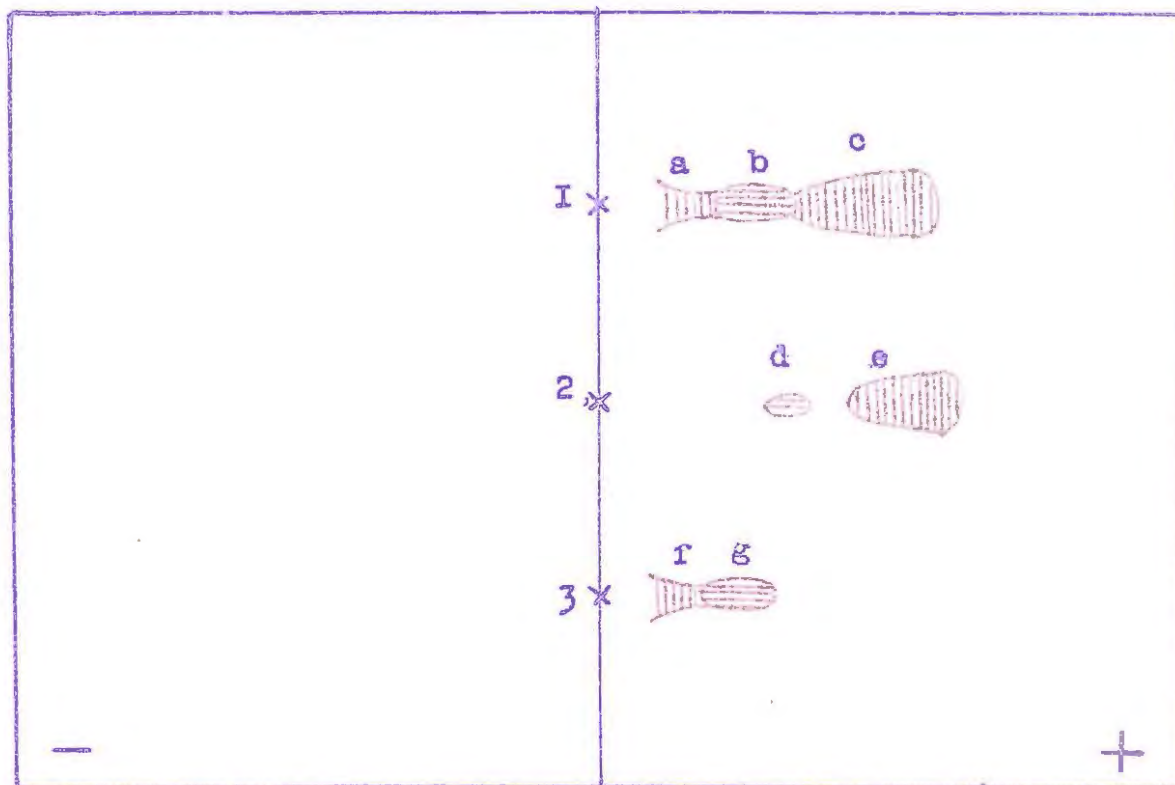
Distances of Migration:

(a) 2.9 cms. - 9.0 cms.

(b) 5.0 cms. - 10.2 cms.

(c) 3.0 cms. - 8.4 cms.

ELECTROCHROMATOGRAM 6.



1. Mixture of 2 and 3 below.

2. 20 % Recrystallised Potassium Trioxalatochromate.

3. 10 % Potassium cis-dioxalatodiaquochromate prepared by aging the recrystallised trans-salt.

EXPERIMENTAL CONDITIONS.

375 - 380 volts

17.4 - 20.3 milliamps.

Background Electrolyte: 5 % Propylenediamine.

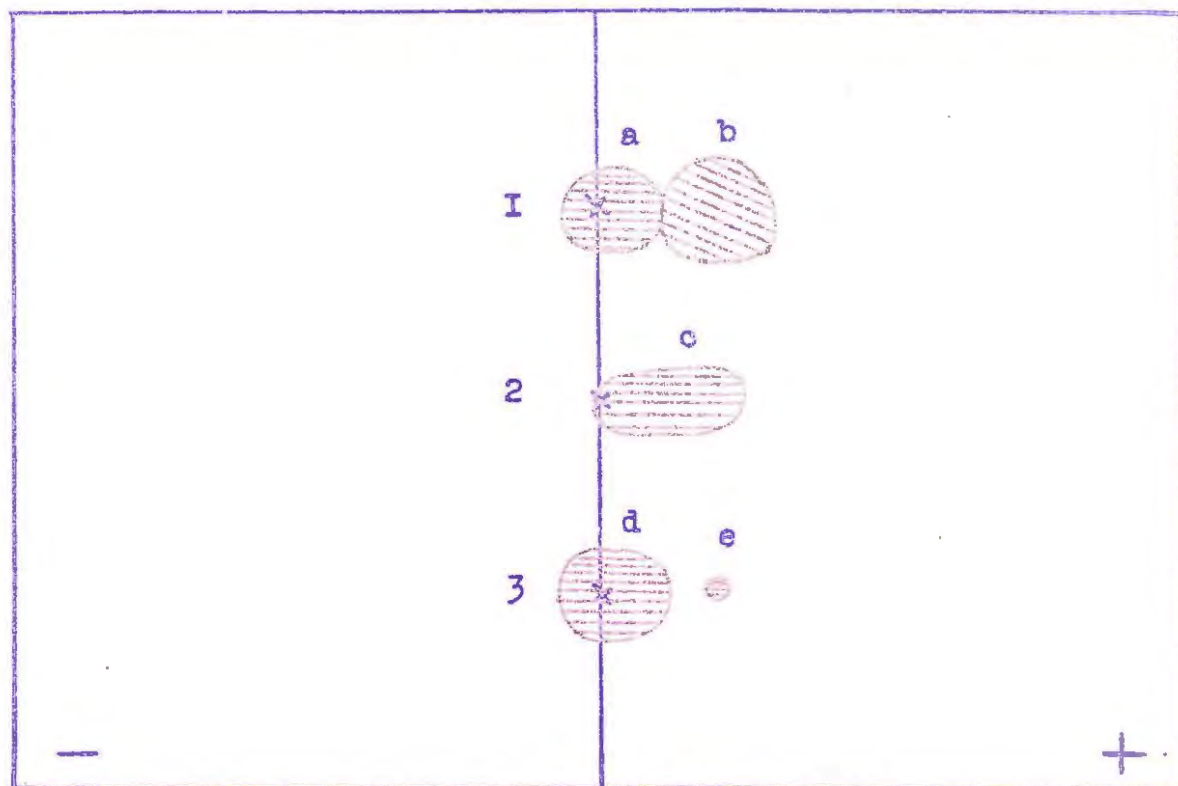
Running Time: 50 mins.

Paper: Whatman 54.

Distances of Migration:

- (a) A trail.
- (b) 3.3 cms. - 5.2 cms.
- (c) 5.2 cms. - 10.4 cms.
- (d) 4.3 cms. - 5.9 cms.
- (e) 6.2 cms. - 10.5 cms.
- (f) A trail.
- (g) 2.5 cms. - 4.4 cms.

ELECTROCHROMATOGRAM 7.



1. Mixture of 2 and 3 below.

2. 20 % Recrystallised Potassium Trioxalatochromiate.

3. 10 % Potassium cis-dioxalatodiaquochromiate prepared by aging the recrystallised trans-salt.

EXPERIMENTAL CONDITIONS.

90 - 190 volts.

5.8 - 27.5 milliamps.

Background Electrolyte: 2 % Propylenediamine hydrochloride.

Running Time: 175 mins.

Paper: Whatman 54.

Distances of Migration:

(a) 1.3 cms.

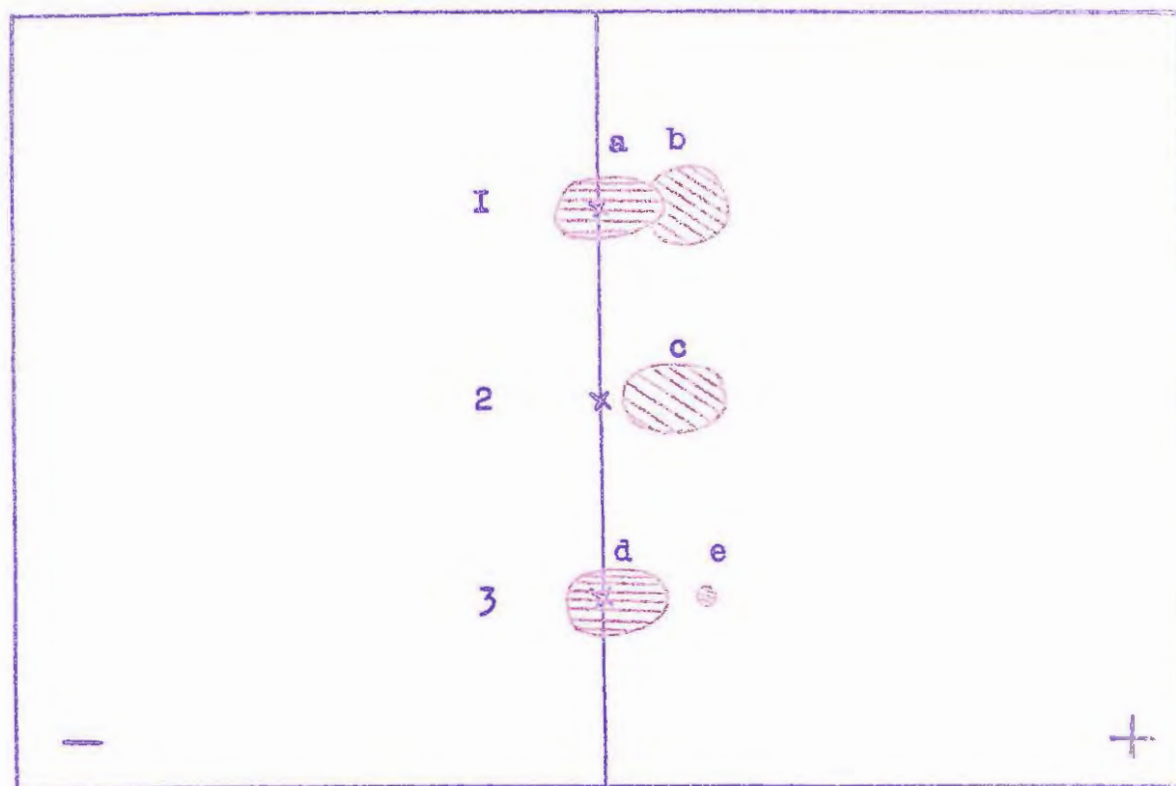
(b) 1.3 - 3.8 cms.

(c) 3.4 cms.

(d) 1.2 cms.

(e) 1.4 - 2.1 cms.

ELECTROCHROMATOGRAM 8.



1. Mixture of 2 and 3 below.

2. 20 % Recrystallised Potassium Trioxalatochromiate.

3. 10 % Potassium cis-dioxalatodiaquochromiate prepared by aging the recrystallised trans-salt.

EXPERIMENTAL CONDITIONS.

90 - 120 volts

22.2 - 29.1 milliamps.

Background Electrolyte: 2 % Methylamine hydrochloride.

Running Time: 70 mins.

Paper: Whatman 54.

Distances of Migration:

(a) 1.2 cms.

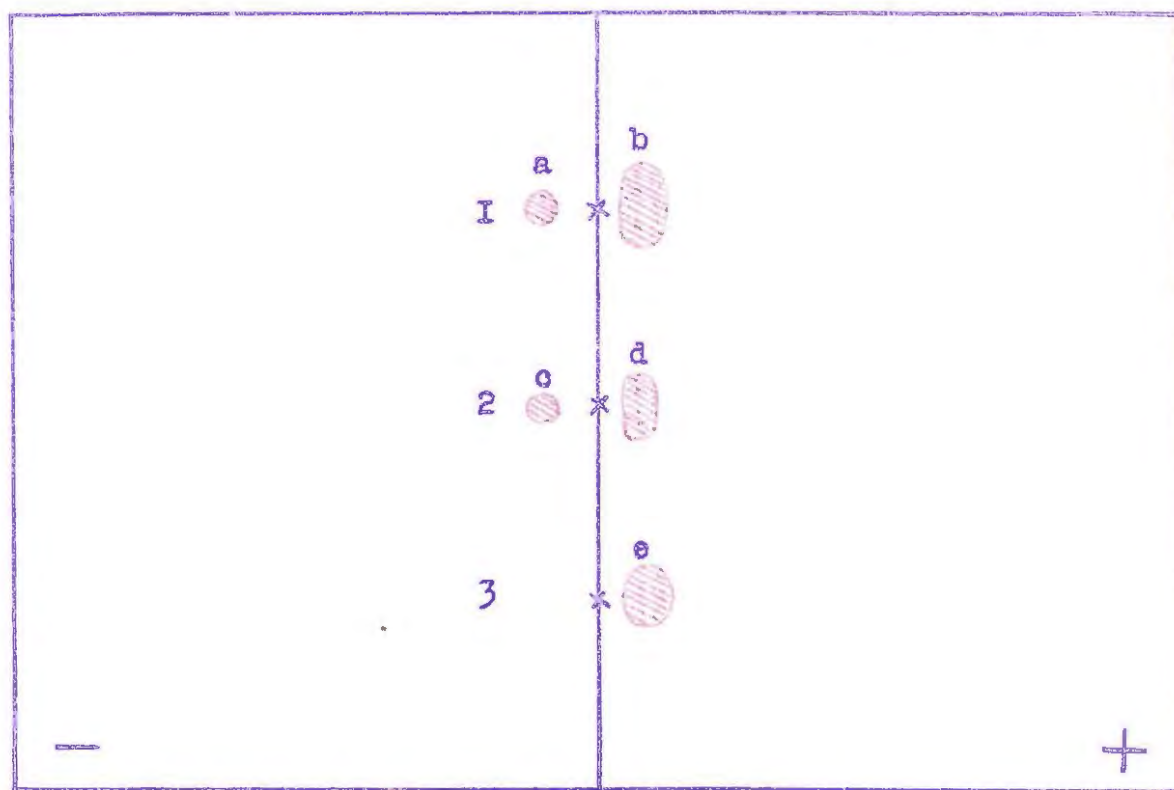
(b) 1.2 - 3.2 cms.

(c) 0.25 - 3.2 cms.

(d) 1.1 cms.

(e) 1.7 - 2.4 cms.

ELECTROCHROMATOGRAM 9.



1. Mixture of 2 and 3 below.

2. 20 % Recrystallised Potassium Trioxalatochromate.

3. 10 % Potassium cis-dioxalatodiaquochromate prepared by aging the recrystallised trans-salt.

EXPERIMENTAL CONDITIONS.

395 - 400 volts.

1.8 - 4.0 milliamps.

Background Electrolyte: 5 % Urea.

Running Time: 70 mins.

Paper: Whatman 54.

Distances of Migration:

- (a) 1.0 cms. - 2.1 cms.
- (b) 0.2 cms. - 1.6 cms.
- (c) 1.0 cms. - 1.9 cms.
- (d) 0.4 cms. - 1.8 cms.
- (e) 0.2 cms. - 1.9 cms.

ELECTROCHROMATOGRAM IO.



1. Mixture of 2 and 3 below.

2. 20 % Recrystallised Potassium Trioxalatochromiate.

3. 10 % Potassium cis-dioxalatodiaquochromiate prepared by aging the recrystallised trans-salt.

EXPERIMENTAL CONDITIONS.

24 - 65 volts.

36.5 - 52.5 milliamps.

Background Electrolyte: 2 % Urea hydrochloride.

Running Time: 150 mins.

Paper: Whatman 54.

Distances of Migration:

(a) 1.0 cms.

(b) 1.0 cms. - 2.3 cms.

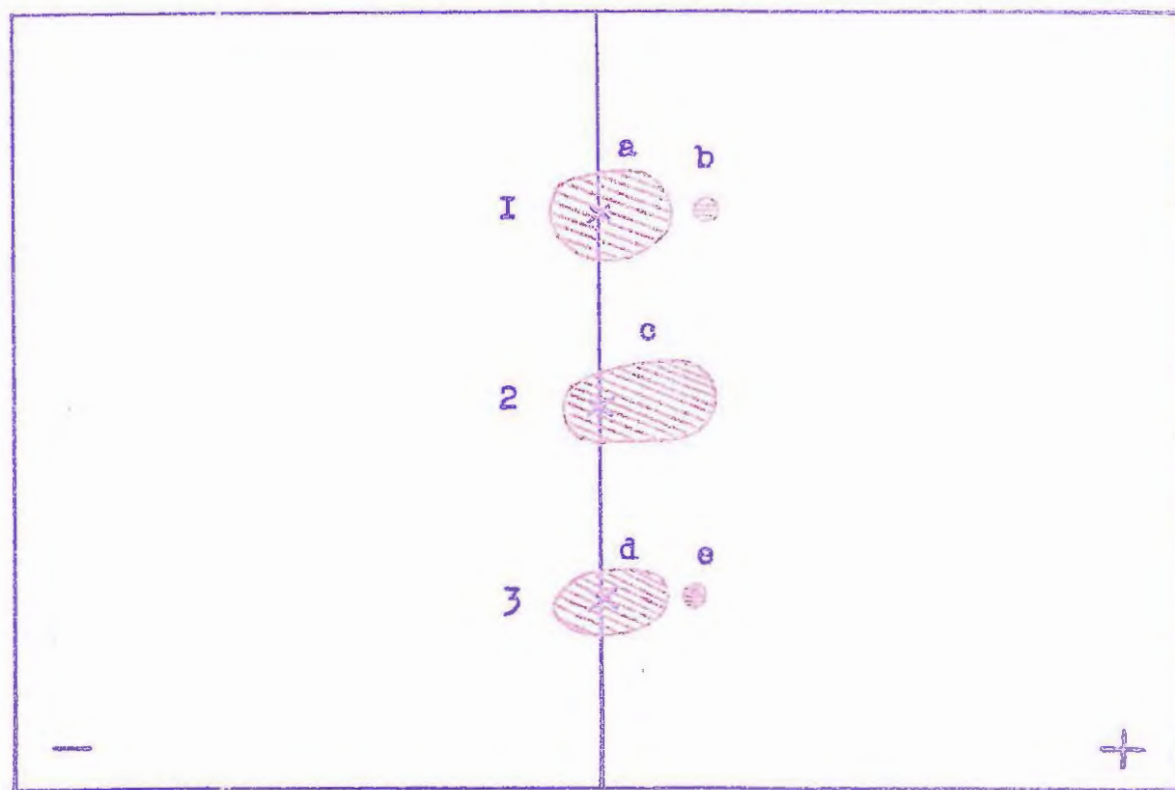
(c) 1.9 cms.

(d) 0.9 cms.

(e) 1.0 - 1.7 cms.

IIA

ELECTROCHROMATOGRAM II.



1. Potassium cis-dioxalatodiaquochromiate prepared by aging Burley's twice recrystallised trans-salt.

2. Potassium Trioxalatochromiate.

3. Potassium cis-dioxalatodiaquochromiate prepared by aging Friend's twice recrystallised trans-salt.

EXPERIMENTAL CONDITIONS.

100 - 110 volts

20.2 - 27.8 milliamps.

Background Electrolyte: 2 % Methylamine hydrochloride.

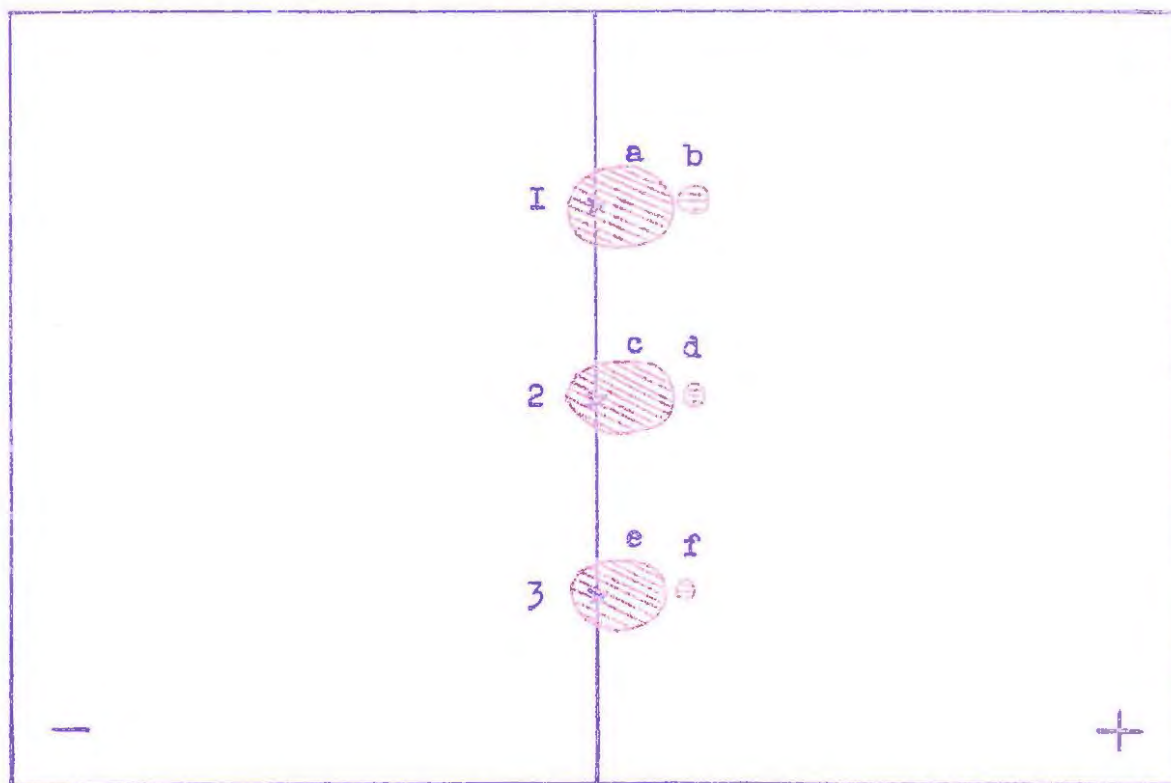
Running Time: 45 mins.

