INVESTIGATION OF THE FORMATION OF COMPLEXES BETWEEN SELECTED ORGANIC COMPOUNDS AND THE CHLORIDES AND SULPHATES OF CHROMIUM.

by

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CONTENTS.

SUMMARY.

Some properties of soluble chromium complex ions containing coordinated aliphatic acids have been studied. The work falls naturally into two sections.

In the first, the coordination of a series of α, β and γ amino acids by chromium chloride has been studied by physical methods. The tanning action of chromium chloride in the presence of these amino acids has also been studied.

The absorption spectra of the complexes were similar to those reported previously for trivalent chromium solutions, having two pronounced maxima in the visible region. From the variations in these absorption maxima, it is suggested that the absorption maximum in the 580 mμ region is influenced by coordination of the chromium with the ligand, while the maximum in the 420 mμ region is also affected by the olation of the basic chromium salts. The spectrophotometric evidence indicates that raising the pH or the concentration of the ligand in the solution increases the amount of coordination, and further, that the tendency for coordination increases as the hydrocarbon chain separating the carboxyl and amino groups becomes longer. This suggests that the stability of the complex is not dependent on chelate ring formation, but is influenced by the pK_1 value of the carboxyl group of the ligand.

Potentiometric/....

Potentiometric titrations support the hypothesis that only the carboxyl group is coordinated, to an extent depending on its pK_1 value, since the curves have shown that the amino group is still free to titrate.

Paper electrophoresis has shown that all the complexes prepared were cationic, indicating that the amino acids were coordinated as dipolar ions.

The tanning action of the masked chromium solutions has confirmed the deductions made from the physical measurements. Increasing the amount of amino acid added to the solution lowered the chromium fixation and the hydrothermal stability of the leather, and further, that for solutions at the same pH containing the same amount of masking agent, tanning action was least for the γ amino acid and greatest for the α amino acids.

Comparison of the present data with the corresponding results obtained with chrome alum solutions showed that coordination of the amino acids was greater in the case of the chromium chloride solutions.

The second section of the experimental work was an investigation of the coordination of substituted acetic and propionic acids by chromium chloride and chromium sulphate. Spectrophotometric and potentiometric methods were applied and the various solutions were also used in miniature tanning experiments. Certain difficulties were encountered in the preparation of some of the complexes, and

it was not possible to carry the work to a point where conclusive results could be obtained. Nevertheless, the work reported suggests that chelate ring formation occurs in the coordination of hydroxy-carboxylic acids, resulting in exceptionally high stability of the complex. In the case of the other ligands, containing amino, chloro and bromo groups, as well as with acetic and propionic acids, the results suggest that coordination involves the carboxyl group only, and that the pK value of this group is an important factor determining the stability of the complexes.

CHAPTER I.

INTRODUCTION.

The Chemistry of the Trivalent Chromium Cation.

Chromium is one of the transition elements, and occupies a position in the first long period of the Periodic Table of the elements, between potassium and bromine. These elements are characterised by, amongst others, such properties as the existence of many coloured compounds, variable valency, and paramagnetism. These unusual properties are caused by the penultimate electron shell of the atom being incomplete.

Under certain conditions electrons can be promoted from the incomplete electron shell to the valence shell of the atom with a comparatively small change of energy, explaining the ease with which these elements can change their oxidation state. The coloured ions and paramagnetic properties are normally associated with the unpaired electron spins commonly present in these elements, since the available orbitals (in the case of chromium, the 3d level) are occupied before pairing of the electrons takes place.

The vacant orbitals in the electron shells of these atoms and their ions can become filled by sharing electron pairs of other atoms or groups, thus forming the coordinate covalent, or semi-polar double bond. This type of bond is not ionic but has directional and stability properties similar to a normal covalent bond; ligands are firmly held, and

lose/.....

lose their separate identity. The charge held by an ion is transferred to the complex ion on coordination, and a cation which coordinates anions can have its charge reduced, neutralised or reversed. Well-known examples of compounds of this type are the ferrocyanide and ferricyanide salts:

$Fe(CN)_6^{4-}$ ferrocyanide ion

$Fe(CN)_6^{3-}$ ferricyanide ion

In the first ion, the iron is in the doubly charged ferrous state. On coordination of six monovalent cyanide anions, this charge is reversed with the formation of a tetravalent anion. The second contains iron in the triply charged ferric state, forming with the cyanide ions a trivalent anion. The cyanide ions are firmly bound to the iron: they cannot be detected in any appreciable concentration in solutions of these salts.

The atomic number of chromium is 24 and in the ground state it has the following electronic configuration:

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$ which becomes

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$ in the trivalent chromic cation. The outer electron orbitals of this ion can be depicted as follows:

4p ○ ○ ○

4s ○

3d ⊙ ⊙ ⊙ ○ ○

with the electrons present in the ion being represented by dots.

The outer (N) electron shell of this ion is complete

when/.....

when it contains eight electrons, and the two vacant 3d orbitals also require to be filled for the formation of a stable ion. Hence it is necessary for the chromic ion to share six pairs of electrons from groups able to supply them for the formation of a stable electronic configuration - these six groups are then bound to the chromic ion.

None of these links have the directional and stability characteristics of d, s and p bonds and it is found that they cannot be distinguished from one another. This is generally characteristic of the so-called hybrid bond, the particular type under consideration being designated d^2sp^3 because of the electrons which interact in its formation.

It has been proposed (1) that these d^2sp^3 hybrid bonds are directed towards the corners of a regular octahedron, and, in the case of potassium trans dioxalato-diaquo chromiate, this fact has been verified by X-ray diffraction analysis (2).

In the case of the normal chromium salts, the coordinating positions of the chromic ion are not vacant, but are occupied by coordinated water molecules. These can be fairly easily displaced, since the water is not strongly coordinated, and give rise to the well known series of chromic chlorides: (3)

α $[Cr(H_2O)_6]Cl_3$ violet coloured

β $[Cr(H_2O)_5Cl]Cl_2$ blue-green

γ $[Cr(H_2O)_4Cl_2]Cl$ green

The first compound, on treatment with silver nitrate, forms an immediate precipitate of silver chloride,

equivalent/.....

equivalent to three chloride ions per chromic ion. However, the other compounds, under the same conditions, are found to yield only two and one chloride ions respectively. This is in agreement with what has been stated above, since in the latter two salts, a portion of the chloride is coordinated to the central chromic ion.

Numerous substances coordinate with the chromic ion; in fact, chloride is one of the weaker coordinating agents. Stiasny [4] and Theis et al [5, 6] have studied the relative ease of penetration of various substances into the coordination complex, and the following list of substances represents the consensus of opinion on the relative affinity of a number of anions. Each ion in the list has a greater tendency for complex formation than those following it:

Oxalate, tartrate, citrate, glycollate, sulphite, acetate, formate, sulphate, chloride, nitrate.

Coordination of these ligands to the chromic ion causes a marked alteration in its properties. The most obvious change is in the colour of the solution: this is seen in the colours of the chromic chlorides discussed above. The effect is observed in all chromium coordination complexes - there is a change of colour, and usually an intensification in the colour of the solution. These effects are capable of quantitative measurement as a shift of the wavelengths of maximum light absorption, and of the optical density of the solution at these wavelengths. It has also been found that the formation of coordination complexes increases the

resistance/.....

resistance of the chromic ion to precipitation by alkali. Thus, while a solution of chromium chloride begins to be precipitated by potassium hydroxide at about pH 3.3, a solution containing an anion capable of forming a strong coordinate bond with the chromic ion has to be raised to a pH value of 8 to 9 before precipitation takes place. Precipitation of the hydroxide is brought about by coordination of hydroxyl ions, which is hindered if strong coordinate bonds to the chromic ion already exist.

Basic Chromic Salts.

The chromic ion readily coordinates hydroxyl ions with the formation of basic salts. The reaction can be brought about by addition of alkali to a chromic solution, or can take place spontaneously in a solution of a chromic salt by hydrolysis, in which case the pH of the solution falls due to liberation of strong acid. A possible equation for the reaction in the case of a chromic chloride solution is:

$$\left[Cr(H_2O)_6\right]Cl_3 \longrightarrow \left[Cr(H_2O)_5OH\right]Cl_2 + HCl$$

For this reason it is probable that the over-all basicity of the solution, as determined by titration (which would be zero in the above example) is different from the basicity of the chromium complex ion present in the solution. Whether the basic salt is formed by addition of alkali or by hydrolysis, the reaction is accelerated by heating the solution.

Formation of basic chromic salts is normally

followed/.....

followed by olation, whereby basic ions are linked together by hydroxyl bridges with the elimination of coordinated water molecules from the ions. For example, in the case of a hypothetical 33% basic chromic solution:

$$2\ Cr(H_2O)_5.OH^{++} \longrightarrow \left[(H_2O)_4Cr\begin{matrix}OH\\OH\end{matrix}Cr(H_2O)_4\right]^{4+} + 2\ H_2O$$

This example is a simplification of the conditions in an experimental solution, since chromic ions can coordinate various numbers of hydroxyl ions, which can then link together in a variety of ways (1).

The ultimate product of this process is the completely basic compound which is insoluble and is precipitated as chromic hydroxide.

The hydroxyl bridges of the olated complex can be changed to oxygen links, when the "oxo compound" is formed. According to the work of Laswick and Plane (7) it appears that the substance stable to prolonged boiling, even in the presence of molar perchloric acid, is a compound corresponding to a partially hydrated chromic oxide.

These aspects of the chemistry of chromium are discussed more fully by Gustavson (8) and Thorstensen (9) in two recently published books.

<u>Experimental Techniques Applicable to the study of Chromium Coordination Compounds</u>.

The properties of trivalent chromium solutions, in particular the ability of the chromium ion to form coordination compounds, can be studied by a number of

experimental/.....

experimental methods, of which a brief survey is given below. All the reviewed methods are applicable to solution chemistry and no mention is made of methods such as X-ray crystallography, which are only applicable to the investigation of pure crystalline materials.

1. Spectrophotometry.

Since the solutions of trivalent chromium compounds are invariably strongly coloured, and the observed colours of the solutions depend to a considerable extent on the anions present, on the pH and on the previous treatment of the solution, light absorption measurements would appear to be an obvious choice as a method for investigating the properties of such solutions. For this reason, considerable use has been made of the method for studies of the constitution of chromium coordination compounds.

Colmar and Schwartz [10], extending the work of some earlier investigators, studied the series of chromium ammine hydrates. They found a regular shift in the wavelength of maximum absorption and of the molar extinction coefficient at this wavelength as the number of ammonia molecules penetrating the complex increased. The changes were attributed to changes in the vibrational energies of the molecule, due to different bond strengths.

Theis and co-workers [11,12,13] investigated the reaction of 33% basic chromium sulphate with oxalic acid, finding an increase in the molar extinction coefficient with

increasing/.....

increasing amounts of oxalic acid, until a molar ratio of 15 moles per mole of chromium was reached, when the extinction coefficient became constant. This fact was used as the basis of an analytical method for chromium which has been described (12,13). It was stated (11) that: "Insulation of the outer incomplete electron shell of the chromium ion by coordinately bound molecules causes the resulting absorption band to be sharper and more regular. In addition, changes in the wavelength of maximum absorption and in the maximum molar extinction coefficient may occur, depending on the energy relations of the bound groups."

Comparing the reactions of chromium under similar conditions with a series of different organic acids (14,6), it was found that increase of the molar extinction coefficient with addition of acid took place even when a ratio of ligand to chromium exceeded 1000, showing that complete penetration had not occurred, and indicating that, of all the ligands studied, oxalate has the highest affinity for coordination with chromium.

When chromium coordinates anions, the charge on the complex falls, causing strong acid to be liberated, and the pH of the solution to drop. This tends to reverse the reaction due partly to depression of the ionisation of the organic compound. In order to overcome this, Shuttleworth (15) suggested the use of salts of organic acids, rather than the acids themselves. The solutions were then adjusted to predetermined pH values by the addition of strong acids

having negligible coordinating powers.

Green and Ang [16] used spectrophotometry in addition to other methods to study the reaction of alanine with chromium. Shuttleworth and Sykes [17] determined the absorption spectra of a series of α, β, γ and ϵ amino acids, and found an inverse linear relation between the maximum molar extinction coefficient and the logarithm of the dissociation constant of the carboxyl group of the amino acid. This, in conjunction with potentiometric data, was used to demonstrate the importance of the carboxyl group rather than the amino group in the reaction of these compounds with the chromium complex under the aqueous acid conditions which are prevalent in tanning operations.

2. Potentiometry.

Potentiometric titrations have been used for investigating coordination reactions by a number of workers, particularly in the biochemical field [18-27]. Variation of pH with addition of alkali has been used to establish the dissociation constants of the ligands under the experimental conditions [18,19]. Interpretation of the curves has enabled the formation constants of a number of coordination complexes, particularly those of amino acids and peptides, to be determined.

Albert [18] noted the difference between the titration curve of a metal with added ligand and the sum of the curves of the separate substances. The magnitude of the

difference was taken as a measure of the extent of coordination of the ligand. Leberman and Rabin [20] applied the same technique to the reaction between cupric ion and histidine. Datta and Rabin [21] used pH titration measurements to determine the stability constants of cobaltous and manganous chelates of glycyl glycine and related compounds. Jones and co-workers [19] determined the dissociation constants of salicylaldehyde and 8-hydroxyquinoline and compared these with the stability constants of their complex ions. Bond and Jones [26], determining pH and redox potential in a ferrous-ferric system to which ethylene diamine tetra-acetic acid and similar coordinating agents had been added, used the pH dependence of the redox potential to determine the relative stabilities of the ferrous and ferric complexes of these ligands. The stability of the ferrous complex was determined in a separate pH titration with only ferrous ion present. This enabled calculation of the stabilities of the ferric chelates.

Application of the methods described above to chromium coordination compounds is complicated by two factors. Chromium readily forms soluble basic salts, the electrovalently bound hydroxyl ions coordinating to the chromium ion. Two chromium ions are readily coordinated by the same hydroxyl ion, leading to olation of the complex, whereby aggregates of two or more chromium ions are joined together by hydroxyl bridges. This complicates theoretical treatment due to the variety of complexes which may be formed under a given set of conditions. In addition, the reactions are slow, even at elevated

temperatures/.....

temperatures, making normal titration methods impossible.

This latter difficulty has been overcome to a certain extent by Green and Ang [16] by adding increasing amounts of alkali to known amounts of chromium and ligand. The solutions were heated in closed tubes for 24 hours, after which the pH's of the solutions were determined. Although this method carries out the titration under equilibrium conditions, it suffers from the disadvantage of the possibility of decomposition of the coordinating compound.

Most potentiometric work on chromium has been carried out in the conventional way after coordination has been carried to equilibrium by ageing or heating of the solution. The object is thus not determination of the stability constants of the complex ions directly, but rather the analysis of the solution for residual ligand, or determination of the acid dissociation constants of the complex ions present.

Britton [28], using the hydrogen electrode, titrated chromium solutions with sodium acetate, oxalate and tartrate. He observed that mixtures of chromium with these salts, after boiling or ageing, could no longer be precipitated at the normal pH on addition of sodium hydroxide. Atkin and Chollet [28], using the quinhydrone electrode, titrated chrome alum solutions in order to determine the free acid present due to hydrolysis. It was found that, on boiling or ageing, the colour of the solution changed and the amount of free acid increased, indicating an increase in hydrolysis.

Burley [30] used titrations with the glass electrode

to study the reactions of potassium oxalato chromiates with certain organic anions. Friend [31] titrated solutions of potassium dioxalato chromiates, obtaining the acid dissociation constants, regarding them as weak dibasic acids. This work was carried out at a reduced temperature to "freeze" the equilibrium, preventing alteration of the coordination state of the chromium ion. Cooper [32], carrying out titrations on similar compounds, deduced the nature of the complexes formed by estimation of the groups on the complex ions which were titrating. Shuttleworth and Sykes [33], investigating the reaction of amino acids with chrome alum, used potentiometric titrations to deduce the nature of the combination of these ligands with chromium.

3. Conductimetric Titration.

Conductivity measurements have been used to estimate the amount of free acid present in chromium solutions due to hydrolysis, the degree of hydrolysis, and the acid and hydroxyl groups associated with the coordinated chromium ion. Theis and Serfass [34] carried out conductimetric titrations to determine the amount of free strong acid present in the solution. On titrating with sodium hydroxide, the conductivity of the chromium solution showed a sharp minimum on completion of the titration of the strong acid.
Shuttleworth [35] applied electrolytic conductivity theory to the study of basic chromium sulphate solutions and showed that it was possible to estimate hydrolysis in the solution as well

as the nature/.....

as the nature of the groups coordinated and electrostatically bound to the chromium ion. These concepts were applied to chromium sulphate complexes [36] and to a series of other systems [37 - 48]. Due to the low concentration of about .0003 molar employed in this work to eliminate the effects of interference between ions, it was found that the slopes of some of the titration curves depended on the speed at which titration was carried out. This was observed with the solutions containing sulphate as ligand and was due to hydrolysis of the complex at high dilution. In order to retard this change, this system was titrated at 5°C [49] when a marked improvement in accuracy was obtained.

4. Polarography.

Reduction potentials of complex chromium ions at a dropping mercury electrode have been used by Hamm and co-workers [50 - 53] to investigate the reactions of chromium solutions. It was found that the half-wave potentials of the different ions in the solution were characteristic. It was observed that the half-wave potential of a freshly prepared chromium chloride solution was different from that of an aged solution. During storage of a fresh solution of chromic chloride, a plateau corresponding to the potential of the fully aged solution appeared, and became more prominent as ageing continued. By plotting the diffusion current at an intermediate potential as a function of time, it was possible to follow the extent of the reaction, and study its

kinetics. In a series of papers [51 - 53] Hamm applied the technique to a number of different systems, including the products of penetration of oxalate, malonate, acetate, glycolate, lactate, phthalate, citrate and tartrate into the hexaquo chromium ion.

5. Paper Electrophoresis.

This method frequently provides a convenient means for separating mixtures of electrolytes. Cooper [32], studying the reactions of the oxalato chromiates, obtained separations using the apparatus described by Strain [54] in which the platinum wire electrodes were placed in contact with the paper, which was moistened with the carrier electrolyte. This was found to be undesirable, due to the acidic and alkaline impurities produced by electrolysis at the electrodes and their effect on the chromium complex ions, which are sensitive to changes of pH. To avoid this, apparatus was constructed in which the electrodes were placed in vessels containing electrolyte into which the ends of the paper were dipped, a method described by Durrum [55] and applied to basic chromium chloride solutions by Gustavson [56].

6. Paper Chromatography.

This technique has proved very useful, particularly in the organic field. Cooper [32] attempted to separate oxalato chromium complexes by one dimensional paper chromatography, but was unsuccessful, though 20 different solvent

mixtures/.....

mixtures were tried.

7. Electro Chromatography.

This is a combination of paper electrophoresis and chromatography. Substances are caused to move vertically on a paper sheet by a capillary flow of background electrolyte down the sheet, and at the same time an electric potential is applied across the sheet. Cooper [32] attempted continuous separation of oxalate complexes by this method, but was not successful.

8. Ion Exchange Methods.

Ion exchange materials have been used both to determine the nature of the ions in chromium solutions, and, by incorporation of specific reactive groups in the inert framework, to elucidate the reactions occurring during chrome tannage.

Gustavson [57] used a synthetic zeolite to study the nature and behaviour of chrome liquors. Adams [58], testing the validity and usefulness of the method, reacted anionic and cationic exchange resins with basic chloride and sulphate solutions of chromium. He showed that, despite limitations due to shifting equilibria in the chromium solutions, the method was useful for determining the amounts of anionic and cationic complex ions present. It was also possible to determine the basicity of the cationic complexes, and follow

the penetration of coordinating agents. Gustavson [59] percolated basic chromic chlorides and sulphates through a sulphonic acid cation exchanger, followed by an anion exchanger, to determine the amounts of cationic, anionic and non-ionic bodies in the solution. By alkalimetric titration of the effluent obtained after passing sulphate solutions through the sulphonic acid resin, the ionic sulphate associated with the chromium was found. The coordinated sulphate was found by difference.

Theis and co-workers [5] reacted an excess of a cation exchange resin with basic chromium sulphate solutions containing organic anions. The resin absorbed the cationic portion of the solution, which was then desorbed by acid. Chromium, sulphate and the organic content were determined in the cationic and non-cationic portions, and the degree of penetration of the ligand into the complex ion was determined.

Gustavson [56] used cation exchangers of both the hydrogen and sodium ion types to determine the amount of cationic material in 66 % basic chromic chloride solutions. Using the column method, it was observed that the proportion absorbed increased with decrease in the size of the resin particles. This was attributed to more intimate contact between the resin and the percolating solution. Thus the finer the resin particles, the more material was retained by the column. However, it was found undesirable to use resin particles which were very fine due to the slow rate of percolation through the column which caused shifts in the equilibrium of the chromium solution. For this reason the shaking method

was preferred since very finely divided resin could be shaken with the solution for a short time, combining the advantages of a fine and a coarser resin. Under these conditions concordant results were obtained, giving a result of 30 % of the chromium being in the cationic form.

Shuttleworth [60] tanned exchange resins containing various reactive groups with chromium solutions of a wide variety of types and charges. The resins contained sulphonic acid, carboxyl and amino groups respectively. In addition, the solutions were used to tan hide powder and pieces of skin. It was found that the charge on the chromium ion was not an important factor in the fixation of chromium from the solution by the resins. The chromium uptake from the various solutions by the resins and by hide powder was compared with the shrinkage temperature of the skin tanned with the same solutions. Very close correlation was obtained between the chromium content of the carboxyl resin and the shrinkage temperature of the skin, giving support to the postulate that the thermal stability characteristic of chrome leather is conferred primarily by coordination of the carboxyl groups in the collagen side chains to the chromium complex.

Kawamura and co-workers used polystyrene based exchange resins for study of chromium complex ions [61-63]. They found that hydrogen, potassium and sodium exchange resins had the greatest exchange capacity, and also that this was not affected by the ligands coordinating to the complex ion. Colloidal ions were absorbed by the resin with a low degree of cross linking [61]. On passing a mixture of anionic,

cationic/.....

cationic and neutral complexes through a sodium or potassium polystyrene-sulphonate column, the cations and some singly charged anions were absorbed [62]. The neutral ions in the effluent could then be separated by passing through an anion exchanger. Kawamura [63] studied the increase in the sizes of chromium complex ions with addition of alkali by comparing the absorption on polystyrene-sulphonate resins with different degrees of cross linking.

9. Diffusion.

Since the rate of diffusion of ions in solution is related to their size [64], diffusion measurements can be used as a means of determining molecular sizes, and to a certain degree, molecular weights. Northrop and Anson [65] used a cell containing a porous diaphragm to separate two solutions of different concentration. McBain and Liu [66] tested the applicability and reproducibility of the method for various systems, concluding that accurately reproducible results could be obtained in a day by the method.

Theis and co-workers [5] used diffusion through a cellophane membrane to determine particle sizes in chromium solutions containing coordinated organic anions. Due to the small pore size of the membrane, some ultrafiltration probably took place, with consequent unreliability in the results obtained.

Stokes [67] pointed out that the method of McBain, relying on convectional stirring, led to concentration

gradients/....

gradients in the compartments separated by the membrane, and further that accomplishing this stirring by placing the denser solution in the upper compartment produced a system which was basically unstable. He found that measurements in a magnetically stirred cell gave more accurate results.

Gustavson[56] applied diffusion measurements using a cellophane membrane, in addition to other physical methods, in an investigation of basic chromic chloride solutions.

Ellis[64] discussed the theory of diffusion and its application to chromium complex ions, describing the use of convectionally and magnetically stirred cells with porous diaphragms. The value of the particle radius of the hexaquo chromic ion obtained by this method was in agreement with that found by X-ray measurements of solid salts. An increase in size with increasing basicity of the solution was observed. In a given solution, particles of different sizes were observed but apparent uniformity was obtained on ageing the solution.

10. Isopiestic Studies.

It is sometimes convenient to determine the activities of substances in solution by determination of the vapour pressure of the solution. However it is not always convenient to determine this from direct measurement, and under these circumstances it is possible to use isopiestic comparison. This method was used by Robinson and Sinclair[68] to measure the activity coefficients of lithium chloride solutions. The solutions, together with potassium chloride solutions were placed in open dishes and kept in a desiccator under vacuum

until/.....

until equilibrium was attained, when the solutions were analysed. The vapour pressure was deduced from the accurately known vapour pressure curve of potassium chloride. This method has been applied to the study of the complex ions of chromium with alanine by Green and Ang[16].

Application of Chromium Co-ordination Chemistry to Leather Manufacture.

Tanned leather in its commonest form differs from raw, untanned skin in several obvious and important respects. Raw skin is a material which is readily putrescible, and when allowed to dry from a wet condition, it forms a hard, translucent mass apparently devoid of fibrous structure. Leather, on the other hand, has considerable resistance to putrefaction, and dries to a porous material in which the fibre structure of the skin can readily be distinguished.

Although it was considered by Knapp, the original discoverer of the tanning properties of chromium salts[69], that the tanning process consisted of depositing on the collagen fibres of skin a layer of insoluble chromium oxide, it is now generally accepted that chemical reaction between the protein and the tanning agent is a characteristic of leather manufacture. The basic reaction in all types of tannage is now considered to be a reaction between the reactive groups of the collagen and the tanning agent, which can lead to the establishment of cross links between adjacent protein molecules.

The tanning agent renders the reactive groups of the collagen less prone to attack by bacteria and enzymes, making the material as a whole less liable to putrefaction in their

presence.

According to recent evidence, it is considered [70] that the protein molecules of collagen consist of polypeptide chains arranged as coiled coils which are twisted about each other to form "ropes". The adjacent polypeptide chains are held in this structure by hydrogen bonds and possibly ionic salt linkages, which are broken in the presence of water at elevated temperatures. This allows the entire structure to collapse as the chains bunch up, and causes a change in the macroscopic dimensions of the skin, which is observed as "shrinkage". In chrome tanned leather, these cross links are supplemented or replaced by chromium complexes, forming links which have a greater hydrothermal stability, and are capable of producing leather which may be dimensionally stable in boiling water.

Knowledge of the properties of the complex ions of chromium, which is useful in providing evidence as to the positions on the protein chains at which co-ordination and cross linking can take place, and more complete knowledge of these reactions, is the underlying reason for the present investigation.

Information Yielded by Miniature Tanning Experiments.

Firstly, miniature tanning experiments can prove useful in the elucidation of the tanning process itself; treatment of normal and modified collagens and of related substances with tanning solutions has been used to determine which of the active groups in the skin protein are responsible for fixing the tanning agent. Secondly, reaction of normal collagen, in the form of either skin or hide powder, with chromium solutions of

different types, yields evidence regarding the tanning ability of these solutions and of the availability of the co-ordination sites on the chromium nucleus. This information is obtained by observing differences in the fixation of tanning agent, and also in the hydrothermal stability of the tanned protein.

In 1926 Thomas and Kelly [71] found that collagen tanned with quinone or vegetable tannins absorbed chromium at a reduced rate, this effect also being noted in deaminated collagen. This was interpreted as evidence that the nitrogen groups play a significant rôle in tanning. Bowes and Kenten[72] studied the effect of esterification and deamination of collagen on its reaction with chromium, and suggested that the chromium complex was fixed by co-ordination of the carboxyl and amino groups of collagen.

Shuttleworth[60] tanned skin, hide powder and a number of ion exchange resins containing sulphonic, carboxyl and amino groups with chromium solutions containing a variety of co-ordinated organic compounds. He obtained good correlation between the shrinkage temperature of skin tanned by a given solution and the chromium uptake by the carboxyl resin from the same solution, and concluded that the important reaction giving chrome leather its characteristic high hydrothermal stability is the co-ordination of the carboxyl groups in the collagen side chains. The charge on the chromium complex is unimportant - the factor determining the tanning ability of an ion being the number and stability of the ligands already present in the complex.

Sykes[73] treated collagen with a variety of reagents

which/.....

which altered the proportion of side-chain carboxyl and amino groups present. He found that while removal of the amino groups in some cases reduced the amount of chromium fixed by the collagen by as much as 50 %, this gave no corresponding decrease in hydrothermal stability of the leather. Decarboxylated collagen, on the other hand, while in some cases fixing an appreciable amount of chromium, lacked the properties of leather.

Study of miniature tannage experiments can also be used to provide evidence concerning the tanning agents. The available coordination positions on the chromium ion may be taken up successively, but the resulting bonds decrease progressively in stability. When a coordinated chromium solution is allowed to react with collagen, there is competition between the collagen and the ligand for the available coordination sites, in which mass action effects, influenced by the concentration of the ligand, and the relative affinity of the ligand and collagen play their parts.

The addition of organic salts to chrome tanning solutions is a commercial practise known as masking. Immendörfer's studies [74] into the effects of polycarboxylic acids as masking agents and their subsequent introduction to the leather industry as patented speciality products by I.G. Farbenindustrie led to renewed interest in this type of material. Claims that masked tannages proceeded rapidly, had strong filling action and improved chromium fixation, were critically reviewed by Holland [75-77]. He not only gave an exhaustive review of the earlier work on this subject but

reported a considerable amount of new experimental data which formed a sound basis for more recent practical and theoretical developments in the field of chrome tanning.

Commercially, formate and phthalate anions have been most widely used, and in both cases it is recommended that the leather be stored for one to two days before neutralising and finishing, and it has been shown that during this period there is an increase in the shrinkage temperature of the leather as the masking agent tends to be displaced from the chromium complex by the reactive groups present in the protein.

CHAPTER II.

EXPERIMENTAL TECHNIQUES.

Preparation of Solutions of Chromium Complexes.

In addition to forming complexes by coordination of added ligands, chromium solutions can also hydrolyse with the formation of basic salts, which in turn can olate to form polynuclear complexes: all these reactions are also pH dependent. Due to these complicating factors, the study of the coordination chemistry of chromium is one of the most difficult of coordination chemistry investigations.

Such factors as the concentration of chromium and of neutral salts, as well as the nature and concentration of inorganic anions are all found to interfere with coordination of the ligand. It is likely that it is these difficulties which have led pure chemists almost to ignore the coordination chemistry of chromium, as is evident from a recent symposium on coordination chemistry [78], in which only two out of about 150 papers submitted refer to soluble chromium complexes. Thus much of the work in this field has been done by leather chemists whose primary interest lies in the technological application of their work.

The factors referred to above set certain limits on the experimental conditions under which chromium complexes are prepared. Thus in comparative work strict control of the concentration of chromium and ligands, of the pH and of

neutral/.....

neutral salt content is advisable in order that equivalent values may be studied. Bearing this in mind, two approaches are available, both of which have been used in this work.

Method I. Essentially this method consists of allowing the chromium at a known concentration to react with the ligand under investigation at a known molar ratio, then allowing the solution to attain equilibrium with or without adjustment of the pH to a predetermined level by addition of acid or alkali. This method has been widely used, particularly when it was desired to study the formation of chromium complexes under conditions similar to those prevailing during leather manufacture (17).

Method 2. In this method, the chromium and ligand are allowed to react together in the presence of known increments of acid or alkali. The properties of a series of these solutions at different pH levels and with various ligands are then compared (16).

In both these methods heat increases the rate of reaction and reduces the time taken for the solutions to reach equilibrium.

Details of the Techniques Employed.

Method I.

In this method the complexes were prepared from a stock chromic chloride solution which was made approximately

.6 molar,/.....