Paper: Whatman 54.

Distances of Migration:

- (a) 1.8 cms.
- (b) 2.0 - 2.6 cms
- (c) 3.7 cms.
- (d) 1.5 cms.
- (e) 1.6 - 2.1 cms.

ELECTROCHROMATOGRAM I2



1. A heated solution of the 1st crop of the 1st recrystallisation of trans-dioxalatodiaquochromate, stood for 12 hours.
2. A heated solution of the 2nd crop of the 1st recrystallisation of trans-dioxalatodiaquochromate, stood for 12 hours.
3. A heated solution of the 3rd crop of the 1st recrystallisation of trans-dioxalatodiaquochromate, stood for 12 hours.

EXPERIMENTAL CONDITIONS.

95 - 100 volts.

19.3 - 24.0 milliamps.

Background Electrolyte: 2 % Methylamine hydrochloride.

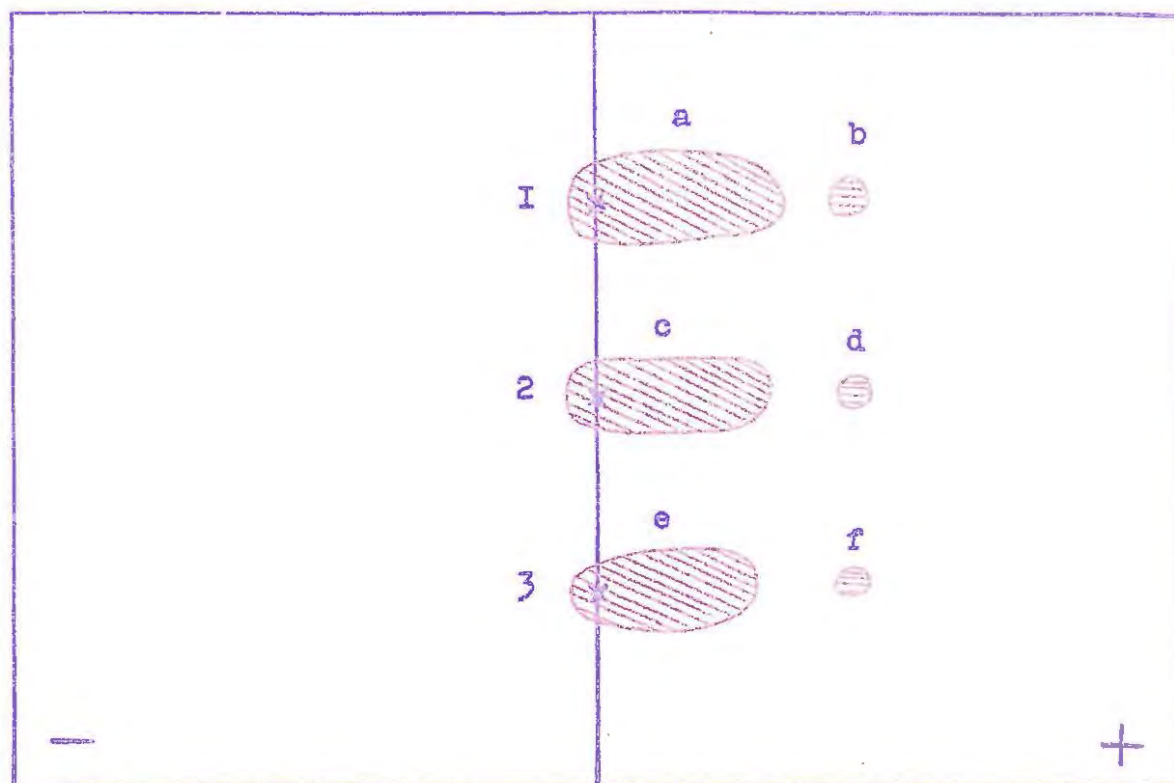
Running Time: 35 mins.

Paper: Whatman 54.

Distances of Migration:

- (a) 1.7 cms.
- (b) 1.8 cms. - 2.4 cms.
- (c) 1.7 cms.
- (d) 1.8 cms. - 2.4 cms.
- (e) 1.8 cms.
- (f) 1.9 cms. - 2.6 cms.

ELECTROCHROMATOGRAM I3.



1. A heated solution of the 1st crop of the 2nd recrystallisation of trans-dioxalatodiaquochromiate, stood for 12 hours.
2. A heated solution of the 2nd crop of the 2nd recrystallisation of trans-dioxalatodiaquochromiate, stood for 12 hours.
3. A heated solution of the 3rd crop of the 2nd recrystallisation of trans-dioxalatodiaquochromiate, stood for 12 hours.

EXPERIMENTAL CONDITIONS.

120 volts.

15.0 - 23.5 milliamps.

Background Electrolyte: 1% Methylamine hydrochloride.

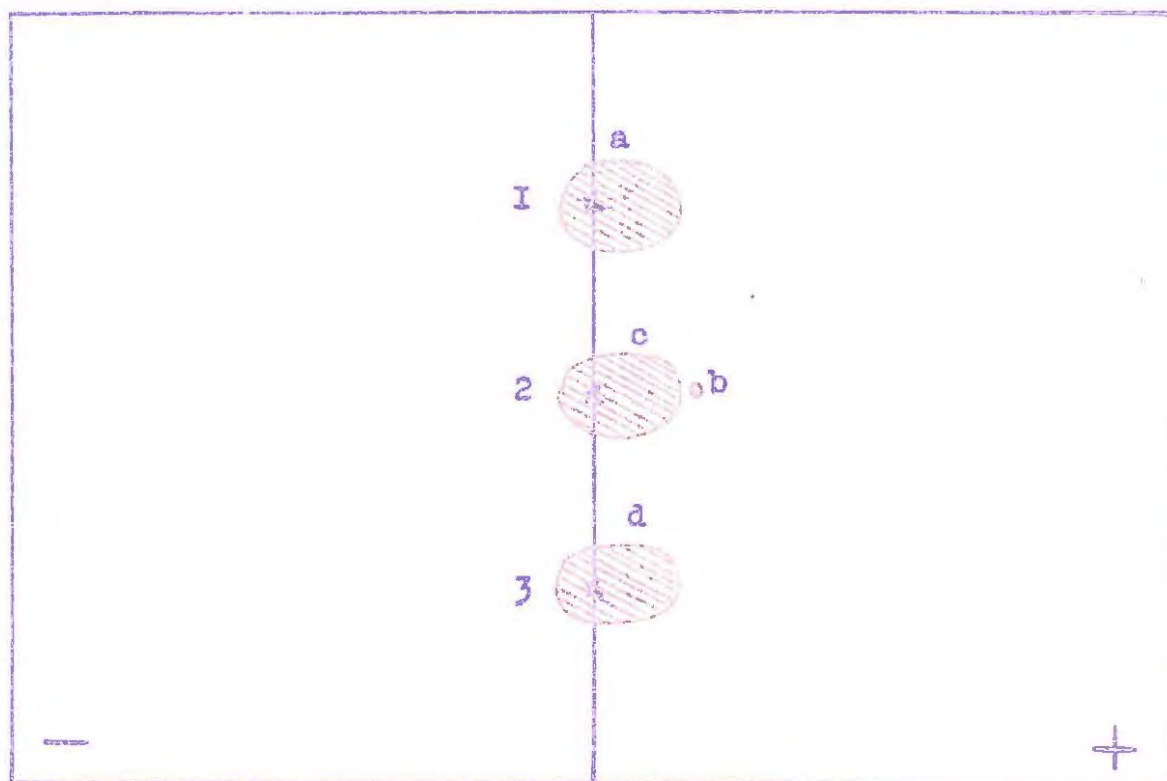
Running Time: 105 mins.

Paper: Asoka White Blotting 38.

Distances of Migration:

- (a) 4.7 cms.
- (b) 6.1 cms - 7.5 cms.
- (c) 4.8 cms.
- (d) 6.3 cms. - 7.7 cms.
- (e) 4.7 cms.
- (f) 5.8 cms. - 7.3 cms.

ELECTROCHROMATOGRAM I4.



1. A cold solution of Potassium cis-dioxalatodiaquochromiate prepared by Werner's Method (a) then washed with alcohol.
2. A cold solution of Potassium cis-dioxalatodiaquochromiate prepared by Werner's Method (a) .
3. A cold solution of Potassium cis-dioxalatodiaquochromiate prepared by Werner's Method (b).

EXPERIMENTAL CONDITIONS.

80 - 110 volts.

16.0 - 25.0 milliamps.

Background Electrolyte: 2 % Methylamine hydrochloride.

Running Time: 90 mins.

Paper: Whatman 54.

Distances of Migration:

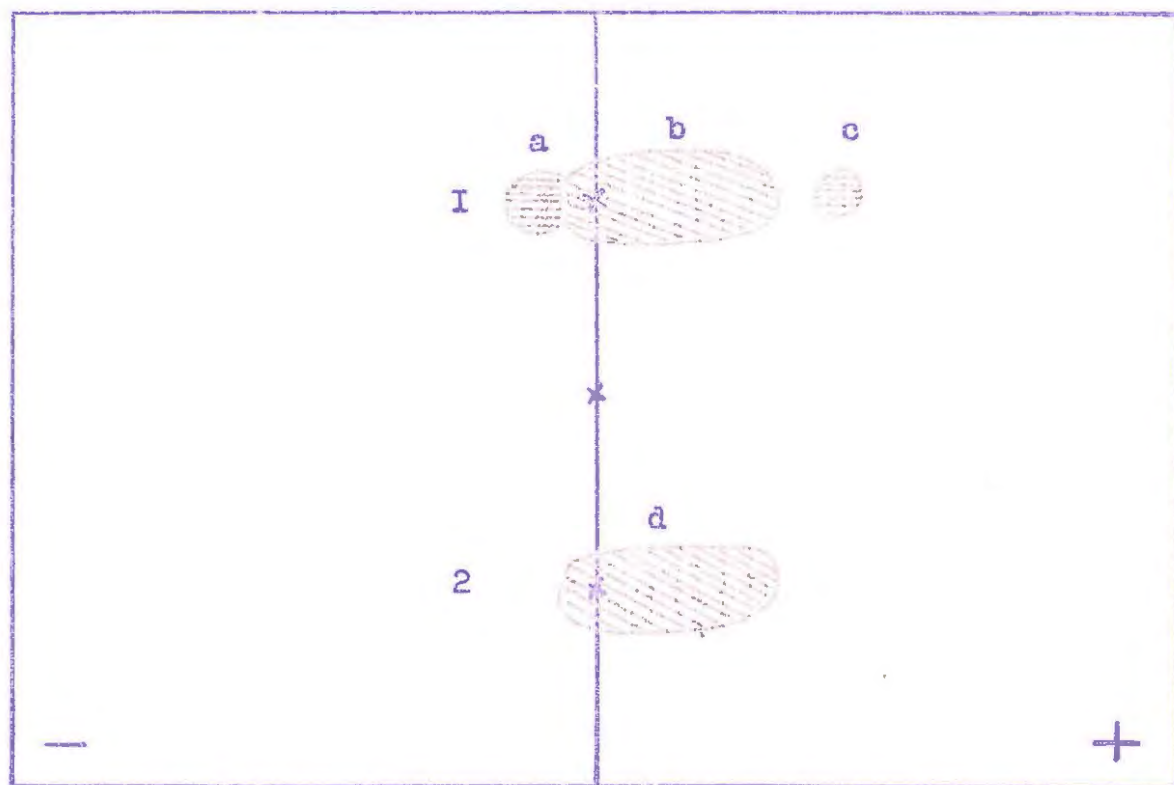
(a) 2.4 cms.

(b) 2.5 cms.- 2.6 cms.

(c) 2.4 cms.

(d) 2.5 cms.

ELECTROCHROMATOGRAM I5.



1. A heated solution of alcohol recrystallised Potassium trans-dioxalatodiaquochromiate stood for 12 hours.

2. A cold solution of alcohol recrystallised Potassium trans-dioxalatodiaquochromiate stood for 12 hours.

EXPERIMENTAL CONDITIONS.

100 - 130 volts

11.5 - 21.0 milliamps.

Background Electrolyte: 1 % Methylamine hydrochloride.

Running Time: 105 mins.

Paper: Asoka White Blotting 38.

Distances of Migration:

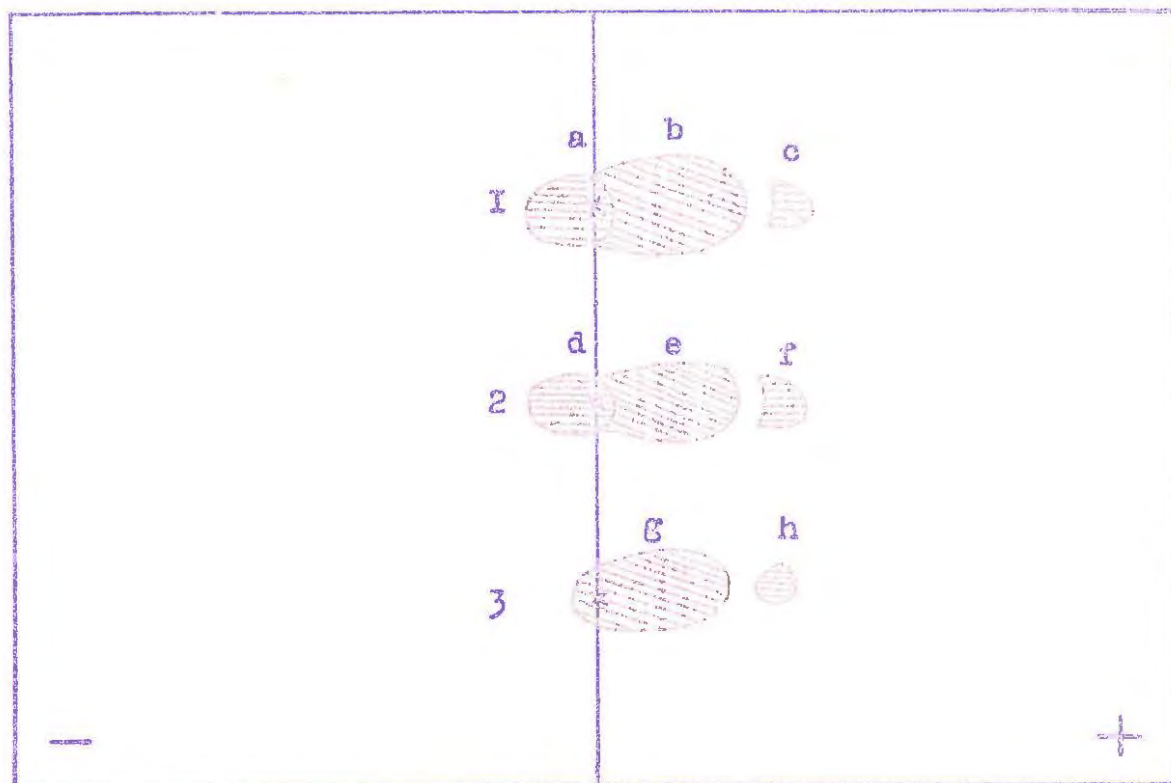
(a) 0.8 cms. - 1.7 cms.

(b) 4.8 cms.

(c) 5.3 cms - 7.3 cms.

(d) 4.6 cms.

ELECTROCHROMATOGRAM I6.



1. A heated solution of Potassium cis-dioxalatodiaquochromiate, prepared from the cis-salt, stood for 4 days.
2. A heated solution of Potassium cis-dioxalatodiaquochromiate, prepared from the twice recrystallised trans-salt, stood for 4 days.
3. A cold solution of Potassium cis-dioxalatodiaquochromiate, prepared from the twice recrystallised trans-salt, stood for 4 days.

EXPERIMENTAL CONDITIONS.

I20 - I40 volts.

I2.0 - 21.0 milliamps.

Background Electrolyte: 1 % Methylamine hydrochloride.

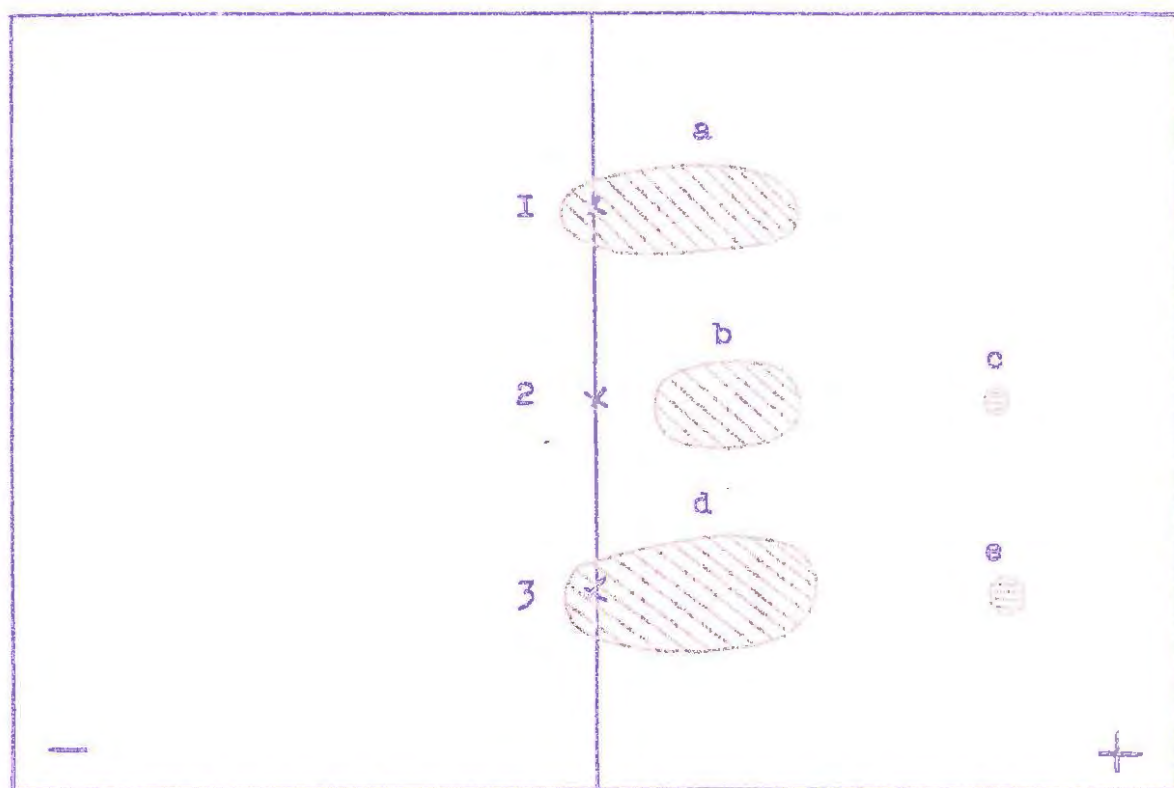
Running Time: 80 mins.

Paper: Asoka White Blotting 38.

Distances of Migration:

- (a) 1.8 cms.
- (b) 3.8 cms.
- (c) 4.2 cms. - 6.0 cms.
- (d) 2.2 cms.
- (e) 4.3 cms.
- (f) 4.6 cms. - 5.9 cms.
- (g) 3.8 cms.
- (h) 4.2 cms. - 5.2 cms.

ELECTROCHROMATOGRAM I7.



1. A heated solution of the crystals of the 1st preparation of Oxalatobisethylenediaminochromic chloride.
2. A heated solution of the crystals of the 2nd preparation of Oxalatobisethylenediaminochromic chloride.
3. 10 % Potassium cis-dioxalatodiaquochromiate prepared by aging the recrystallised trans-salt, as a reference solution.

EXPERIMENTAL CONDITIONS.

I20 - I40 volts.

I6.8 - 27.0 milliamps.