.6 molar, then allowed to age for a month before use, and analysed for chromium.

To each of a series of 30 ml. beakers, a volume of this solution equivalent to 20 ml. of a .333 molar chromium solution was added from an accurate burette. 1.33 molar solutions of the ligands were prepared by weighing out the solids, the purity being assumed 100 % for this purpose. Volumes of these solutions equivalent to molar ratios of $\frac{1}{2}$, 1, 2 and 3 per chromium atom were added to the chromium chloride solutions from a micro-burette, three separate solutions at each molar ratio being prepared.

These solutions were now adjusted to equilibrium pH values of 2.50, 3.16 and 3.82 by addition of potassium hydroxide solution. To accelerate the changes accompanying alteration of the pH of chromium solutions, the following procedure was followed: alkali was added until the pH reached the desired value (or, in the initial stages, a slightly higher value), after which the solution was heated on a hot-plate at 70°C for 1 hour and allowed to cool. This procedure was repeated until the pH remained constant at the desired value after two successive periods of heating without addition of alkali. The solution was now transferred to a 20 ml. volumetric flask and made to the mark. To minimise the change in pH with dilution at this stage, the volume of the solution when the pH was measured was made such that about 2 ml. was required to transfer the solution to the flask and make to the mark. The solutions were allowed to age for 1 month

before/.....

before any measurements were carried out on them.

Method 2.

A series of complexes was prepared using the method proposed by Green and Ang [16] for study of the coordination of alanine by chromium.

The complexes were prepared from stock solutions of chromic chloride and chromic sulphate, which had been assayed for chromium. Volumes of these solutions equivalent to 100 ml. of .666 molar chromium solution were transferred to flasks from an accurate burette. The ligand was added in the ratio of 3 moles of ligand per gram atom of chromium and the solution boiled under reflux for 20 hours. Since complex formation is slight in strongly acid solution, some of the ligands were used in the form of their potassium salts. While addition of the alkali salt frequently caused precipitation of the chromium solution, it was found that this could be prevented by adding the acid and then adding an equivalent amount of standard potassium hydroxide solution through the condenser over a period of about an hour while the solution was boiling under reflux. After refluxing, the solution was cooled and made to a volume of 100 ml.

5 ml. aliquots were pipetted into a 10 ml. volumetric flask, and to these were added volumes of standard potassium hydroxide solution corresponding to 0 - 4 moles of alkali per gram atom of chromium, in increments of .333 mole. The solutions were then made to the mark, giving solutions .333 molar with respect to chromium, and transferred to dry tubes

which were sealed and heated in a boiling water bath for 20 hours.

The solutions were cooled, and the pH's determined, this representing a form of potentiometric titration. Portions were retained without any dilution for spectrophotometric measurement.

Modifications to Method 2.

Since it was found that some of the ligands were hydrolysed during the periods of boiling, attempts were made to carry out the coordination reaction under less drastic conditions.

Modification 1.

The periods of refluxing and also of the subsequent heating of the series were both reduced to 1 hour.

Modification 2.

The entire preparation was carried out at room temperature. After addition of ligand and initial alkali, the solution was allowed to stand for 24 hours. The series with increasing additions of alkali was then prepared, and these were allowed to stand for a further period of 24 hours before measurements were made.

In order to ascertain whether these modifications produced a similar amount of coordination to the method proposed by Green and Ang, the three methods were compared

with/.....

with glycine as ligand. The maximum molar extinction coefficients are given in Table 2.1.

Table 2.1.

Comparison of modifications to Green and Ang's method of preparing chromium complexes in solution.

Ligand added to 33 % basic chromic chloride	Treatment	Maximum Molar Extinction Coefficient	
		420 mμ region	580 mμ region
3 moles of glycine per gram atom of chromium	Heating for 20 hours	32.2	38.3
	Heating for 1 hour	31.7	37.5
	Cold reaction for 24 hours	29.4	35.3
Nil	Heating for 20 hours	25.9	18.7
	Cold reaction for 24 hours	23.9	18.5

The variations caused by the modified methods were found to be relatively small and gave more reliable results for ligands unstable to prolonged heating than did the method as originally proposed. Moreover, for purely comparative work this is quite adequate and will be discussed more fully in Chapter IV.

INVESTIGATION OF THE CHROMIUM SOLUTIONS.

Spectrophotometric Investigations.

The absorption of monochromatic light by solutions is described by two laws, both of which were originally derived from experimental observation. The first, proposed by Bouguer in 1729 states: "Each layer of equal thickness absorbs an equal fraction of the radiant energy which traverses it." The second law, proposed by Beer in 1852 states: "The absorptive capacity is directly proportional to the concentration of the solute" [79]. These laws can be expressed in the following symbolic form:

$$I = Io.10^{-dt}$$
$$= Io.10^{-\varepsilon ct}$$

where I = light transmitted through the solution

Io = light transmitted through an equal thickness of the solvent

t = thickness of absorbing solution

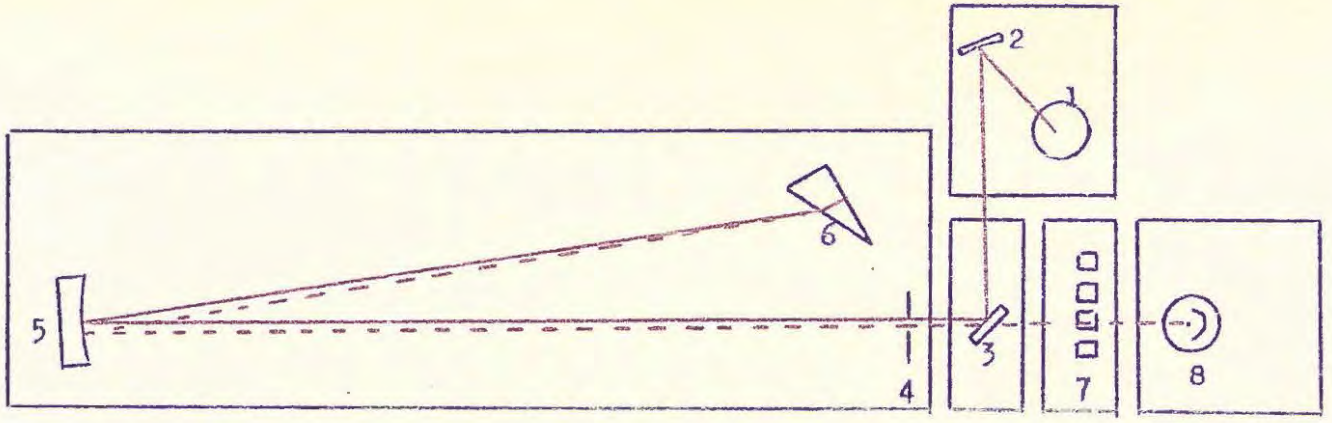
d = constant for a given solution
= optical density of solution

ε = constant for a given solute
= molar extinction coefficient

This relation is known as the Beer-Bouguer Law.

In practice, the solution must be contained in a transparent cell, at the walls of which a proportion of the light is reflected. By taking Io as the light transmitted through pure solvent in an identical cell, these reflection losses are balanced out.

Strong/.....



1. Tungsten lamp.
2. Condensing mirror.
3. Diagonal slit entrance mirror.
4. Entrance and exit slits.
5. Collimating mirror.
6. Quatrz prism, rotated to select desired wavelength.
7. Corex cells containing solutions under investigation.
8. Photo-electric cell whose amplified output signal is measured by a potentiometer.

Fig. 2.1. Optical System of the Beckman Model DU Spectrophotometer.

Strong [80] has derived the Beer-Bouguer Law threoretically from probability and capture cross section concepts. It is shown that the optical density is additive for a solution containing different solutes, and that if a finite wavelength band is considered, it is necessary to integrate the energy/wavelength function. It is also shown that apparant deviations from the law are caused by variation in the nature of the solution with variation of concentration, or variations in the width of the wavelength band passed.

In the present investigation, the Beckman Model DU Spectrophotometer was used for determination of the absorption spectra. This instrument has found wide application both as an analytical tool and for research. Castor [81], after carrying out experiments on a number of these instruments, discusses the reproducibility of the model DU. A diagram of the optical system of the instrument is given in Fig. 2.1.

Two different instruments were used in the present work. The one on which the majority of the measurements were made was fitted with the blue-sensitive photoelectric tube normally fitted to the instrument, while the later measurements were made on another instrument in which this tube had been replaced by a photomultiplier tube designed to increase the sensitivity of the instrument at the lower end of its spectral range.

Corex resistance glass absorption cells of 1 cm light path were used to contain the solutions under

investigation/.....

investigation.

Solutions at the high concentration used in the present work were almost opaque, and for this reason much too dense for spectrophotometric investigation. It was therefore necessary to dilute them: a dilution of 25 times (to 1/75 molar) being found to give solutions with a convenient value of optical density in the complexes studied. Since dilution causes a change of pH, leading to hydrolysis and other changes which might affect the previously attained equilibrium, and alteration of the molar extinction coefficient, the absorption curve was completed as rapidly as possible after dilution. The measurements were carried out in a room thermostatically controlled at 22°C.

The absorption density was determined at wavelengths between 320 and 620 mμ. In agreement with previous workers' findings [11,16], there were found to be two maxima in this region of the absorption spectra of all the solutions studied, one with its peak at about 420 mμ, and the other with its peak at about 590 mμ. These absorption maxima will be referred to respectively as the "blue peak" and "yellow peak" in this thesis. Since these maxima were the portions of the spectra with the greatest interest, readings were taken at intervals of 4 mμ in these regions, while the interval was increased to 20 mμ at other portions of the spectrum, merely serving to demonstrate the general shape of the curve. In the latter portion of the work, readings only in the regions of the absorption maxima were taken. This enabled the time

between/.....

between dilution of the solution and completion of the measurements to be further reduced.

The instrument was operated at or near its maximum sensitivity, enabling the potentiometer circuit to be balanced with a slit-width of .06 - .01 mm, giving a nominal spectral band about .5 mμ [82]. Balancing was done by adjusting the slit-width, with a cell containing distilled water in the light path. Three other cells containing complex solutions in the cell carrier were successively placed in the light path, and measurements at the same wavelength were made on them.

Potentiometric Titration.

The potentiometric titrations were made using the method suggested by Shuttleworth [33]. The titrations were carried out rapidly to minimise the changes in the equilibrium of the solution due to dilution and change of pH during the titration.

The apparatus used was the following:
Titrations were carried out in a 150 ml. resistance glass beaker. pH measurement was effected by a Cambridge wide range glass electrode (Cat. No.42558) and a dipping saturated calomel electrode, connected to a Cambridge Bench-type pH meter. The glass electrode used has an effective range of pH 0 - 13 according to the manufacturers. The pH meter was standardised at pH 4.00 by means of a .05 molar solution of potassium hydrogen phthalate [83]. The solution being titrated was stirred by a glass stirrer driven by a small

air/.....

air turbine. This, while stirring the solution adequately, caused no electrical interference to the electrodes, as shown by the steadiness of the pH meter galvanometer.

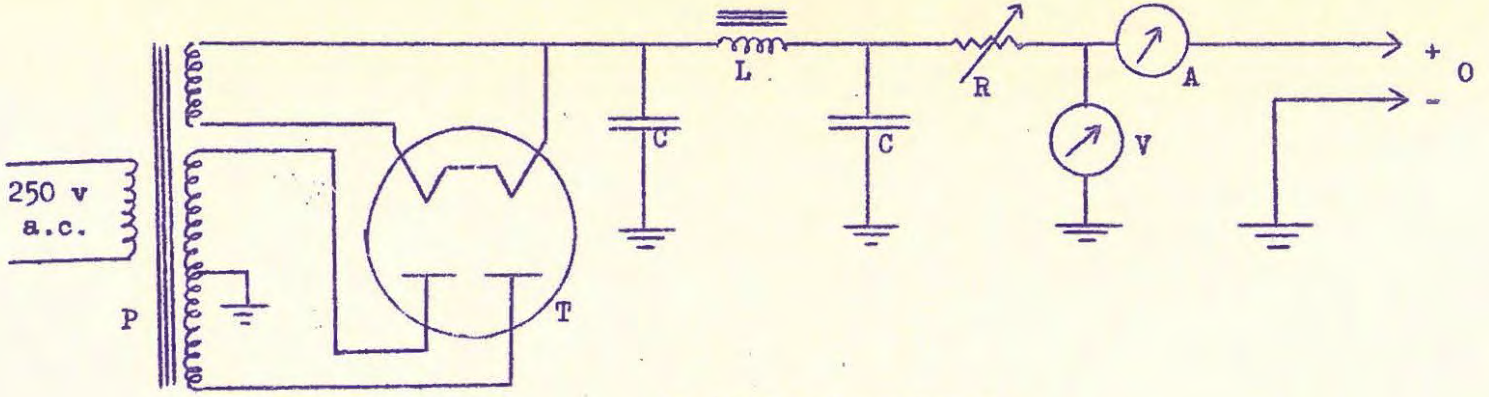
The experimental procedure used was as follows: 2 ml. of the solution to be titrated was pipetted into the titration beaker and diluted to 50 ml. with water. The solution was titrated with 0.5 normal potassium hydroxide solution, allowing only sufficient time between additions of alkali to permit the pH of the solution to be read, approximately 30 seconds. Titration was continued to a pH value of 12. A separate aliquot was then titrated with 0.5 normal hydrochloric acid, the pH being taken to 1.4.

The potassium hydroxide solution was standardised with potassium hydrogen phthalate, and the hydrochloric acid with borax, and in addition the two solutions were titrated against each other.

Paper Electrophoresis.

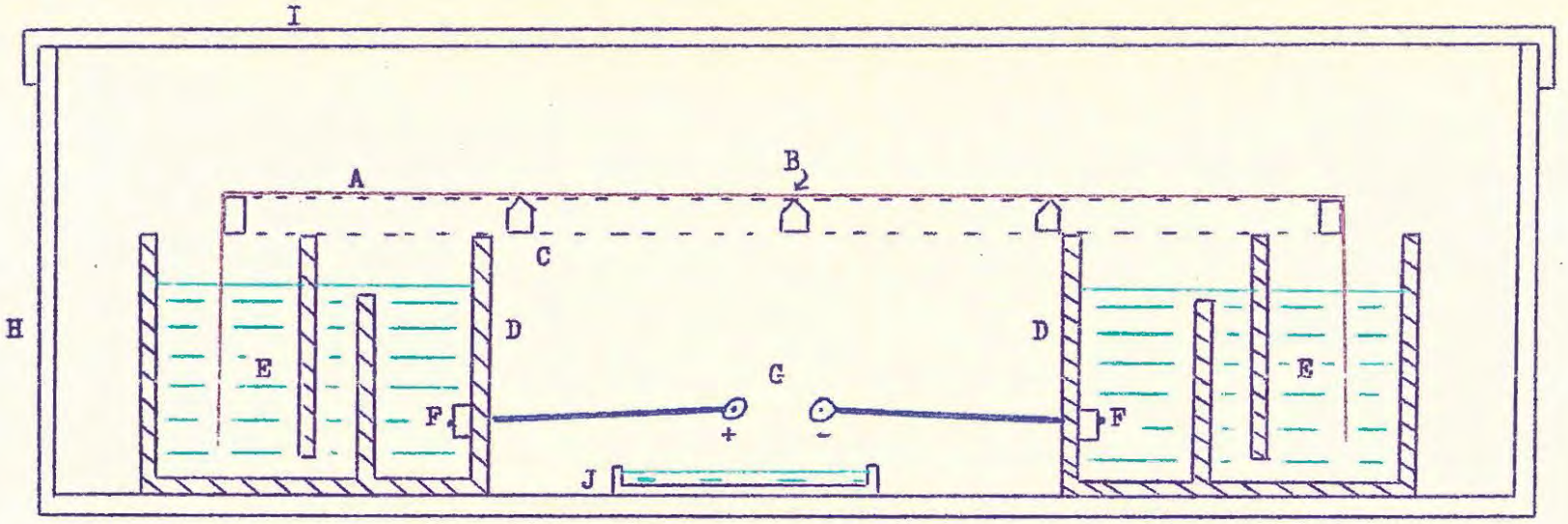
Electrophoresis was carried out on strips of Whatman No. 3 MM filter paper which were cut to a width of 2.5 cm. The background electrolyte used was 0.01 normal sodium nitrate solution, which was adjusted to the same pH as the solution under examination with nitric acid. This solution was used in place of a buffer solution to avoid the possibility of coordination of the chromium by the weak acid anion of these solutions. A concentration of 0.01 molar was chosen to give sufficient conductivity for a reasonable rate

of/.....



P Power transformer.
T Rectifier tube.
C 8 μF condensers.
L Choke.
R Rheostat.
A Milliammeter.
V Voltmeter.
O High voltage d.c. output to paper electrophoresis apparatus.

Fig. 2.3. Current Source for Paper Electrophoresis.



A Filter paper strips.

B Point of application of Chromium Complex.

C Perspex supporting grid.

D Electrode vessels.

E Background electrolyte.

F Electrodes.

G Terminals for current supply.

H Perspex box.

I Perspex lid.

J Flat dishes of background electrolyte.

Fig. 2.2. Paper Electrophoresis Apparatus.

of movement while maintaining the current sufficiently low to cause only slight heating effects on the paper.

The apparatus used is shown : Fig. 2.2 being the assembly holding the paper strips, and Fig. 2.3 being the source of high voltage direct current.

The experimental procedure used was the following: The electrode vessels were filled with background electrolyte adjusted to the appropriate pH and placed in the perspex box. They were connected by means of a siphon tube and allowed to stand for 30 minutes to equalise the levels of the solution in the two vessels in order to prevent any siphoning action during the run. Flat dishes containing electrolyte were placed on the bottom of the box to increase the evaporating surface and hasten saturation of the atmosphere.

Six strips were run at a time. The centre of each strip was marked with a pencil line, and the strips saturated with background electrolyte, lightly blotted to remove the excess, and stretched over the supporting grid with their ends dipping into the solution in the electrode vessels. The centre of each strip was now further blotted to prevent spreading of the chromium solution, 0.05 mL of which was applied along the pencil line from a micropipette in the form of a strip 5 mm wide. The box was closed, and allowed to stand for 30 minutes to allow the atmosphere surrounding the strips to become saturated.

The current was now switched on, a total voltage of 190 - 210 volts being applied, and the current being

between/.....

between 2.5 ma. and 4.5 ma., the higher values being registered with the more acid solutions which have a higher conductivity. These values gave a potential gradient of about 5.5 volts per cm and a current density of 0.17 to 0.3 ma. per cm width of paper.

During the run a certain amount of moisture was observed to condense on the lid of the box, indicating a certain amount of electrical heating of the strips, since the run was conducted in a thermostatically controlled room at 23°C. This caused a certain amount of concentration of the electrolyte in the strips during the run, causing a slight rise in the current. During the run the current and voltage were read at intervals, the time of the run, usually about 6 hours, also being recorded.

At the end of the run, the grid with the paper strips was removed from the apparatus, and the strips allowed to dry on the grid in a horizontal position to avoid any flow of electrolyte. The position of the chromium bands was determined and the amount of movement of the complex determined.

In order to observe the movement of the amino acid in the solution the strips were sprayed with a 0.1 % solution of Ninhydrin in citric acid/sodium citrate buffer and heated in an oven at 105°C to develop the colour (84). The amino acid was revealed by the intense blue colour formed by it.

Miniature/....

Miniature Tanning Experiments.

The solutions of chromium complexes prepared as described in the previous section (pp 26-29) were used as the tanning agents in a series of miniature tannages.

1. Preparation of Skin.

Drysalted goatskin was soaked, depilated with lime/sodium sulphide, neutralised with acetic acid, and washed free of salts, then dried by sublimation of water vapour from the frozen skin (i.e. freeze-dried). In this form it could be kept indefinitely, but could be readily wet out to its original moisture content by soaking in water. The flesh and grain surfaces of the skin were mechanically removed in order to give a more uniform composition through the thickness of the skin, after which it was cut into strips 3" by ½", which weighed approximately 0.25 gm. These strips were stored in sealed bottles until required for use.

2. Tannage.

Immediately before tannage, the strips of skin were wet-out overnight. In the case of pieces to be tanned by the chromium complexes prepared by Method 1 (p 26), which had been adjusted to three pre-determined pH levels, the skin strips were soaked in hydrochloric acid solutions of such concentration that the equilibrium pH was that of the appropriate chromium solution. In the case of the complexes prepared by Method 2 (p28), it would have been difficult to

bring/.....

bring the skin to an equilibrium at the same pH as the solution. These pieces were therefore wet out in distilled water and transferred to the chromium solution. Though this difference in pH causes a change in basicity, this is not considered to be serious in comparative work of this kind.

Tannage was carried out in glass sample tubes which were securely sealed with waxed corks to prevent leakage. 5 ml. of the chromium solution was measured into each tube, one of the wet strips added, and the tube sealed, this giving a ratio of approximately 1 gm. of dry protein to 20 ml. of solution. Tannage was continued for 96 hours, the tubes being shaken continuously at 60 r.p.m. Controls were included in the form of skin strips shaken in water for the same period, or in hydrochloric acid at the required pH where appropriate for the first series.

3. Testing of the Leather.

a. Determination of Fixed Chromium.

In order to determine the chromium combined with the skin, it was necessary to remove non-combined chromium, which was of two kinds: that dissolved in the water held between the fibres of the skin by capillary action, and that dissolved in the water of hydration of the collagen fibres.

In order to determine the most efficient method for removing this chromium, a number of strips of skin were tanned by the above method in a 50 % basic chromium sulphate solution containing 5 % Cr_2O_3, then divided up and six strips

subjected/.....

Table 2.2.

Comparison of methods for removal of excess chromium from tanned skin.

Details of treatments:

i. Removed from chromium solution and dried overnight at 105°C.

ii. Washed in running water (pH 7.5 - 8.0, alkaline hardness 20 p.p.m.) for 24 hours, then dried as in i.

iii. Pressed between layers of blotting paper in a hydraulic press, then dried as in i.

iv. Pressed as in iii, soaked in water for 5 minutes, pressed again, then dried as in i.

The following figures are % Cr_2O_3 in the dry leather.

	Treatment prior to analysis			
Replicate	i	ii	iii	iv
1	12.38	5.73	9.30	6.52
2	9.41	5.31	8.92	7.09
3	9.60	5.63	9.60	7.51
4	12.73	5.60	9.44	6.84
5	12.55	5.55	9.46	6.70
6	8.79	5.58	9.50	7.15
Mean	10.91	5.57	9.37	6.97
Standard Deviation	1.82	.14	.24	.36
Coefficient of variation	.167	.025	.026	.050

subjected to each of the following treatments:

i. Removed from the chromium solution and dried overnight at 105°C.

ii. Washed in running water (pH 7.5 - 8.0, alkaline hardness 20 p.p.m.) for 24 hours, then dried as in i.

iii. Pressed between layers of blotting paper in a hydraulic press, then dried as in i.

iv. Pressed as in iii, soaked in water for 5 minutes, pressed again, then dried as in i.

The chromium content of the pieces treated by the different methods is given in Table 2.2.

It is apparent that method ii removes the largest amount of uncombined chromium from the leather and gives the most precise results. This method was slightly modified for use in the tanning experiments, the strips being pressed between blotting paper to remove most of the chromium before being washed for 24 hours in running tap water.

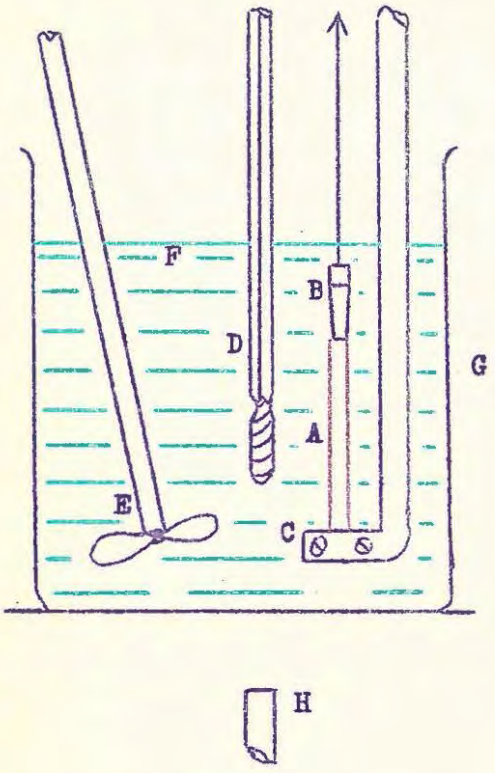
After washing, the strips were split, one strip being dried at 105°C overnight for analysis, and the other being retained for determination of the shrinkage temperature.

b. Determination of Shrinkage Temperature.

The apparatus used for this determination is shown in Fig. 2.4.

The wet specimen was secured in the two clamps, when it was subjected to a tension of 5 gms. It was immersed

in/.....



A Specimen.

B Movable clamp attached to indicator.

C Fixed clamp.

D 200°C thermometer.

E Electric stirrer.

F Heat transfer medium.

G 600 ml. beaker.

H Gas burner.

Fig. 2.4. Shrinkage Temperature Apparatus.

in the heat transfer medium at a temperature of approximately 15°C below the anticipated shrinkage temperature, and was then heated at a fairly rapid rate of 5°C per minute, rapid stirring being used to prevent temperature variations in different parts of the beaker. This method was used to avoid the changes caused when the wet leather is subjected to prolonged heating, which are discussed by Gustavson (84) and overcome by the "shocking" technique suggested by him, whereby a preliminary experiment is carried out to determine the approximate shrinkage temperature and allow the heating period to be minimised.

The shrinkage temperature was recorded as the temperature of the liquid when the first reduction of the length of the specimen occurred.

Where the anticipated shrinkage temperature was below 98°C, distilled water was used as the heat transfer medium. Where this temperature was expected to be exceeded, medicinal paraffin was used, as suggested by Bowes (85) in place of the 75 % aqueous glycerol used in the American Leather Chemists' Association official method, as the results obtained with medicinal paraffin are closer to those obtained with water heated under pressure.

Analytical Methods.

1. Determination of Chromium.

Both the chromium solutions and the leathers were analysed by the official wet oxidation method of the Society of Leather Trades' Chemists [86], the determination being scaled down where necessitated by the existence of only a small sample.

2. Determination of Basicity.

The basicity of the chromium solutions was determined by the official method of the Society of Leather Trades' Chemists [86].

3. Determination of Nitrogen.

The Kjeldahl method proposed by Chibnall, Rees and Williams [87] was used, as modified by Yuen and Pollard [88] and Eastoe and Eastoe [89] using the still described by Markham [90].

CHAPTER III.

COORDINATION OF AMINO ACIDS BY CHROMIUM CHLORIDE UNDER AQUEOUS ACID CONDITIONS.

The solutions whose properties are reported in this chapter were prepared by adding known amounts of the amino acids to standard solutions of chromium chloride, allowing them to come to equilibrium at predetermined pH values, and ageing for one month. This method of preparation is described in more detail as Method 1, page 26.

In a recent series of investigations in these laboratories, Shuttleworth and Sykes have studied the co-ordination of the same ligands by chrome alum under similar conditions, using spectrophotometric [17], potentiometric [33] and miniature tanning methods [92]. The present work was done as a comparison with this previous work, in order to observe the effects on these reactions of the lesser coordinating affinity of chloride compared with sulphate ions. It is interesting to note that chromium sulphate solutions are generally considered to have superior tanning properties to chloride liquors.

Table 3.1./....

Table 3.1.

Logarithmic dissociation constants of the functional groups of the ligands.

Ligand	pK_1 (carboxyl group)	pK_2 (amino group)
Glycine	2.3	9.6
α amino-n-butyric acid	2.5	9.6
β amino-n-butyric acid	3.6	10.3 +
γ amino-n-butyric acid	4.2	10.4

+ Estimated value.

The ligands studied are listed in Table 3.1, together with the dissociation constants of their carboxyl and amino groups. These figures are taken from the literature [93] with the exception of the dissociation constant of the amino group of β amino-n-butyric acid, which was estimated by potentiometric titration of 0.04 molar solution.

RESULTS.

It was evident from visual examination of the masked solutions that a reaction between the chromium and the ligand had taken place. While solutions containing no amino acid were green, the presence of ligand produced a purple colour, the extent of the colour change increasing with higher concentration of ligand, and with higher pH. These changes were quantitatively measured with the spectrophotometer.

Spectrophotometric/....

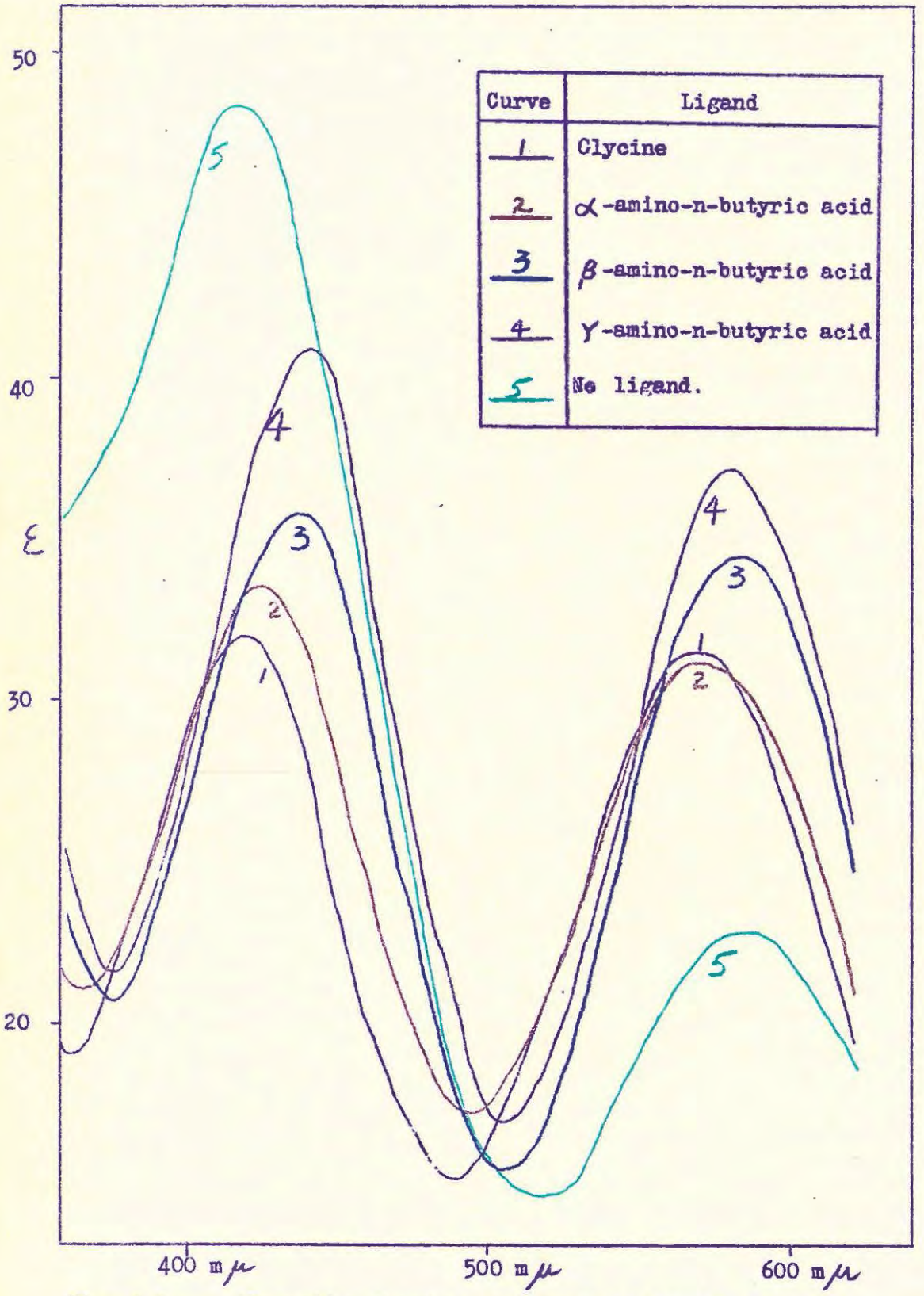


Fig. 3.1. Absorption Spectra of Chromium Chloride solutions masked with 2 moles of amino acid per gram atom of Chromium, at an equilibrium pH value of 3.16.

Spectrophotometric Examination.

Spectrophotometric measurements were carried out between wavelengths of 320 mμ and 620 mμ on solutions containing the four ligands, each at four concentrations (0.5, 1, 2, 3 moles of ligand per gram atom of chromium) and three pH levels (2.50, 3.16, 3.82). In order to observe the effects of higher ligand concentrations, solutions containing four and six moles of glycine per gram atom of chromium at the three pH levels were also prepared and examined. Solutions containing no added ligand were prepared as blanks at the two lower pH values and at pH 3.5, which was the highest value attainable without precipitation when using this method.

A total of 57 absorption spectra were determined and these are plotted as Figs. A.1 - A.19 in the Appendix. The absorption spectra of the solutions containing 2 moles of the ligands per gram atom of chromium at an equilibrium pH of 3.16, and the unmasked solution at this pH value, are plotted opposite in Fig. 3.1. These curves have a similar form to the absorption spectra of trivalent chromium solutions reported by previous workers [11,16,17], showing two absorption maxima in the visible region. For convenience, the absorption maximum in the region of 420 mμ has been referred to as the "blue peak", that at about 580 mμ as the "yellow peak".

The/.....

Table 3.3.

Wavelengths of Maximum Absorption of Chromium Chloride Solutions masked with Amino Acids. (Millimicrons)

Ligand	Moles Ligand per mole chromium	Blue Peak			Yellow Peak		
		pH 2.50	pH 3.16	pH 3.82	pH 2.50	pH 3.16	pH 3.82
Nil		416	416	420	582	586	584
Glycine	½	420	412	416	576	575	566
	1	416	416	412	576	574	575
	2	418	418	410	576	568	564
	3	428	418	412	572	562	550
	4	424	414	406	568	556	544
	6	420	410	408	560	550	544
α amino-n-butyric acid	½	418	414	416	576	578	576
	1	418	420	418	576	578	570
	2	428	424	416	574	568	560
	3	434	425	416	572	566	552
β amino-n-butyric acid	⅓	412	410	414	576	572	575
	1	416	410	412	577	572	566
	2	435	433	432	584	584	578
	3	442	446	442	582	586	586
γ amino-n-butyric acid	½	408	408	410	574	575	576
	1	416	412	413	574	572	568
	2	419	420	432	582	576	576
	3	442	444	444	580	578	578

Table 3.2.

Maximum molar extinction coefficients of chromium chloride solutions masked with amino acids.

Ligand	Moles of Ligand per mole Chromium	Blue Peak			Yellow Peak		
		pH 2.50	pH 3.16	pH 3.82	pH 2.50	pH 3.16	pH 3.82
Nil		31.0	48.3	49.4	19.3	22.7	23.3
Glycine	½	26.1	44.6	48.4	21.6	23.7	27.2
	1	25.9	33.8	50.9	24.8	27.0	30.3
	2	28.7	32.2	44.6	29.1	31.4	34.6
	3	32.1	34.7	40.3	32.3	34.9	39.0
	4	34.4	36.8	46.6	33.4	38.0	52.5
	6	36.0	39.3	46.5	36.8	44.9	52.5
α amino-n-butyric acid	½	26.1	43.1	48.9	21.4	25.4	27.8
	1	26.2	34.1	46.9	24.5	27.4	29.4
	2	31.4	33.6	42.4	30.3	31.4	36.1
	3	36.2	36.4	40.8	33.0	35.3	40.5
β amino-n-butyric acid	½	25.1	38.2	46.1	21.8	24.8	28.8
	1	23.9	32.9	43.1	27.2	30.4	34.7
	2	34.4	35.9	36.8	33.2	34.5	36.3
	3	45.0	45.8	43.9	35.6	36.4	36.4
γ amino-n-butyric acid	½	25.5	37.8	45.0	22.5	25.1	29.6
	1	24.0	33.0	42.1	27.4	31.6	35.3
	2	37.2	40.9	43.1	34.5	36.8	37.7
	3	47.0	47.6	47.6	38.0	38.0	38.0

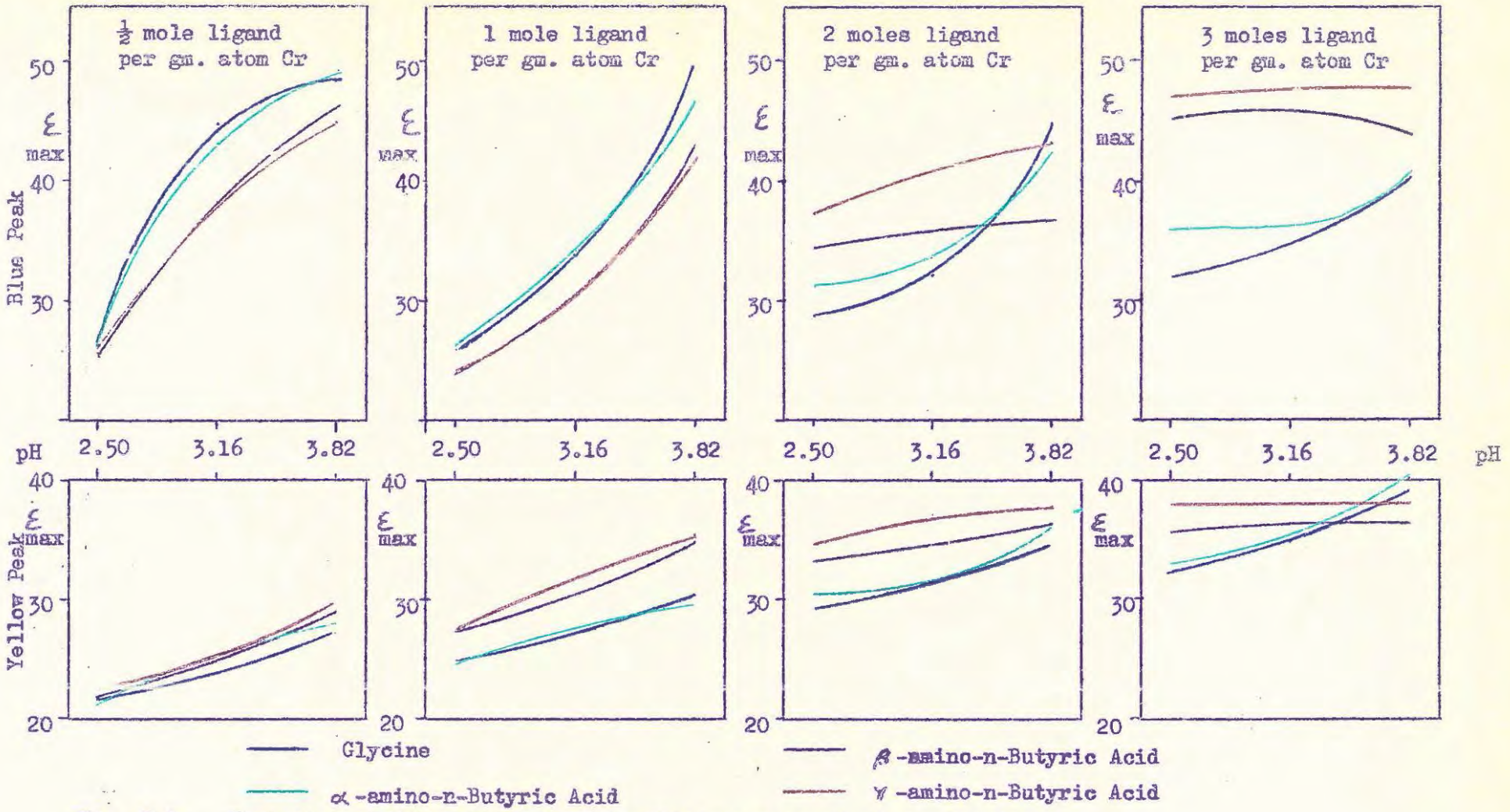


Fig. 3.2. Variation of Molar Extinction Coefficient with pH of the Solutions.

The molar extinction coefficient (ε) is calculated from the optical density readings taken by application of the Beer-Bouguer relation quoted on page 31:

$$d = \varepsilon c \quad \therefore \quad \varepsilon = \frac{d}{c}$$

where d = optical density
c = concentration of solution
$= \frac{1}{75}$ gm. atoms of Cr per litre.

The molar extinction coefficient of the two absorption maxima of the solutions will be referred to as the "ε max" values.

Examination of Fig. 3.1 shows that the ε max of the solutions at the two peaks vary between the different ligands, increasing in the order: glycine, α-, β-, γ-amino-n-butyric acid. This is similar to the observations of Shuttleworth and Sykes [17], but a marked difference is noted in that the absorption of the blue peak in the case of the unmasked solution is higher than those of the masked solutions. The significance of this point will be discussed later.

The wavelengths of maximum absorption and molar extinction coefficients at the solutions' two absorption maxima are given in Tables 3.2 and 3.3.

Inspection of Table 3.2 shows that the ε max values of the solutions tend to increase at the higher pH levels, but reference to Fig. 3.2 shows that this effect is most pronounced at the lower concentrations of ligand.

The variation of ε max of the solutions with the concentration of the ligand is shown in Fig. 3.3. A marked

difference/.....

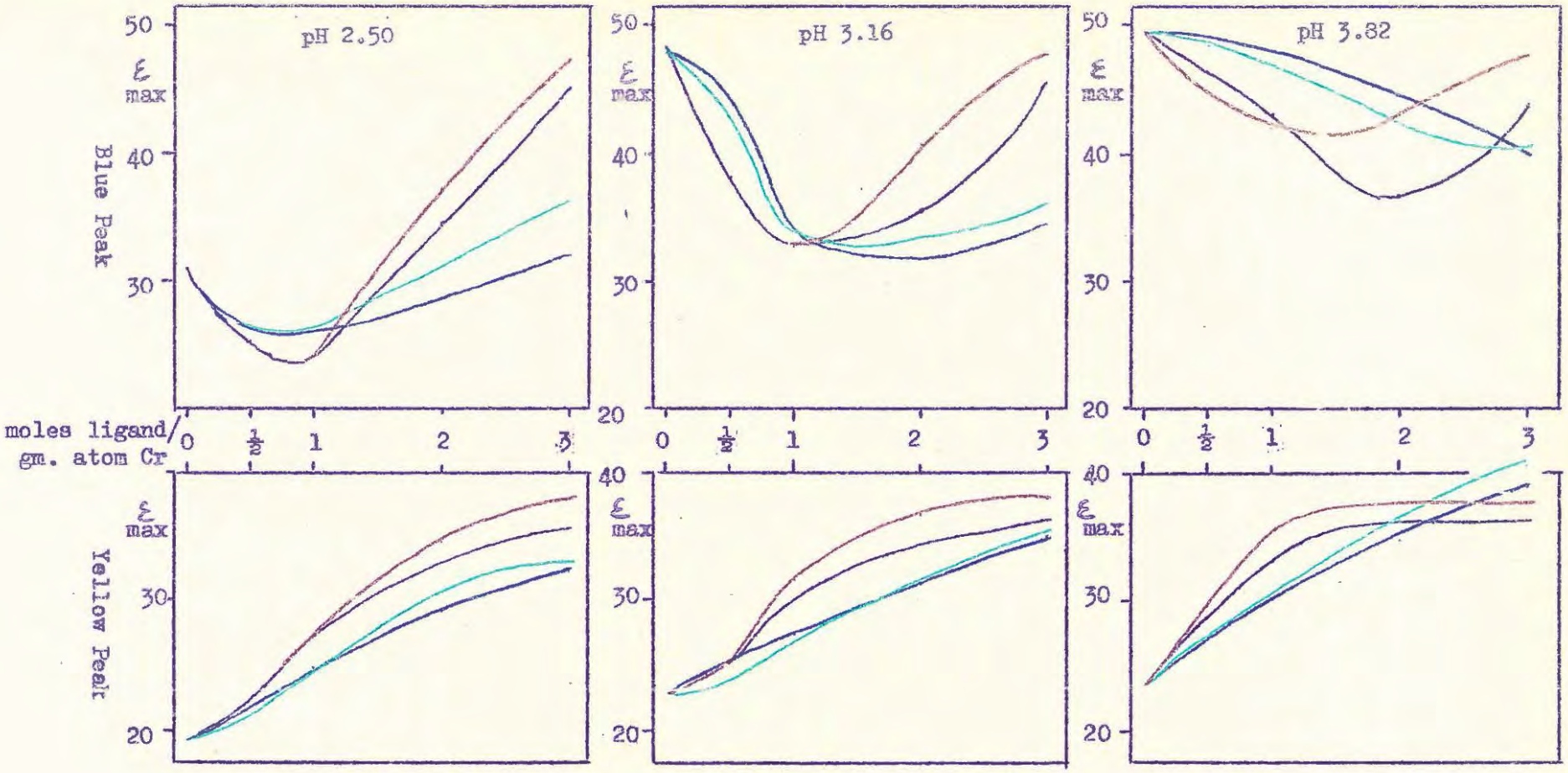
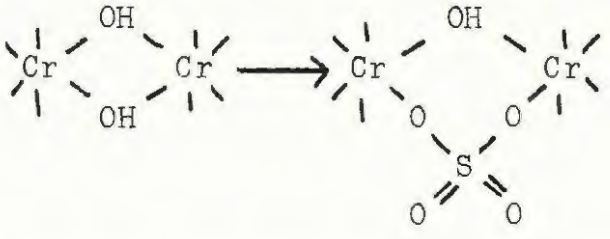


Fig. 3.3. Variation of Molar Extinction Coeffieient with Molar Ratio of Ligand.

difference between the effect on the absorption of the blue and yellow peaks is immediately apparent. Inspection of the curves representing ε max of the yellow peak indicates the occurrence of a normal mass action equilibrium between the total amount of ligand present and the extent of coordination of the chromium. However, an apparent contradiction is found in the variation of the absorption of the blue peak, where there is a reduction in ε max with rising concentration of the ligand until a minimum is reached, after which the value increases again. A similar effect was observed by Shuttleworth [94] in studies of the coordination of sulphate ions, when the absorption of a 33 % basic chromium nitrate solution initially fell on increasing the concentration of sulphate ions. The proposed explanation of this phenomenon was a change in the composition of the solution from a highly absorbing olated complex to a less absorbant solution in which hydroxyl bridges were replaced by sulphate links:



A similar explanation is suggested in the present case: that the presence of amino acid reduces the degree of olation of the complex and initially forms a solution of lower absorption, before the mass action effect increases the extent of coordination with the ultimate formation of a solution of higher ε max. It is interesting to compare the solutions at the three pH levels, when it is observed that in the solutions

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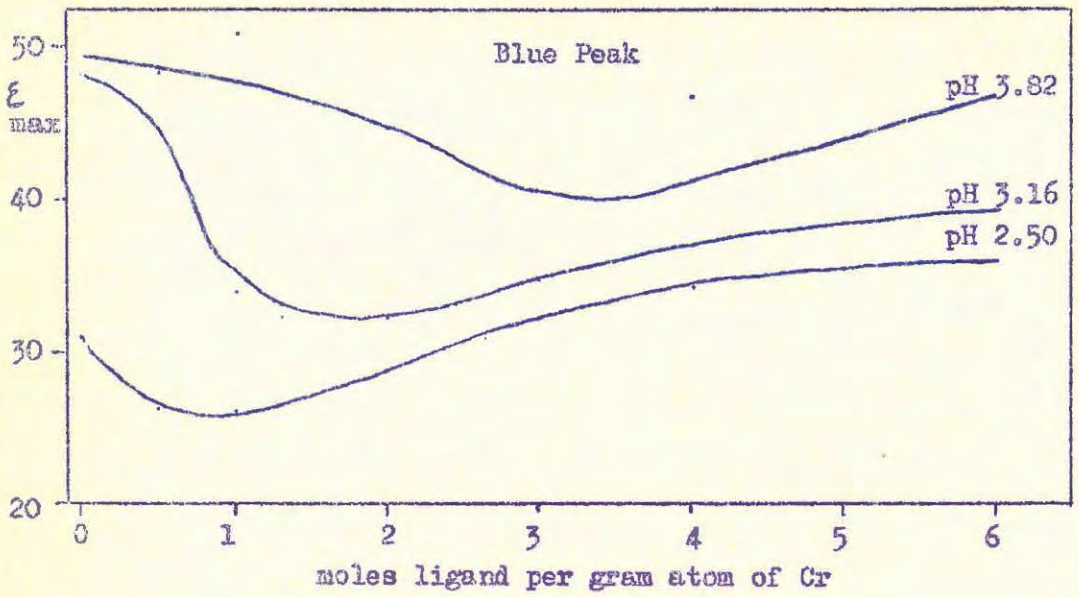

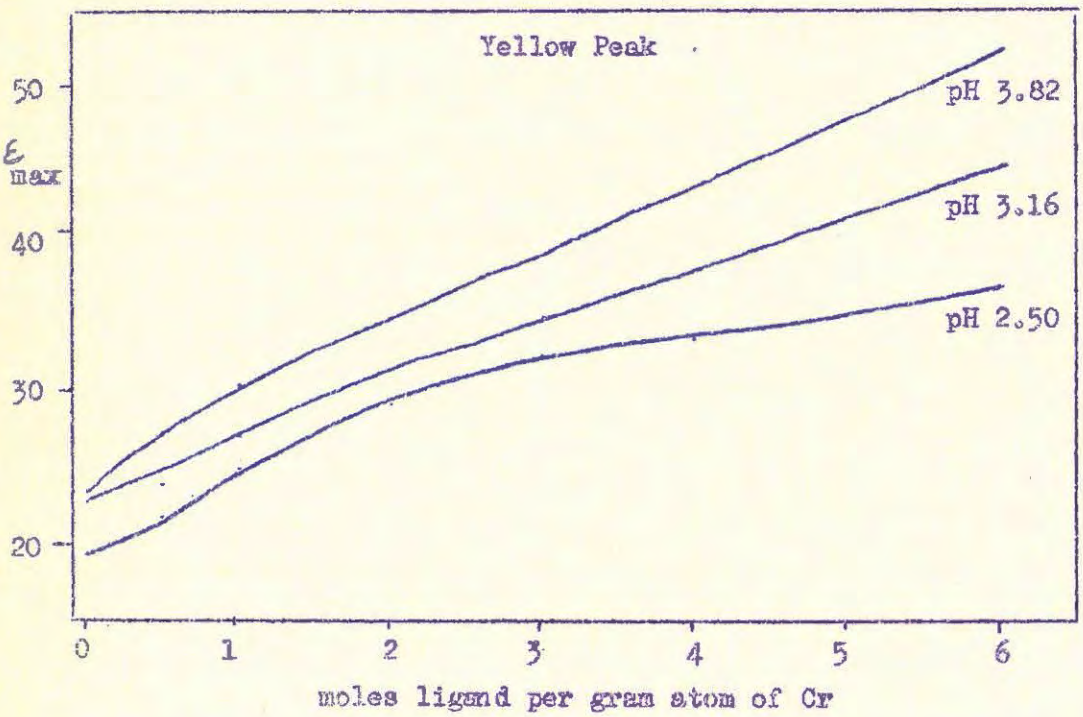

Fig. 3.4. Variation of Molar Extinction Coefficient with Molar Ratio of Glycine.

of higher pH, having a higher basicity, the minima of absorption tend to be displaced to a higher molar ratio of ligand, indicating that a larger quantity of hydroxyl has to be removed from the complex before the effect of coordination on absorption predominates.

From the regular increase in ε max of the yellow peak it appears that absorption in this region of the spectrum is not affected to any marked extent by olation of the complex, but that this peak is primarily a measure of the degree of coordination of ligand to the chromium. This concept is also supported by the considerably greater effect of pH on the blue peak compared with the yellow peak at the lower molar ratios of ligand which can be seen on inspection of Fig. 3.2. At the higher molar levels, where the effect of the pH on olation is expected to be lower, the pH effect on the blue peak is in fact considerably reduced.

Fig. 3.4 shows the variation in ε max on solutions containing glycine in amounts up to 6 moles per gram atom of chromium. The ε max values at the blue peak, after reaching the minimum values discussed above, appear to approach maximum limiting values, this being particularly noticeable at the lowest pH level. In the case of the yellow peak, there is a steady increase of absorption as the concentration increases, with indication of reaching a limiting value in the case of solutions at the lowest pH value. These curves lend support to the concept of the coordination reaction obeying a mass action relationship.

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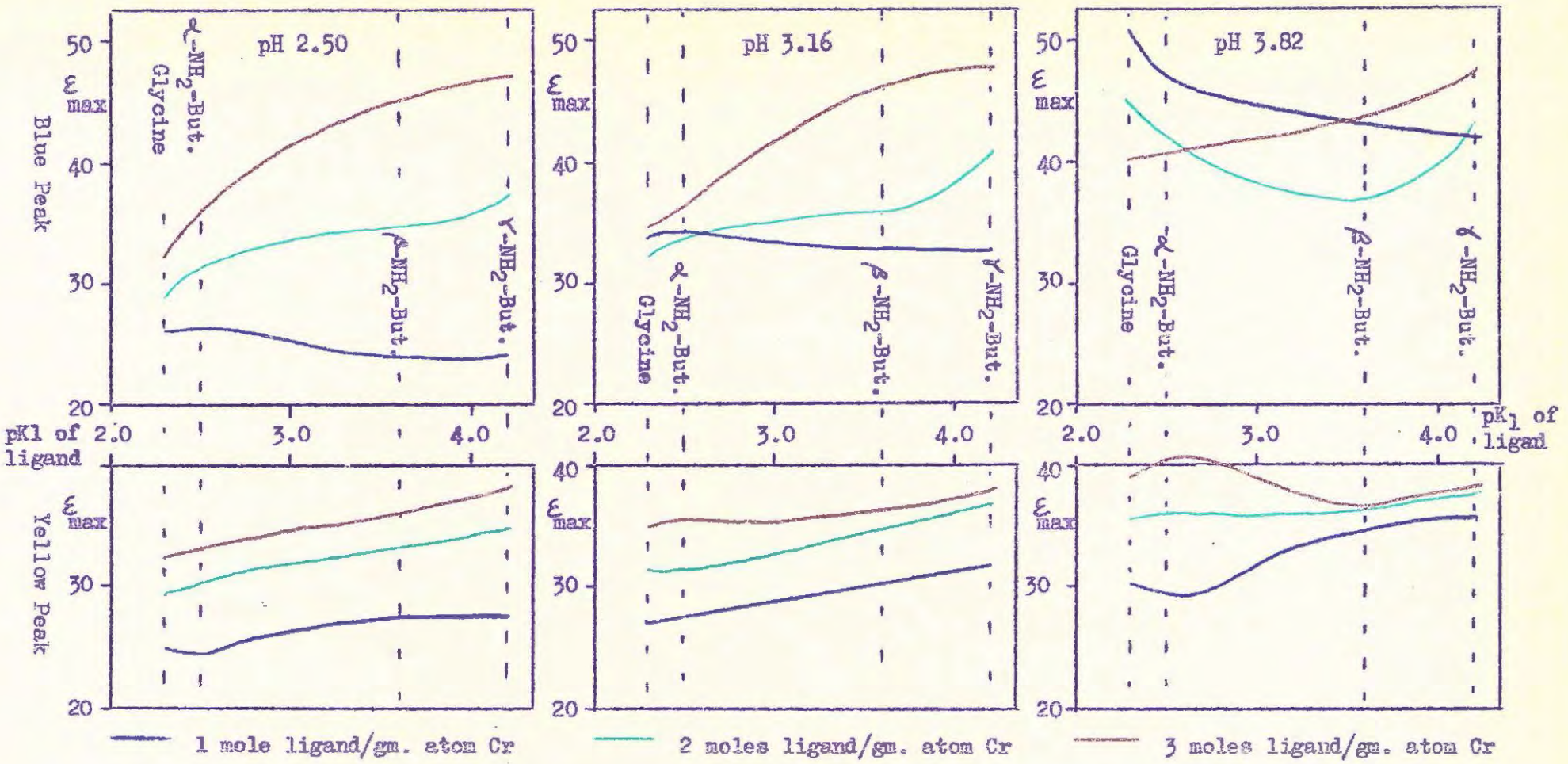

Fig. 3.5. Variation of Molar Extinction Coefficient with pK_1 value of the Carboxyl Group of the Ligand.

The differences between the absorptions of solutions prepared from different ligands at the same concentration and pH is shown in Fig. 3.5, where the ε max values are plotted as functions of the logarithmic dissociation constant (pK_1) of the carboxyl groups of the ligands.

Examination of the curves representing the yellow peak indicates that there is an increase in absorption with increasing pK_1 value in most cases, indicating that there is a positive, approximately linear correlation between the extent of coordination of an amino acid and the pK_1 value of its carboxyl group. It is suggested that apparent anomalies in the case of the blue peak are due to the contrary effects of coordination and de-olation. However, it may be seen that at the highest molar ratio of ligand, where coordination probably predominates due to the mass action effect, a positive correlation between ε max and pK_1 is observed.

These results appear to indicate that, under the acidic conditions of the present experiment, the dissociation constant of the carboxyl group is the main factor influencing the stability of the coordination complexes of chromium with amino acids. If the stability were increased by chelate ring formation due to both functional groups entering the complex, α-amino acids would be expected to form the most stable complexes, while in fact the reverse is indicated by the above results.

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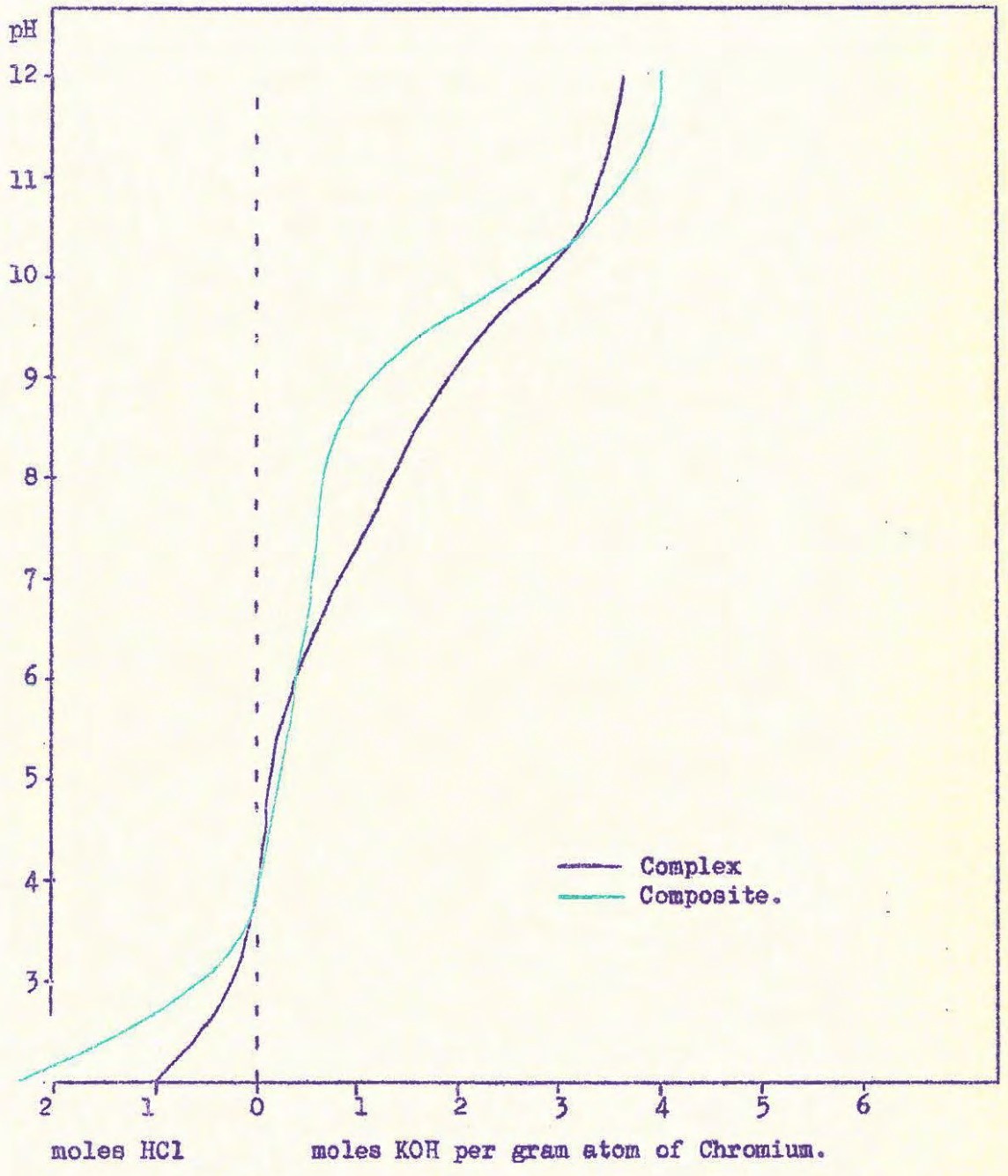

Fig. 3.7. Titration Curves of Chromium Chloride Solution with 3 moles of Glycine per gram atom of Chromium, at Equilibrium pH value of 3.82.