Background Electrolyte: 1 % Methylamine hydrochloride.

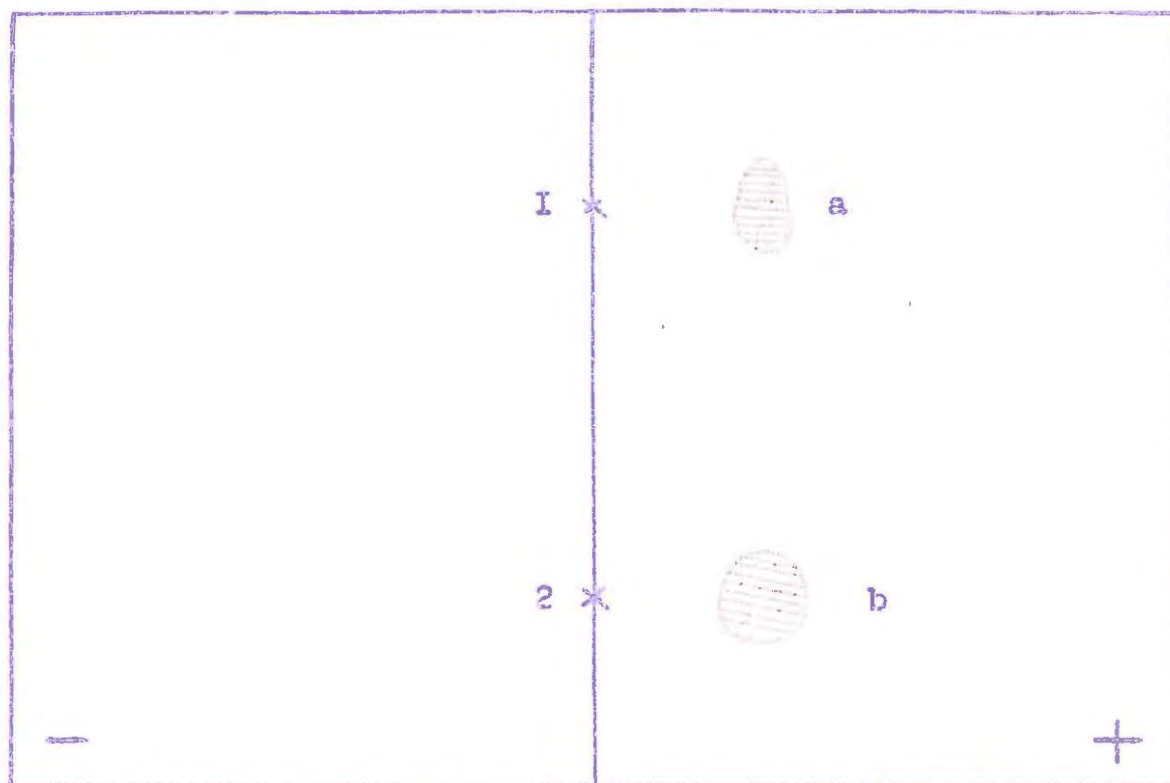
Running Time: 150 mins.

Paper: Asoka White Blotting 38.

Distances of Migration:

- (a) 5.3 cms.
- (b) 1.6 cms. - 5.8 cms.
- (c) 10.0 cms. - 10.9 cms.
- (d) 7.0 cms.
- (e) 9.8 cms - 11.1 cms.

ELECTROCHROMATOGRAM 18.



1. A heated solution of the alcohol washed crystals of the 1st preparation of Oxalatobisethylenediaminochromic chloride.
2. A heated solution of the alcohol washed crystals of the 2nd preparation of Oxalatobisethylenediaminochromic chloride.

EXPERIMENTAL CONDITIONS.

210 - 270 volts.

12.0 - 17.5 milliamps.

Background Electrolyte: 0.05M Potassium Nitrate.

Running Time: 35 mins.

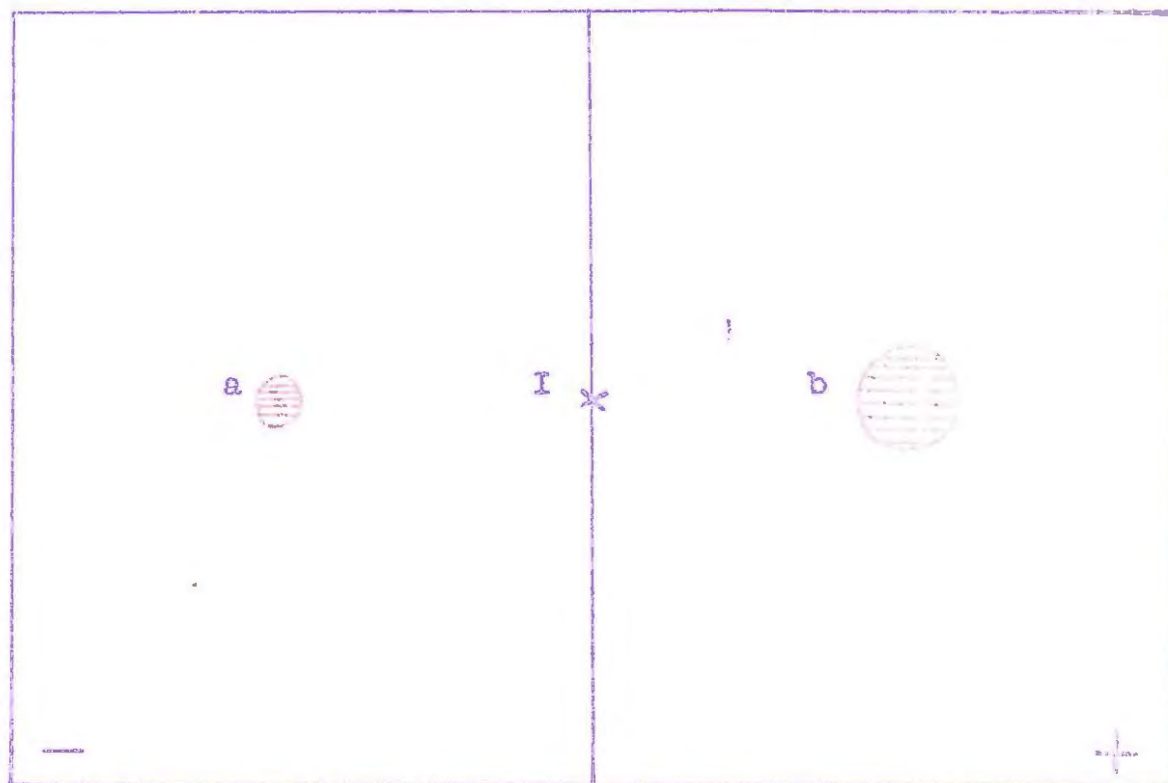
Paper: Asoka White Blotting. 38.

Distances of Migration:

(a) 3.2 cms. - 4.0 cms.

(b) 2.3 cms. - 4.3 cms.

ELECTROCHROMATOGRAM I9.



I. A heated solution of recrystallised Potassium Dioxalatoethylenediaminochromate.

EXPERIMENTAL CONDITIONS.

280 - 300 volts.

17.2 - 20.2 milliamps.

Background Electrolyte: 0.05M Potassium Nitrate.

Running Time: 80 mins.

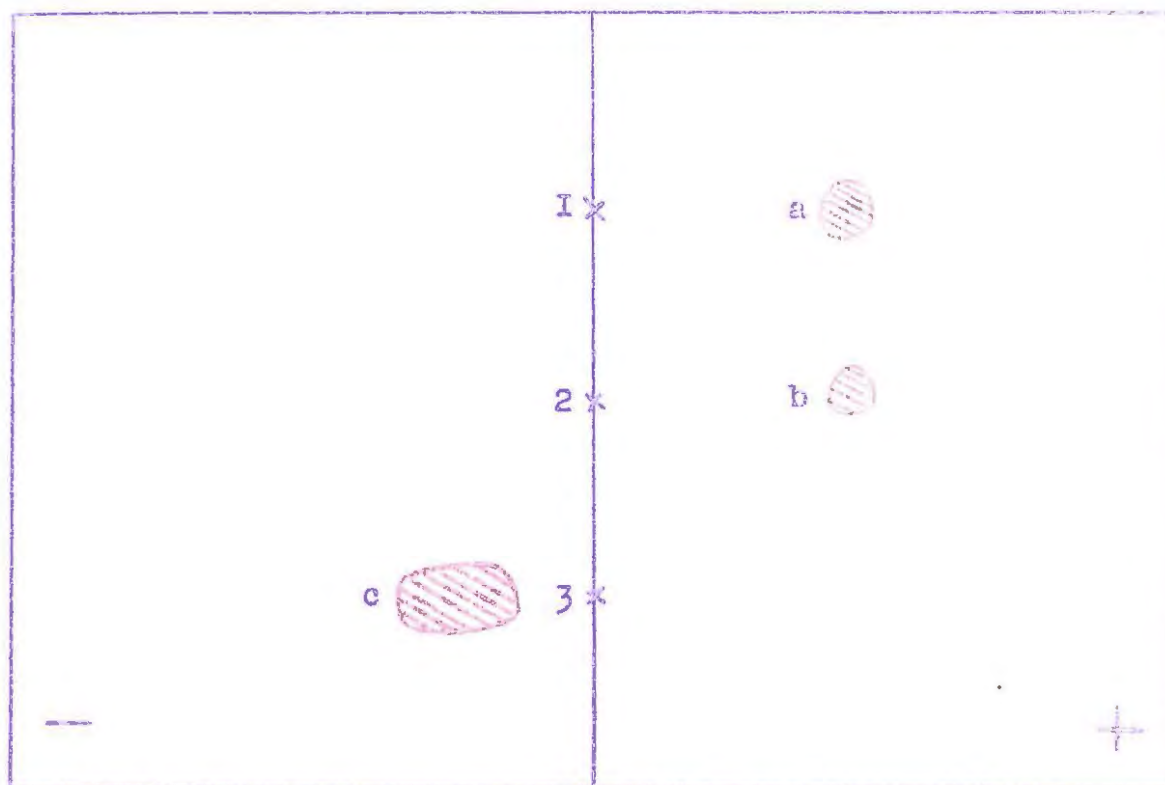
Paper: Asoka White Blotting. 33.

Distances of Migration:

(a) 6.9 cms. - 8.5 cms.

(b) 1.9 cms. - 7.0 cms.

ELECTROCHROMATOGRAM 20.



1. Potassium cis-dioxalatodiaquochromate and propylene-diamine (1:1 moles) heated for 4 hours at $101 - 108^{\circ}\text{C}$ then aged for 21 days at 18°C (0.009208 M).
2. Potassium cis-dioxalatodiaquochromate and propylene-diamine (1:2 moles) heated for 4 hours at $101 - 108^{\circ}\text{C}$ then aged for 21 days at 18°C (0.009208 M).
3. Potassium cis-dioxalatodiaquochromate and propylene-diamine (1:3 moles) heated for 4 hours at $101 - 108^{\circ}\text{C}$ then aged for 21 days at 18°C (0.009208 M).

EXPERIMENTAL CONDITIONS.

220 - 250 volts

12.5 - 15.0 milliamps.

Background Electrolyte: 0.05M Potassium Nitrate.

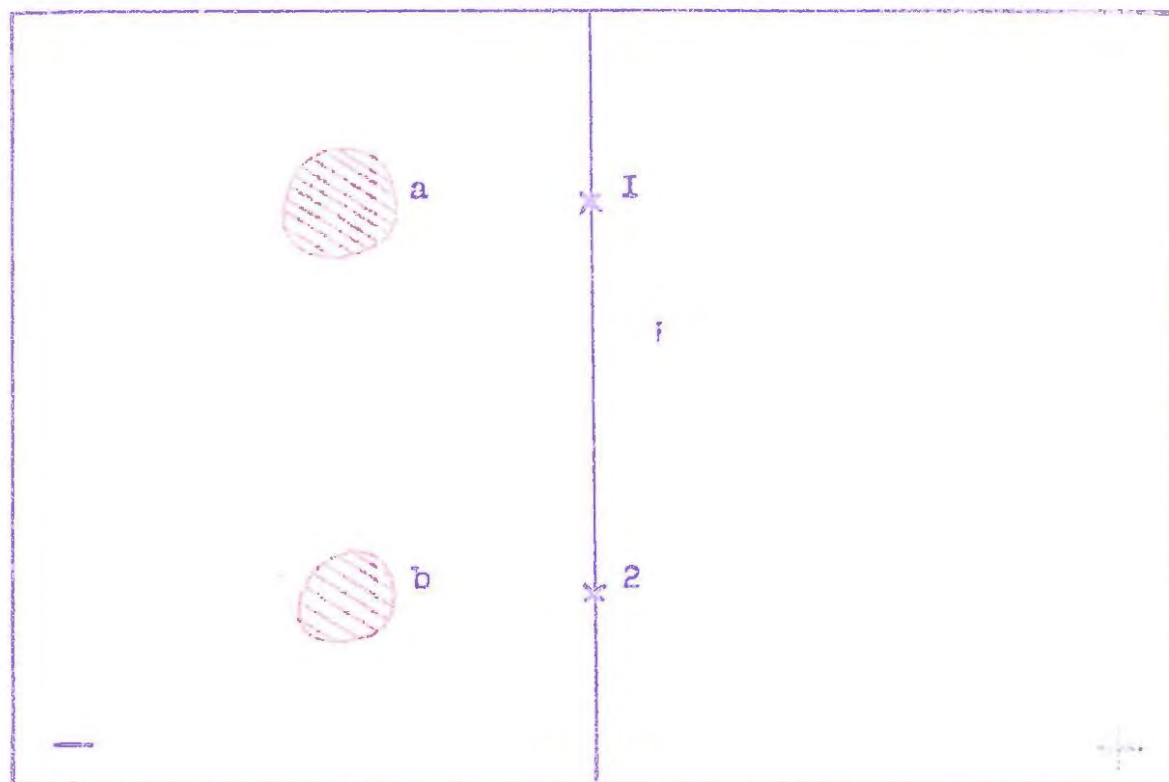
Running Time: 120 mins.

Paper: Asoka White Slotting 38.

Distances of Migration:

- (a) 5.7 cms. - 8.0 cms.
- (b) 6.4 cms. - 8.2 cms.
- (c) 1.5 cms. - 5.8 cms.

ELECTROCHROMATOGRAM 21.



1. Potassium cis-dioxalatodiaquochromate and propylene-diamine (1:10 moles) heated for 7 hours at 85 - 95°C then aged for 4 days at 18°C (0.009208 M).
2. Potassium cis-dioxalatodiaquochromate and ethylene-diamine (1:9 moles) heated for 7 hours at 85 - 95°C then aged for 4 days at 18°C (0.009208 M).

EXPERIMENTAL CONDITIONS.

220 - 240 volts.

10.0 - 11.8 milliamps.

Background Electrolyte: 0.05M Potassium Nitrate.

Running Time: 60 mins.

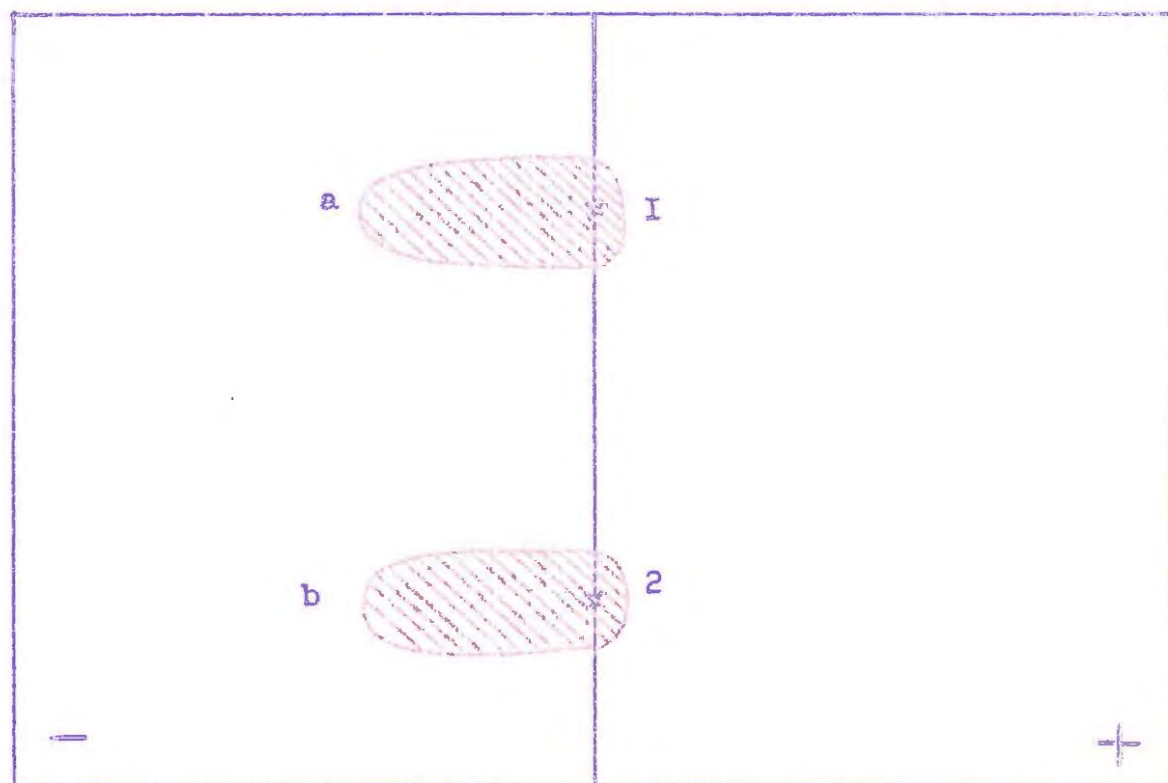
Paper: Asoka White Blotting 38.

Distances of Migration:

(a) 5.0 cms. - 9.0 cms.

(b) 5.6 cms. - 9.2 cms.

ELECTROCHROMATOGRAM 22.



1. Potassium cis-dioxalatodiaquochromate and propylene-diamine (1:10 moles) aged for $17\frac{1}{2}$ hours at 20°C (0.009208 M).
2. Potassium cis-dioxalatodiaquochromate and ethylenediamine (1:9 moles) aged for $17\frac{1}{2}$ hours at 20°C (0.009208 M).

EXPERIMENTAL CONDITIONS.

230 - 250 volts.

11.5 - 15.5 milliamps.

Background Electrolyte: 0.05M Potassium Nitrate.

Running Time: 90 mins.

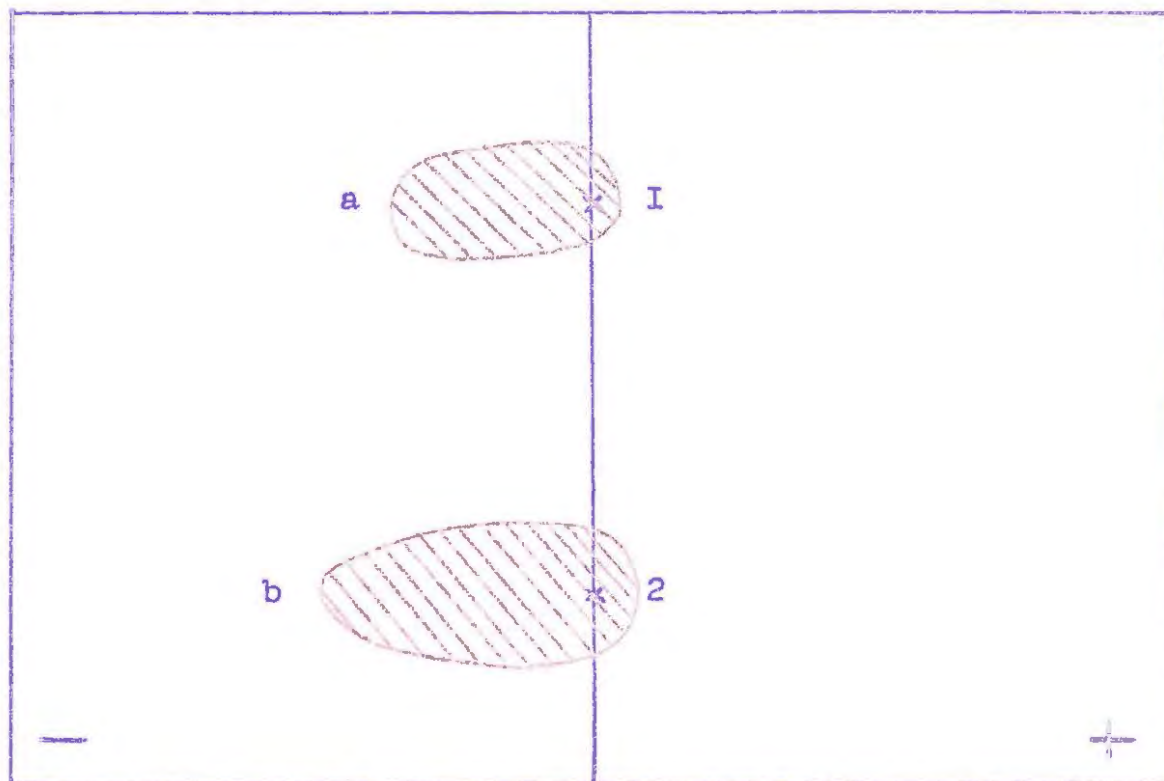
Paper: Asoka White Blotting 38.