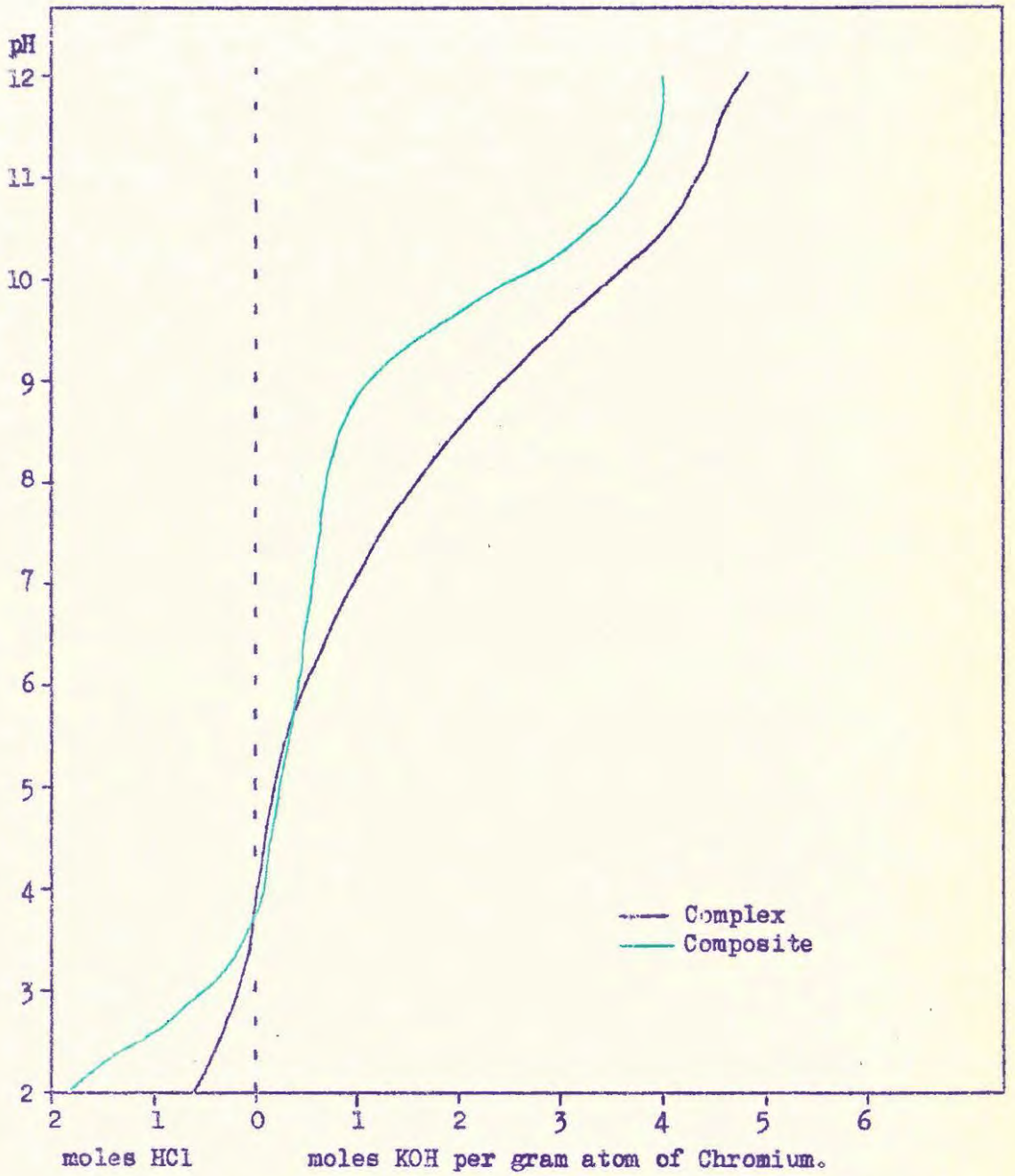

Fig. 3.8. Titration Curves of Chromium Chloride Solution with 3 moles of α-amino-n-Butyric Acid per gram atom of Chromium, at Equilibrium pH value of 3.82.

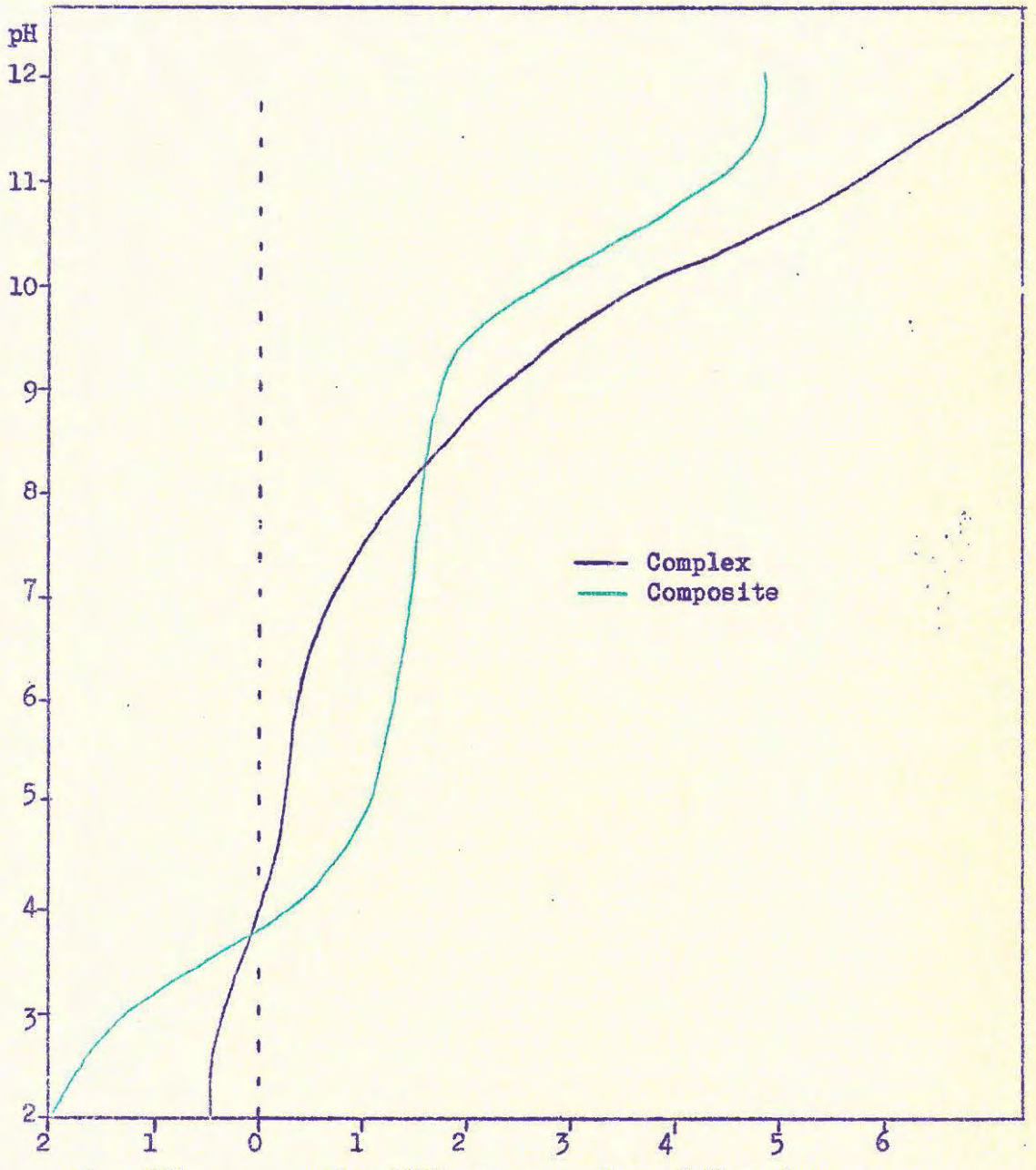

Fig. 3.9. Titration Curves of Chromium Chloride Solution with 3 moles of β-amino-n-Butyric Acid per gram atom of Chromium, at Equilibrium pH value of 3.82.

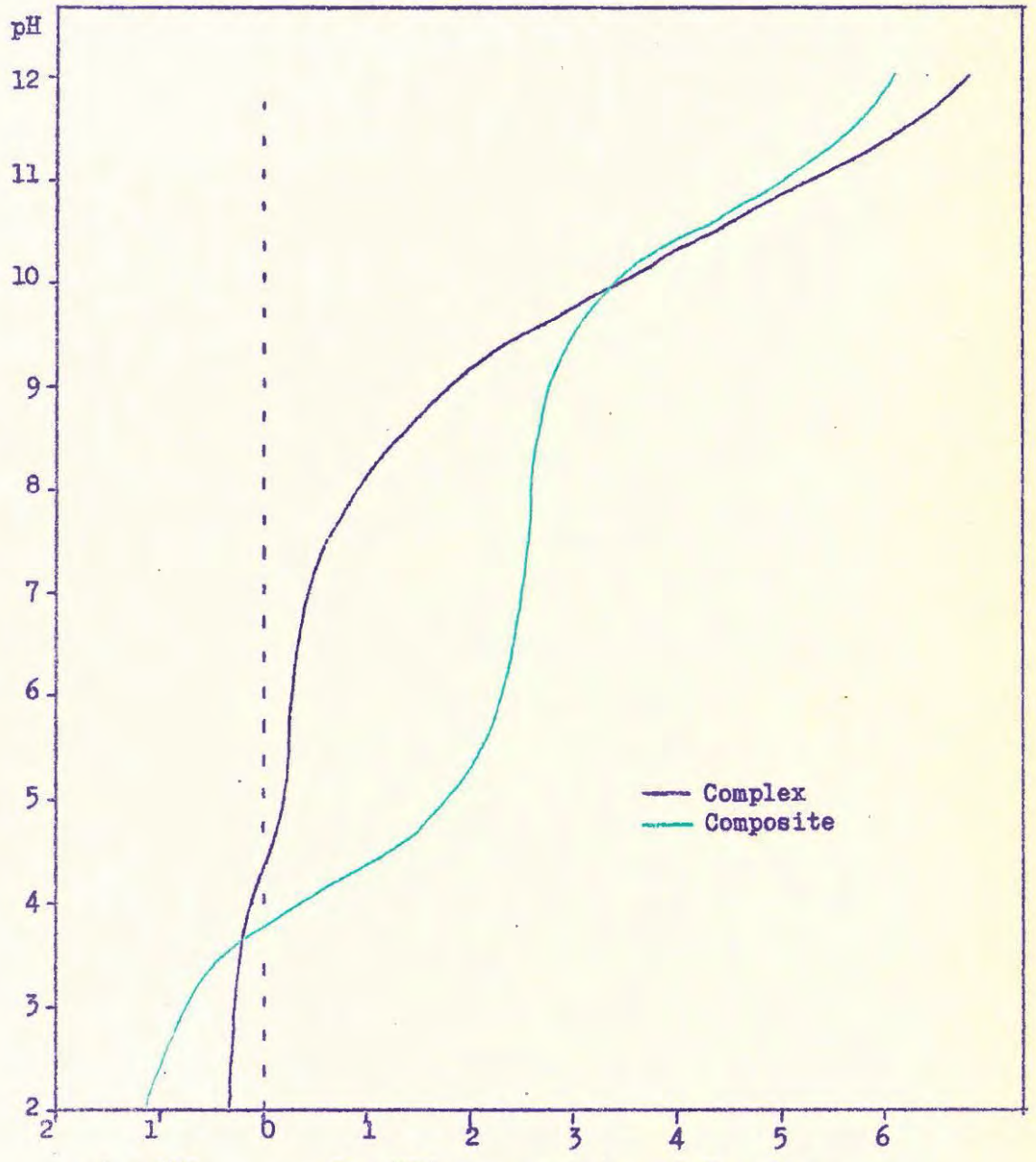

Fig. 3.10. Titration Curves of Chromium Chloride Solution with 3 moles of γ-amino-n-Butyric Acid per gram atom of Chromium, at Equilibrium pH value of 3.82.

Potentiometric Titrations

In order to confirm the qualitative and semi-quantitative information regarding the relative extents of coordination which is provided by the spectrcphotometric results, and to allow a quantitative estimation of the degree of coordination to be made, a number of the solutions were examined by potentiometric titration. The titrations were carried out on the solutions containing the ligands at a ratio of 3 moles per gram atom of chromium, at an equilibrium pH of 3.82, as well as on equivalent quantities of the ligands adjusted to pH 3.82 and the unmasked chromium chloride solution at pH 3.5.

Two separate aliquots of each solution were titrated, one with alkali to pH 12, the other being back-titrated down to pH 2 with hydrochloric acid, employing the procedure described in the experimental section, page 14. The results in all cases were combined in a single titration curve. In order to eliminate the confusion due to the effect of dilution on the titration curves, which becomes large as the extreme pH values are approached, the titration curve of water was determined between the pH limits 2 and 12 and the appropriate amounts, determined from this curve, were deducted from all volume readings before plotting the titration curves reported.

The titration curve of each of the four ligands was added to that of the aged chromium chloride solution, and the resulting curves, which are referred to as the "composite"

curves/.....

curves, are plotted alongside the titration curves of the corresponding complexes in Figs. 3.7 - 3.10. The titration curve of the aged chromium chloride solution is plotted in Fig. 3.6.

The amount of ligand coordinated was estimated by measuring the difference between the complex and composite titration curves at appropriate pH values.

This method of estimating the extent of coordination of metals by noting the differences between the sum of the titres of the metal and ligand and the titre of the mixture is not confined to chromium, but has been used in a number of investigations of this type. Among investigations on other metals, Albert [96] has used the differences between analagous composite and complex titration curves to estimate the co-ordination of a number of metals by amino acids. Datta and Rabin [21] have used similar methods to study the chelation of peptides and similar substances to copper, cobalt and manganese, where the method is sufficiently exact to permit the stability constants of the complex ions to be determined.

The present titration curves may be divided into two main portions. In the acid pH range, the free carboxyl groups in the solutions are titrated over an interval depending on the pK_1 value of the amino acid. In the composite curves, the titrations are equivalent to all the carboxyl ions in the solutions, plus small amounts absorbed by the chromium chloride. In the case of the complexes, the titration in this region is equivalent to the uncoordinated ligand present, with a certain

contribution/.....

contribution by the chromium in the complex. This aspect is discussed more fully below. Examination of Figs. 3.7 - 3.10 shows that the reaction between the ligand and the chromium has reduced the amount of carboxyl titrating in this region, and indicates that coordination of the carboxyl groups has taken place.

In the upper pH range of the titration curves, the amino groups of the ligands are titrated. In the case of the composite curves, all the amino groups titrate according to their normal pK_2 values. Examination of the complex curves reveals that the amino groups in the complexes are now titrating over a much wider pH range, the titration commencing about 2 - 3 pH units lower than in the case of the composite curve. It is evident that coordination of the carboxyl groups of the amino acids has caused a lowering of the pK_2 values of the amino groups. A similar effect has been reported for the pK_2 values of amino acids and their esters, when it was found that esterification caused a lowering of pK_2 (93). It is evident that there is no reduction in the quantity of amino groups titrating in the case of the complexes.

The quantity of carboxyl groups coordinated to the chromium was estimated by application of the well-known equation:

$$pH = pK + \log_{10} \frac{\text{conc. of salt}}{\text{conc. of acid}}$$

relating the pH of a solution containing a weak acid and its salt with a strong base to the dissociation constant of the acid and the relative concentrations of the salt and acid.

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In the range between pH = pK and pH = pK + 2, approximately 50 % of the weak acid present is titrated.

The difference between titrations for the composite curve and for the complex between these pH limits, was measured for each ligand, and this quantity, with certain reservations, was taken to represent half of the amount of carboxyl coordinated. The results of these estimations are given in Table 3.4.

Table 3.4.

Moles of carboxyl coordinated as estimated from the potentiometric titration curves in range pH = pK_1 to pH = pK_1 + 2.

Ligand	pH range	Difference between composite and complex curves, equivalent to half bound carboxyl.	Moles of carboxyl coordinated
Glycine	2.3 - 4.3	.90	1.8
α amino-n-butyric acid	2.5 - 4.5	.80	1.6
β amino-n-butyric acid	3.6 - 5.6	1.15	2.3
γ amino-n-butyric acid	4.2 - 6.2	1.30	2.6

An assumption has been made in arriving at these results which is not strictly valid: this is that the difference between the composite and complex curves is due only to coordinated carboxyl groups. Reference to Fig.3.6 shows that chromium chloride itself does not titrate to any appreciable extent in the range below pH 4. Since absorption

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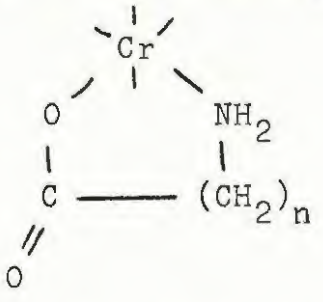
of strong acid by non-olated basic groups forms the basis of a standard method for determination of the degree of olation [97], this suggests that the chromium chloride solution is 100 % olated, and agrees with Shuttleworth's findings [95] that the uptake of strong acid by olated chromium solutions is a slow process.

It has been assumed that the chromium in the complex behaves in a similar manner to the unmasked solution. However, it is possible that coordination, which the spectrophotometric results indicate causes a reduction of olation, might change the absorption of acid and alkali by the chromium. Although this may alter the results obtained, it is considered that the errors caused in this way are comparatively small.

These potentiometric results provide confirmation that only the carboxyl groups enter the chromium complex under the conditions of the experiment. In a solution of a complex containing a chelate ring of the type:



which is similar to that formed with oxalate, the amino group would not be free to titrate.

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Table 3.5.

Electrolytic mobilities of complexes of chromium chloride with amino acids.

Ligand	Molar ratio of ligand	Mobility (cm/sec/unit voltage grad. x 10^{-5}) pH 2.50	pH 3.16	pH 3.82
Nil		1.4	2.2	1.6
Glycine	½	.9	1.9	1.5
	1	2.0	2.5	1.6
	2	2.0	3.0	2.3
	3	2.3	3.2	2.0
α amino-n-butyric acid	½	1.1	1.8	1.7
	1	1.3	2.3	2.2
	2	2.0	1.7	1.8
	3	2.2	2.9	2.3
β amino-n-butyric acid	½	1.8	1.3	1.5
	1	1.2	2.5	2.3
	2	1.7	2.6	2.2
	3	2.1	2.8	2.2
γ amino-n-butyric acid	½	.9	2.7	1.3
	1	1.2	2.8	2.4
	2	1.7	2.0	1.0
	3	1.7	2.7	1.1

Paper Electrophoresis.

The method described in the experimental section (page 35) is subject to a number of complicating factors which may alter the mobilities of the ions to a certain extent, thus limiting the deductions which may be made from the results. Dilution of the complex may cause its state to change during the six hour period of the run, though this effect may be reduced as the pH of the medium is the same as that of the complex. In addition, the electric field separates the components of the solution, and mass action effects will tend to favour a reversal of coordination.

At the end of the run the complex was visible as a sharp band on the electrogram without development by colour reagents, the direction of movement showing that all the complexes were cationic. On spraying the electrogram with Ninhydrin, the amino acid was detected over the whole area of the strip between the origin and the cathode vessel. It is suggested that this amino acid was liberated from the complex during the run, and, having a much greater mobility, moved ahead of the complex by different distances depending on the time at which it was liberated.

The mobilities of the complexes, calculated from the distance moved by the bands, the mean voltage gradient and the time of the run, are given in Table 3.5.

The most noticeable feature of the table is the fact that, with two exceptions, the complexes at pH 3.16 had a

higher/.....

higher mobility than the corresponding solutions at the other pH levels. Since penetration of hydroxyl ions into the complex lowers the mobility by reducing the charge, and olation, by tending to make the structure more compact, should have the effect of increasing the mobility, it seems likely that the maximum mobility at pH 3.16 represents a state at which the interaction of these two contrary effects reaches a turning point. It is noted that penetration of amino acid has no direct effect on the total charge of the complex, though it is likely to have indirect effects.

Table 3.6.

Chromium fixation by skin tanned with complexes of chromium chloride with amino acids (m.moles of Cr per gram collagen).

Ligand	Moles Ligand per mole chromium	pH 2.50	pH 3.16	pH 3.82
Nil		1.53	1.63	2.20
Glycine	½	.72	1.08	1.75
	1	.62	.81	1.20
	2	.40	.54	.66
	3	.27	.41	.47
α amino-n-butyric acid	½	.56	1.05	1.93
	1	-	.70	1.13
	2	.36	.48	.65
	3	.27	.35	.50
β amino-n-butyric acid	½	.55	.97	1.59
	1	.44	.65	.81
	2	.39	.35	.32
	3	.12	.14	.22
γ amino-n-butyric acid	½	.51	.97	1.57
	1	.37	.66	.77
	2	.28	.32	.36
	3	.09	.10	.11

Table 3.7.

Increase in shrinkage temperature of skin tanned with complexes of chromium chloride plus amino acids. (Δ °C).

Ligand	Moles Ligand per Mole Chromium	pH 2.50	pH 3.16	pH 3.82
Nil		39	58	56
Glycine	½	31	59	54
	1	37	56	52
	2	33	52	46
	3	30	38	35
α amino-n-butyric acid	½	38	56	57
	1	36	56	55
	2	31	45	39
	3	27	36	38
β amino-n-butyric acid	½	38	56	48
	1	38	54	53
	2	29	34	34
	3	26	28	29
γ amino-n-butyric acid	½	36	58	49
	1	34	43	40
	2	30	37	34
	3	21	20	25

Miniature Tanning Experiments.

This work was done in order to provide confirmation of the conclusions which were drawn from the results of the physical measurements reported in the earlier sections of this chapter. Shuttleworth has shown [60] that the principal factor affecting the tanning power of a chromium solution is the number and stability of the ligands already present in the complex. For this reason, the tanning action of the complexes under comparable conditions has been used as a measure of the relative stability of the various chromium-amino acid complexes.

Visual examination of the skin strips after tannage showed that the ligands had reduced the tanning power of the chromium solutions. The strips tanned with the solutions containing little or no amino acid appeared to be well tanned, while those with larger amounts of ligand appeared untanned, and collapsed on drying. In comparing the appearance of the strips tanned with the different complexes, there seemed to be a small decrease in efficiency in the order: glycine, α-, β-, γ-amino-n-butyric acid. The strips tended to assume the colour of the complexes with which they were tanned.

The amounts of chromium fixed from the complexes are given in Table 3.6, the figures being calculated from the analytical results for chromium and nitrogen. A certain inaccuracy should be mentioned at this stage - the amino acid fixed in the pelt by the chromium complex will alter the figure for "hide substance" to a certain extent. This error,

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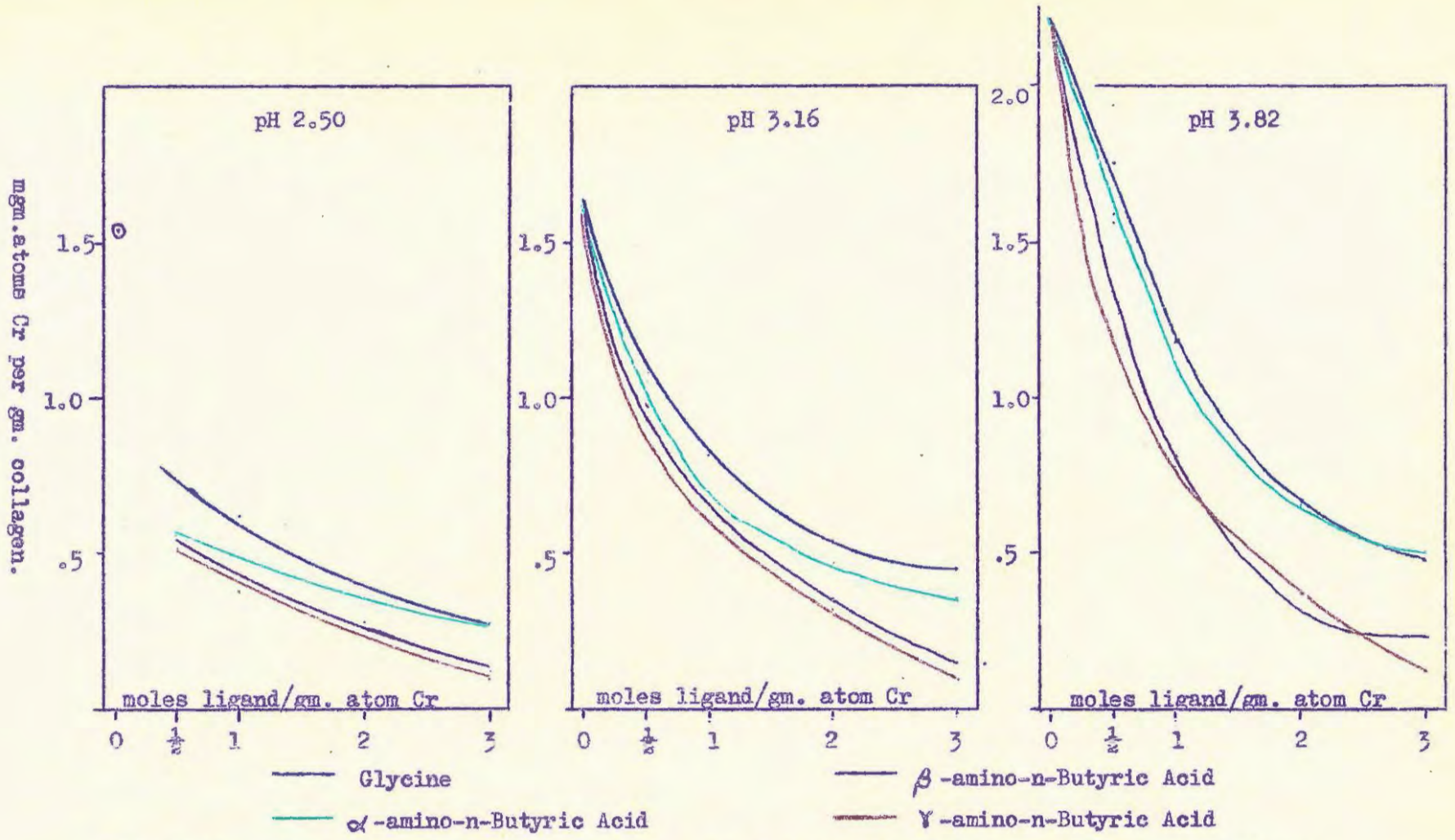

Fig. 3.11. Variation of Chromium Fixation with Molar Ratio of Ligand in Tanning Solutions.

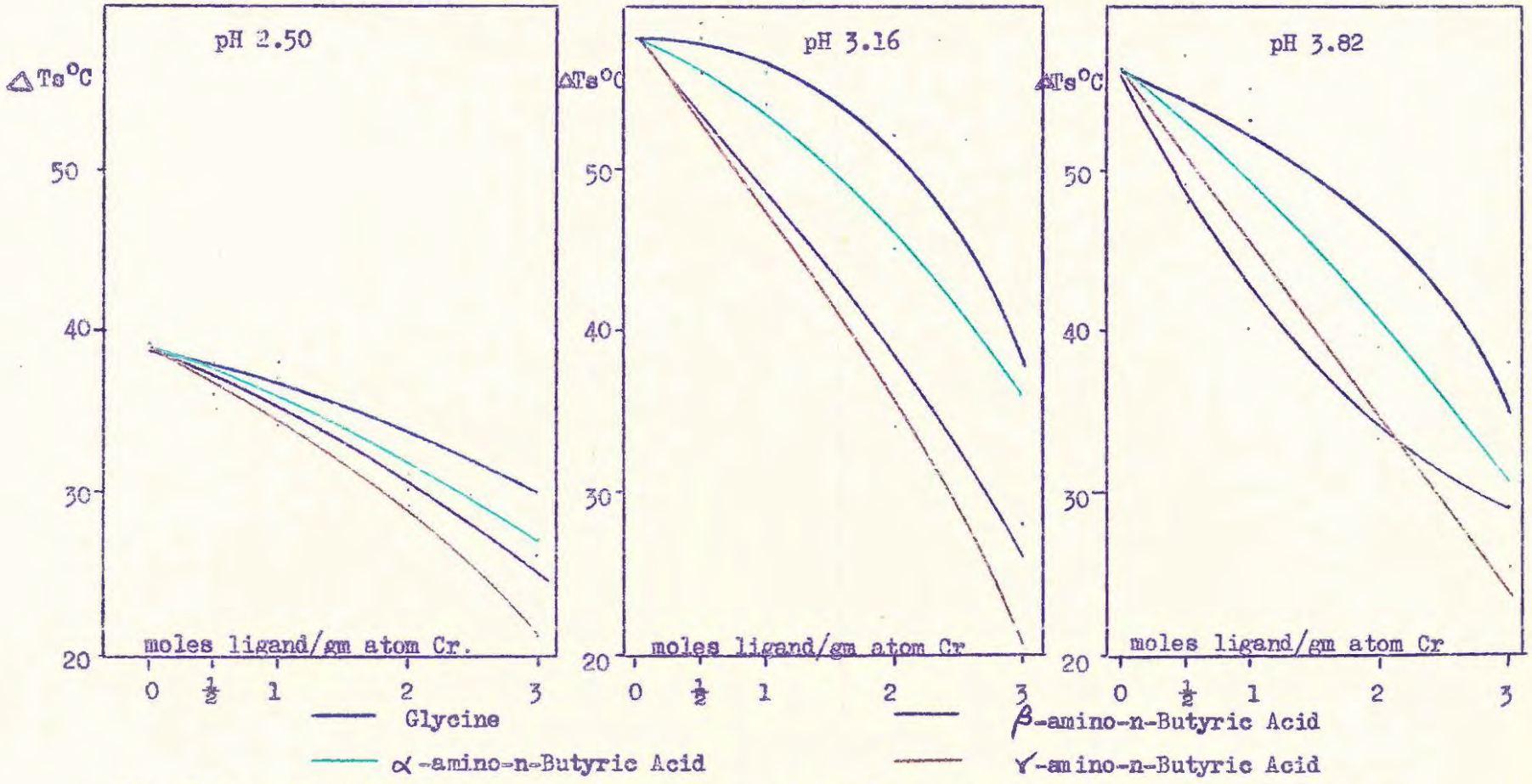

Fig. 3.12. Variation of Shrinkage Temperature with molar ratio of Ligand in Tanning Solution.

which is relatively small because of similar nitrogen contents of the amino acids under consideration, is not a serious factor in the present comparative work.

The increases in the shrinkage temperature of the tanned strips compared with strips treated for the same time with hydrochloric acid solutions at the appropriate pH levels, are given in Table 3.7.

Fig. 3.11 shows the variation of the chromium fixation from the complexes with different amounts of ligand in the solution. Increasing the ligand concentration is seen to decrease chromium fixation in all cases and the curvelinear relation existing suggests that there is a mass action equilibrium between the penetration of the complex by the active groups of the collagen and the ligand, governed by their relative affinities.

The variation in chromium fixation is reflected in the increase in the shrinkage temperature of the skin after tannage. This effect is shown in Fig. 3.12, where it is seen that the decreased chromium fixation caused by the presence of the ligand has brought about a corresponding decrease in hydrothermal stability of the leather.