Distance of Migration:

(a) 6.0 cms.

(b) 6.8 cms.

ELECTROCHROMATOGRAM 23.



- I. Potassium cis-dioxalatodiaquochromiate and propylene-diamine (1:10 moles) aged for 68 hours at 20°C (0.009208 M).
2. Potassium cis-dioxalatodiaquochromiate and ethylene-diamine (1:9 moles) aged for 68 hours at 20°C (0.009208 M).

EXPERIMENTAL CONDITIONS.

220 - 230 volts.

11.0 - 12.0 milliamps.

Background Electrolyte: 0.05M Potassium Nitrate.

Running Time: 70 mins.

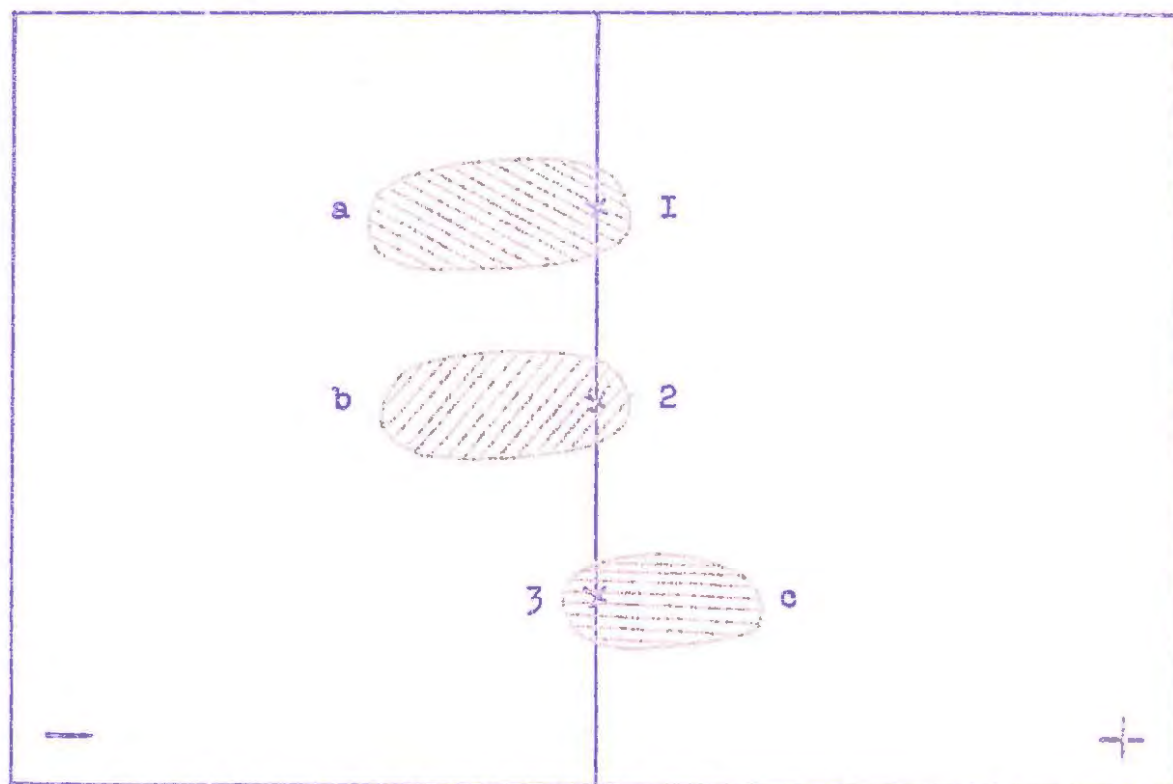
Paper: Asoka White Blotting 38.

Distances of Migration:

(a) 5.3 cms.

(b) 7.2 cms.

ELECTROCHROMATOGRAM 24.



1. Potassium cis-dioxalatodiaquochromiate and propylene-diamine (1:10 moles) aged for 24 days at 20°C (0.009208 M).
2. Potassium cis-dioxalatodiaquochromiate and ethylenediamine (1:9 moles) aged for 24 days at 20°C (0.009208 M).
3. Potassium cis-dioxalatodiaquochromiate and 2 equivalents of Potassium Hydroxide per mole of Chromium, aged for 20 days at 20°C (0.009208 M).

EXPERIMENTAL CONDITIONS.

210 - 260 volts.

10.0 - 14.0 milliamps.

Background Electrolyte: 0.05M Potassium Nitrate.

Running Time: 60 mins.

Paper: Asoka White Blotting 38.

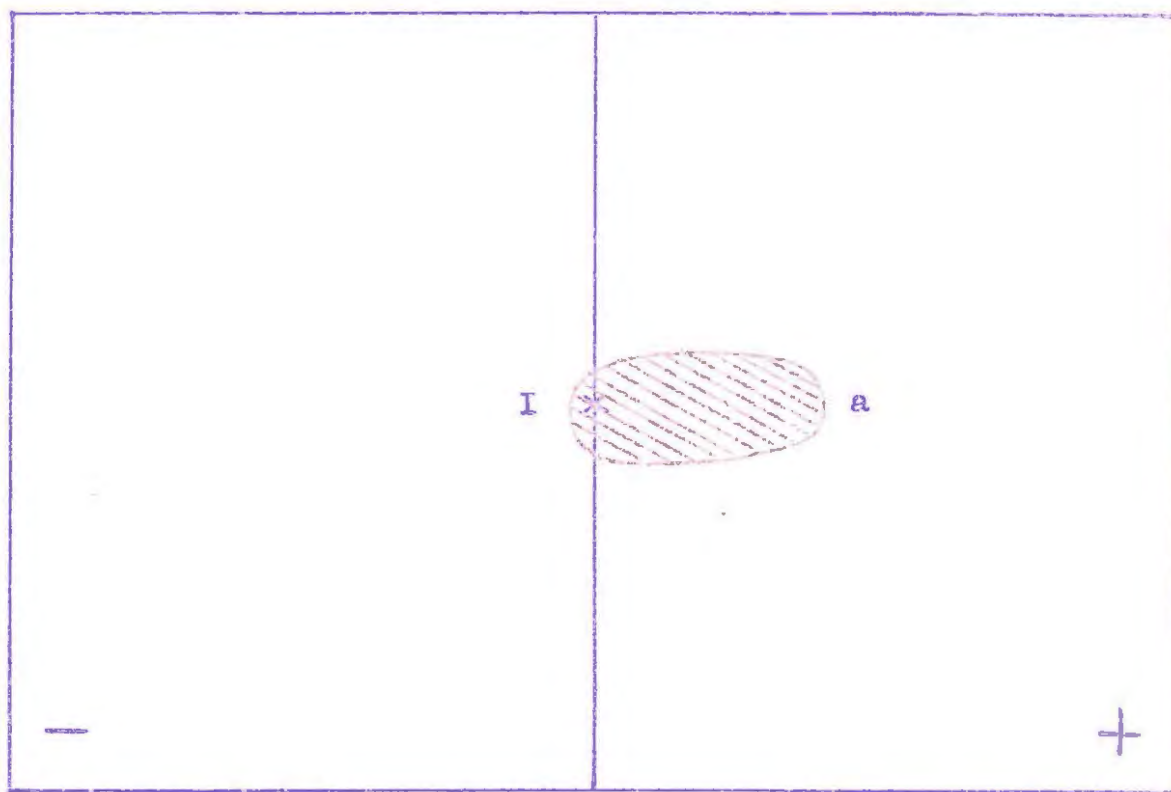
Distances of Migration:

(a) 6.0 cms.

(b) 6.0 cms.

(c) 4.1 cms.

ELECTROCHROMATOGRAM 25.



I. Potassium cis-dioxalatodiaquochromate and 2 equivalents of Potassium Hydroxide per mole of Chromium, aged for $17\frac{1}{2}$ hours at 20°C (0.009208 M).

EXPERIMENTAL CONDITIONS.

160 - 220 volts.

9.0 - 11.0 milliamps.

Background Electrolyte: 0.05M Potassium Nitrate.

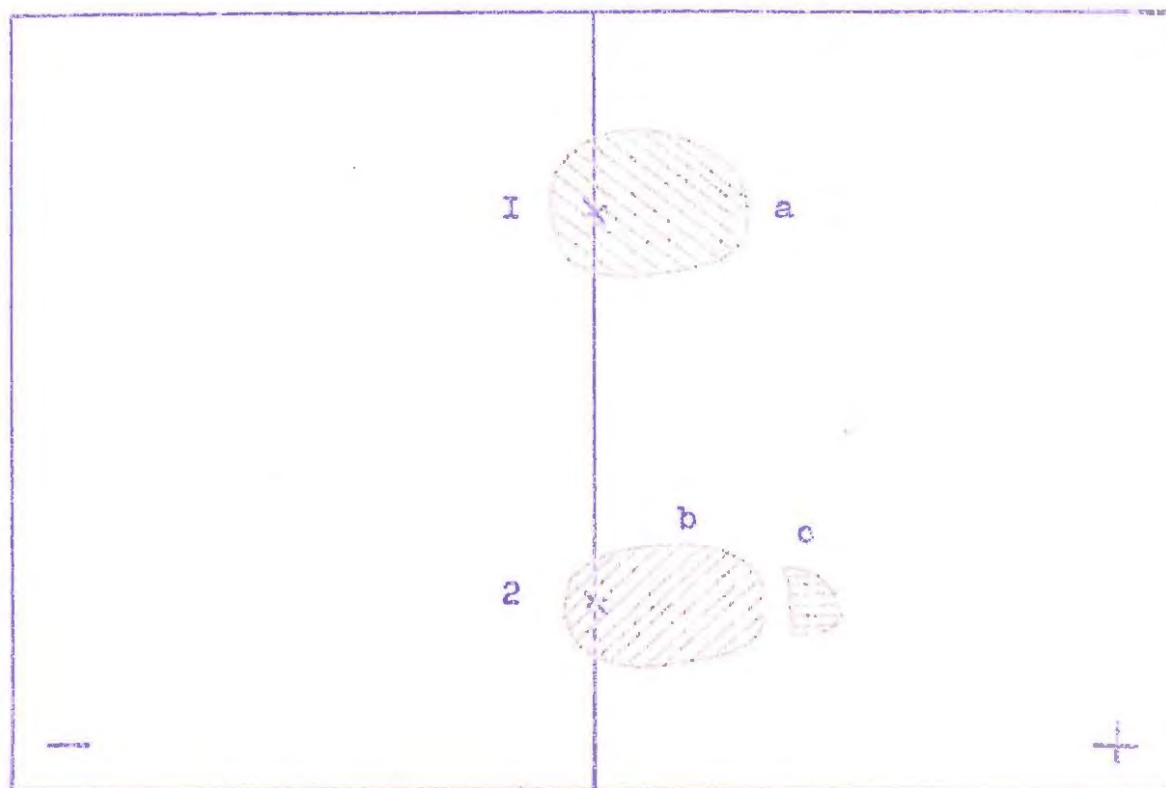
Running Time: 60 mins.

Paper: Asoka White Blotting 38.

Distances of Migration:

(a) 6.1 cms.

ELECTROCHROMATOGRAM 26.



1. Potassium cis-dioxalatodiaquochromate and 2 equivalents of Potassium Hydroxide per mole of Chromium, aged for 68 hours at 20°C (0.009208 M).

2. 10 % Potassium cis-dioxalatodiaquochromate prepared by aging the recrystallised trans-salt (as a reference).

EXPERIMENTAL CONDITIONS.

210 - 260 volts.

10.0 - 15.0 milliamps.

Background Electrolyte: 0.05M Potassium Nitrate.

Running Time: 55 mins.

Paper: Asoka White Blotting 38 .

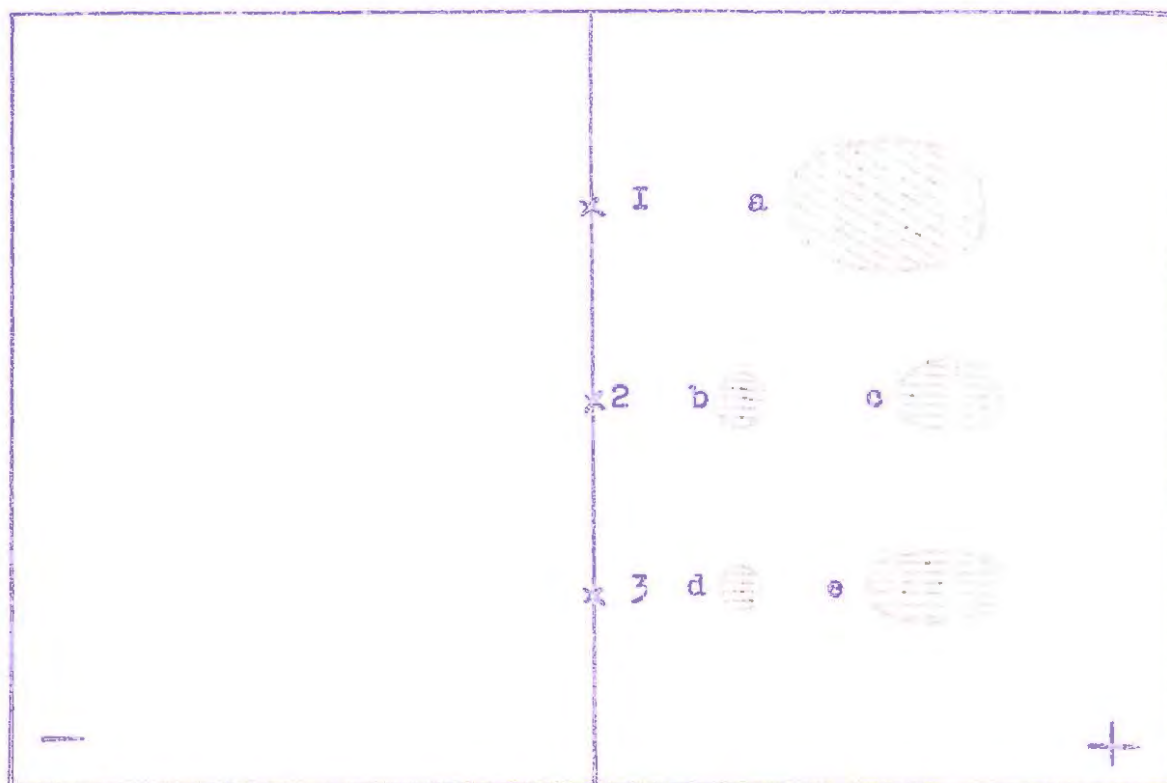
Distances of Migration:

(a) 3.9 cms.

(b) 4.3 cms.

(c) 4.5 cms. - 5.9 cms.

ELECTROCHROMATOGRAM 27.



Continuous Variation Method applied to Potassium cis-dioxalato-diaquo-chromate and Propylenediamine at pH 8.0.

50(I - X) mls. 0.009208 M Potassium cis-dioxalato-diaquo-chromate and
50X mls. 0.009208 M Propylenediamine.

1. $X = 0.0$

2. $X = 0.1$

3. $X = 0.2$

EXPERIMENTAL CONDITIONS.

210 - 280 volts.

11.0 - 16.0 milliamps.

Background Electrolyte: 0.05M Potassium Nitrate.

Running Time: 60 mins.

Paper: Aeoka White Blotting 38.

Distances of Migration:

(a) 5.1 cms. - 10.0 cms.

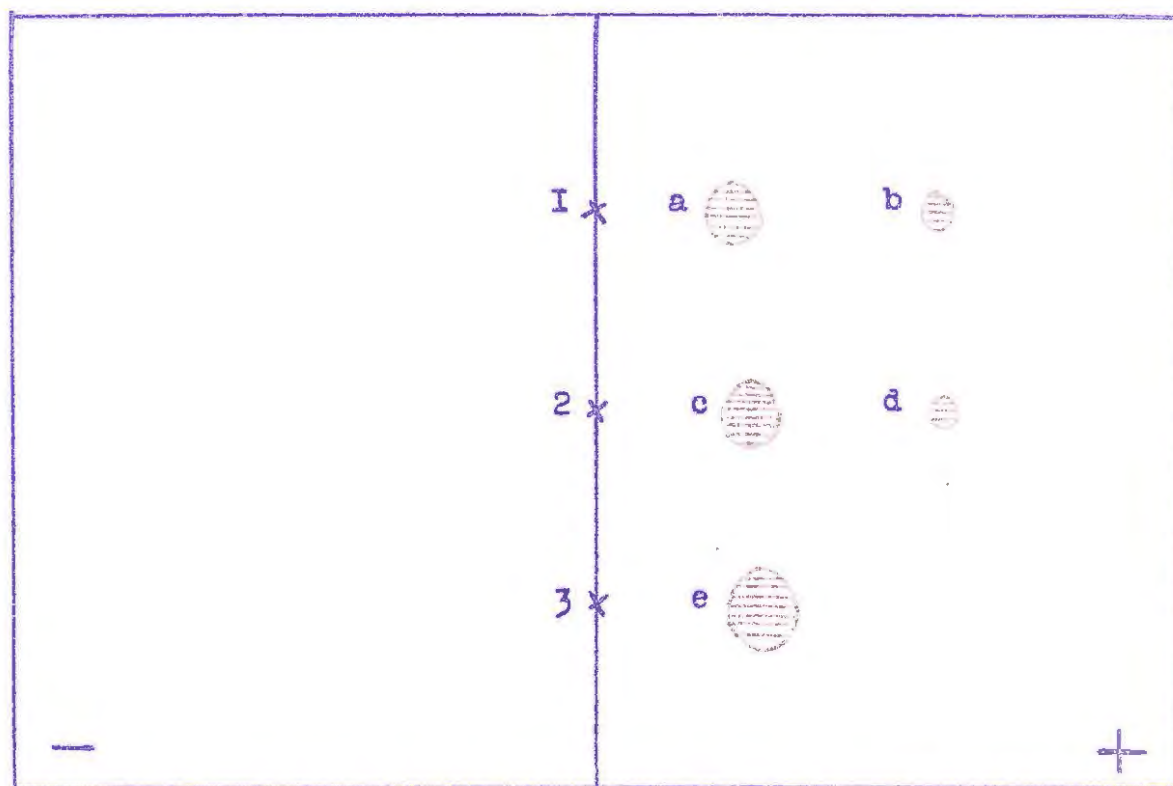
(b) 3.1 cms. - 4.6 cms.

(c) 7.8 cms. - 10.3 cms.

(d) 3.4 cms. - 4.7 cms.

(e) 6.6 cms. - 10.0 cms.

ELECTROCHROMATOGRAM 28.



Continuous Variation Method applied to Potassium cis-dioxalato-diaquochromate and Propylenediamine at pH 8.0.

50(I - X) mls. 0.009208 M Potassium cis-dioxalatodiaquochromate and
50X mls. 0.009208 M Propylenediamine.

1. $X = 0.3$

2. $X = 0.4$

3. $X = 0.5$

EXPERIMENTAL CONDITIONS.

270 - 280 volts.

16.0 - 16.5 milliamps.

Background Electrolyte: 0.05M Potassium Nitrate.

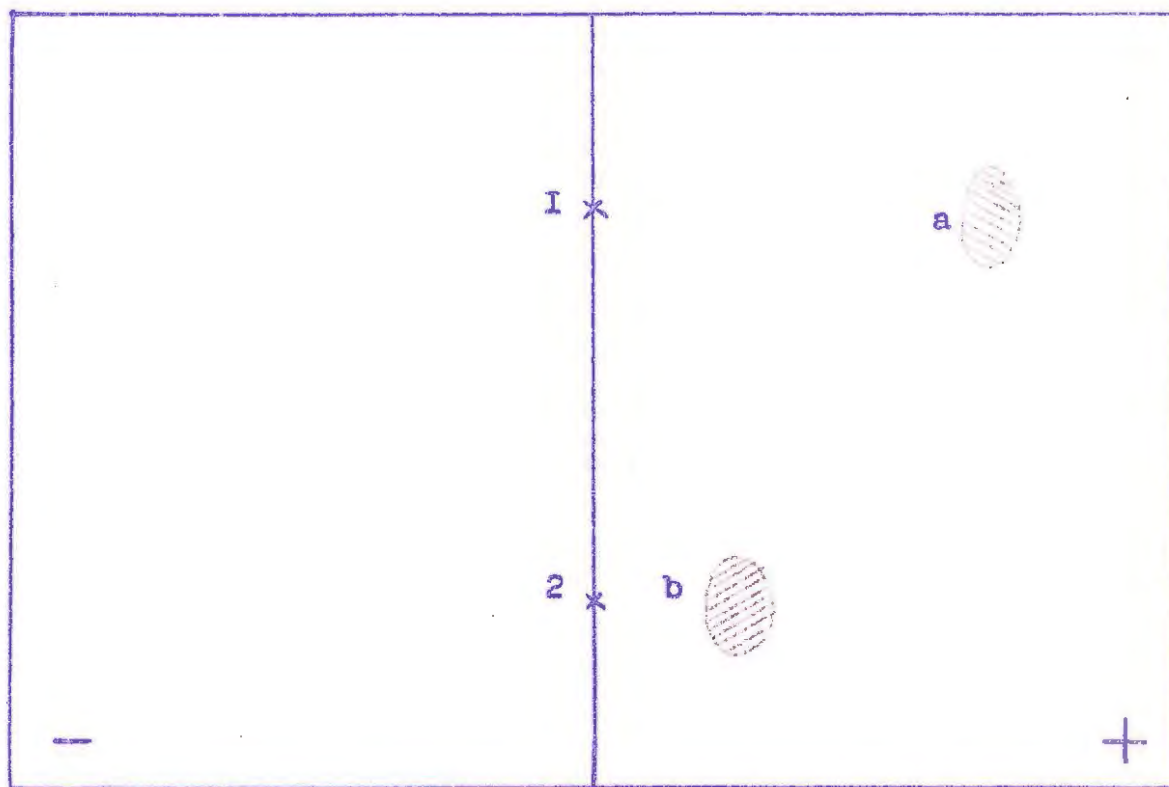
Running Time: 50 mins.