The effect of the presence of different ligands on the chromium uptake is shown in Fig. 3.13 where the fixation is plotted as a function of the pK_1 values of the amino acids. There is a decrease in chromium fixation in the order of increasing pK_1 values, confirming the spectrophotometric and potentiometric evidence that there is increasing penetration

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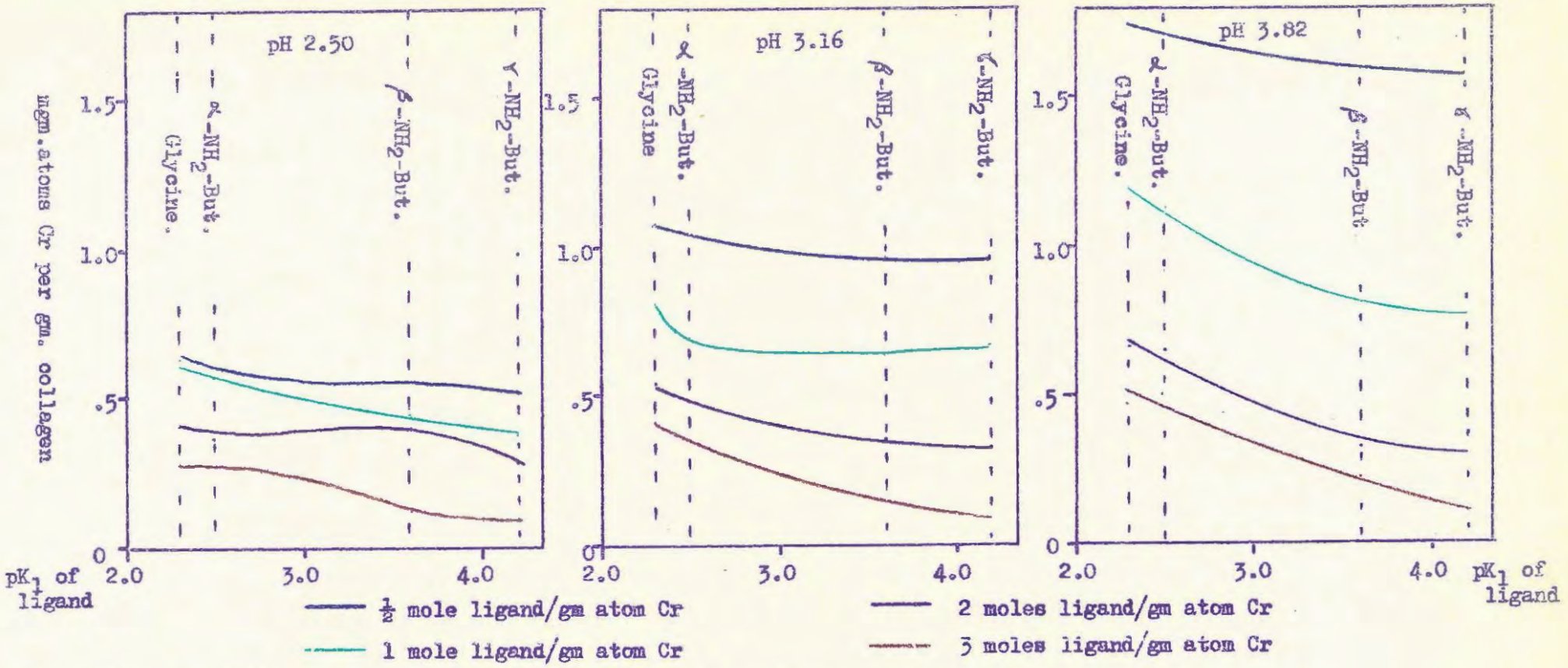


Fig. 3.13. Variation of Chromium Fixation with pK_1 value of Carboxyl Group of Ligand.

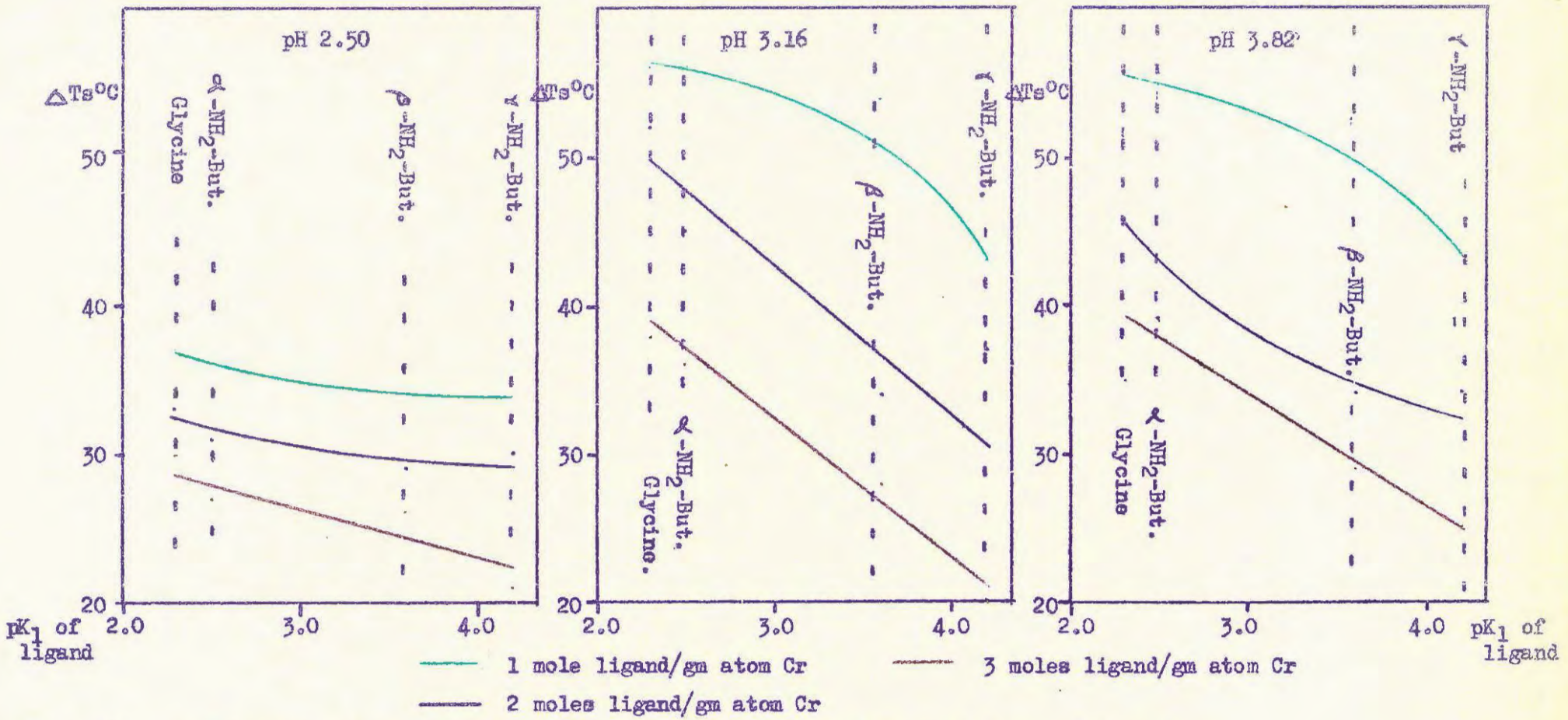


Fig. 3.14. Variation of Shrinkage Temperature with pK_1 value of Carboxyl Group of Ligand.

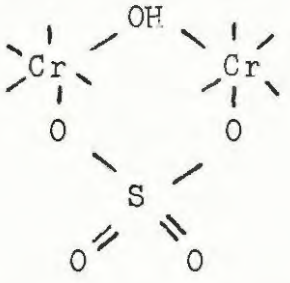
by the ligand in this order. Fig. 3.14 shows that the hydrothermal stability of the leather conforms to a similar pattern.

The tanning properties of the complexes seem to indicate that there is an increase in the stability of the complexes in the order of increasing pK_1 values, since the tanning action of a complex is influenced by the ease with which the ligands can be displaced from it by collagen, as well as the number of coordination sites occupied.

The similarity of the effects of coordination on the chrome fixation and shrinkage temperature indicates that the action of the ligands has been to prevent entry of the active groups of the collagen into the complex with the formation of stable cross links.

DISCUSSION OF RESULTS AND COMPARISON WITH THE WORK ON CHROME ALUM.

It has long been known that sulphate ions have a greater coordinating affinity for chromium than chloride ions [4] and Theis and co-workers [14] and Shuttleworth [42,49], among others, have studied the coordination of sulphate ions to chromium. The greater stability of coordination of sulphate compared with chloride is associated with the formation of a six membered ring of the type



which is somewhat similar to the structure formed by other bidendate ligands and suggests that ring formation is the reason for the generally greater stability of these compared with monodendate ligands.

This chelate ring formation by sulphate ions resists penetration of the complex by other ligands, including hydroxyl ions, and has the effect of reducing the amounts of ligands added to chromium sulphate solutions which are coordinated. The reduced penetration in the case of hydroxyl ions coupled with the fact that sulphuric is a somewhat weaker acid than hydrochloric, causes sulphate solutions to be less basic than chloride solutions at similar pH values.

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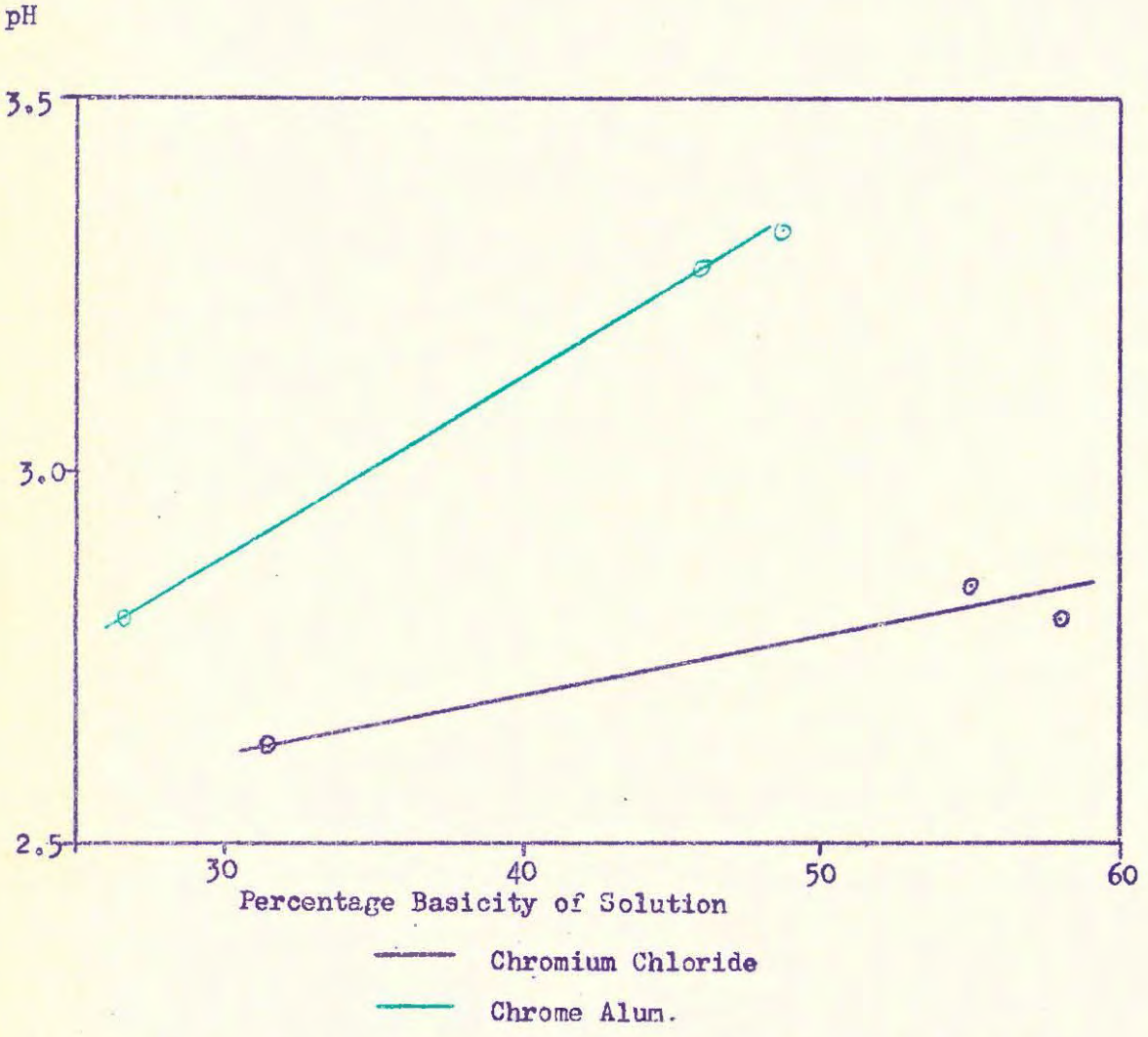


Fig. 3.15. Variation of pH with Basicity of Chromium Chloride and Chrome Alum Solutions.

This point has been verified in the present work by preparing a series of solutions of various basicities and determining their pH values. The results are given in Table 3.8, and are plotted for comparison in Fig. 3.15, from which it may be seen that the chrome alum solutions have pH's of .25 - .5 higher than chromium chloride solutions of the same basicity.

Table 3.8.

pH values and basicities of chromium chloride and chrome alum solutions.

Anion	Concentration (molar)	Basicity (%)	pH
Chloride	.327 .336 .295	57.9 31.4 54.9	2.80 2.63 2.84
Sulphate	.330 .338 .283	26.5 45.9 48.3	2.80 3.27 3.32

The order in which the different ligands come into contact with the chromium probably plays a part in the extent to which they coordinate. In both series of experiments, the amino acid was added before adjustment of the pH by alkali, and olation would tend to take place only at the coordination sites left vacant by these ligands. It is likely that different results would have been found had the ligands been added to chromium solutions after olation was brought about by addition of alkali.

In the case of the chrome alum solutions, the

sulphate/.....

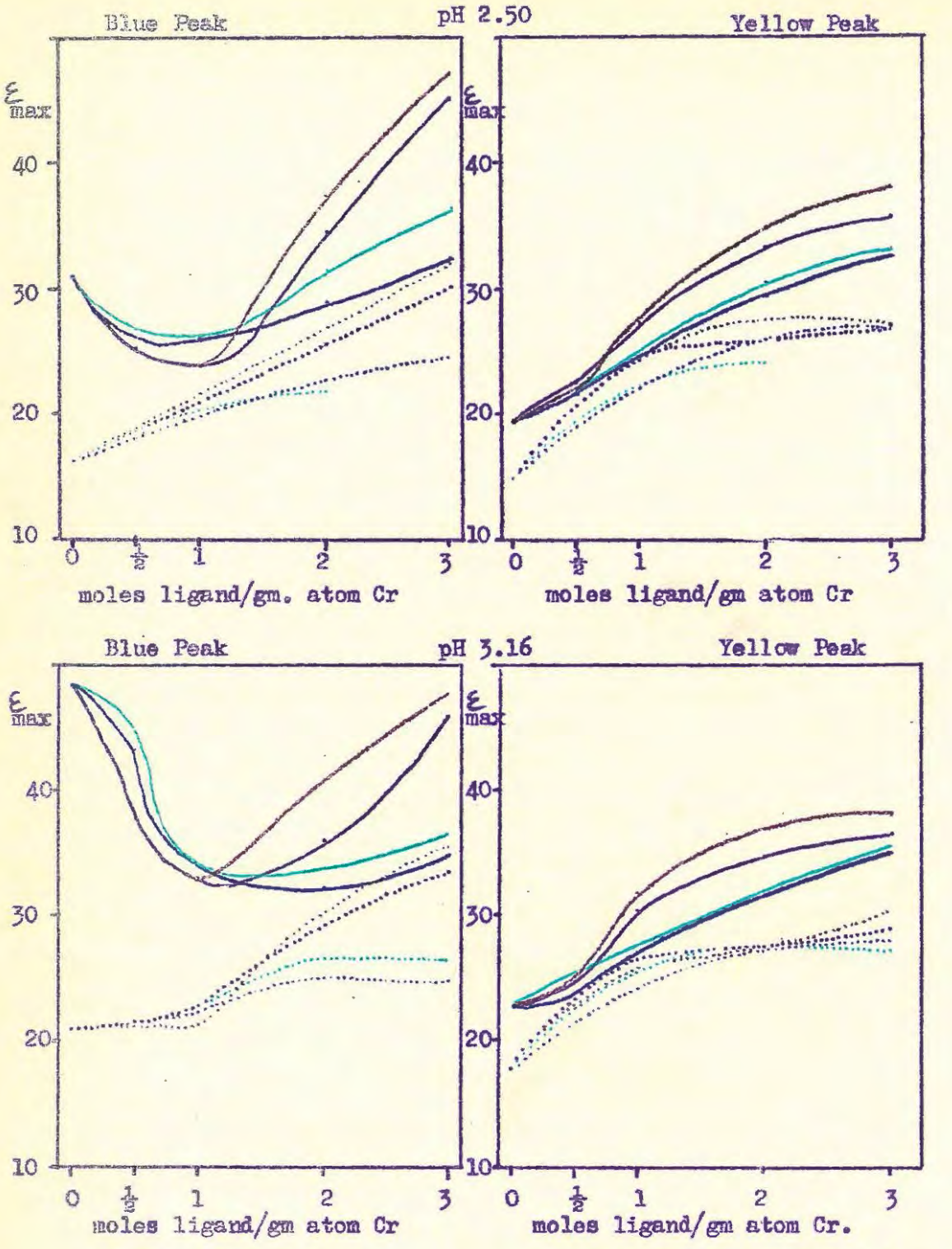


Fig. 3.16. Comparison of Molar Extinction Coefficients of Complexes Prepared from Chromium Chloride and Chrome Alum.

sulphate was present in the solution before the ligand was added, and for this reason the fairly stable sulphate rings had to be displaced, at two different points in the complex, before coordination of the carboxyl groups could take place.

Comparing the spectrophotometric data from the two series of experiments, it was found that the chloride solutions had considerably higher ε max values than the corresponding sulphate solutions at the same chromium concentration. This may be seen in Fig. 3.16, in which the variation of ε max with ligand concentration is plotted for both the chrome alum and chloride solutions, at the 2.50 and 3.16 pH levels.

The fall of ε max in the 420 mμ or blue peak region, when a small amount of ligand has been added to the chloride solution is reduced in the case of the sulphate solutions. At the 2.50 pH level, this effect is observed to a small extent in the chloride, due to displacement of a relatively small number of olated rings, and is not apparent with the sulphate solutions. At the 3.16 pH level this effect is much more pronounced in the chloride, due to the larger number of olation bridges that have to be displaced. In the sulphate solutions an indication of this effect is received in that the rate at which ε max rises with the amount of ligand increases at the 1 molar level where Shuttleworth and Sykes have shown 0.6 - 0.8 moles of amino acid to be coordinated per gram atom of chromium. In this case the initial slow rise in ε max is probably due to displacement of sulphate rings and a certain amount of olated rings.

These/.....

These comparisons seem to provide additional evidence for the hypothesis that while the yellow peak is affected predominantly by penetration of ligands other than hydroxyl, the blue peak is affected by both olation and coordination.

The amounts of carboxyl coordinated to the chromium complex, as estimated from the potentiometric results, are compared with the corresponding figures for chrome alum in Table 3.9, from which it appears that a larger amount has been coordinated to the chromium in the case of the chloride solutions than in the case of the sulphate. Additional qualitative support for this is obtained by comparing the resistance to penetration of the complexes by alkali. Shuttleworth and Sykes found the glycine complex to precipitate at pH 9.0, while the precipitation points of the complexes of the other ligands are given as "greater than 10". In the present work none of the complexes were found to precipitate during the titration up to pH 12.

Table 3.9./....

Table 3.10.

Comparative figures for the tanning action of solutions of chromium chloride and chrome alum masked with amino acids.

a. Chromium fixation from solutions containing 2 moles of amino acid per gram atom of chromium, at equilibrium pH 3.16.

Ligand	chromium chloride	chrome alum
Nil	1.63	0.74
α-amino-n-butyric acid	0.48	0.35
β-amino-n-butyric acid	0.35	0.23
γ-amino-n-butyric acid	0.32	0.17

b. Increase in shrinkage temperature produced by tannage with solutions of chromium chloride and chrome alum containing 2 and 3 moles of amino acid per gram atom of chromium, at equilibrium pH 3.82.

Ligand	2 moles ligand		3 moles ligand	
	chromium chloride	chrome alum	chromium chloride	chrome alum
Nil	56 °C	60 °C	56 °C	60 °C
amino acetic acid	46	46	35	45
β-amino-n-butyric acid	34	35	29	27
γ-amino-n-butyric acid	34	27	25	6

Table 3.9.

Comparison of amounts of ligands coordinated from sulphate and chloride solutions at pH 3.82, with 3 moles of ligand per gram atom of chromium.

Ligand	Sulphate	Chloride
Glycine	1.1	1.8
α amino-n-butyric acid	1.3	1.6
β amino-n-butyric acid	1.5	2.3
γ amino-n-butyric acid	1.6	2.6

Comparing the results of the tanning experiments reveals that the presence of the ligands has a similar effect on the chromium fixation and shrinkage temperature in both cases. It was found that in general, chromium fixation and shrinkage temperature were higher with the chloride solutions than with the sulphate complexes. This fact does not necessarily contradict the view that sulphate solutions generally have a superior tanning action, however, as the effect of the higher basicity of the chloride solutions would be to increase both these values, as reference to the variation with pH of the solution will show.

In conclusion it may be said that chloride and sulphate solutions have shown similar variations in all the properties measured due to the additions of ligands, with generally reduced amounts of penetration in the case of the

chrome/.....

chrome alum solutions due to the resistance to displacement of the relatively stable chelate ring formed by the sulphate ion.

Unlike normal carboxylic acids, coordination of amino acids has not reversed the change on the complex, due to the fact that these ligands are dipolar ions, and have no net charge in the form in which they are coordinated.

The amino groups do not appear to contribute to the stability of the complexes due to formation of chelate rings, but only indirectly due to their influence on the pK_1 values of the amino acids, which is the quantity directly influencing the coordination of monocarboxylic ligands.

CHAPTER IV.

COMPLEXES OF SUBSTITUTED ACETIC AND PROPIONIC ACIDS.

The results which were reported and discussed in Chapter III, in conjunction with the analagous results obtained in experiments involving similar complexes of chrome alum, have provided a certain amount of evidence as to the mode of coordination of amino acids by chromium. As a result of this work the hypothesis has been put forward that no stable bond between the amino group and the chromium nucleus is formed under aqueous acidic conditions, but that the link is through the carboxyl group only, the effect of the amino group being an indirect one through its influence on the pK_1 value of the carboxyl group.

As an extension of this work, the coordination of a number of substituted carboxylic acids was studied, in order to observe the effects of other substituent groups on the coordination of the carboxyl group. Two series of acids were used in this work - acetic and propionic acids, and these with amino, hydroxyl, chloro and bromo substituent groups. In most cases, coordination of both chromium chloride and chromium sulphate was studied.

The aim of this work has been to discover whether these other polyfunctional ligands showed evidence of chelate ring formation under aqueous acid conditions, or whether they react in a similar manner to that proposed for the amino acids

studied/.....

studied in the first section, i.e. merely by their effect on the dissociation constant of the carboxyl group, with possibly an additional influence due to steric effects.

The complexes whose properties are described in this chapter were prepared by allowing the solutions to attain equilibrium after definite amounts of alkali had been added to them, rather than adding small amounts of alkali over a period in order to bring the solutions to predetermined pH values. This method of preparation, which is similar to that used by Green and Ang [16], in studies of the coordination of alanine by chromium chloride, is described on page 28.

The method as described originally by Green and Ang for alanine was in effect the addition of a carboxylic acid salt to the chromium solution. Shuttleworth [15] has shown that in the case of masking with organic acids, equilibrium is reached much more quickly if the ligand is added as a salt. Although in Shuttleworth's work, sodium acetate was added to chrome alum solution of similar concentration to that used in chrome tanning, and the pH subsequently adjusted to 4.9, no precipitation was reported. Serfass and Theis [14], on the other hand, found that addition of sodium salts of organic acids to 33 % basic chromium sulphate at a concentration of 4.5 % Cr_2O_3 caused precipitation, and for this reason they used the free acids in their investigations.

At the concentration used in the present work, (0.333 molar with respect to chromium), precipitation

occurred/.....

occurred when the potassium salt of the ligand was added to the chromium solution of zero basicity. If, however, the acid were added to the chromium solution first, and an equivalent amount of alkali to neutralise the organic acid added over a period afterward, precipitation could in most cases be avoided. Up to three moles of additional alkali per gram atom of chromium were then added to yield curves comparable to those obtained by the addition of alkali to a mixture of chromium salt and amino acid.

In the solutions where the initial reaction was carried out by boiling under reflux, the alkali was conveniently added dropwise down the reflux condenser during boiling. In the solutions where the preparation was carried out in the cold, the alkali was added dropwise with constant stirring.

In some cases, precipitation still occurred at this stage, or possibly after the addition of a small amount of alkali above the equivalent for the potassium salt, so in order to extend the range of pH over which the soluble complexes could be studied, smaller quantities of alkali were added initially in some cases, i.e:- readings were first taken on chromium salt to which had been added a mixture of organic acid and organic acid salt.

The halogen-substituted acids were found to hydrolyse during the prolonged periods of heating used in the original method of preparation. Attention was first

drawn/.....

drawn to this effect by the low pH values of solutions containing these ligands and confirmed by the formation of a silver halide precipitate when a boiled solution of chromium sulphate and bromo-acetic acid was treated with nitric acid and silver nitrate. Since no such precipitate was produced by this solution prior to boiling, decomposition must have occurred. It was, therefore, decided to attempt preparation of complexes of these ligands by less drastic methods.

These modifications to the original method were tested using glycine as ligand, in order to discover the differences between the properties of complexes produced by the different methods. These results are given in Figs. 4.4, 4.5 and 4.6.

It was found that the shorter period of heating of the halogen-substituted acids still produced hydrolysis, and for this reason the complexes of these ligands were prepared without heating at any stage. The properties of some complexes of bromo-propionic acids, prepared by the original method before the limitations were noticed, are given in Figs. 4.14, and 4.15.

It will be appreciated that the method of preparation is in effect one technique for obtaining a titration curve of a chromium complex, as the pH corresponding to any particular increment of alkali will be dependent on the four factors:

a./.....

a. displacement of coordinated water by:

   i. organic ligand

   ii. alkali

b. displacement of coordinated inorganic ligand by

   i. organic ligand

   ii. alkali.

Additional information on the reactions taking place can be obtained by spectrophotometric analysis of the solutions at the various pH values. This was done by diluting 25 times to the same chromium concentration as in Chapter III and measuring the absorption characteristics of the solutions over the restricted ranges 400 - 440 $m\mu$ and 540 - 600 $m\mu$ and determining the ε max values and the wavelengths of maximum absorption.

Detailed results are given in tabular form in Appendix B, for the pH, λ max and ε max values for each particular increment of alkali.

Finally, each of the solutions prepared was used for miniature tanning experiments, the fixation of chromium per gram of oven-dry leather and the rise in shrinkage temperature were determined: detailed results of these determinations are given in the same tables in Appendix B.

Presentation/....

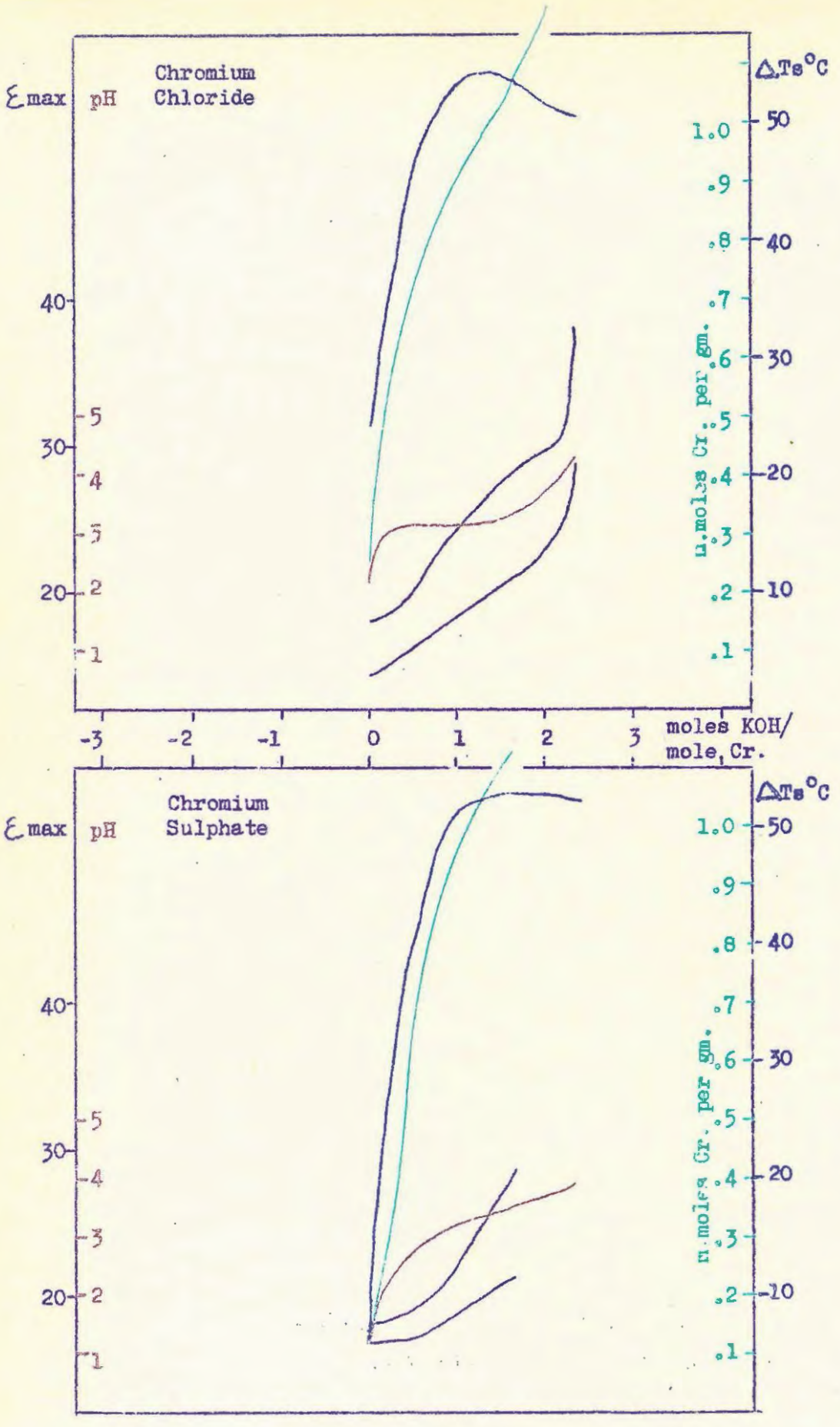


Fig. 4.1. No ligand.
24 hours cold reaction.

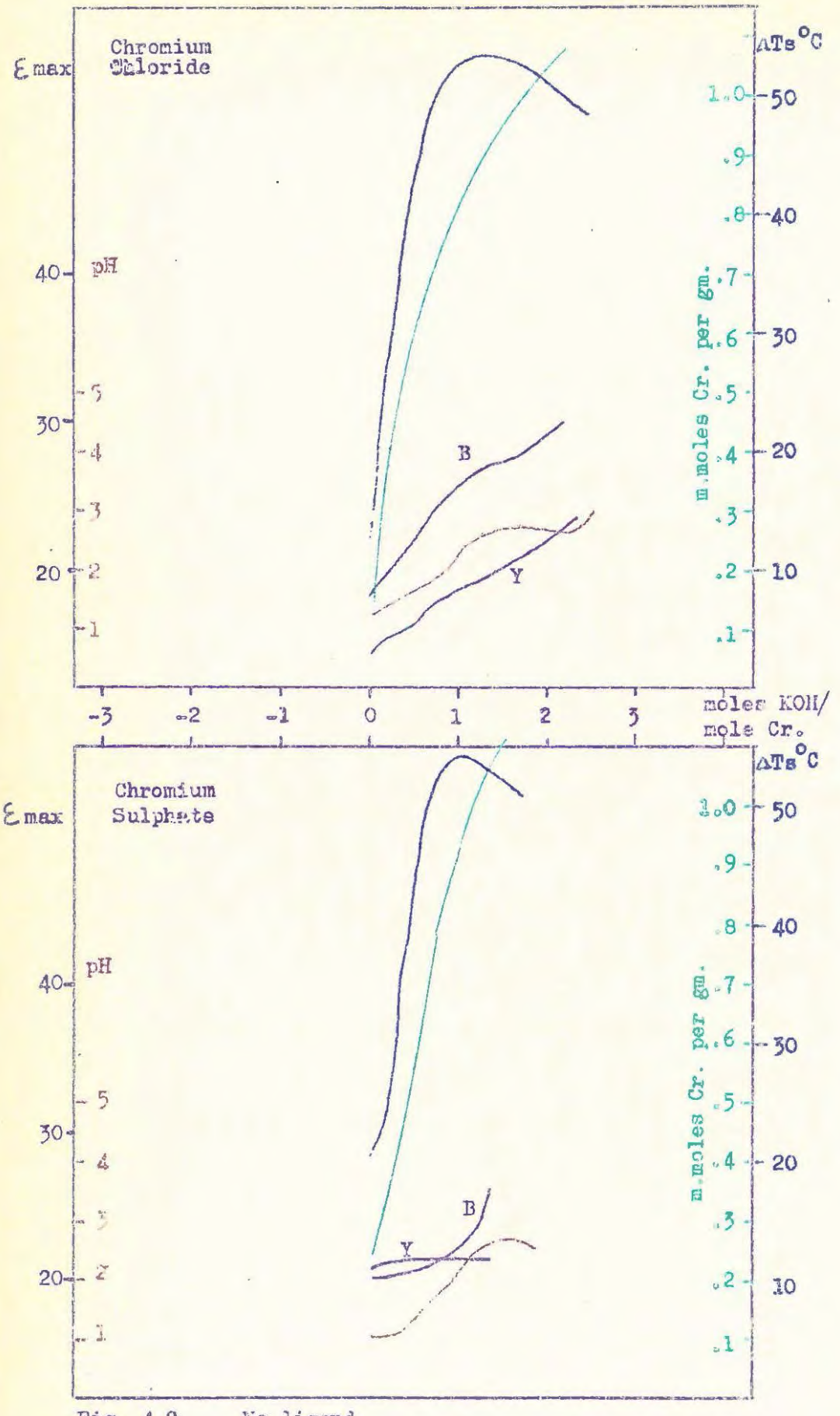


Fig. 4.2. No ligand.
Heating for 20 hours.

Presentation of Results.

In the following pages, each of the various ligands studied will be considered individually and the results presented in graphical form. In most cases the ligands were studied in conjunction with chromium chloride and chromium sulphate, and for case of comparison, graphs relevant to both salts are given on the same page opposite to the corresponding text.

The ligands studied fall into two series, one based on substituted acetic acids, and the other on substituted propionic acids. A full list of the complexing agents, along with their pK_{acid} values is given in Table 4.1.

Table 4.1.

Dissociation Constants of the Carboxyl Groups of the Ligands.

Ligand.	pK_{acid}.
Acetic acid.	4.7
Amino acetic acid (glycine)	2.3
Hydroxy acetic acid (glycollic)	3.8
Chloro acetic acid	2.9
Bromo acetic acid	2.9
Propionic acid	4.9
α -amino propionic acid (alanine)	2.4
β -amino propionic acid (β alanine)	3.6
α -hydroxy propionic acid (lactic)	3.9
α -bromo propionic acid	3.0
β -bromo propionic acid	4.0

The nett quantity of base in the solution is plotted as the abscissa of the curve, as moles of alkali

per/.....

per mole of chromium. The zero point represents the addition of carboxylic acid as a salt, whether internal as in the case of the amino acids, or as the potassium salt for the other materials. When addition of the potassium salt caused precipitation, either free acid was added to the chromium solution or a partially neutralised acid. Points on the extreme left of the graphs will therefore indicate the amount of neutralisation of the organic acid as originally added, and the other figures the increments of alkali required to theoretically neutralise the added organic acid.

In all the graphs, the same legends have been used to enable them to be read more easily. Thus:

1. The pH values of the solutions are plotted in red.
2. The ε max values of the two absorption maxima of the solutions are plotted in purple, the values corresponding to the blue (420 mμ region) and yellow (580 mμ region) peaks being marked "B" and "Y" respectively.

The scales for these potentiometric and spectrophotometric properties are drawn on the left of the figures.

The scales for the tanning properties of the solutions are drawn on the right of the figures:

3. The chromium fixation from the solutions by collagen is plotted in green, in mg. atoms of chromium per gram of leather.
4. The hydrothermal stability of the leather produced is plotted in blue, as the increase in shrinkage temperature (in degrees Centigrade) ($\Delta Ts^{o}C$) of the leather compared with raw skin.

No ligand.

Solutions of chromium chloride and chromium sulphate were prepared by two of the methods described:

i. addition of increments of alkali to aliquots of the chromium solutions, which were then allowed to react for 24 hours at room temperature;

ii. boiling the solutions under reflux for 20 hours, adding increments of alkali to aliquots of the solutions, and heating these for a further 20 hours.

The properties of these solutions are given graphically in Figs. 4.1 and 4.2.

The differences between the pH values of the solutions of chromium chloride and chrome alum at the same basicity, which were discussed in the previous section, (page 61), are not so apparent in the present solutions, and this is probably due to the absence of neutral sulphates which are present in chrome alum solutions.

The solutions which were heated had lower pH values than unheated solutions to which similar amounts of alkali had been added. Addition of alkali to a solution of a chromium salt brings about a rapid increase in the pH of the solution, which tends to fall with the passage of time. This is due to the comparatively slow reaction:

$$Cr(SO_4)_{1\frac{1}{2}} + KOH \rightleftharpoons Cr.OH.SO_4 + K(SO_4)_{\frac{1}{2}}$$

Even in the absence of alkali the pH of a solution of a chromium salt is low due to hydrolysis with the formation

of a basic chromium complex [1] by the reaction:

$$Cr(SO_4)_{1\frac{1}{2}} + H_2O \rightleftharpoons Cr.OH.SO_4 + \tfrac{1}{2} H_2SO_4$$

Thus the action of added alkali is to neutralise this free acid, altering the original equilibrium and causing further hydrolysis. This reaction is slow at room temperature, but is speeded up if the solution is heated to boiling point, when equilibrium is generally approached after 30 minutes.

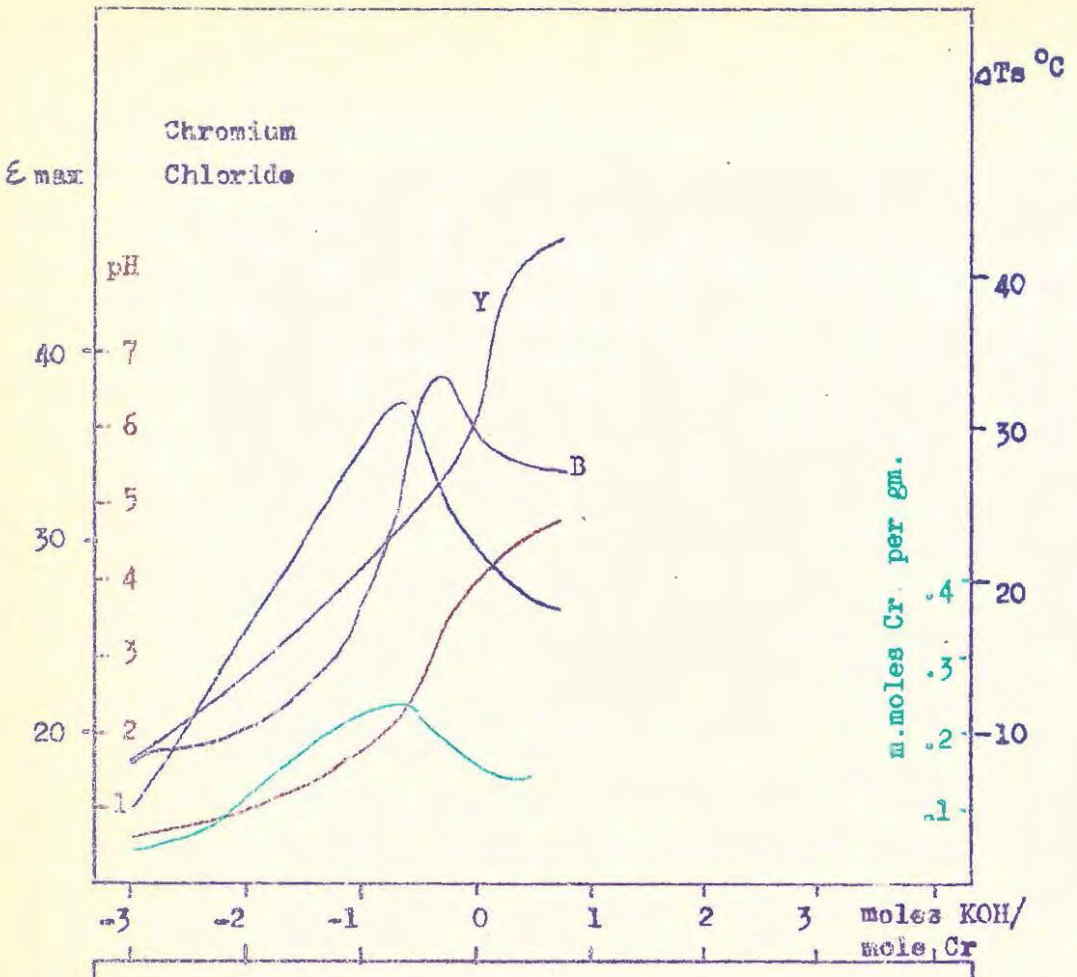
This accounts for the lower pH of the solutions which were heated, and the lower pH values of the solutions in the cold preparation series containing no additional alkali, in which hydrolysis had proceeded to equilibrium by ageing.

In both the heated and unheated solutions, the sulphate was precipitated after addition of less alkali than the chloride, due to chelation of sulphate causing formation of an incompletely basic precipitate. This has long been known and is allowed for in the official method for the determination of basicity of chrome liquors [87].

Although prepared by a different technique, these solutions exhibit similar properties to those reported in Chapter III. For instance, the ε max value in the 420 mμ region is greater than that in the 580 mμ region of the spectrum, and increases at a greater rate as the amount of alkali added to the solution is increased. This might be expected if the ε max value of the blue peak is influenced to a greater extent by olation than is the yellow peak.

The/....

The chromium fixation by collagen from the unmasked solutions rises rapidly as the additions of alkali are increased. There is a corresponding rise in the shrinkage temperature ($\triangle Ts^{o}C$), but it is observed that this quantity reaches a maximum of approximately $50^{o}C$ in the vicinity of 1 - 1½ moles of added alkali per gram atom of chromium, after which, though the figure for chromium fixation continues to increase, the hydrothermal stability ceases to rise, or in some cases falls. This is probably due to precipitation of chromium hydroxide in the skin leading to a higher chromium content but no increase in cross linking, as reflected in the shrinkage temperature increase.



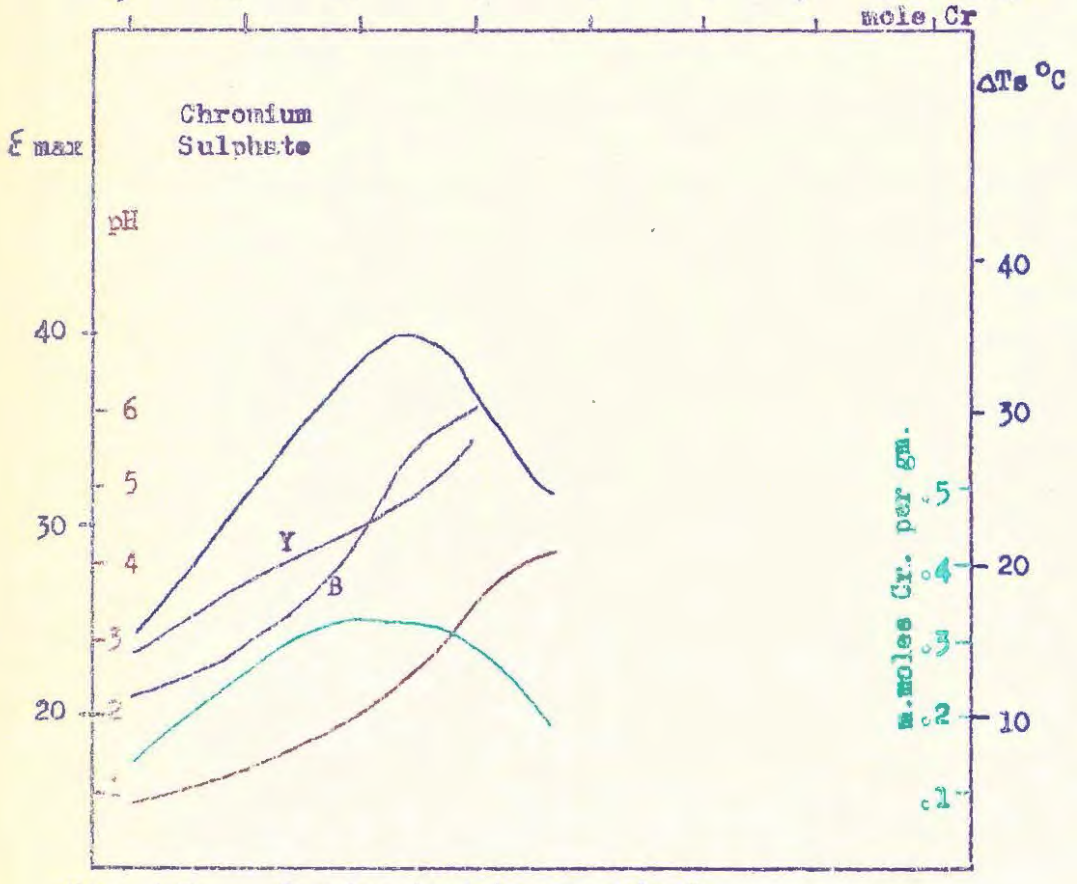


Fig. 4.3. 3 moles Acetate per mole Cr.
20 hours heating.

Acetate.

Three moles of acetic acid were added per gram atom of chromium and the solutions boiled under reflux for 20 hours. Increments of alkali were then added to aliquots of these solutions, which were heated for a further 20 hours. The properties of the solutions are plotted in Fig. 4.3.

The pH values of the complexes are considerably higher than the values for unmasked chromium solutions containing the same amount of added alkali, due to hydrolysis of the potassium acetate causing liberation of strong base. The complexes remained soluble at pH values higher than in the case of the unmasked solutions, indicating stabilisation by coordination of the ligand. The precipitation of the solutions, after smaller additions of alkali than with the unmasked solutions, is due to hydrolysis of potassium acetate increasing the hydroxyl ion concentration for a given increment of alkali, at a corresponding point at the right of the origin.

Coordination is indicated by the increased ε max values compared with the unmasked solutions, the value for the yellow peak being the higher in the more acid solutions.

Chromium fixation by collagen is much less than in the case of the unmasked solutions, and reaches a maximum after the addition of approximately 1 mole of alkali per gram atom of chromium less than the amount equivalent to the acetic acid added. Above this point the ionisation of the acetic

acid/.....

acid evidently increases the stability with which it is coordinated to the chromium complex, and consequently reduces the penetration by carboxyl groups from the collagen, with the result that both the chromium fixation and the hydrothermal stability of the leather fall.

Both the chromium fixation and the hydrothermal stability of the skin tanned with the solutions prepared from chromium sulphate are higher than those of the skin tanned with the masked chromium chloride solutions.

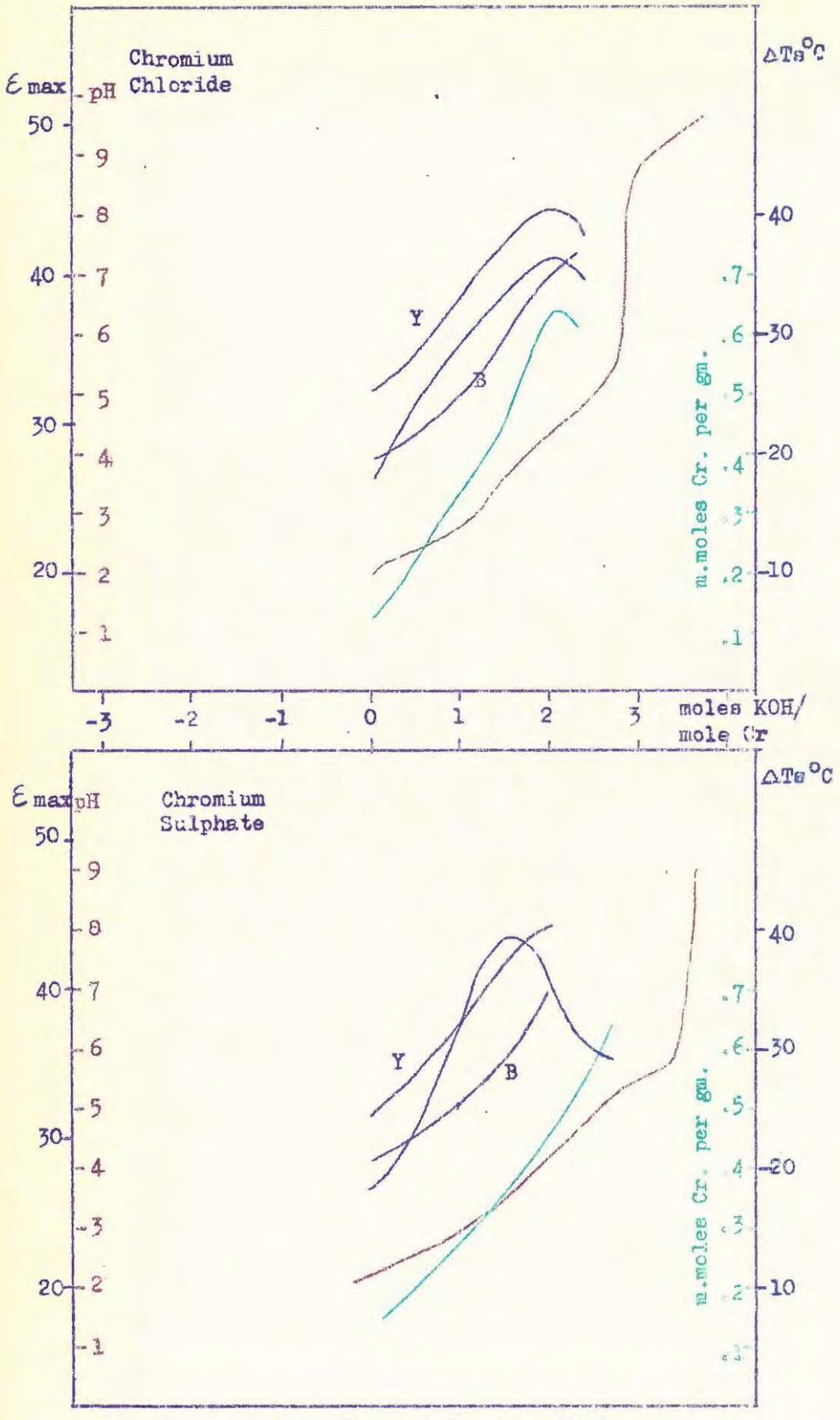


Fig. 4.4. 3 moles NH_2-acetate per mole Cr.
20 hours heating.

Amino-acetate. (Glycine).

Complexes were prepared from chromium chloride and sulphate by adding three moles of glycine per gram atom of chromium and boiling under reflux for 20 hours, after which increments of alkali were added to aliquots of these solutions, which were heated for a further period of 20 hours. The properties of these complexes are plotted in Fig. 4.4. The position of the curves relative to the horizontal scale allows for the fact that the amino acid is an internal salt due to its basic amino groups.

The pH values of the solutions are higher than the corresponding values for the unmasked solutions due to the effect of the basic groups of the amino acid.

The ε max values are higher than the corresponding values for the unmasked solutions. The value for the yellow peak has increased to a greater extent than that of the blue peak, indicating an increased amount of coordination compared with the unmasked solutions.

Chromium fixation by collagen from the complexes, and Δ Ts^{o}C are much lower than with the unmasked solutions, but higher than with the acetate complexes containing the same amount of added alkali.

Modifications to the Preparation of Glycine-containing Complexes.

Complexes were prepared from chromium chloride solutions containing three moles of glycine per gram atom of chromium by the following methods:

i. heating the chromium chloride with the ligand for 1 hour, adding increments of alkali to aliquots of this solution, and heating these for a further period of 1 hour;

ii. by allowing the ligand and chromium chloride to react at room temperature for 24 hours, adding increments of alkali to aliquots of this solution, and allowing these to react at room temperature for 24 hours.

These experiments were done in order to compare the modifications with Green and Ang's original method. The properties of these complexes are plotted in Figs. 4.5 and 4.6.

Comparison of the curves representing the pH values and the ε max values of the blue and yellow peaks of the complexes prepared by the 1 hour periods of heating, with those prepared by the 20 hour periods of heating, shows that the two sets of results are very similar, and indicates that the reduced reaction period still allows equilibrium conditions to be very closely approached.

Fig. 4.5 however, shows that the properties of complexes prepared without heating are somewhat different

from/.....

from those prepared by heating, due either to the reduced speed of the reaction at the lower temperature not allowing equilibrium to be reached, or possibly due to slightly different equilibrium properties at room temperature. It is found that the pH values of the unheated solutions were higher, while the ϵ max values were generally lower, particularly at the lower additions of alkali. Both these effects indicate less coordination and olation.

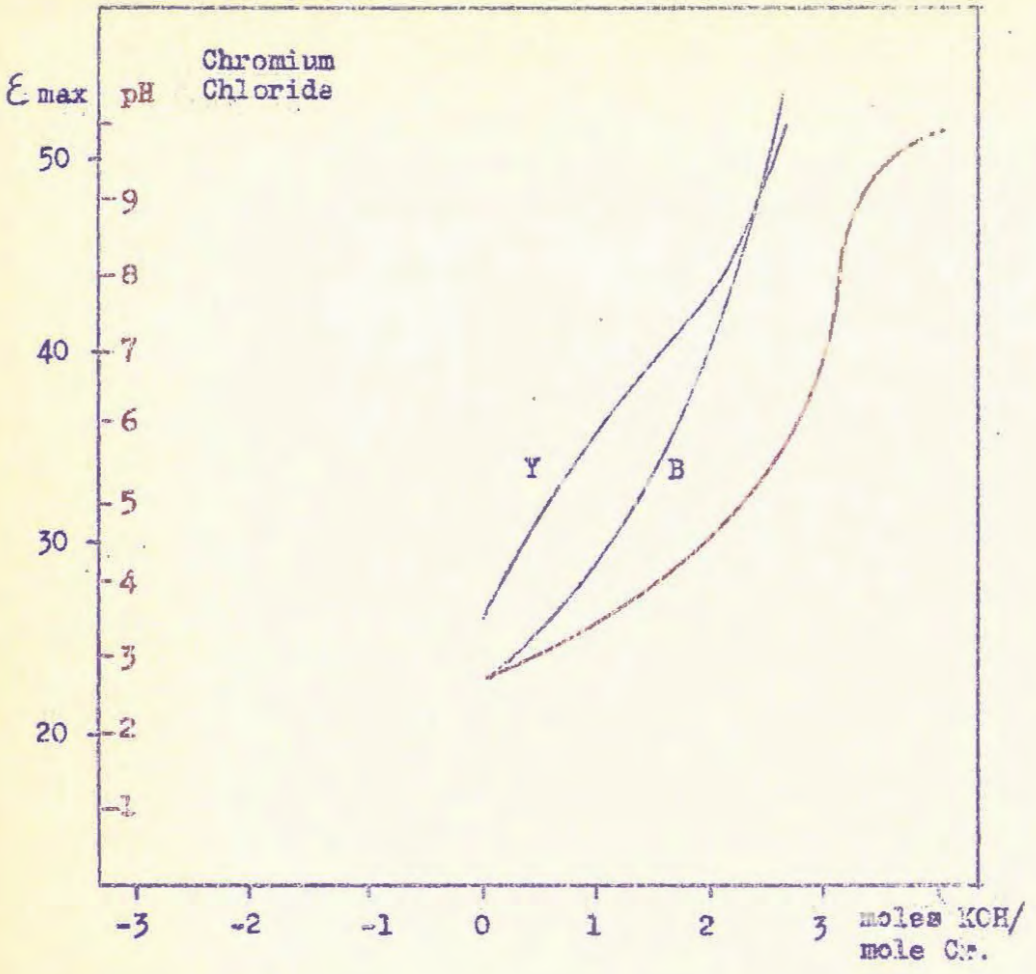


Fig. 4.5. 3 moles NH_2-acetate per mole Cr.
24 hours cold reaction.

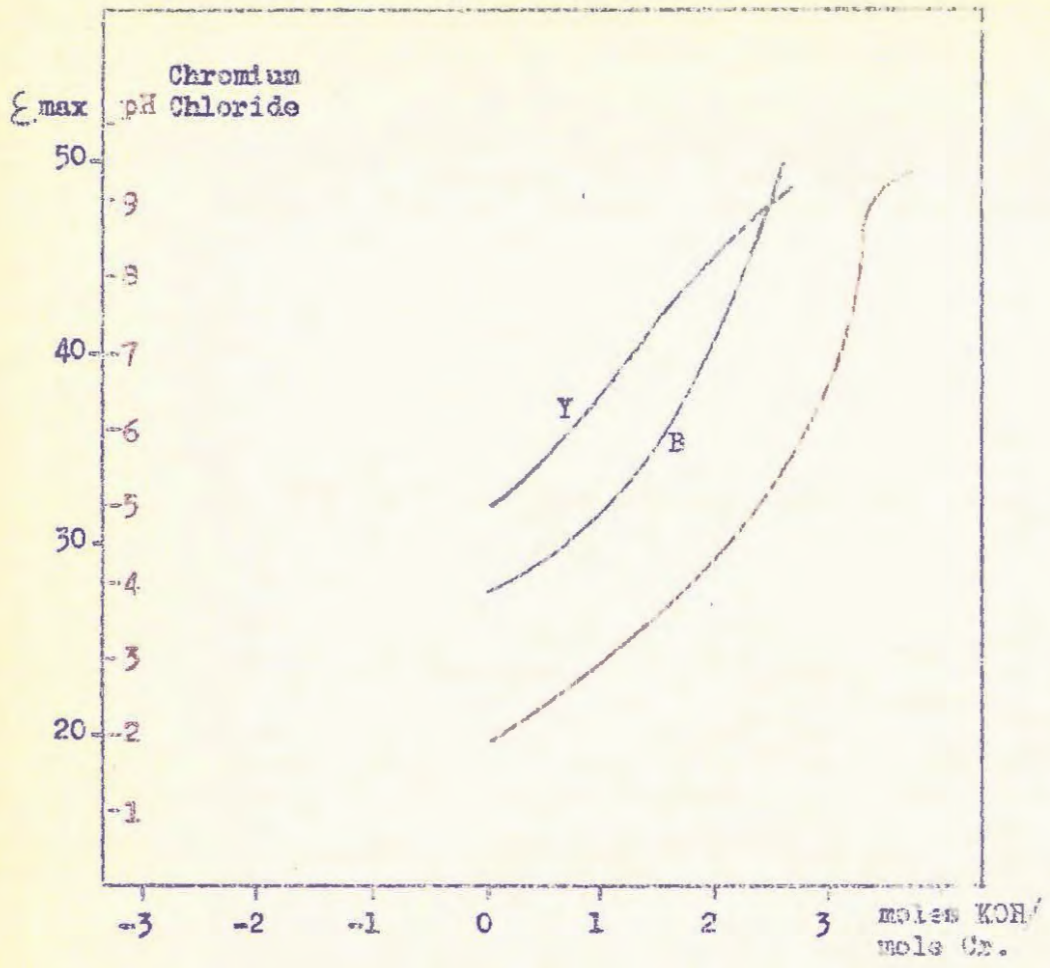


Fig. 4.6. 3 moles NH_2-acetate per mole Cr.
1 hour heating.

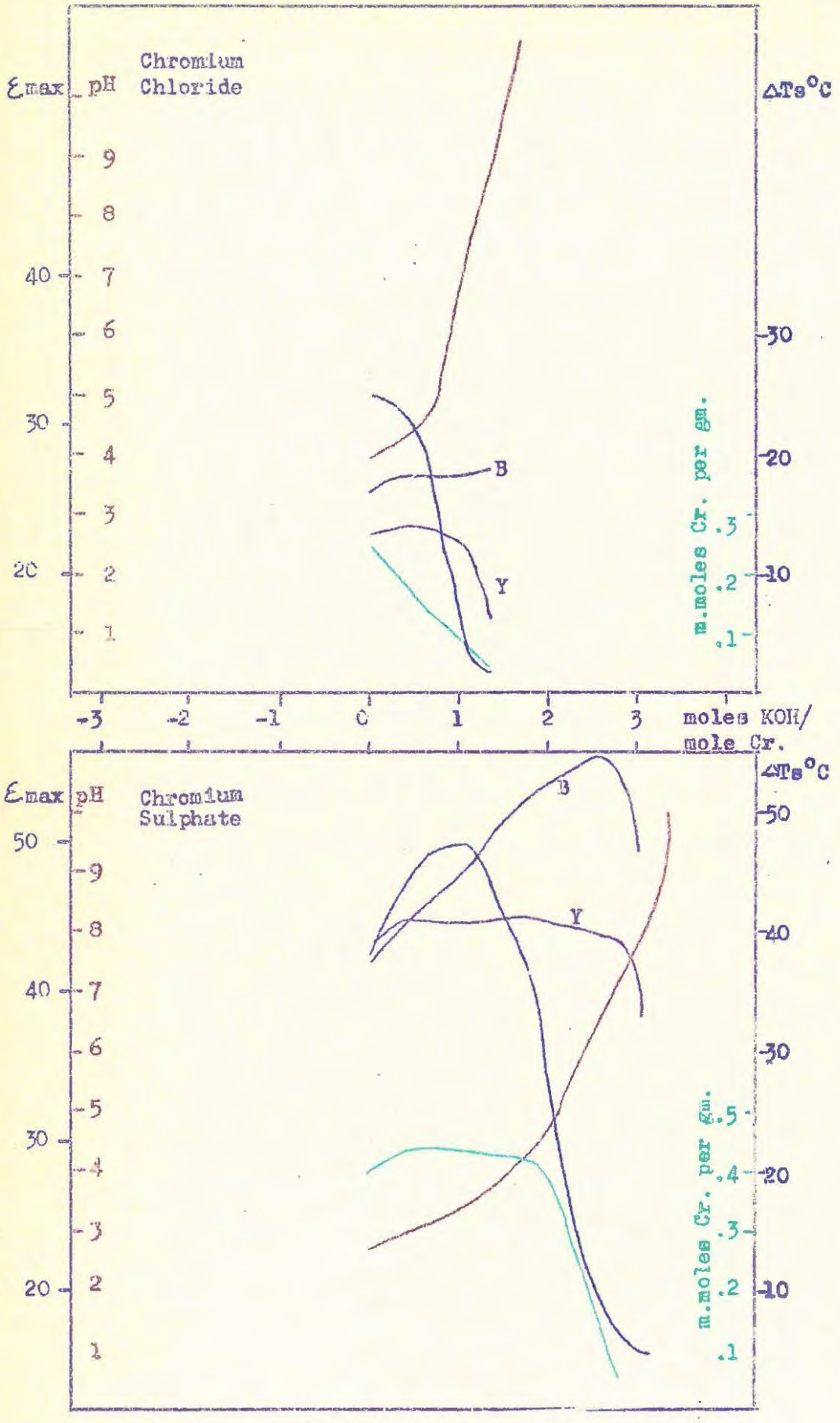


Fig. 4.7. 3 moles OH-acetate per mole Cr.
20 hours heating.

Hydroxy-acetate. (Glycollate).

The complexes were prepared from chromium chloride and sulphate by adding 3 moles of glycollic acid and boiling the solutions under reflux for 20 hours, adding sufficient alkali during the initial portion of this period to form potassium glycollate. Increments of alkali were then added to aliquots of these solutions which were heated for a further period of 20 hours. The properties of the complexes are plotted in Fig. 4.7.