Paper: Asoka White Blotting 38.

Distances of Migration:

- (a) 3.3 cms. - 4.7 cms.
- (b) 7.2 cms. - 8.2 cms.
- (c) 4.0 cms. - 5.5 cms.
- (d) 7.9 cms. - 9.0 cms.
- (e) 3.4 cms. - 5.0 cms.

ELECTROCHROMATOGRAM 29.



1. Potassium cis-dioxalatodiaquochromiate and Urea (1:6 moles) boiled for 1 hour (0.009208 M).
2. Potassium cis-dioxalatodiaquochromiate and Urea (1:6 moles) aged for 169 hours at 20°C. (0.009208 M).

EXPERIMENTAL CONDITIONS.

260 - 280 volts.

13.8 - 17.0 milliamps.

Background Electrolyte: 0.05M Potassium Nitrate.

Running Time: 60 mins.

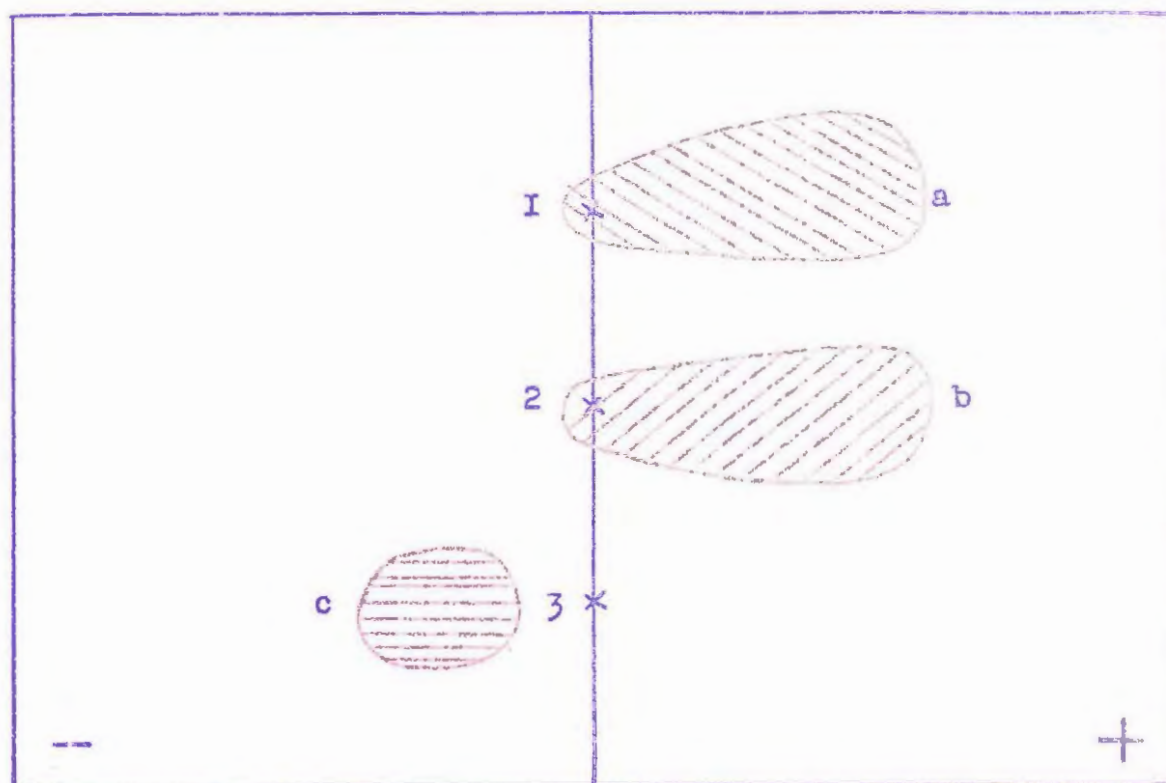
Paper: Asoka White Blotting 38.

Distances of Migration:

(a) 9.6 cms. - 11.0 cms.

(b) 2.8 cms. - 5.5 cms.

ELECTROCHROMATOGRAM 30.



1. Potassium Trioxalatochromiate and propylenediamine (1:1 moles) heated for 4 hours at $101 - 108^{\circ}\text{C}$ then aged for 21 days at 18°C (0.009208 M).
2. Potassium Trioxalatochromiate and propylenediamine (1:2 moles) heated for 4 hours at $101 - 108^{\circ}\text{C}$ then aged for 21 days at 18°C (0.009208 M).
3. Potassium Trioxalatochromiate and propylenediamine (1:3 moles) heated for 4 hours at $101 - 108^{\circ}\text{C}$ then aged for 21 days at 18°C (0.009208 M).

EXPERIMENTAL CONDITIONS.

255 - 280 volts.

13.6 - 15.0 milliamps.

Background Electrolyte: 0.05M Potassium Nitrate.

Running Time: 85 mins.

Paper: Asoka White Blotting 38.

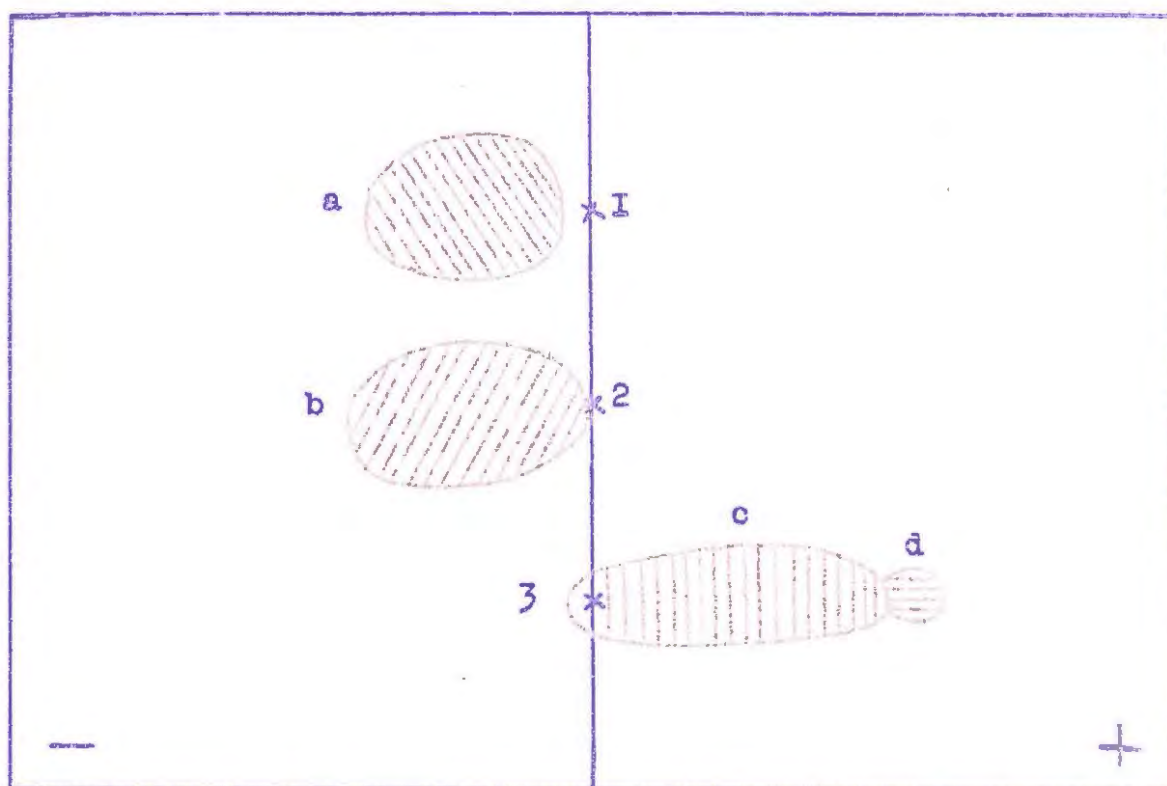
Distances of Migration:

(a) 8.4 cms.

(b) 8.8 cms.

(c) 1.3 cms. - 6.0 cms.

ELECTROCHROMATOGRAM 31.



1. Potassium Trioxalatochromiate and propylenediamine (1:10 moles) heated for 7 hours at 85 - 95°C then aged for 4 days at 18°C (0.009208 M).
2. Potassium Trioxalatochromiate and ethylenediamine (1:9 moles) heated for 7 hours at 85 - 95°C then aged for 4 days at 18°C (0.009208 M).
3. 10 % Potassium cis-dioxalatodiaquochromiate prepared by aging the trans-salt (as a reference).

EXPERIMENTAL CONDITIONS.

230 - 240 volts.

13.0 - 14.0 milliamps.

Background Electrolyte: 0.05M Potassium Nitrate.

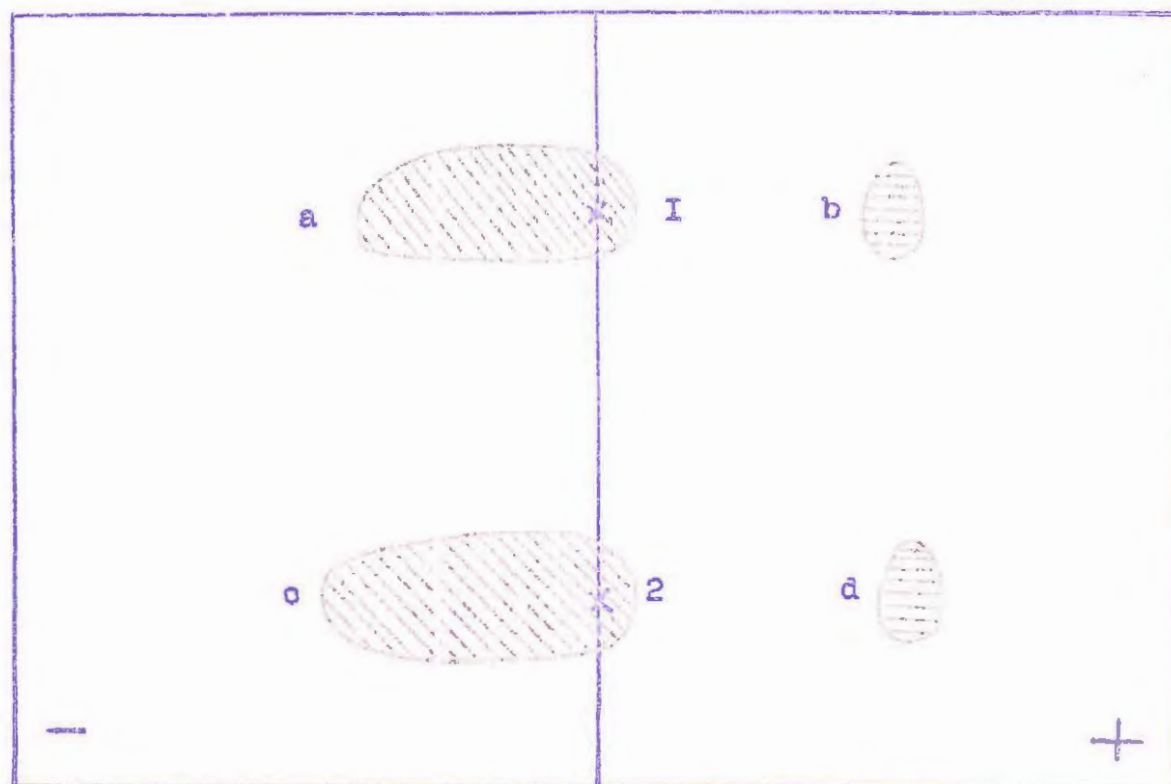
Running Time: 60 mins.

Paper: Asoka White Blotting 38.

Distances of Migration:

- (a) 0.3 cms. - 5.2 cms.
- (b) 5.6 cms.
- (c) 7.6 cms.
- (d) 7.6 cms. - 9.0 cms.

ELECTROCHROMATOGRAM 32.



1. Potassium Trioxalatochromiate and propylenediamine
(1:10 moles) aged for 19 hours at 20°C (0.009208 M).
2. Potassium Trioxalatochromiate and ethylenediamine
(1:9 moles) aged for 19 hours at 20°C (0.009208 M).

EXPERIMENTAL CONDITIONS.

230 - 340 volts.

10.8 - 14.0 milliamps.

Background Electrolyte: 0.05M Potassium Nitrate.

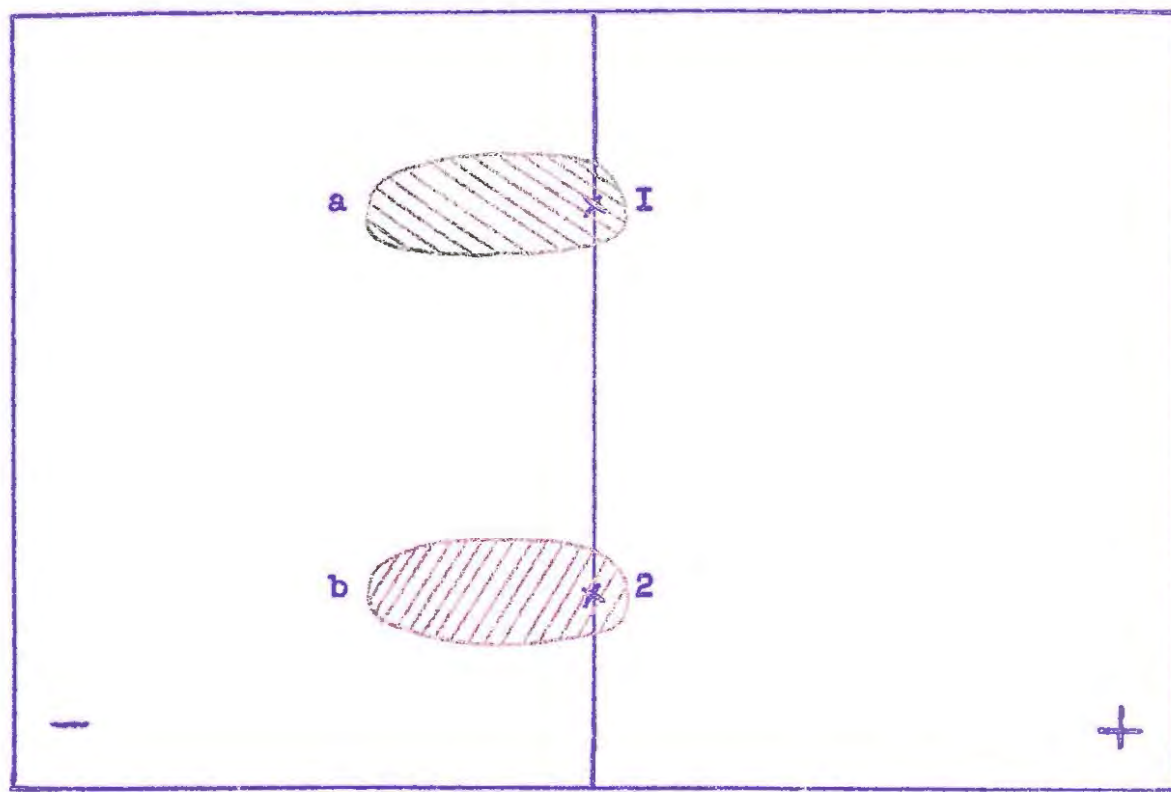
Running Time 50 mins.

Paper: Asoka White Blotting 38.

Distances of Migration:

- (a) 6.3 cms.
- (b) 7.5 cms. - 9.1 cms.
- (c) 7.0 cms.
- (d) 8.2 cms. - 9.4 cms.

ELECTROCHROMATOGRAM 33.



1. Potassium Trioxalatochromiate and propylenediamine
(1:10 moles) aged for 93 hours at 20°C (0.009208 M).
2. Potassium Trioxalatochromiate and ethylenediamine
(1:9 moles) aged for 93 hours at 20°C (0.009208 M).

EXPERIMENTAL CONDITIONS.

270 - 300 volts.

16.0 - 18.0 milliamps.

Background Electrolyte: 0.05M Potassium Nitrate.

Running Time: 55 mins.

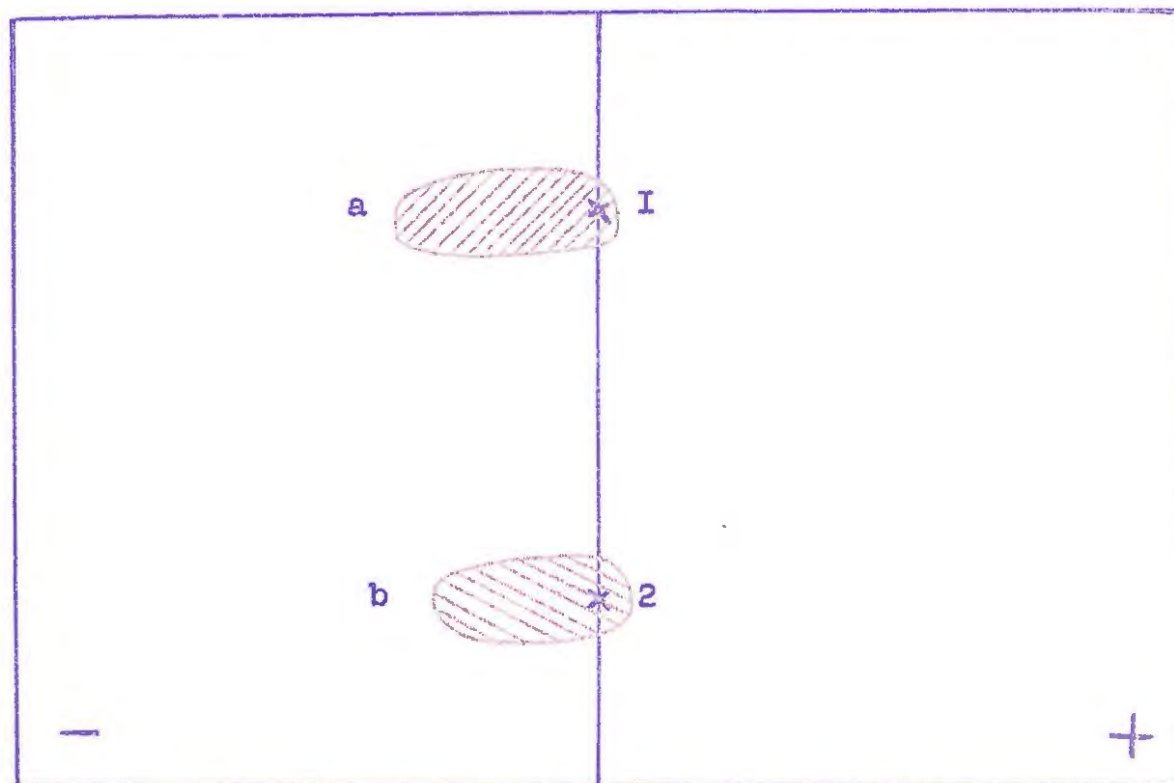
Paper: Asoka White Blotting 38.

Distances of Migration:

(a) 5.7 cms.

(b) 5.5 cms.

ELECTROCHROMATOGRAM 34.



1. Potassium Trioxalatochromiate and propylenediamine
(1:10 moles) aged for 24 days at 20°C (0.009208 M).
2. Potassium Trioxalatochromiate and ethylenediamine
(1:9 moles) aged for 24 days at 20°C (0.009208 M).

EXPERIMENTAL CONDITIONS.

220 - 300 volts.

11.6 - 16.0 milliamps.

Background Electrolyte:

0.05M Potassium Nitrate.

Running Time: 50 mins.

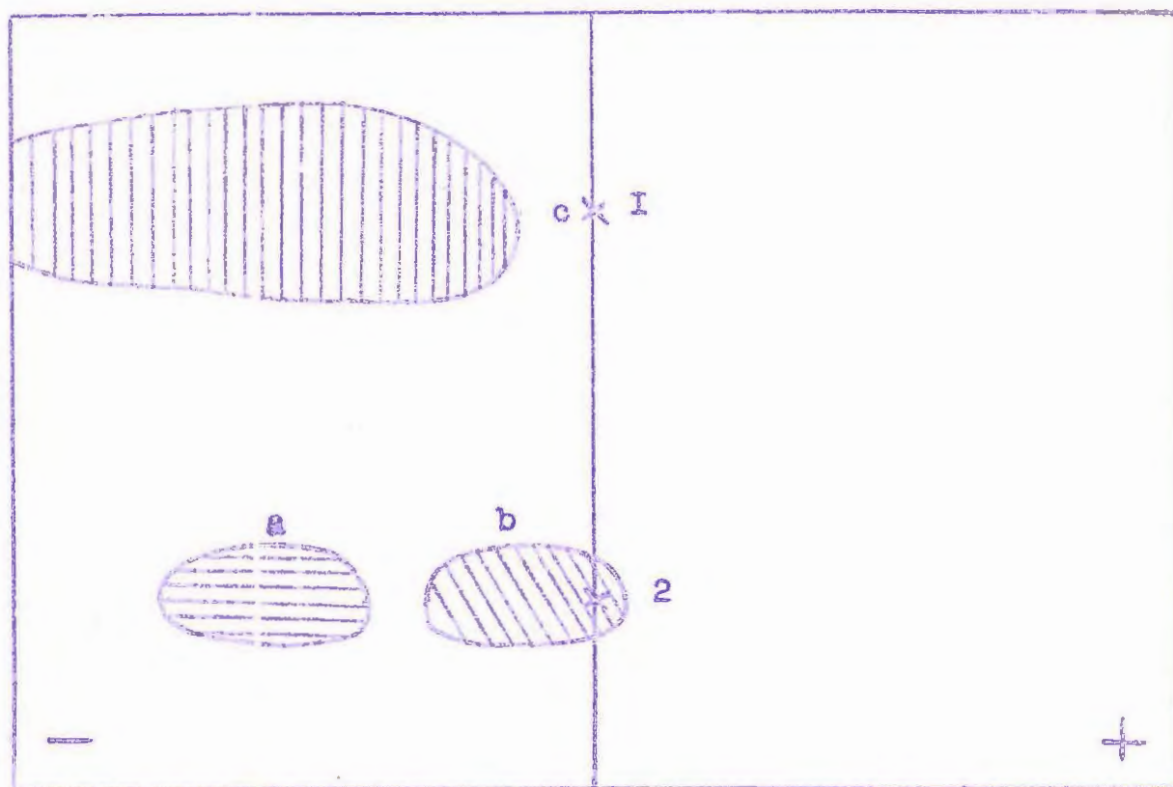
Paper: Asoka White Blotting 38.

Distances of Migration:

(a) 5.4 cms.

(b) 5.1 cms.

ELECTROCHROMATOGRAM 35.



1. A solution of Triethylenediaminochromic chloride in cold water and used immediately (0.009208 M).
2. Triethylenediaminochromic chloride aged for 6 days at 18°C (0.009208 M).

EXPERIMENTAL CONDITIONS.

225 - 280 volts.

11.8 - 18.0 milliamps.

Background Electrolyte: 0.05M Potassium Nitrate.

Running Time: 85 mins.

Paper: Asoka White Blotting 38.

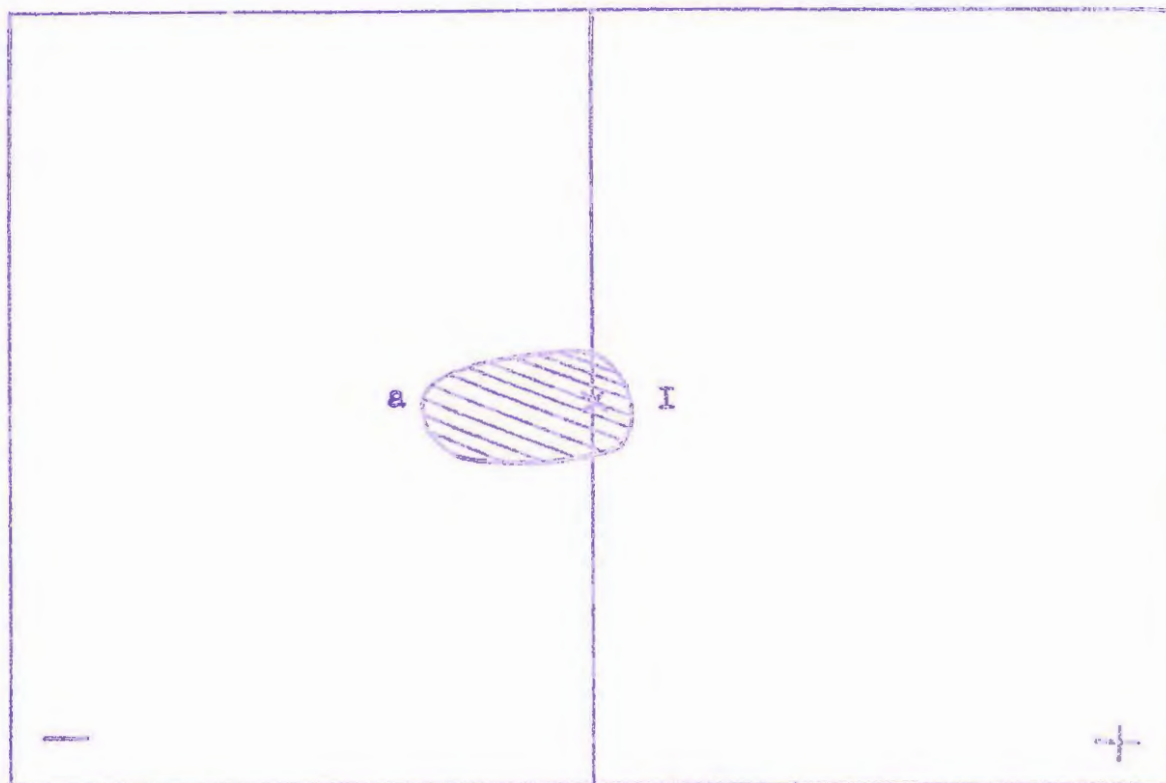
Distances of Migration:

(a) 5.8 cms. - 11.4 cms.

(b) 4.5 cms.

(c) 1.8 cms. - 12.8 cms.

ELECTROCHROMATOGRAM 36.



I. Potassium Triethylenediaminochromic chloride aged for
12 days at 18°C (0.009208 M).

EXPERIMENTAL CONDITIONS.

240 - 260 volts.

14.0 - 20.0 milliamps.

Background Electrolyte: 0.05M Potassium Nitrate.

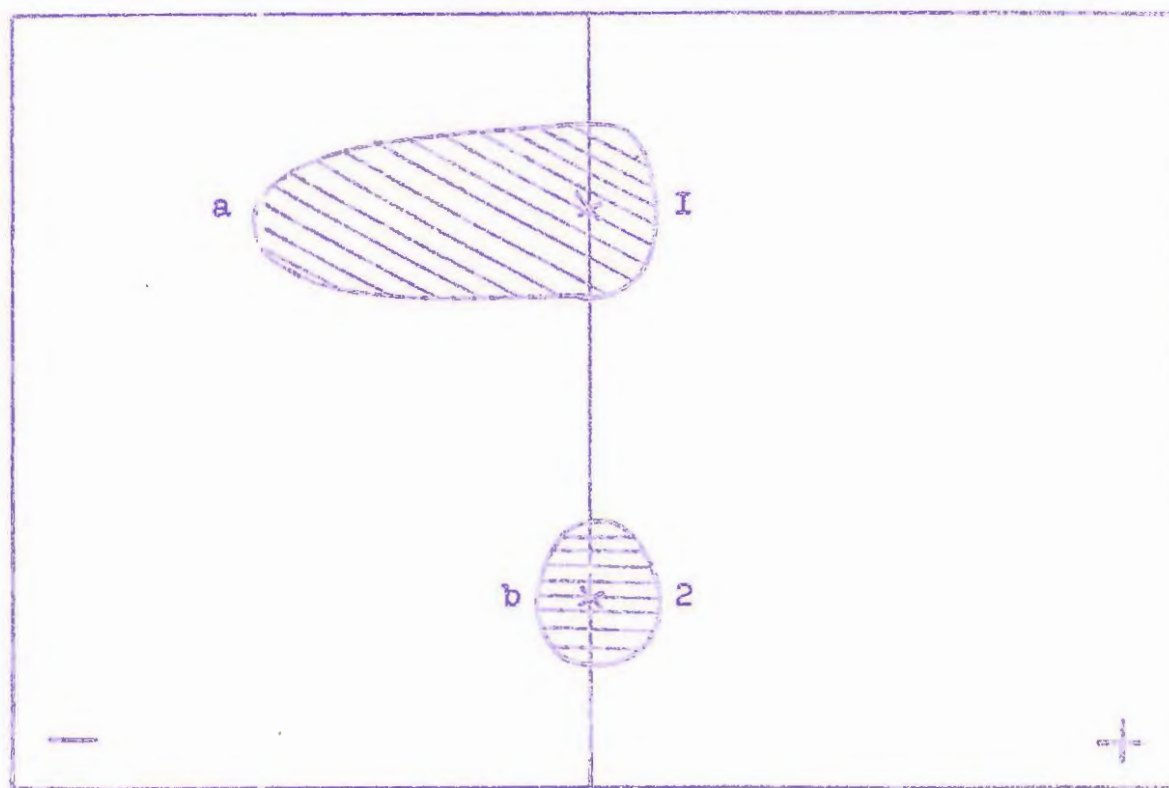
Running Time: 80 mins.

Paper: Asoka White Blotting 38.

Distances of Migration:

(a) 4.4 cms.

ELECTROCHROMATOGRAM 37.



1. A solution of Potassium Triethylenediaminochromic chloride in cold water used immediately (as a reference).
2. Potassium Triethylenediaminochromic chloride aged for 18 days at 18°C (0.009208 M).

EXPERIMENTAL CONDITIONS.

230 - 260 volts.

12.0 - 15.0 milliamps.

Background Electrolyte: 0.05M Potassium Nitrate.

Running Time: 50 mins.

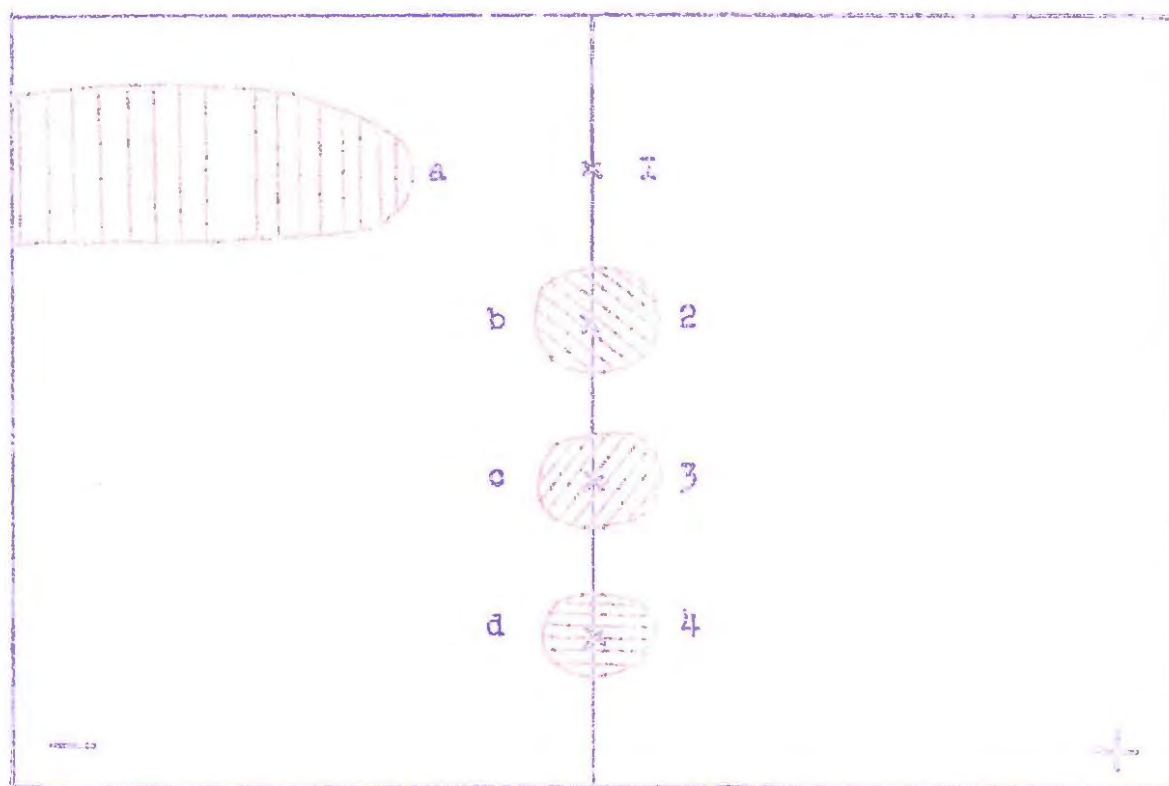
Paper: Asoka White Blotting 38.

Distances of Migration:

(a) 8.5 cm.

(b) No visible migration.

ELECTROCHROMATOGRAM 38.



1. A solution of Potassium Triethylenediaminochromic chloride in cold water used immediately (0.009208 M).
2. Potassium Triethylenediaminochromic chloride aged for 18 days at 18°C pH 7.7 (0.009208 M).
3. Potassium Triethylenediaminochromic chloride aged for 18 days at 18°C then brought to pH 4.5 (0.009208 M).
4. Potassium Triethylenediaminochromic chloride aged for 18 days at 18°C then brought to pH 12.0 (0.009208 M).

EXPERIMENTAL CONDITIONS.

240 - 250 volts.

16.0 - 18.5 milliamps.

Background electrolyte: 0.05M Potassium Nitrate.

Running Time: 100 mins.

Paper: Asks White Flopping 36.

Distances of Migration:

- (a) 4.2 cms. - 12.5 cms.
- (b) No visible migration.
- (c) No visible migration.
- (d) No visible migration.

A P P E N D I X B

S P E C T R O P H O T O M E T R I C

D A T A .

In this appendix, the following symbols are used :-

- λ = Wavelength in millimicrons ($m\mu$).
- D = Optical Density.
- S = Slit width in millimeters.

TABLE B.1.

Absorption curve of Potassium trioxalatochromiate.

0.0092 M

16°C

Fig. 14.

λ	S	D	$-\log D$	λ	S	D	$-\log D$
320	1.200	1.260	-0.1004	470	0.071	0.223	0.6517
325	0.970	0.809	0.0921	480	0.065	0.176	0.7545
330	0.800	0.477	0.3215	490	0.062	0.169	0.7721
335	0.680	0.280	0.5528	500	0.060	0.201	0.6968
340	0.585	0.171	0.7670	510	0.055	0.272	0.5654
345	0.510	0.115	0.9393	520	0.055	0.365	0.4377
350	0.450	0.097	1.0132	530	0.055	0.476	0.3224
355	0.400	0.103	0.9872	540	0.055	0.583	0.2343
360	0.360	0.129	0.8894	550	0.058	0.676	0.1701
365	0.330	0.174	0.7595	560	0.058	0.737	0.1325
370	0.300	0.231	0.6364	570	0.060	0.752	0.1238
375	0.285	0.304	0.5171	580	0.065	0.728	0.1379
380	0.280	0.387	0.4123	590	0.075	0.667	0.1759
385	0.280	0.482	0.3170	600	0.095	0.587	0.2314
390	0.300	0.578	0.2381	610	0.245	0.493	0.3072
395	0.350	0.673	0.1720	620	0.235	0.384	0.4157
400	0.450	0.766	0.1158	630	0.220	0.284	0.5467
410	0.135	0.916	0.0381	640	0.210	0.211	0.6757
420	0.120	0.958	0.0186	650	0.194	0.146	0.8356
430	0.105	0.887	0.0521	660	0.180	0.107	0.9706
440	0.095	0.737	0.1325	670	0.170	0.071	1.1487
450	0.085	0.536	0.2708	680	0.160	0.045	1.3468
460	0.080	0.353	0.4522	690	0.154	0.036	1.4437
				700	0.145	0.028	1.5528

TABLE B.2.

Absorption curve of Potassium cis-dioxalatodiaquochromate prepared by Werner's method (a) and unwashed with alcohol.

0.0092 M

18°C.

Fig. 15.

λ	D	$-\log D$	λ	D	$-\log D$
310	0.660	0.1805	490	0.160	0.7959
320	0.350	0.4559	500	0.183	0.7375
325	0.297	0.5272	510	0.228	0.6421
332	0.298	0.5258	522	0.304	0.5171
340	0.342	0.4660	528	0.340	0.4685
345	0.368	0.4342	540	0.410	0.3872
350	0.388	0.4112	552	0.454	0.3429
355	0.403	0.3947	560	0.468	0.3298
360	0.415	0.3820	570	0.458	0.3391
365	0.425	0.3716	582	0.422	0.3747
370	0.443	0.3536	588	0.394	0.4045
380	0.490	0.3098	600	0.334	0.4763
390	0.558	0.2534	610	0.271	0.5670
400	0.623	0.2055	620	0.217	0.6635
410	0.671	0.1733	630	0.162	0.7905
420	0.660	0.1805	640	0.121	0.9172
432	0.578	0.2381	650	0.090	1.0458
440	0.488	0.3116	660	0.064	1.1938
452	0.354	0.4510	680	0.031	1.5086
464	0.247	0.6073	690	0.031	1.5086
470	0.207	0.6840	700	0.015	1.8239
482	0.165	0.7825	710	0.008	2.0969

TABLE B.3.

Absorption curve of Potassium cis-dioxalatodichromate (using the cis - salt prepared by Werners method (a) and washed with alcohol).

0.0092 M

18°C

Fig. 17.

λ	S	D	$-\log D$	λ	S	D	$-\log D$
320	1.200	0.210	0.6778	480	0.067	0.143	0.8447
325	0.970	0.114	0.9431	490	0.065	0.144	0.8416
330	0.800	0.063	1.2007	500	0.060	0.174	0.7595
335	0.680	0.042	1.3768	510	0.056	0.225	0.6478
340	0.582	0.032	1.4959	520	0.054	0.285	0.5452
345	0.510	0.038	1.4202	530	0.053	0.351	0.4547
350	0.450	0.048	1.3188	540	0.055	0.413	0.3840
355	0.400	0.064	1.1938	550	0.056	0.452	0.3449
360	0.360	0.090	1.0458	560	0.058	0.471	0.3270
365	0.330	0.125	0.9031	570	0.061	0.463	0.3344
370	0.302	0.168	0.7747	580	0.065	0.429	0.3675
375	0.285	0.218	0.6615	590	0.077	0.381	0.4191
380	0.280	0.280	0.5528	600	0.096	0.326	0.4868
385	0.280	0.346	0.4609	610	0.220	0.286	0.5436
390	0.300	0.411	0.3862	620	0.210	0.221	0.6556
395	0.350	0.469	0.3288	630	0.198	0.163	0.7878
400	0.450	0.521	0.2832	640	0.188	0.122	0.9136
410	0.140	0.602	0.2204	650	0.178	0.089	1.0506
420	0.122	0.602	0.2204	660	0.168	0.063	1.2007
430	0.110	0.548	0.2612	670	0.158	0.043	1.3665
440	0.096	0.437	0.3595	680	0.150	0.032	1.4949
450	0.087	0.325	0.4881	690	0.143	0.029	1.5376
460	0.080	0.238	0.6234	700	0.137	0.016	1.7959
470	0.073	0.174	0.7595				

TABLE B.4.

Absorption curve of Potassium cis-dioxalatodichromate (using the cis-salt prepared by Werner's method (a) and washed with alcohol) boiled for 1 hour in aqueous solution, cooled and then made up to volume.

0.0092 M

18°C

Fig. 17.