Inspection of the curves shows that there are marked differences between the complexes prepared from chromium chloride and chromium sulphate. The pH values of the chloride solutions rise considerably more rapidly with addition of alkali than those of the sulphate solutions, and the chloride solutions were found to gelatinise after the addition of 1½ moles of additional alkali. The sulphate solutions remained clear until three equivalents of alkali per gram atom of chromium had been added.

The high solubility of the sulphate solutions shows that a very stable complex has been formed by the glycollate, probably indicating chelate ring formation involving both the carboxyl and hydroxyl groups, in the presence of two or more equivalents of alkali per gram atom of chromium. Gel formation in the case of the reaction between chromium chloride and glycollate in the presence of small amounts of added alkali is a point which requires

further/.....

further investigation, but may indicate the formation of polynuclear complexes.

The extremely high ε max values of the sulphate complexes are further evidence for their high stability. The high values of the chromium fixation and hydrothermal stability of the skin tanned by the sulphate solutions are unusual in view of the high ε max values, but may be due to relatively easy penetration of collagen carboxyl into the complex and formation of cross links by polynuclear complexes in a manner similar to that proposed by Holland [75, 77] for the action of long-chain dicarboxylic acids in the tanning properties of chrome liquors. After the addition of 2 moles of alkali per gram atom of chromium however, the chromium fixation and hydrothermal stability fall abruptly, probably due to formation of a very stable complex where penetration of the collagen carboxyl is largely prevented.

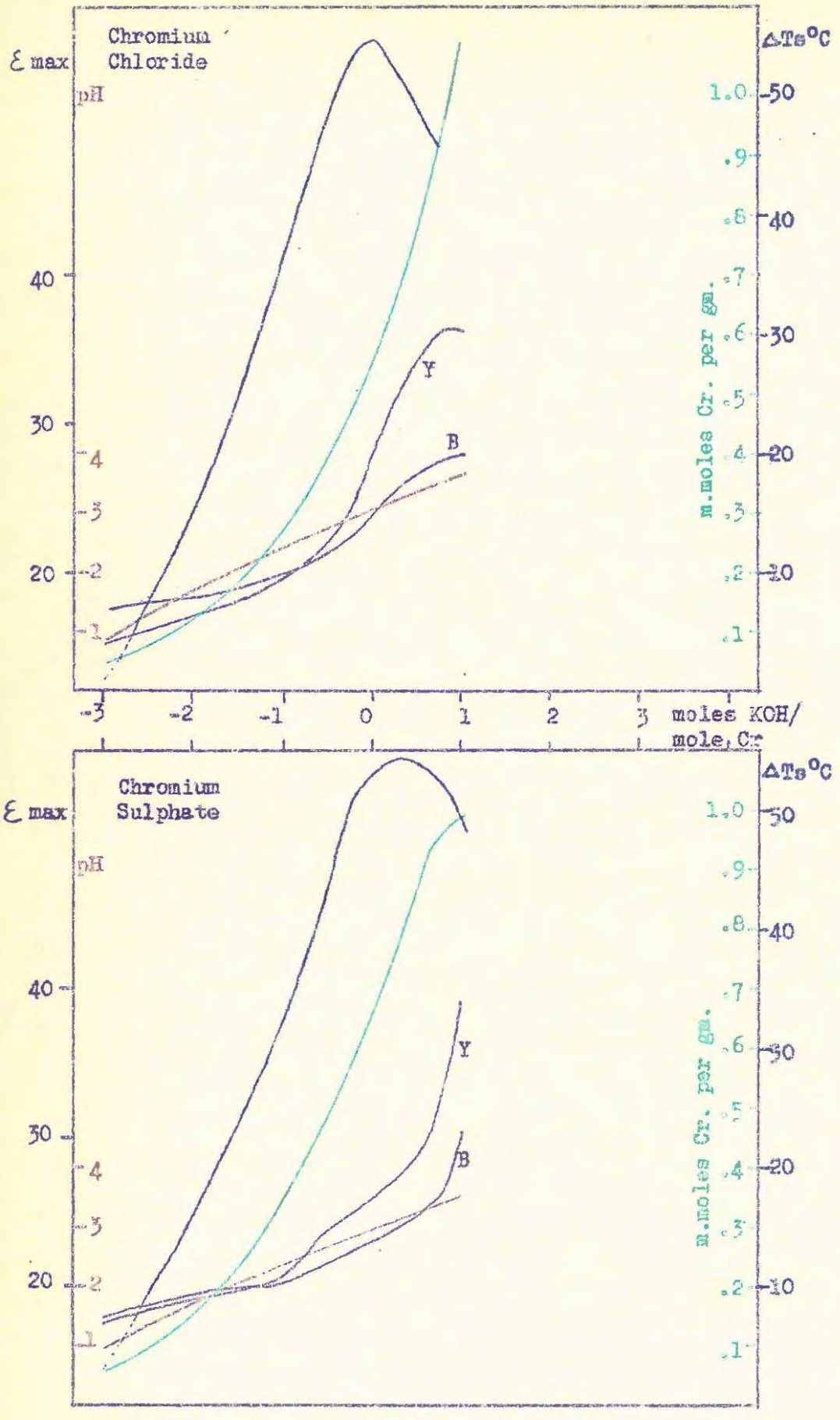


Fig. 4.8. 3 moles Cl-acetate per mole Cr.
24 hours cold reaction.

Chloro-acetate.

This ligand was found to decompose on heating, and the complexes were therefore prepared by reactions at room temperature. Complexes were prepared from chromium chloride and sulphate by adding three moles of chloro-acetic acid per gram atom of chromium, and allowing it to react at room temperature for 24 hours. Increments of alkali were then added to aliquots of this solution and allowed to stand for a further period of 24 hours. The properties of the resulting complexes are plotted in Fig. 4.8.

The variation of the pH with the amount of alkali added is similar for the solutions prepared from chromium chloride and sulphate.

The ε max values indicate that the extent of coordination is fairly small, the low values of εmax in the 420 mμ region indicating that in addition the degree of olation is low in the fairly acid solutions.

The curves showing the chromium fixation by collagen and the hydrothermal stability of the leather also indicate a comparatively low level of coordination. The fall of ΔTs in the leathers formed at the higher pH levels may be an indication of the precipitation of highly basic chromium salts in the skin.

In the case of the solutions prepared from chromium sulphate, the absence of hydrolysis of the ligand

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under the conditions of the preparation was verified by treating portions of the complexes with nitric acid and silver nitrate, when the absence of a precipitate indicated that no hydrolysis had taken place.

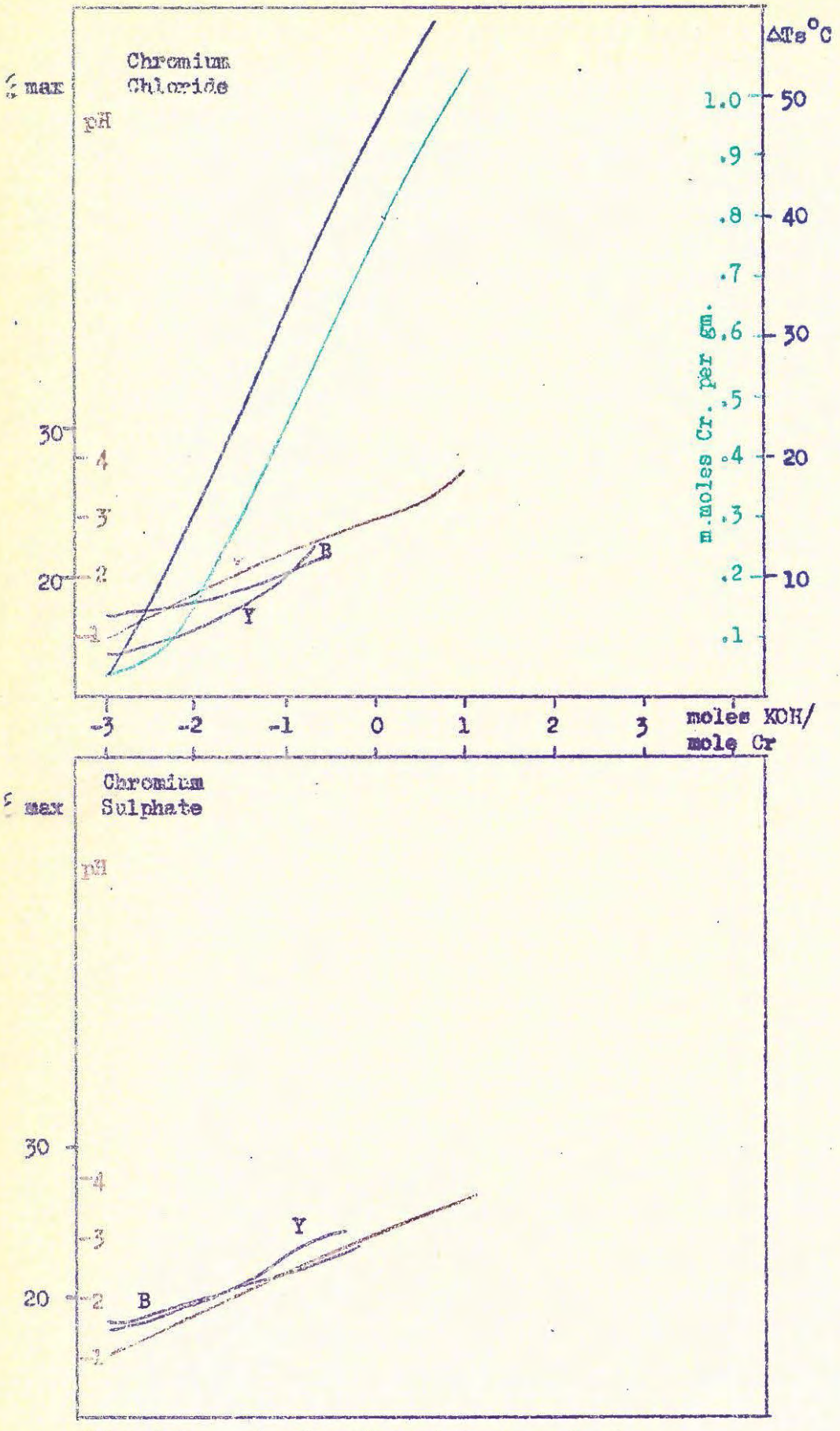


Fig. 4.9. 3 moles Br-acetate per mole Cr.
24 hours cold reaction.

Bromo-acetate.

The complexes were prepared without heating for the same reason as in the case of chloro-acetate. The complexes were prepared from chromium chloride and sulphate by adding three moles of bromo-acetic acid per gram atom of chromium and allowing the reaction to proceed at room temperature for 24 hours. Increments of alkali were then added to aliquots of this solution, which were allowed to react for a further 24 hours at room temperature. The properties of the complexes are plotted in Fig. 4.9.

Comparison of these results with those obtained from the chloro-acetate complexes show that the two ligands behave in a very similar manner, which might be expected from the similar nature of their substituent groups and their almost indentical pK_{acid} values.

One point of difference between the chloro-acetic and bromo-acetic complexes is the lower precipitation point of the latter, which may be due to steric effects, or the more hydrophobic nature of the bromine atom.

As in the case of the chloro-acetate complexes, absence of hydrolysis was verified by treatment with nitric acid and silver nitrate.

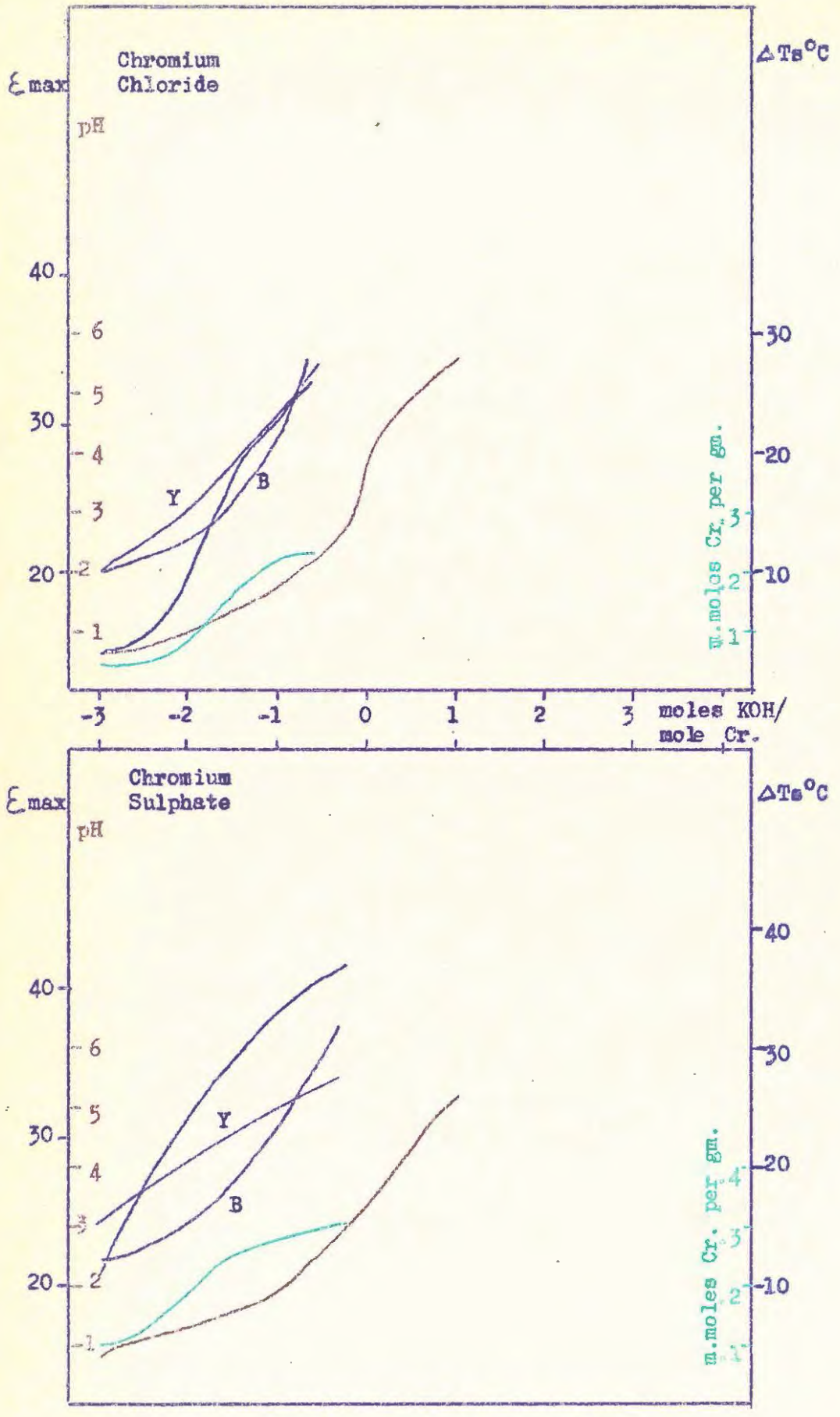


Fig. 4.10. 3 moles propionate per mole Cr.
20 hours heating.

Propionate.

The complexes were prepared from chromium chloride and sulphate by adding three moles of propionic acid and boiling under reflux for 20 hours. Increments of alkali were then added to aliquots of this solution, and heated for a further period of 20 hours. The properties of the complexes are plotted in Fig. 4.10.

Precipitation of the solutions took place before sufficient alkali had been added to completely neutralise the propionic acid. This is probably accounted for by two factors: the weak nature of propionic acid (pK = 4.9) causing hydrolysis of the potassium salt with liberation of strong base; and the presence of the comparatively large hydrocarbon chain which is likely to limit the solubility of the complexes.

The ε max values of the complexes indicate that coordination of the ligand is comparatively stable, and the poor tanning action of the solutions, as shown by the low chromium fixation and hydrothermal stability of the leather, furnish additional evidence of this.

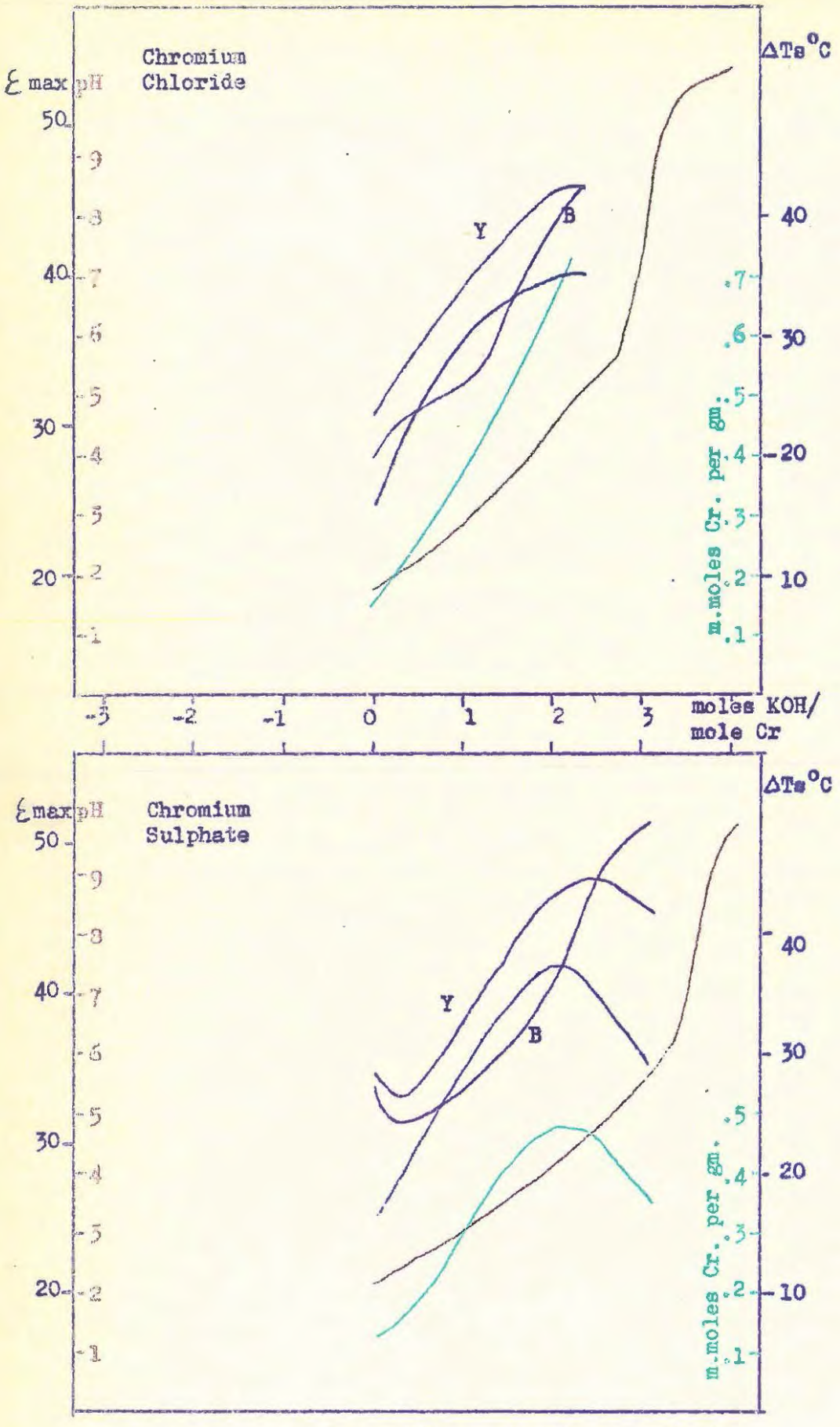
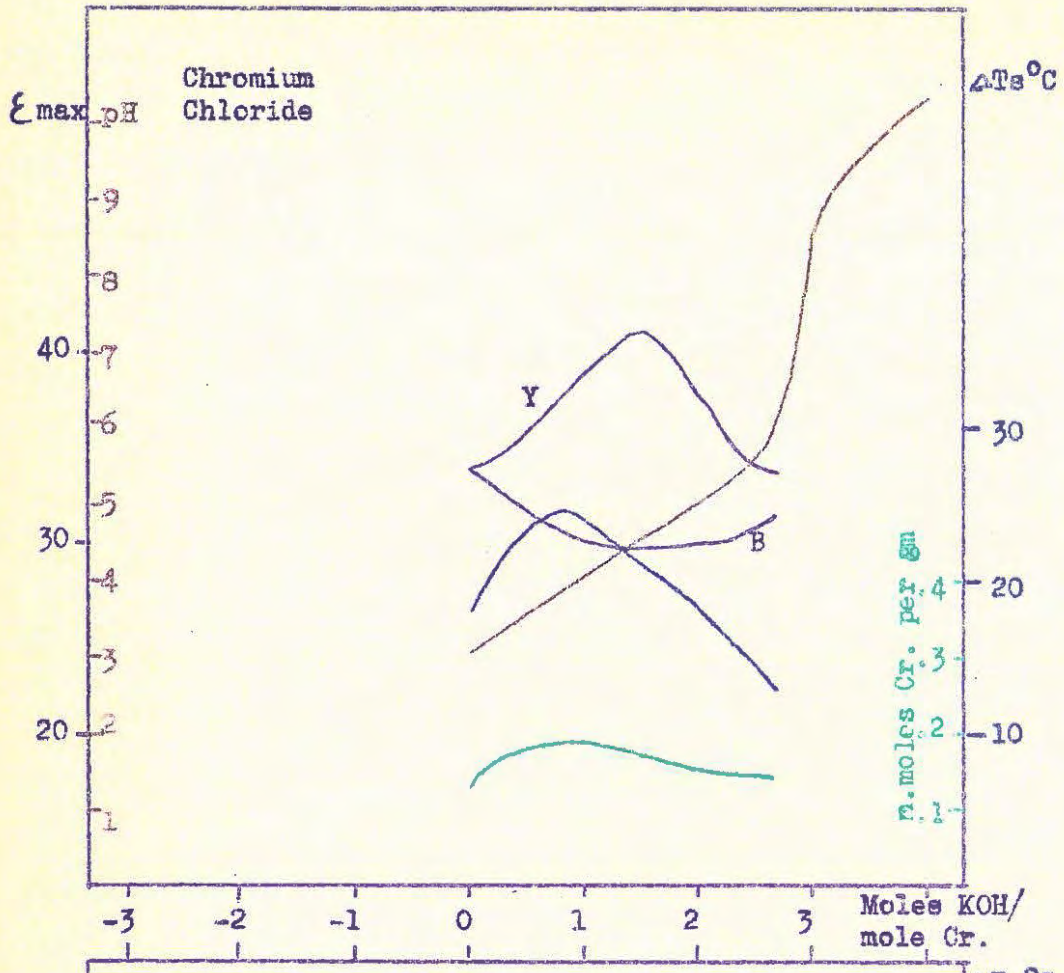


Fig. 4.11. 3 moles αNH_2-propionate per mole Cr
20 hours heating.

α Amino-propionate. (Alanine).

The complexes were prepared from chromium chloride and sulphate by adding three moles of alanine per gram atom of chromium and boiling the solutions under reflux for 20 hours. Increments of alkali were then added to aliquots of these, and heated for a further period of 20 hours. The properties of the complexes are plotted in Fig. 4.11, the position of the curves relative to the horizontal scale allowing for the fact that the amino acid is an internal salt.

The high ε max values of the complexes appear to be evidence of a high degree of coordination of the ligand, but the comparatively high chromium fixation from the solutions by collagen, and the hydrothermal stability of the leather formed, indicate that penetration of the complex by collagen carboxyl groups can still take place to an appreciable extent.



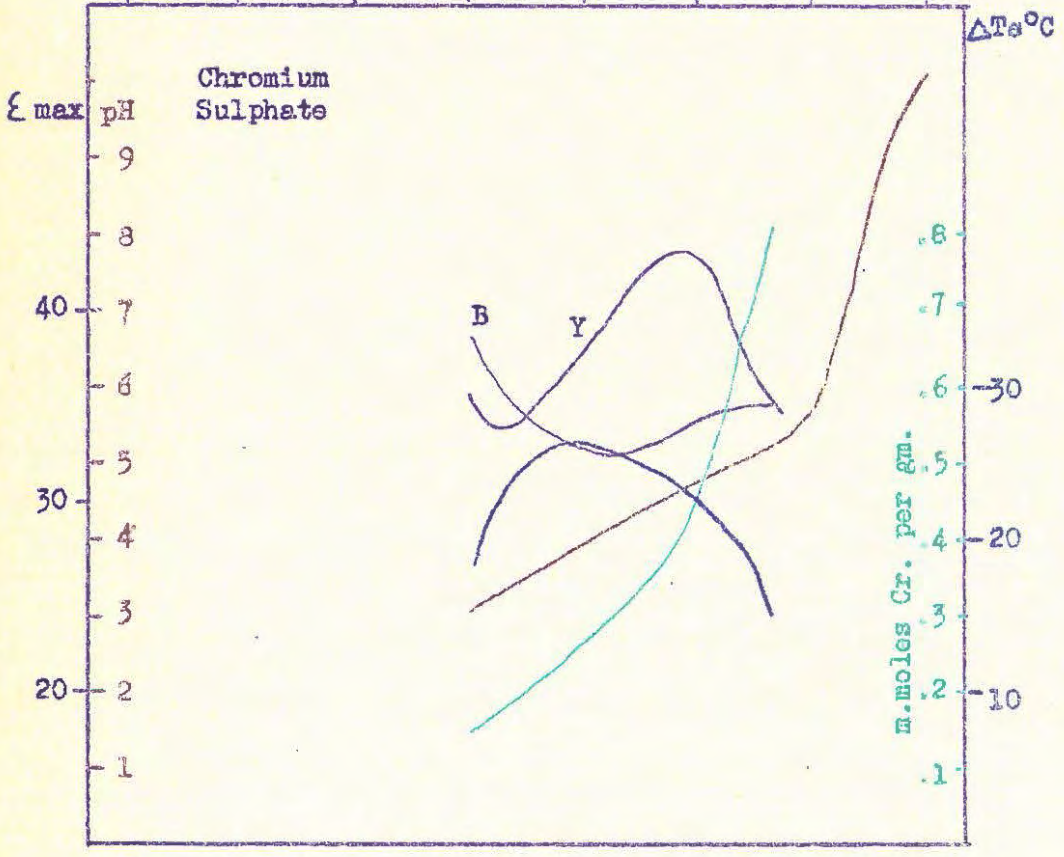


Fig. 4.12. 3 moles β NH_2-propionate per mole Cr. 20 hours heating.

β Amino-propionate. (β Alanine).

The method of preparation of these complexes was the same as that used in the case of α alanine. The properties of the complexes are plotted in Fig. 4.12.

Comparison of the curves of the alanine and β alanine complexes shows that there are marked differences between their properties. The possible causes of these will be discussed later.

The pH values of the complexes are fairly high, due to the high pK_1 value (3.6) of β alanine.

The curves representing ε max are similar for the chloride and sulphate solutions, but it is observed that the ε max. value of the blue peak goes through a minimum after the addition of about $1\frac{1}{2}$ moles of alkali per gram atom of chromium, while the yellow peak goes through a maximum at about this point.

The chromium fixation from the solutions is seen to be almost constant in the case of the chloride solutions, while in the case of the sulphate solutions, the fixation rises steadily as the amount of alkali added to the solution increases. In both cases however, the shrinkage temperature of the leather reaches a maximum value after the addition of about 1 mole of alkali per gram atom of chromium and falls in the solutions containing a larger amount of alkali. This suggests that the increased fixation in the case of the sulphate solutions is due to the precipitation of a basic salt of chromium in the skin.

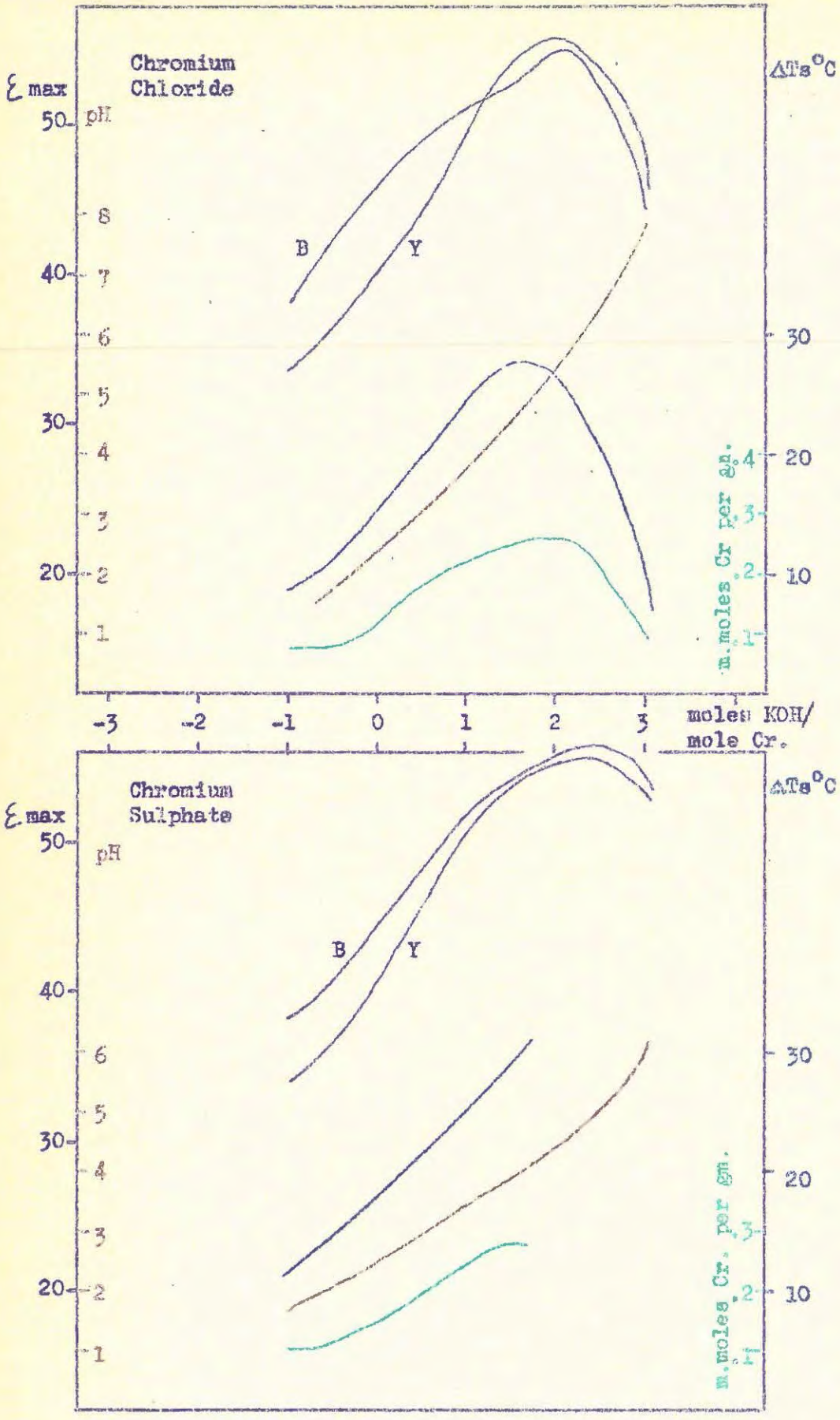


Fig. 4.1½. 3 moles α-OH-propionate per mole Cr. 20 hours heating.

α Hydroxy-propionate. (Lactate).