λ	S	D	$-\log D$	λ	S	D	$-\log D$
320	1.200	0.236	0.6271	480	0.067	0.141	0.8508
325	0.970	0.140	0.7339	490	0.065	0.144	0.8416
330	0.800	0.079	1.1024	500	0.060	0.173	0.7620
335	0.680	0.057	1.2441	510	0.056	0.220	0.6576
340	0.582	0.042	1.3768	520	0.054	0.284	0.5467
345	0.510	0.044	1.3565	530	0.053	0.352	0.4535
350	0.450	0.051	1.2924	540	0.055	0.413	0.3840
355	0.400	0.068	1.1675	550	0.056	0.452	0.3449
360	0.360	0.093	1.0315	560	0.058	0.473	0.3251
365	0.330	0.128	0.8928	570	0.061	0.466	0.3316
370	0.302	0.171	0.7670	580	0.065	0.435	0.3615
375	0.285	0.223	0.6517	590	0.077	0.387	0.4123
380	0.280	0.239	0.6216	600	0.096	0.336	0.4737
385	0.280	0.346	0.4609	610	0.220	0.292	0.5346
390	0.300	0.411	0.3862	620	0.210	0.227	0.6440
395	0.350	0.470	0.3279	630	0.198	0.168	0.7747
400	0.450	0.523	0.2815	640	0.188	0.125	0.9031
410	0.139	0.605	0.2182	650	0.178	0.090	1.0468
420	0.122	0.606	0.2175	660	0.168	0.064	1.1938
430	0.110	0.550	0.2596	670	0.158	0.044	1.3565
440	0.096	0.443	0.3536	680	0.150	0.033	1.4815
450	0.087	0.329	0.4828	690	0.143	0.031	1.5086
460	0.080	0.239	0.6216	700	0.137	0.018	1.7447
470	0.073	0.174	0.7595				

TABLE B.5.

Absorption curve of Potassium cis-dioxalatodiaquochromate (using the cis-salt prepared by Werners method (a) and washed with alcohol) boiled for $\frac{1}{2}$ hour in 1% nitric acid, cooled and then made up to volume.

0.0092 M

18°C

Fig. 17.

λ	S	D	$-\log D$	λ	S	D	$-\log D$
320	1.200	0.516	0.2874	480	0.067	0.128	0.8929
325	0.970	0.311	0.5072	490	0.065	0.131	0.8827
330	0.800	0.165	0.7825	500	0.060	0.158	0.8013
335	0.680	0.090	1.0458	510	0.056	0.202	0.6945
340	0.582	0.058	1.2366	520	0.054	0.255	0.5935
345	0.510	0.048	1.3188	530	0.053	0.315	0.5017
350	0.450	0.053	1.2757	540	0.055	0.359	0.4449
355	0.400	0.066	1.1805	550	0.056	0.392	0.4067
360	0.360	0.087	1.0605	560	0.058	0.402	0.3958
365	0.330	0.115	0.9393	570	0.061	0.392	0.4067
370	0.302	0.150	0.8239	580	0.065	0.358	0.4461
375	0.285	0.190	0.7212	590	0.077	0.318	0.4976
380	0.280	0.240	0.6198	600	0.096	0.271	0.5670
385	0.280	0.293	0.5331	610	0.220	0.240	0.6198
390	0.300	0.343	0.4647	620	0.210	0.186	0.7305
395	0.350	0.391	0.4078	630	0.198	0.135	0.8697
400	0.450	0.432	0.3645	640	0.188	0.100	1.000
410	0.139	0.496	0.3045	650	0.178	0.070	1.1549
420	0.122	0.498	0.3028	660	0.168	0.050	1.3010
430	0.110	0.453	0.3439	670	0.158	0.035	1.4559
440	0.096	0.368	0.4342	680	0.150	0.028	1.5528
450	0.087	0.280	0.5528	690	0.143	0.023	1.6383
460	0.080	0.208	0.6819	700	0.137	0.013	1.8861
470	0.073	0.154	0.8125				

TABLE B.6.

Absorption curve of Potassium cis-dioxalatodiaquochromiate prepared by aging the trans-salt, once recrystallised from 1% nitric acid and once recrystallised from 1 : 1 alcohol-water.

0.0092 M

18°C.

Fig. 19.

λ	S	D	$-\log D$	λ	S	D	$-\log D$
320	0.885	0.194	0.7122	362	0.261	0.104	0.9830
322	0.810	0.154	0.8125	364	0.255	0.118	0.9281
324	0.741	0.121	0.9172	366	0.245	0.133	0.8761
326	0.690	0.094	1.0269	368	0.240	0.150	0.8239
328	0.640	0.073	1.1367	370	0.230	0.169	0.7721
330	0.595	0.058	1.2366	372	0.225	0.188	0.7258
332	0.555	0.048	1.3188	374	0.220	0.208	0.6819
334	0.520	0.041	1.3872	376	0.218	0.234	0.6308
336	0.490	0.036	1.4437	378	0.214	0.256	0.5918
338	0.462	0.035	1.4685	380	0.210	0.282	0.5498
340	0.440	0.032	1.4949	382	0.210	0.319	0.4962
342	0.415	0.032	1.4949	384	0.210	0.347	0.4597
344	0.394	0.036	1.4437	386	0.215	0.356	0.4486
346	0.370	0.037	1.4318	388	0.220	0.384	0.4157
348	0.350	0.041	1.3872	390	0.230	0.411	0.3862
350	0.328	0.046	1.3372	392	0.240	0.434	0.3625
352	0.320	0.053	1.2756	394	0.260	0.459	0.3382
354	0.305	0.058	1.2366	396	0.280	0.483	0.3161
356	0.295	0.068	1.1675	398	0.305	0.503	0.2984
358	0.282	0.079	1.1024	400	0.340	0.526	0.2790
360	0.275	0.090	1.0458				

TABLE B.7.

Absorption curve of Potassium cis-dioxalatodiaquochromiate prepared by aging the trans-salt, twice recrystallised from 1% nitric acid.

0.0092 M

18°C.

Fig. 19

λ	S	D	$-\log D$	λ	S	D	$-\log D$
320	0.885	0.185	0.7328	362	0.261	0.102	0.9914
322	0.810	0.147	0.8327	364	0.255	0.115	0.9393
324	0.741	0.115	0.9393	366	0.245	0.134	0.8729
326	0.690	0.089	1.0506	368	0.240	0.149	0.8268
328	0.640	0.069	1.1612	370	0.230	0.169	0.7721
330	0.595	0.052	1.2840	372	0.225	0.188	0.7258
332	0.555	0.043	1.3665	374	0.220	0.207	0.6810
334	0.520	0.037	1.4318	376	0.218	0.233	0.6326
336	0.490	0.033	1.4815	378	0.214	0.254	0.5952
338	0.462	0.031	1.5086	380	0.210	0.280	0.5528
340	0.440	0.029	1.5376	382	0.210	0.307	0.5129
342	0.415	0.030	1.5229	384	0.210	0.340	0.4685
344	0.394	0.033	1.4815	386	0.215	0.354	0.4510
346	0.370	0.034	1.4685	388	0.220	0.383	0.4168
348	0.350	0.039	1.4089	390	0.230	0.410	0.3872
350	0.328	0.045	1.3468	392	0.240	0.433	0.3635
352	0.320	0.051	1.2924	394	0.260	0.457	0.3401
354	0.305	0.057	1.2441	396	0.280	0.481	0.3179
356	0.295	0.067	1.1739	398	0.305	0.501	0.3002
358	0.282	0.077	1.1135	400	0.340	0.524	0.2807
360	0.275	0.090	1.0458				

TABLE B.8.

Absorption curve of Triethylenediaminochromic chloride immediately after preparing the solution.

0.0105 M

20°C.

Fig.21.

λ	S	D	$-\log D$	λ	S	D	$-\log D$
320	1.275	0.174	0.7595	460	0.085	0.722	0.1415
325	1.025	0.242	0.6162	470	0.075	0.657	0.1824
330	0.840	0.323	0.4868	480	0.070	0.542	0.2660
335	0.710	0.417	0.3768	485	0.068	0.463	0.3344
340	0.620	0.492	0.3063	490	0.066	0.392	0.4067
350	0.470	0.570	0.2426	495	0.065	0.321	0.4935
360	0.380	0.520	0.2840	500	0.062	0.257	0.5901
370	0.320	0.371	0.4306	505	0.061	0.204	0.6904
375	0.300	0.296	0.5287	510	0.060	0.157	0.8041
380	0.290	0.235	0.6289	520	0.058	0.095	1.0223
390	0.320	0.160	0.7959	530	0.057	0.055	1.2596
400	0.480	0.161	0.7932	540	0.058	0.034	1.4685
410	0.145	0.228	0.6421	550	0.060	0.024	1.6198
420	0.130	0.341	0.4672	560	0.063	0.018	1.7447
430	0.110	0.483	0.3161	570	0.066	0.013	1.8861
440	0.100	0.618	0.2090	580	0.071	0.010	2.0000
450	0.090	0.704	0.1524	600	0.102	0.007	2.1549

TABLE B.9.

Absorption curve of Trisethylenediaminochromic sulphate
boiled for 15 minutes.

0.00092M

21.5°C

Fig.25.

λ	S	D	$-\log D$	λ	S	D	$-\log D$
320	1.250	0.082	1.0862	490	0.065	0.053	1.2757
330	0.820	0.061	1.2147	500	0.060	0.059	1.2291
340	0.600	0.052	1.2840	510	0.058	0.066	1.1805
350	0.460	0.046	1.3372	520	0.056	0.073	1.1367
360	0.360	0.048	1.3188	530	0.055	0.078	1.1079
370	0.310	0.061	1.2147	540	0.056	0.081	1.0915
380	0.285	0.074	1.1308	550	0.057	0.081	1.0915
390	0.310	0.084	1.0757	560	0.060	0.078	1.1079
400	0.460	0.093	1.0315	570	0.065	0.075	1.1249
410	0.140	0.087	1.0605	580	0.068	0.070	1.1549
420	0.120	0.083	1.0809	590	0.080	0.062	1.2076
430	0.110	0.074	1.1308	600	0.280	0.057	1.2441
440	0.097	0.063	1.2007	610	0.260	0.050	1.3010
450	0.088	0.055	1.2596	620	0.240	0.041	1.3872
460	0.080	0.051	1.2924	630	0.225	0.031	1.5086
470	0.074	0.049	1.3098	640	0.210	0.026	1.5850
480	0.068	0.050	1.3010				

TABLE B.10

Absorption curve of a solution prepared by heating the
crystals of Preparation 1 of $[\text{Cr en}_2 (\text{C}_2\text{O}_4)] \text{Cl}$.

0.005 M

17°C

Fig. 27

λ	S	D	$-\log D$	λ	S	D	$-\log D$
320	1.300	0.254	0.5952	490	0.065	0.209	0.6799
330	0.860	0.133	0.8761	500	0.063	0.250	0.6021
340	0.630	0.099	1.0044	510	0.060	0.285	0.5452
350	0.480	0.121	0.9172	520	0.059	0.309	0.5100
360	0.390	0.184	0.7352	530	0.058	0.321	0.4935
370	0.320	0.262	0.5817	540	0.059	0.319	0.4962
380	0.300	0.324	0.4895	550	0.060	0.301	0.5214
390	0.320	0.351	0.4547	560	0.064	0.273	0.5638
400	0.480	0.345	0.4622	570	0.066	0.237	0.6253
410	0.145	0.305	0.5157	580	0.070	0.200	0.6990
420	0.130	0.249	0.6038	590	0.085	0.159	0.7986
430	0.115	0.190	0.7212	600	0.105	0.127	0.8962
440	0.100	0.146	0.8356	610	0.270	0.100	1.000
450	0.090	0.124	0.9066	620	0.260	0.073	1.1367
460	0.085	0.125	0.9031	630	0.240	0.052	1.2840
470	0.078	0.144	0.8416	640	0.220	0.042	1.3768
480	0.070	0.173	0.7620	650	0.210	0.032	1.4949

TABLE B.11.

Absorption curve of a solution prepared by heating the crystals of Preparation 2 of $(Cr en_2 (C_2O_4)_2)Cl$.

0.0054 M

17°C

Fig. 27.

λ	S	D	$-\log D$	λ	S	D	$-\log D$
320	1.300	0.318	0.4976	490	0.065	0.225	0.6478
330	0.860	0.151	0.8210	500	0.063	0.281	0.5513
340	0.630	0.099	1.0044	510	0.060	0.331	0.4802
350	0.480	0.118	0.9281	520	0.059	0.367	0.4353
360	0.390	0.192	0.7167	530	0.058	0.390	0.4089
370	0.320	0.288	0.5406	540	0.059	0.387	0.4123
380	0.300	0.375	0.4260	550	0.060	0.363	0.4401
390	0.320	0.426	0.3706	560	0.064	0.325	0.4881
400	0.480	0.424	0.3726	570	0.066	0.377	0.5575
410	0.145	0.375	0.4260	580	0.070	0.229	0.6402
420	0.130	0.296	0.5287	590	0.085	0.177	0.7520
430	0.115	0.213	0.6716	600	0.105	0.137	0.8633
440	0.100	0.152	0.8182	610	0.270	0.102	0.9914
450	0.090	0.121	0.9172	620	0.260	0.075	1.1249
460	0.085	0.121	0.9172	630	0.240	0.054	1.2676
470	0.078	0.142	0.8477	640	0.220	0.042	1.3768
480	0.070	0.178	0.7496	650	0.210	0.032	1.4949

TABLE B.12.

Absorption curve of Potassium cis-dioxalatodihydroxochromiate.

0.0092 M

18°C

Fig. 39.

λ	D	$-\log D$	λ	D	$-\log D$
322	1.550	-0.1903	470	0.297	0.5272
325	1.320	-0.1206	480	0.227	0.6440
330	0.990	0.0044	490	0.182	0.7399
340	0.530	0.2757	500	0.164	0.7852
350	0.308	0.5114	510	0.172	0.7645
360	0.265	0.5768	520	0.194	0.7122
370	0.351	0.4547	530	0.232	0.6345
380	0.541	0.2668	540	0.273	0.5638
390	0.780	0.1079	550	0.315	0.5017
400	0.980	0.0088	560	0.345	0.4622
410	1.040	-0.0170	570	0.363	0.4401
420	0.987	0.0052	580	0.373	0.4283
430	0.820	0.0862	590	0.373	0.4283
440	0.648	0.1884	600	0.363	0.4401
450	0.498	0.3028	610	0.348	0.4584
460	0.380	0.4202	620	0.328	0.4841
			630	0.302	0.5200

TABLE B.13.

Molar Ratio method applied to Potassium cis-dioxalato-diaquochromiate and propylenediamine at pH 4.8.

0.0092 M

Figs. 40, 41.

moles of propylene- diamine per mole chrome	pH of solution after heating	-Log Optical Density		
		340 mu	380 mu	480 mu
8.0	4.37	0.8861	0.4828	0.8447
7.5	4.16	0.8794	0.4841	0.8416
7.0	4.16	0.8794	0.4841	0.8416
6.5	4.10	0.8962	0.4881	0.8447
6.0	4.15	0.9101	0.4895	0.8447
5.5	4.07	0.8996	0.4895	0.8447
5.0	4.02	0.9101	0.4895	0.8477
4.5	4.04	0.9101	0.4895	0.8447
3.5	4.05	0.9318	0.4935	0.8477
3.0	4.00	0.9355	0.4976	0.8477
2.5	4.08	0.9469	0.4935	0.8447
2.0	4.07	0.9586	0.4962	0.8477
1.5	4.02	0.9586	0.4976	0.8477
0.5	4.05	0.9872	0.5003	0.8477
0.0	4.34	0.9957	0.5003	0.8477

TABLE B.14.

Continuous variation method applied to Potassium cis-dioxalatodiaquochromiate and propylenediamine at pH 8.0. mixed 50 (1 - x) mls. 0.0092 M cis-dioxalatohydroxo-aquochromiate and 50 x mls 0.0092 M propylenediamine, boiled for 30 mins., cooled and made up to volume (0.0092M)

D_2 = Optical density of reaction mixture after treatment.

D_3 = Optical density of cis-dioxalatohydroxo-aquochromiate treated in the same way as the reaction under observation, at the same dilutions as those used in the reactions.

Fig. 42.

X	Y = $D_2 - D_3$				
	360 mμ	380 mμ	400 mμ	440 mμ	460 mμ
0.00	.000	.000	.000	.000	.000
0.05	.013	.022	.013	-.012	-.004
0.10	.026	.044	.025	-.030	-.011
0.15	.038	.070	.043	-.043	-.015
0.20	.050	.091	.055	-.057	-.022
0.25	.062	.113	.074	-.064	-.025
0.30	.071	.130	.083	-.080	-.030
0.35	.083	.153	.099	-.092	-.033
0.40	.090	.162	.105	-.102	-.035
0.45	.095	.169	.111	-.103	-.036
0.50	.096	.170	.109	-.104	-.034
0.55	.093	.165	.105	-.104	-.033
0.60	.089	.156	.099	-.098	-.033
0.65	.082	.145	.091	-.090	-.030
0.70	.074	.128	.080	-.082	-.024
0.75	.063	.110	.067	-.070	-.022
0.80	.052	.089	.055	-.057	-.018
0.85	.041	.068	.043	-.044	-.013
0.90	.029	.046	.026	-.029	-.007
0.95	.016	.022	.013	-.014	-.003
1.00	.003	.001	.003	+.001	+.001

TABLE B.15.

Absorption curve of :

(a) Potassium cis-dioxalatohydroxoquoachromiate.

(b) Olated complex.

0.0092 M

18°C

Fig. 48

λ	D_a	D_b	$-\log D_a$	$-\log D_b$
320	0.900	0.990	0.0458	0.0044
322	0.632	-	0.1993	-
325	-	0.648	-	0.1884
330	0.433	0.423	0.3635	0.3737
335	0.298	0.280	0.5258	0.5528
340	0.215	0.203	0.6676	0.6925
345	0.164	0.155	0.7852	0.8097
350	0.145	0.127	0.8386	0.8962
355	0.153	0.115	0.8153	0.9393
360	0.183	0.123	0.7375	0.9101
365	0.227	-	0.6445	-
370	0.283	0.186	0.5482	0.7305
380	0.407	0.293	0.3904	0.5331
390	0.501	0.425	0.3002	0.3716
395	0.541	-	0.2668	-
400	0.565	0.553	0.2480	0.2573

TABLE B.16.

Continuous variation method applied to Potassium trioxalatochromiate and propylenediamine mixed 50(1-X) mls. 0.0092M trioxalatochromiate and 50X mls. 0.0092M propylenediamine boiled for 30 minutes, recorded the pH of the solution, added nitric acid to bring pH to 6.1 and then made up to volume (0.0092M).

D_2 = Optical density of reaction mixtures after treatment.

D_3 = Optical density of trioxalatochromiate, treated in same way as the reaction under observation, at the same dilution as those used in the reactions.

Fig. 60.

X	pH after heating	N/5 HNO ₃ to bring pH to 6.1	Y = $D_2 - D_3$					
			350mμ	370mμ	420mμ	440mμ	560mμ	580mμ
0.00	5.90	—	-.005	-.005	-.016	-.017	-.010	-.010
0.05	6.80	0.05	+.006	+.013	.013	.024	.009	.015
0.10	7.08	0.10	.009	.025	.026	.042	.013	.027
0.15	7.29	0.14	.016	.039	.034	.052	.011	.033
0.20	7.44	0.15	.019	.048	.056	.071	.022	.050
0.25	7.59	0.23	.025	.061	.063	.084	.024	.060
0.30	7.62	0.25	.032	.074	.077	.097	.029	.067
0.35	7.76	0.40	.034	.079	.089	.109	.030	.082
0.40	7.89	0.45	.036	.080	.100	.118	.042	.083
0.45	7.93	0.50	.041	.090	.108	.129	.041	.091
0.50	8.04	0.60	.043	.094	.117	.137	.048	.099
0.55	8.18	0.85	.042	.083	.114	.126	.050	.094
0.60	8.31	1.05	.041	.076	.118	.126	.054	.094
0.65	8.49	1.10	.042	.074	.118	.125	.055	.095
0.70	8.70	1.45	.044	.070	.110	.112	.056	.088
0.75	9.22	1.90	.040	.056	.093	.087	.053	.075
0.80	9.53	2.20	.034	.043	.083	.074	.050	.065
0.85	9.78	2.70	.032	.034	.064	.054	.041	.051
0.90	10.10	3.20	.026	.030	.043	.037	.031	.038
0.95	10.32	3.80	.017	.017	.020	.015	.013	.016
1.00	10.54	4.30	.005	.003	+.002	+.002	+.003	+.001

TABLE B.17:

Continuous variation method applied to Potassium Trioxalatochromate and enta.
mixed 50 (1-x) mls 0.0046 M Potassium trioxalatochromate (pH = 6.02) and 50x mls 0.0046 M enta (pH = 2.62), boiled for 30 mins, aged for 12 hours and then made up to volume (0.0046 M).

D₂ = Optical density of reaction mixture after treatment.

D₃ = Optical density of trioxalatochromate, treated in the same way as the reaction under observation, at the same dilutions as those used in the reactions.

Fig. 65.

X	- Y = - (D ₂ - D ₃)			
	340 mu	400 mu	420 mu	560 mu
0.00	.002	.005	.006	.003
0.05	.002	.006	.008	.002
0.10	.004	.007	.013	.006
0.15	.007	.009	.020	.009
0.20	.008	.013	.027	.013
0.25	.011	.014	.027	.011
0.30	.010	.015	.029	.011
0.35	.011	.017	.033	.015
0.40	.015	.019	.035	.015
0.45	.010	.016	.033	.010
0.50	.011	.016	.036	.012
0.55	.012	.017	.033	.014
0.60	.012	.015	.033	.013
0.65	.009	.014	.033	.010
0.70	.008	.014	.030	.010
0.75	.006	.012	.024	.009
0.80	.000	.010	.023	.010
0.85	-.003	.007	.016	.004
0.90	-.003	.006	.013	.004
0.95	-.006	.000	.005	.002
1.00	-.010	-.003	-.001	.000

TABLE B.18.

Solutions from Fig. 65 aged for 4 days then spectrophotometric readings recorded. (see previous table).

Fig. 66.

X	- Y $\pm$ -(D ₂ - D ₃)			
	400 mu	420 mu	430 mu	560 mu
0.00	.004	.036	- .016	.004
0.05	.007	.037	- .012	.004
0.10	.007	.044	- .003	.006
0.15	.009	.047	.003	.010
0.20	.010	.048	.006	.012
0.25	.014	.049	.010	.010
0.30	.012	.052	.016	.009
0.35	.017	.052	.018	.015
0.40	.016	.054	.023	.015
0.45	.014	.051	.023	.011
0.50	.015	.053	.027	.012
0.55	.018	.048	.025	.015
0.60	.013	.046	.025	.014
0.65	.014	.044	.026	.012
0.70	.012	.039	.023	.010
0.75	.013	.035	.020	.010
0.80	.008	.029	.019	.010
0.85	.006	.023	.015	.006
0.90	.005	.015	.010	.005
0.95	.001	.008	.005	.004

TABLE B.19.

Continuous variation method applied to Potassium cis-dioxalatodiaquochromiate and propylenediamine at pH 4.8, mixed 50 (1 - x) mls. 0.0092 M Potassium cis-dioxalatodiaquochromiate (pH 4.8) and 50 x mls 0.0092 M propylene-diamine (pH 4.8), boiled for 25 mins, cooled and made up to volume (0.0092 M).

D₂ = Optical density of reaction mixture after treatment.

D₃ = Optical density of cis-dioxalatodiaquochromiate, treated in the same way as the reaction under observation, at the same dilutions as those used in the reaction.

(no graph).

X	Y = D ₂ - D ₃				
	360 mu	380 mu	400 mu	420 mu	560 mu
0.00	.000	.000	.000	.000	.000
0.05	.001	.001	.001	.003	.006
0.10	.000	.000	.000	.000	.004
0.15	.002	.000	.002	.000	.004
0.20	.003	-.003	.002	-.001	.001
0.25	.003	-.001	.004	.003	.006
0.30	.001	.000	.001	.002	.005
0.35	.003	.001	.003	.004	.006
0.40	.000	.000	.000	.000	.000
0.45	.002	-.001	.004	.005	.006
0.50	.001	.001	.003	.006	.003
0.55	.002	.002	.005	.003	.004
0.60	.002	.000	.003	.002	.003
0.65	.005	.002	.005	.005	.005
0.70	.002	.001	.002	.005	.001
0.75	.004	.000	.003	.004	.002
0.80	.003	.001	.002	.001	.001
0.85	.003	.000	.002	.001	.002
0.90	.002	.002	.002	.001	.000
0.95	.004	.002	.002	.002	.001
1.00	.003	.003	.003	.001	.002

APPENDIX C.

POTENTIOMETRIC

DATA.

TABLE C1

Titration of Potassium nitrate against 0.05N KOH and
0.05 HNO_3

0.00092M

20°C

Fig. 12.

mls. acid	pH	mls. alkali	pH
0.0	6.38	0.00	6.05
0.1	4.79	0.073	8.90
0.2	4.16	0.146	9.58
0.3	3.92	0.219	9.85
0.4	3.75	0.292	10.07
0.5	3.64	0.365	10.18
0.7	3.48	0.438	10.32
0.9	3.34	0.584	10.42
1.2	3.21	0.730	10.56
1.6	3.08	0.876	10.66
2.0	2.98	1.022	10.72
3.0	2.81	1.168	10.78
4.0	2.68	1.460	10.89
5.0	2.58	1.825	10.99
6.5	2.48	2.190	11.06
8.0	2.38		
10.0	2.29		
12.0	2.21		
14.0	2.15		
16.0	2.09		
18.0	2.05		
20.0	2.00		

TABLE C.2.

Titration of a freshly prepared solution of Triethylene-
diaminochromic chloride with 0.05 N HNO_3 and 0.05 N KOH.

(Blank corrected at the appropriate temperature).

0.00092 M

20°

Fig. 23.

Equivalents of acid/Cr	pH	Equivalents of alkali/Cr	pH
0.000	6.57	0.000	6.00
0.027	4.37	0.039	6.80
0.055	4.08	0.080	7.85
0.109	3.39	0.119	9.37
0.163	3.31	0.050	9.86
0.190	3.18		
0.218	3.06		
0.326	2.89		
0.380	2.76		
0.545	2.66		
0.815	2.55		
1.090	2.37		
1.630	2.24		
2.060	2.18		
2.180	2.14		
2.720	2.01		

TABLE C.3.

Titration of a solution of Triethylenediaminochromic chloride, aged for 6 days at ca 20°C, with 0.05 N HNO₃ and 0.05 N KOH.

(Blank corrected at the appropriate temperature).

0.00092 M

21°C

Fig. 23.

Equivalents of acid/Cr	pH	Equivalents of alkali/Cr	pH
0.000	7.16	0.000	7.20
0.054	7.06	0.082	7.28
0.109	6.94	0.158	7.42
0.218	6.78	0.239	7.54
0.324	6.60	0.315	7.70
0.435	6.40	0.358	7.82
0.545	6.20	0.397	7.94
0.650	5.92	0.478	8.16
0.705	5.77	0.515	8.38
0.760	5.48	0.555	8.54
0.815	5.18	0.600	8.72
0.842	4.85	0.635	8.82
0.870	4.25	0.712	9.06
0.925	4.06	0.793	9.24
0.900	3.81	0.875	9.42
0.900	3.56	0.950	9.52
0.870	3.45	0.980	9.66
0.815	3.35	1.030	9.77
		1.080	9.87
		1.170	10.02
		1.240	10.13
		1.340	10.27
		1.460	10.42
		1.580	10.54
		1.710	10.64
		1.790	10.72
		2.020	10.84
		2.200	10.94
		2.400	11.01

TABLE C.4.

Titration of a solution of Triethylenediaminochromic chloride, aged for 18 days at ca 20°C, with 0.05 N HNO_3 and 0.05 N KOH.

(Blank corrected at the appropriate temperature).

0.00092 M

20°C

Fig. 23.

Equivalents of acid/Cr.	pH	Equivalents of alkali/Cr.	pH
0.000	7.57	0.000	7.42
0.055	7.52	0.040	7.46
0.109	7.46	0.080	7.50
0.163	7.40	0.159	7.58
0.218	7.34	0.318	7.79
0.376	7.26	0.396	7.92
0.435	7.16	0.475	8.10
0.545	7.08	0.555	8.28
0.650	7.00	0.635	8.50
0.815	6.87	0.715	8.72
0.980	6.72	0.760	8.93
1.090	6.64	0.835	9.06
1.250	6.50	0.910	9.23
1.410	6.32	1.030	9.36
1.630	5.94	1.140	9.49
1.790	5.54	1.265	9.65
1.900	4.96	1.480	9.84
1.930	4.54	1.650	9.98
1.960	4.28	1.800	10.13
2.010	4.10	2.110	10.38
2.040	3.84	2.310	10.61
2.060	3.73	2.480	10.81
2.120	3.44	2.660	10.94
2.120	3.24	2.770	11.07
2.060	2.94		
2.010	2.56		

TABLE C.5.

Titration of ethylenediamine, purified by dehydration and distillation, with 0.05 N HNO_3 and 0.05 N KOH

(Blank corrected at the appropriate temperature).

0.00092

22°C

Fig. 24

Equivalents of acid/Cr.	pH	Equivalents of alkali/Cr.	pH
0.000	10.31	0.000	10.31
0.027	10.00	0.039	10.36
0.109	9.86	0.063	10.43
0.163	9.73	0.087	10.48
0.245	9.60	0.174	10.63
0.272	9.54	0.265	10.74
0.380	9.36	0.293	10.86
0.490	9.22	0.326	10.93
0.597	8.99	0.358	11.00
0.706	8.72	0.445	11.05
0.815	8.31		
0.870	8.02		
0.925	7.82		
0.980	7.82		
0.980	7.66		
1.030	7.52		
1.140	7.24		
1.250	7.08		
1.360	6.88		
1.470	6.68		
1.580	6.49		
1.685	6.30		
1.800	5.93		
1.900	5.24		
1.850	4.30		
1.900	4.06		
1.900	3.79		
1.900	3.66		
1.850	3.57		
1.875	3.49		
1.875	3.24		

TABLE C.6.

Titration with 0.05 N HNO_3 and 0.05N KOH of a solution prepared from the crystals of Preparation I of $[\text{Cr en}_2 (\text{C}_2\text{O}_4)] \text{Cl}$.

(Blank corrected at the appropriate temperature)

0.001 M

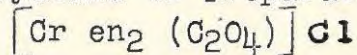
22°C

Fig. 26.

Equivalents of acid/Cr.	pH	Equivalents of alkali/Cr	pH
0.000	7.29	0.000	7.30
0.05	7.11	0.036	7.40
0.10	6.96	0.073	7.52
0.15	6.81	0.109	7.73
0.20	6.63	0.146	7.90
0.25	6.41	0.183	8.05
0.30	6.24	0.219	8.20
0.35	6.06	0.255	8.42
0.40	5.83	0.292	8.49
0.45	5.58	0.328	8.72
0.50	5.27	0.365	8.84
0.53	4.90	0.400	8.96
0.53	4.37	0.438	9.11
0.55	4.00	0.475	9.22
0.50	3.71	0.585	9.58
0.50	3.58	0.640	9.73
0.45	3.47	0.667	9.86
0.45	3.32	0.739	9.96
		0.810	10.16
		0.845	10.30
		0.940	10.45
		0.988	10.55
		1.106	10.69
		1.175	10.79
		1.340	10.93
		1.450	11.03

TABLE C.7.

Titration with 0.05 N HNO_3 and 0.05 N KOH of a solution prepared from the crystals of Preparation II of



(Blank corrected at the appropriate temperature).

0.001 M

22°C

Fig. 26.

Equivalents of acid/Cr.	pH	Equivalents of alkali/Cr.	pH
0.000	7.53	0.000	7.80
0.046	7.32	0.034	7.98
0.093	7.17	0.068	8.14
0.140	7.02	0.102	8.37
0.186	6.87	0.135	8.53
0.232	6.67	0.170	8.70
0.279	6.50	0.205	8.85
0.325	6.30	0.237	8.99
0.372	6.12	0.272	9.18
0.418	5.86	0.307	9.30
0.465	5.64	0.340	9.43
0.510	5.26	0.373	9.53
0.510	4.79	0.405	9.77
0.510	4.17	0.450	9.94
0.510	3.86	0.472	10.08
0.465	3.65	0.510	10.30
0.465	3.50	0.560	10.48
		0.600	10.63
		0.642	10.72
		0.685	10.82
		0.730	10.89
		0.750	10.94
		0.770	11.00

TABLE C.8.

Titration of Potassium cis-dioxalatodiaquochromate and propylenediamine (1:1 moles), heated for 4 hours at ca 100°C then aged for 21 days, with 0.05N HNO₃ and 0.05N KOH.

(Blank corrected at the appropriate temperature)

0.00092M

14°C

Fig. 32.

Equivalents of acid/Cr.	pH	Equivalents of alkali/Cr	pH
0.000	6.52	0.000	6.88
0.034	6.41	0.037	7.12
0.095	6.30	0.073	7.33
0.155	6.22	0.083	7.62
0.211	6.10	0.094	8.00
0.250	5.88	0.111	8.29
0.300	5.58	0.120	8.60
0.344	5.18	0.127	8.82
0.380	4.71	0.140	8.95
0.398	4.48	0.159	9.07
0.423	4.34	0.166	9.17
0.435	4.22	0.177	9.27
0.445	4.12	0.187	9.39
0.451	3.97	0.194	9.53
0.467	3.91	0.215	9.58
0.473	3.86	0.234	9.66
0.495	3.77	0.251	9.74
0.527	3.69	0.265	9.77
0.560	3.66	0.277	9.82
0.565	3.57	0.290	9.86
0.598	3.52	0.299	9.90
0.652	3.48	0.316	9.93
0.700	3.42	0.330	9.96
0.765	3.34	0.337	10.01
0.830	3.29	0.353	10.08
0.925	3.24	0.353	10.12
0.982	3.16	0.413	10.26
1.095	3.06	0.472	10.40
1.210	2.98	0.505	10.52
		0.645	10.78

TABLE C.9.

Titration of Potassium cis-dioxalatodiaquochromate and propylenediamine (1:2 moles), heated for 4 hours at ca 100°C then aged for 21 days, with 0.05N HNO₃ and 0.05N KOH

(Blank corrected at the appropriate temperature).

0.00092M

14°C

Fig. 32.

Equivalents of acid/Cr.	pH	Equivalents of alkali/Cr	pH
0.0	7.84	0.0	7.84
0.034	7.75	0.019	8.11
	7.61	0.057	8.27
0.162	7.48	0.082	8.48
0.222	7.39	0.109	8.67
0.288	7.32	0.140	8.85
0.354	7.23	0.177	9.00
0.388	7.14	0.214	9.09
0.481	7.07	0.278	9.30
0.555	7.01	0.312	9.38
0.610	6.94	0.358	9.48
0.670	6.86	0.435	9.62
0.730	6.78	0.495	9.71
0.847	6.63	0.548	9.76
1.000	6.36	0.625	9.88
1.115	6.08	0.685	9.95
1.230	5.61	0.705	10.07
1.268	5.40	0.815	10.14
1.365	4.86	0.880	10.21
1.520	4.43	0.950	10.30
1.630	4.22	1.045	10.43
1.663	4.13	1.150	10.61
1.730	3.96	1.250	10.72
1.820	3.86	1.340	10.80
1.886	3.72	1.360	10.90
1.936	3.53		
2.010	3.41		
2.120	3.20		
2.240	3.10		
2.280	3.01		
2.320	2.94		
2.350	2.82		
2.450	2.70		

TABLE C.10.

Titration of Potassium cis-dioxalatodiaquochromate and propylenediamine (1:3 moles), heated for 4 hours at ca 100°C then aged for 21 days, with 0.05N HNO₃ and 0.05N KOH.

(Blank corrected at the appropriate temperature).

0.00092M

14°C

Fig. 32:

Equiva- lents of acid/Gr.	pH	Equiva- lents of acid/Gr.	pH	Equiva- lents of alkali/Gr.	pH	Equiva- lents of alkali/Gr.	pH
0.0	9.08	2.230	6.48	0 0	8.99	0.890	10.01
0.040	8.82	2.340	6.37	0.013	9.16	0.978	10.09
0.106	8.65	2.470	6.19	0.039	9.24	1.105	10.19
0.177	8.48	2.580	6.02		9.27	1.158	10.23
0.250	8.34	2.690	5.79	0.116	9.32	1.220	10.28
0.311	8.19	2.740	5.64	0.150	9.36	1.280	10.31
0.326	8.06	2.800	5.51	0.184	9.40	1.330	10.36
0.443	7.93	2.840	5.26	0.213	9.45	1.400	10.39
0.526	7.80	2.910	5.10	0.245	9.50	1.440	10.44
0.575	7.76	2.950	4.94	0.282	9.53	1.495	10.47
0.641	7.70	3.010	4.82	0.313	9.55	1.615	10.54
0.701	7.63	3.060	4.70	0.345	9.60	1.630	10.62
0.825	7.50	3.110	4.60	0.382	9.63	1.730	10.69
0.890	7.46	3.230	4.43	0.418	9.66	1.860	10.78
1.000	7.38	3.340	4.30	0.454	9.68	1.930	10.88
1.140	7.27	3.420	4.14	0.492	9.71	1.970	10.96
1.270	7.19	3.520	4.04	0.545	9.75		
1.395	7.12	3.800	3.66	0.560	9.78		
1.640	6.94	3.850	3.57	0.598	9.81		
1.760	6.88	4.020	3.39	0.630	9.84		
1.885	6.78	4.150	3.27	0.690	9.88		
2.010	6.68	4.200	3.12	0.760	9.92		
2.120	6.60	4.350	2.92	0.820	9.97		
		4.480	2.78				
		4.500	2.73				
		4.600	2.68				

TABLE C 11

Titration of Potassium trioxalatochromate and propylene-diamine (1:1 moles), heated for 4 hours at ca 100°C then aged for 21 days, with 0.05N HNO₃ and 0.05N KOH.

(Blank corrected at the appropriate temperature).

0.00092M

16°C

Fig. 53.

Equivalents of acid/Cr.	pH	Equivalents of alkali/Cr.	pH
0.0	7.17	0.0	7.14
0.019	7.12	0.026	7.32
	7.04	0.047	7.52
	6.96		7.72
0.124	6.90	0.130	8.30
0.177	6.72	0.146	8.77
0.202	6.64	0.166	9.02
0.229	6.56	0.187	9.34
0.252	6.48	0.206	9.50
0.308	6.18	0.234	9.61
0.327	6.00	0.265	9.75
0.348	5.83	0.296	9.83
0.372	5.66	0.318	9.92
0.385	5.44	0.342	9.98
0.405	5.30	0.364	10.08
0.435	5.15	0.375	10.13
0.460	5.01	0.418	10.23
0.490	4.92	0.472	10.43
0.515	4.83	0.555	10.59
0.560	4.69	0.620	10.70
0.620	4.56	0.685	10.81
0.670	4.44	0.717	10.94
0.717	4.33	0.760	11.01
0.770	4.24		
0.835	4.16		
0.895	4.01		
0.966	3.86		
1.042	3.74		
1.075	3.68		
1.120	3.63		
1.158	3.45		
1.231	3.32		
1.348	3.19		
1.410	3.07		
1.445	2.97		
1.600	2.89		

TABLE C.12.

Titration of Potassium trioxalatochromate and propylene-diamine (1:2 moles), heated for 4 hours at ca 100°C then aged for 21 days, with 0.05N HNO₃ and 0.05N KOH.

(Blank corrected at the appropriate temperature.

0.00092M

16°C

Fig. 53.

Equivalents of acid/Cr.	pH	Equivalents of alkali/Cr.	pH
0.0	8.09	0.0	7.94
0.023	7.92	0.019	8.19
0.089	7.74	0.077	8.60
0.155	7.58	0.140	8.91
0.189	7.48	0.203	9.13
0.282	7.38	0.261	9.34
0.348	7.29	0.378	9.46
0.475	7.14	0.380	9.60
0.608	6.97	0.455	9.70
0.728	6.80	0.515	9.78
0.836	6.64	0.586	9.87
0.945	6.43	0.695	10.03
1.064	6.18	0.815	10.16
1.162	5.80	0.906	10.30
1.260	5.36	1.000	10.42
1.380	5.04	1.100	10.54
1.490	4.80	1.270	10.68
1.600	4.63	1.385	10.87
1.705	4.48	1.440	10.96
1.810	4.36		
1.972	4.19		
2.090	4.07		
2.220	3.95		
2.310	3.84		
2.445	3.74		
2.500	3.63		
2.605	3.54		
2.720	3.46		
2.770	3.37		
2.930	3.23		
3.040	3.10		
3.100	3.00		
3.205	2.93		
3.250	2.85		

TABLE 0.13.

Titration of Potassium trioxalatōchromiate and propylene-diamine (1:3 moles), heated for 4 hours at ca 100°C then aged for 21 days, with 0.05N HNO₃ and 0.05N KOH.

(Blank corrected at the appropriate temperature).

0.0092M

16°C

Fig. 53.

Equivalents of acid/Cr.	pH	Equivalents of alkali/Cr.	pH
0.0	9.09	0.0	9.05
0.042	8.84	0.039	9.27
0.178	8.55	0.113	9.37
0.310	8.24	0.239	9.54
0.435	7.98	0.307	9.60
0.570	7.78	0.380	9.67
0.700	7.64	0.456	9.73
0.820	7.53	0.520	9.78
0.950	7.41	0.592	9.84
1.075	7.32	0.723	9.95
1.205	7.23	0.842	10.05
1.304	7.14	0.962	10.14
1.520	7.02	1.085	10.23
1.765	6.84	1.240	10.34
2.120	6.53	1.330	10.43
2.340	6.26	1.465	10.54
2.510	5.98	1.594	10.64
2.620	5.72	1.710	10.74
2.720	5.43	1.805	10.83
2.840	5.18	1.875	10.92
3.110	4.75		
3.230	4.58		
3.510	4.33		
3.800	4.13		
4.100	3.93		
4.260	3.76		
4.470	3.60		
4.650	3.44		
4.860	3.31		
4.960	3.19		
5.100	3.09		
5.250	3.00		
5.300	2.93		
5.480	2.84		
5.700	2.74		