The complexes were prepared from chromium chloride and sulphate by adding three moles of lactic acid and boiling under reflux for 20 hours. During the initial part of this period, two equivalents of alkali per gram atom of chromium were added slowly. To aliquots of the solutions, increments of alkali were added, and heated for a further period of 20 hours. The properties of the complexes are plotted in Fig. 3.13.

The high ε max values of the complexes indicate that coordination of the ligand by chromium is very stable and possibly includes chelate ring formation involving the carboxyl and hydroxyl groups.

The low chromium fixation from the solutions is further evidence of the difficulty of displacing the ligand from the complex, though the hydrothermal stability conferred on the leather is quite appreciable, and may be due to formation of cross links consisting of polynuclear complexes as was suggested for the complexes of glycollic acid. Both the chromium fixation and the hydrothermal stability rise to a maximum value in the case of the chromium chloride solutions after the addition of about 1½ equivalents of alkali per gram atom of chromium, after which the values fall, indicating that penetration of the complex by the collagen carboxyl groups becomes increasingly difficult. In the

case/.....

case of the chromium sulphate solutions this was not observed due to precipitation of the complexes containing two or more equivalents of alkali per gram atom of chromium between measurement of the absorption spectra and use of the solutions in the tanning experiments.

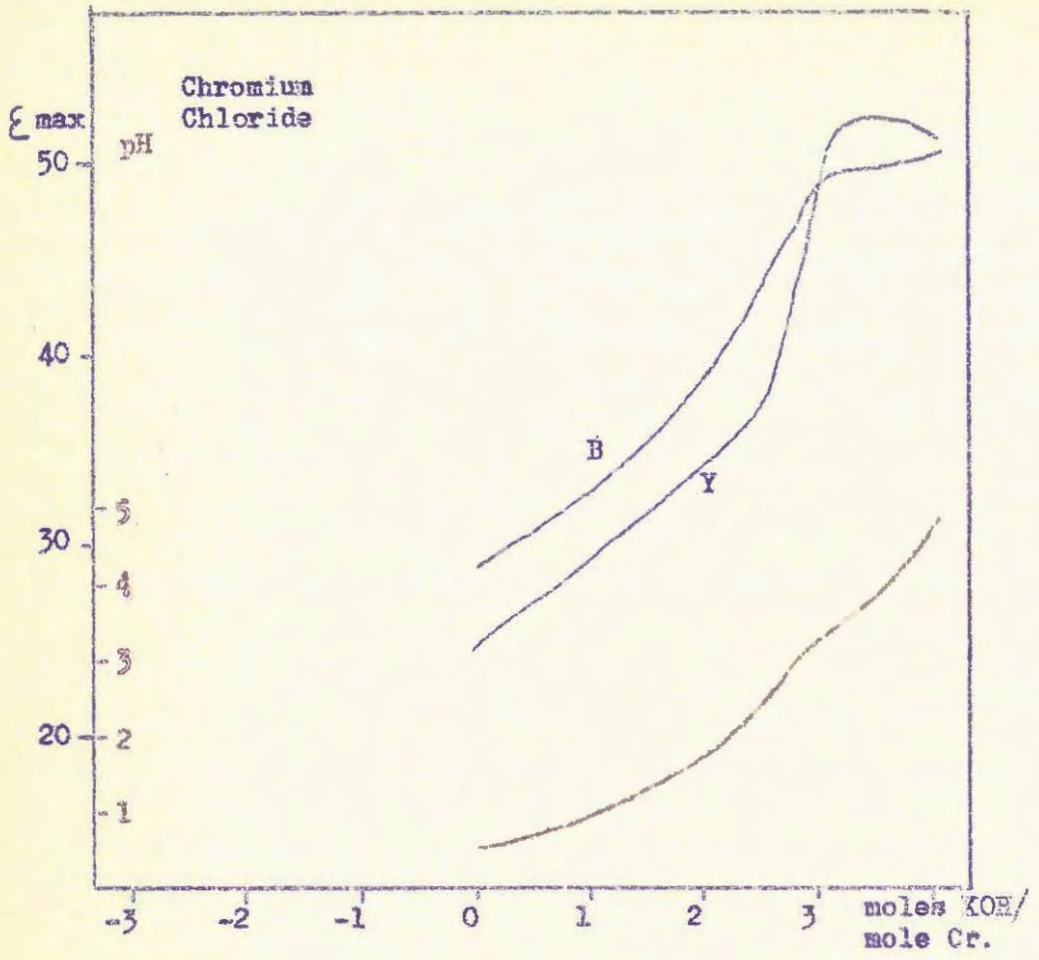


Fig. 4.14 3 moles ∝ Br-propionate per mole Cr.
20 hours heating

<u>∝ Bromo-propionate</u>.

These complexes were prepared from chromium chloride and sulphate by adding three moles of ∝ bromo-propionic acid per gram atom of chromium and boiling the solutions under reflux for 20 hours, during the initial portion of which three moles of alkali were added slowly. Further increments of alkali were added to aliquots, which were heated for a further period of 20 hours. These complexes were prepared before it was realised that decomposition of the ligand would occur under these preparative conditions, and it is unfortunate that time did not allow repetition of the experiments. The properties of the complexes formed are plotted in Fig. 4.14.

Hydrolysis of the ligand accounts for the low pH values of the solutions after the addition of comparatively large amounts of alkali to the solution, and it is probable that the following reaction occurred.

$$CH_3 - \underset{\underset{Br}{|}}{CH} - COOH \xrightarrow[H_2O]{} CH_3 - \underset{\underset{OH}{|}}{CH} - COOH + HBr$$

Formation of a hydroxy acid would account for the high ε max values of these complexes, and in fact the form of the curves suggests that there is partial decomposition of the ligand with the formation of lactic acid.

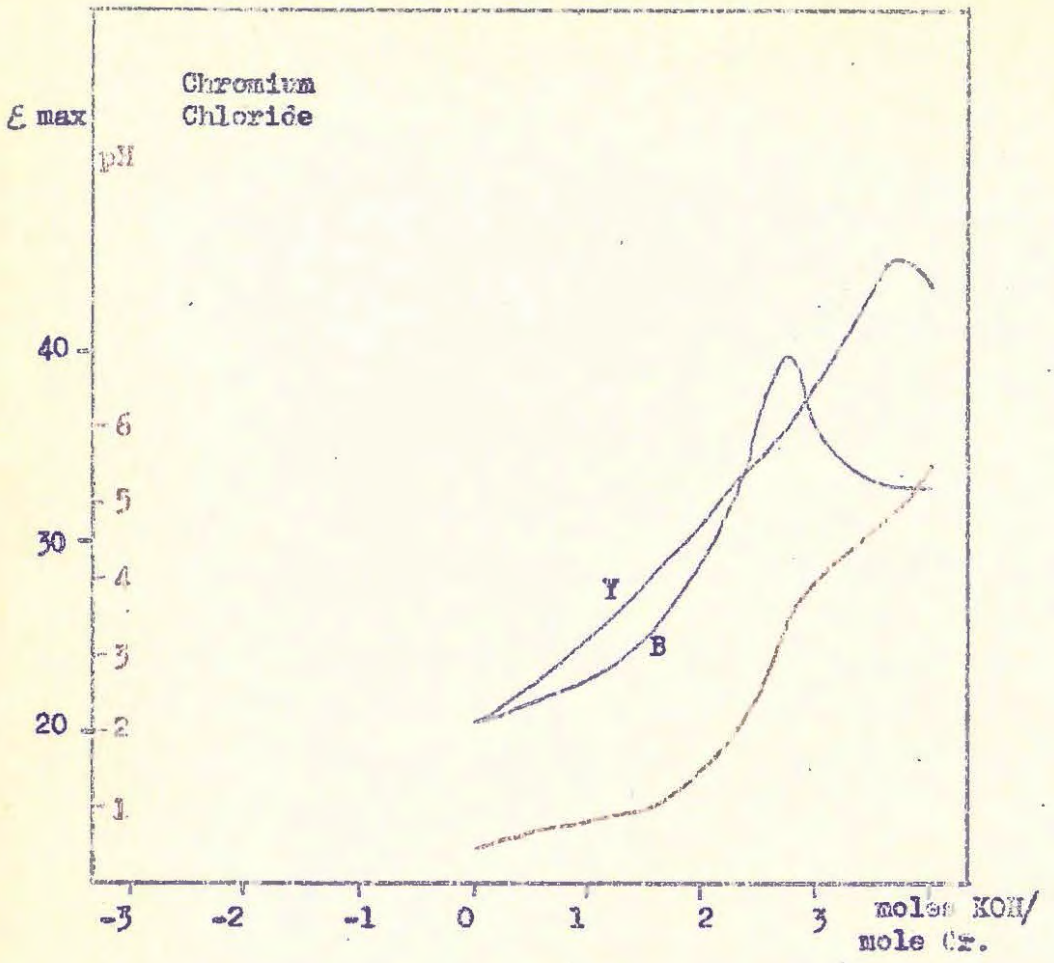


Fig. 4.15. 3 moles βBr-propionate per mole Cr.
20 hours heating.

β Bromo-propionate.

These complexes were prepared by the same method as those of β bromo-propionic acid, and it is likely that the ligand decomposed in a similar manner, though it is possible that a variety of products might be formed in view of the somewhat unstable nature of β hydroxy-propionic acid.

The properties of the solutions, plotted in Fig. 4.15, suggest the presence of a hydroxy acid in the solution.

DISCUSSION..

1. Critical Review of the Method of Preparation.

The method of preparation of the complexes discussed in this chapter was adapted from that published by Green and Ang [16] for preparation of complexes of alanine with chromium chloride. The experimental details of the method are given in Chapter II on page 28, where they are designated "Method 2."

In the present work, the method has proved suitable without alteration for the preparation of complexes with amino acids as ligands, as these substances are internal salts, and their carboxyl groups are normally almost entirely in the dissociated form in which they penetrate the complex. In order that the complexes of other ligands containing no basic groups should be comparable with those of the amino acids, these ligands were first added in the form of their potassium salts. Unfortunately, the hydrolysis of these salts of weak acids, with formation of free strong base, brought about precipitation of the chromium. In certain cases this could be overcome by forming the salt after addition of the free acid to the chromium solution, by addition of an equivalent quantity of potassium hydroxide solution. Some complexes still precipitated under this treatment, and these ligands were either not neutralised, or only partially neutralised.

Whether/.....

Whether the use of a weaker base such as ammonia to adjust the pH would have brought about less drastic changes in basicity has not been investigated, but it would be worthy of trial in future work, especially in view of the fact that addition of amino acids, even in the solid form, in no cases caused any precipitation of the chromium.

Another disadvantage of the method proved to be the rather drastic conditions which were used to promote coordination - namely boiling the chromium solution with the organic ligand under reflux for 20 hours, followed by a further period of 20 hours heating at boiling point after the addition of the further increments of alkali. The work on glycine appears to indicate that periods of heating as long as these are unnecessary for the establishment of equilibrium in these solutions, since the solutions prepared by reducing the periods of heating from 20 hours to 1 hour produced complexes with almost identical properties. The use of even milder reaction conditions, for example, allowing the reaction to proceed for 24 hours at room temperature (21 - 25^{o}C), caused the reactions to proceed to about 90 % completion (see Chapter II, page 30).

2. Discussion of Results.

a. Limitations of the Experimental Method.

Before the properties of complexes of the different ligands are compared, it should be stressed that this series of experiments is somewhat incomplete, although a considerable amount of work has been reported. Lack of sufficient time prevented a more thorough investigation into the method of preparation of the complexes, with the result that optimum conditions are unlikely to have been used for the reactions between carboxylic acids and chromium solutions. Furthermore, inspection of the list of the ligands studied(Table 4.1), reveals that the series of substituted propionic acids is not complete, since only one of the hydroxy acids was used, and the treatment of the solutions containing halogen acids resulted in their decomposition. In order that more reliable conclusions might be drawn from this work, it would also be desirable to take all the solutions to their precipitation points, and to complete the series of ligands. It would, in addition, be worthwhile to extend the work to further series of ligands, for example, substituted butyric, valeric and caproic acids.

In spite of these limitations of the present work, a comparison of the complexes of the different ligands, largely of a qualitative and descriptive nature, has been made, and tentative conclusions drawn as to the nature of the reactions of the ligands with chromium.

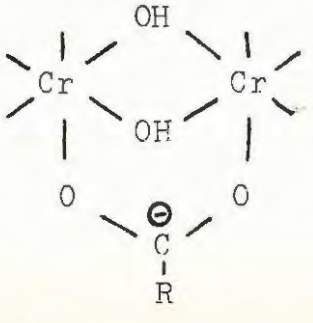
b. Comparison/...

b. Comparison of the Complexes containing Ligands of Similar Type.

i. Unsubstituted Carboxylic Acids.

Comparison of Figs. 4.3 and 4.10 shows that the properties of the acetate and propionate complexes after addition of equal amounts of alkali to the solutions are very similar. The differences are due to the slightly longer hydrocarbon chain of propionic acid, which causes the pK value to be slightly higher than that of acetic acid. Comparison of the ε_{max} values indicates that this causes slightly more stable coordination of the propionate ion. The slightly more hydrophobic nature of this longer hydrocarbon chain is the probable reason for the propionate complexes precipitating after the addition of less alkali than in the case of the acetate complexes.

The chromium fixation and hydrothermal stability of the skin tanned with these complexes initially rises as the amount of alkali added to the solutions is increased, but, in the case of the acetate complexes, both reach a limiting value and then fall as more alkali is added. From the shape of the curves it seems likely that the propionate complexes would have behaved in a similar manner had they remained soluble. This is an indication that stable complexes of little tanning action have been formed, most likely having a structure similar to the following:



ii. Amino/...

ii. Amino Acids.

The properties of the complexes prepared from amino acids are plotted in Figs. 4.4, 4.11 and 4.12. Comparison of the curves in Figs. 4.4 and 4.11, relating to glycine and α alanine, shows that the variation of the properties of the complexes of the α amino acids with the amount of alkali added to the solutions are similar for the two ligands, and indicates that their reactions are also similar. Fig. 4.12 shows however, that β alanine behaves in a somewhat different manner, this being particularly noticeable in the maximum reached by the ε max values of the yellow peak after the addition of $1\frac{1}{2}$ - 2 moles of alkali per gram atom of chromium; further addition of alkali causes the absorption to fall. It appears likely that the cause of this phenomenon is a change in the electron distribution in the complex, brought about by the more alkaline environment.

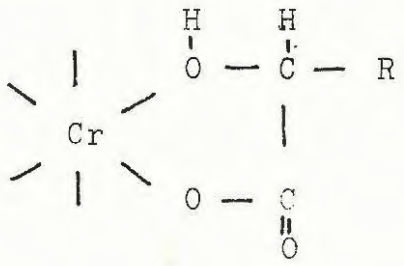
iii. Hydroxy Acids.

The properties of the complexes of glycollic and lactic acids are plotted in Figs. 4.7 and 4.13 respectively.

The very high ε max values of these solutions, particularly after the addition of fairly large amounts of alkali, indicates the existence of very strong coordinate bonds, probably including the formation of five-membered

chelate/.....

chelate rings of the type:

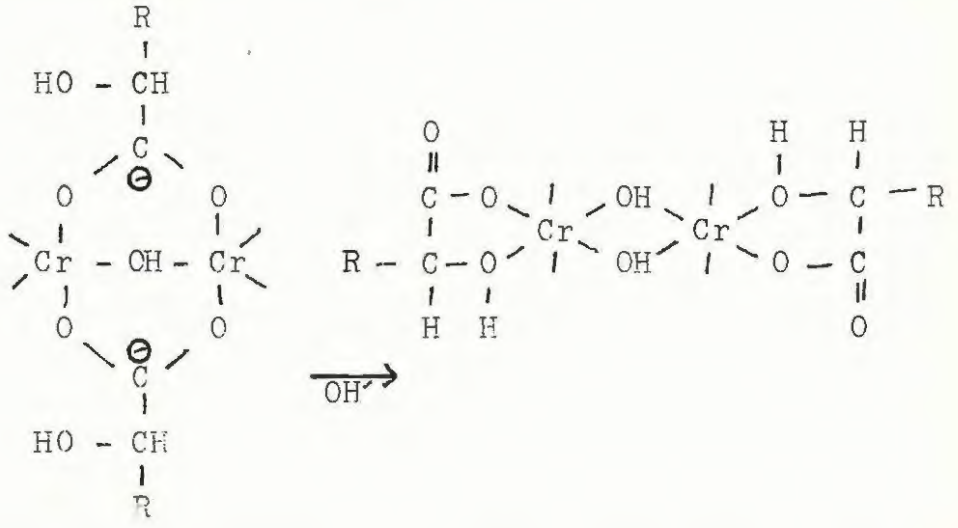


These high ε max values were not observed with the glycollate complexes prepared from chromium chloride, in which gel formation took place after the addition of a relatively small quantity of alkali. This obviously requires further study as it is indicative of large polynuclear complexes having been formed. The stability of the soluble complexes in this series is indicated by the low chromium fixation and hydrothermal stability of the leather produced by them.

The higher chromium fixation and high hydrothermal stability of skin tanned with the complexes prepared from glycollic acid with chromium sulphate may be due to formation of cross links involving large polynuclear complexes. This may be compared with Holland's suggestions (75 - 77) regarding the action of dibasic acids. A similar, though somewhat less pronounced effect is observed with the complexes of lactic acid. In all cases however, chromium fixation and hydrothermal stability fall sharply after the addition of larger amounts of alkali, possibly due to a

transformation/.....

transformation of the type:



leading to the formation of stable complexes in which displacement of the ligand held as a five-membered ring by the carboxyl groups of collagen would be unlikely. Somewhat similar structures have been proposed by Ramaswamy and Nayudamma [99] for products of reactions between chromium and hydroxy-carboxylic acids under similar conditions of concentration and pH.

Due to the probable nature of the decomposition products of α and β bromo propionic acids, it is appropriate to consider the complexes formed after addition of these ligands in this section. Comparison of Figs. 4.11 and 4.14 shows that the properties of solutions to which lactic and α bromo propionic acids were added are similar if allowance is made for the formation of approximately three equivalents of strong acid in the latter case. The curves relating to β bromo propionic acid suggest that the reactions of the decomposition products are different

in/.....

in the more highly alkaline solutions, which might be expected if the decomposition product is a β hydroxy acid.

c. Relationships between Different Classes of Ligands.

There are various criteria by which the stability of coordination complexes of chromium can be judged, including the resistance to precipitation by alkali, and the properties of the solutions under equivalent conditions. The former method will be applied first:

i. Resistance to Precipitation by Alkali.

A number of limitations to the use of the resistance of complexes to precipitation, as a measure of stability, should be born in mind. Precipitation need not necessarily be caused by complete penetration of hydroxyl groups with the formation of chromium hydroxide, but may involve a partially basic compound of low solubility. Furthermore, the degree of hydrolysis of the organic salts can cause uncertainty as to the amount of free alkali in the solution.

The ranges over which precipitation occurred are given in Table 4.2. The first figure is the value for the last completely clear solution, whilst the second refers to the solution containing the first trace of permanent precipitate. In the cases where no precipitation occurred in the range studied, the single figure refers to the solution containing the largest amount of added alkali.

Examination/.....

Table 4.2.

Precipitation Ranges of Solutions containing 3 moles of Ligand per gram atom of Chromium.

Ligand	pK_{acid}	Moles alkali per gram atom Cr in addition to amt. reqd. to form carboxylic acid salt.		pH	
		chromium chloride	chromium sulphate	chromium chloride	chromium sulphate
Nil (cold preparation)	-	>2.33	1.66 - 1.83	>4.35	3.46 - 3.56
(hot preparation)	-	2.17 - 2.33	1.33 - 1.5	2.50 - 2.62	2.66 - 2.69
Acetate	4.7	>0.67	0 - 0.33	>4.72	3.48 - 3.87
Propionate	4.9	-0.67 - -0.33	-0.33 - 0	2.05 - 2.42	3.00 - 3.50
Chloro acetate	2.9	>1	>1	>3.67	>3.51
Bromo acetate	2.9	-0.67 - -0.33	-0.33 - 0	2.66 - 2.86	2.81 - 3.07
Amino acetate	2.3	2.33 - 2.67	2.67 - 3	4.74 - 5.13	5.00 - 5.53
α amino propionate	2.4	2.33 - 2.67	3 - 3.33	5.06 - 5.52	5.58 - 6.10
β amino propionate	3.6	2.67 - 3	2.67 - 3	5.96 - 8.52	5.25 - 5.64
Hydroxy acetate	3.8	1.33 - 1.67	3 - 3.33	8.60 - 10.80	7.64 - 9.94
α hydroxy propionate	3.9	>3	>3	>6.86	>6.16

N.B. Negative values refer to solutions to which less alkali has been added than the amount required to form the carboxylic acid salt.

Examination of the table indicates that no simple relationship between the precipitation points and the pK_{acid} values of the ligands exists. It is therefore more convenient to group the ligands according to their substituent groups.

From the pH values at which the first precipitate forms, it appears that the ligands confer resistance to penetration of the chromium by hydroxyl in the following order:

hydroxy acids > amino acids > unsubstituted acids > halogen acids.

It is seen that this order does not follow decreasing pK_{acid} values of the ligands. In the case of the hydroxy acids, this is probably due to formation of stable five-membered rings in the more alkaline solutions, which prevent penetration of hydroxyl groups. In the case of the amino acids, a possible explanation of the enhanced solubility is a solvation effect of the charged amino group ($-NH_3^+$) left free after coordination of the carboxyl group (see Chap. III).

Comparison of the amounts of alkali required to precipitate the complexes shows that this tends to be slightly greater for the halogen acids than for the unsubstituted acids. Though it seems unlikely that the halogen groups would play a direct part in increasing the solubility of complexes, the higher pK values of the unsubstituted acids cause their salts to have a higher

degree/.....

degree of hydrolysis in solutions of similar pH value, and give rise to a greater concentration of strong base in the solution.

ii. Comparison of the Complexes under Equivalent Conditions.

There are a number of different ways in which to define "equivalent" conditions for the comparison of the properties of chromium complexes. All of these criteria of equivalence offer advantages from certain points of view, but all have disadvantages from others. Possible points of comparison are:

a. After the addition of equivalent amounts of alkali to the solutions. This suffers from the disadvantage that the different carboxylic acid salts will have different degrees of hydrolysis, depending on the pK values of the acids, causing differences in the hydroxyl ion concentration of the solution and thus in the basicity of the chromium.

b. At pH's equal to the pK_{acid} values of the ligands, where the carboxylic acids are 50 % ionised. In this case, the extent of neutralisation of the chromium at the different pH values will vary.

c. At equal pH values. An advantage of this method is that any differences between the properties are due only to the effects of the ligands. This does not give a true comparison of the different ligands,

since/.....

Table 4.3.

Properties of Chromium Complexes at Equilibrium pH value of 3.5.

Ligand	pK_{acid}	ε max (420 mμ region)		ε max (580 mμ region)	
		chromium chloride	chromium sulphate	chromium chloride	chromium sulphate
Nil (cold preparation)	-	29.0	(29.5)	21.0	(22.0)
(Hot preparation)	-	(30.0)	(28.0)	(23.0)	(22.0)
Acetate	4.7	38.0	36.2	35.6	34.4
Propionate	4.9	(40.0)	(40.0)	(37.0)	(35.0)
Chloro acetate	2.9	27.4	26.0	35.6	31.2
Bromo acetate	2.9	(22.0)	(24.0)	(24.0)	(26.0)
Amino acetate	2.3	36.0	35.8	41.2	41.2
α amino propionate	2.4	37.0	37.0	41.0	42.6
β amino propionate	3.6	31.6	33.8	36.4	35.0
Hydroxy acetate	3.8	-	48.6	-	44.4
α hydroxy propionate	3.9	50.0	52.0	52.0	51.4

N.B. Values in parenthesis were estimated by extrapolation.

since at any arbitary pH value they will be dissociated to extents depending on their pK values, which will influence their tendency for coordination. However, this method of comparison is attractive from a practical point of view, especially if a pH value applicable to chrome tanning is chosen, when a useful comparison of the masking action of the ligands can be made. This is essentially the method of comparison used in Chapter III, where a number of interesting results emerged. For these reasons, this method of comparison has been adopted for the present series.

A pH value of 3.5 has been chosen as being of interest, and the properties of the solutions at this pH level are given in Table 4.3, for the spectrophotometric properties of the solutions, and Table 4.4 for the results of the tanning experiments.

Examination of Table 4.3 reveals that, in general, the molar extinction coefficients of the complexes vary in the order: hydroxy acids $>$ amino acids $>$ unsubstituted acids $>$ halogen acids.

Examination of Table 4.4, giving the tanning properties of the various complexes, suggests a slightly different order for the stability of the complexes: hydroxy acids, $>$ unsubstituted acids $>$ amino acids $>$ halogen acids.

With the exception of the hydroxy acids, it is

seen/.....

Table 4.4.

Properties of Skin tanned with Chromium Complexes at Equilibrium pH value of 3.5.

Ligand	pK_{acid}	mg: atoms Cr per gram leather.		$\Delta Ts^{o}C.$	
		chromium chloride	chromium sulphate	chromium chloride	chromium sulphate
Nil (cold preparation)	-	1.06	1.30	52	52
(hot preparation)	-	(1.07)	(1.15)	(50)	(52)
Acetate	4.7	.18	.30	25	32
Propionate	4.9	(.30)	(.32)	(35)	(35)
Chloro acetate	2.9	.90	.95	50	52
Bromo acetate	2.9	.91	-	53	-
Amino acetate	2.3	.37	.47	33	40
α amino propionate	2.4	.50	.42	31	38
β amino propionate	3.6	.18	.22	23	25
Hydroxy acetate	3.8	-	.43	-	43
α hydroxy propionate	3.9	.20	.27	24	26

- N.B. Values in parenthesis were estimated by extrapolation.

seen that this is in the order of decreasing pK_{acid} values. The different position of the amino acids when the order is according to the ε max values of the complexes may be due to electron shifts involving the amino group which increase the optical absorption of the chromium ion. The high stability of the hydroxy acid complexes has already been discussed and attributed to chelate ring formation involving both the carboxyl and hydroxyl groups.

d. General Deductions.

When chelate ring formation does not take place, pK_1 is an important factor in coordination, and much evidence is available [14, 17, 33, 100] to indicate that for a series of similar ligands, for example, amino acids, the amount of complex formation is, to a first approximation, a linear function of the pK value (c.f. Chapter III). However, although direct relationships may be expected for a series of, for instance, carboxylic or bromo-carboxylic acids, it is unlikely to be identical to the one found for amino acids. Unfortunately, insufficient results are available from the present work to confirm this hypothesis, although the trend is apparent. It is interesting to note that Datta et al [27] have come to somewhat similar conclusions from their studies of complex formation between divalent metals and glycyl, leucyl and sarcosyl compounds.

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APPENDIX A.

Figs. A.1 - A.19 are the absorption spectra of complexes prepared from Chromium Chloride Solutions by adding amino acids, in quantities of 0.5, 1, 2, 3, 4 and 6 moles per gram atom of chromium and adjusting to equilibrium pH values of 2.50, 3.16 and 3.82 by addition of KOH solution. The final concentration of chromium was 0.333 gm atom per litre. The solutions were diluted 25 times immediately before taking the spectrophotometric readings. Molar Extinction Coefficients (ε) plotted were calculated from Beer-Bouguer relationship (page 31). The curves are plotted over the wavelength range 360 mμ to 620 mμ.

The following colour code is used:

——— denotes solutions at equilibrium pH 2.50

——— . . . . . pH 3.16

– – – – . . . . . pH 3.82

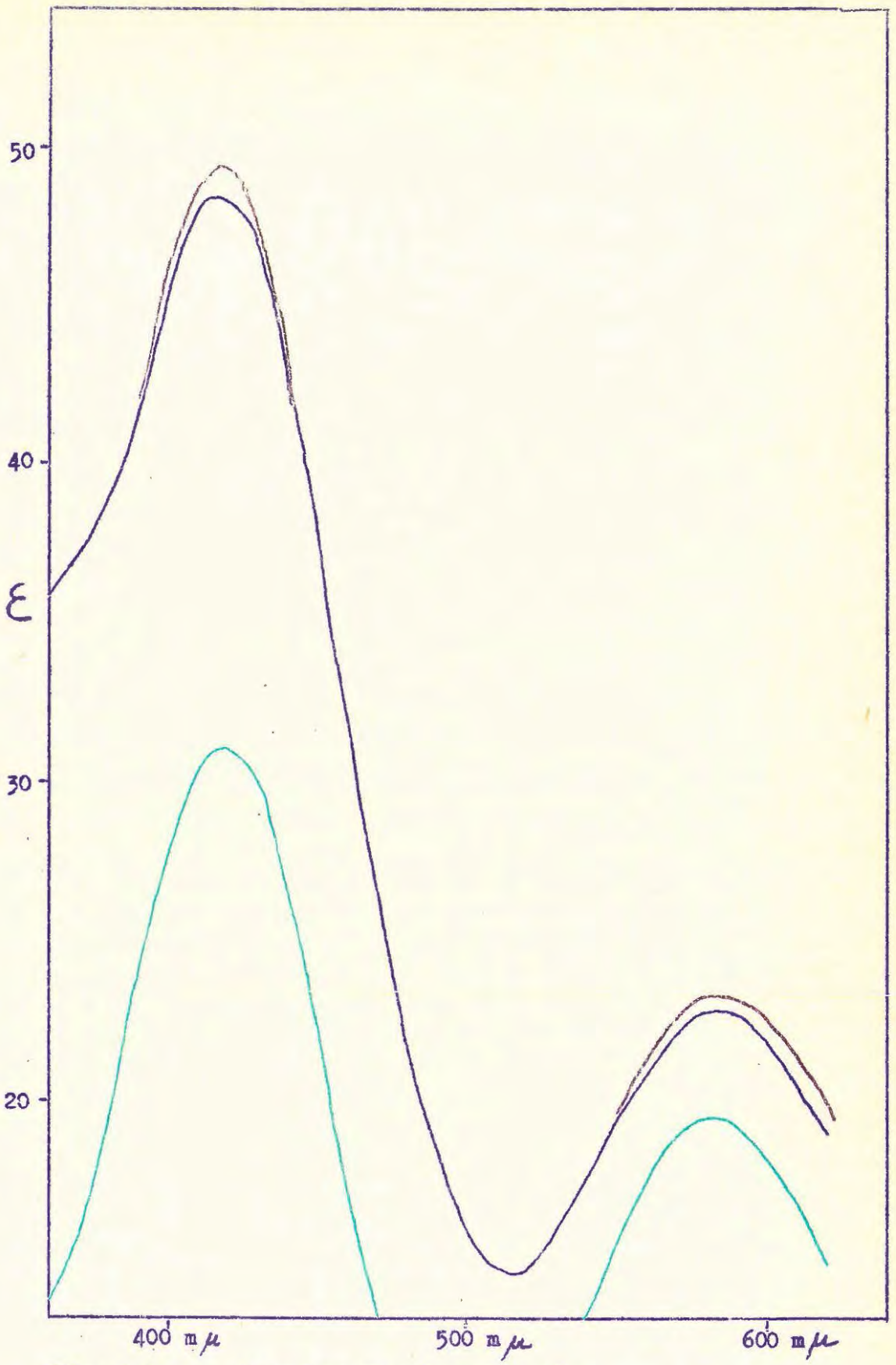

Fig. A.1. .333 molar Chromium Chloride.

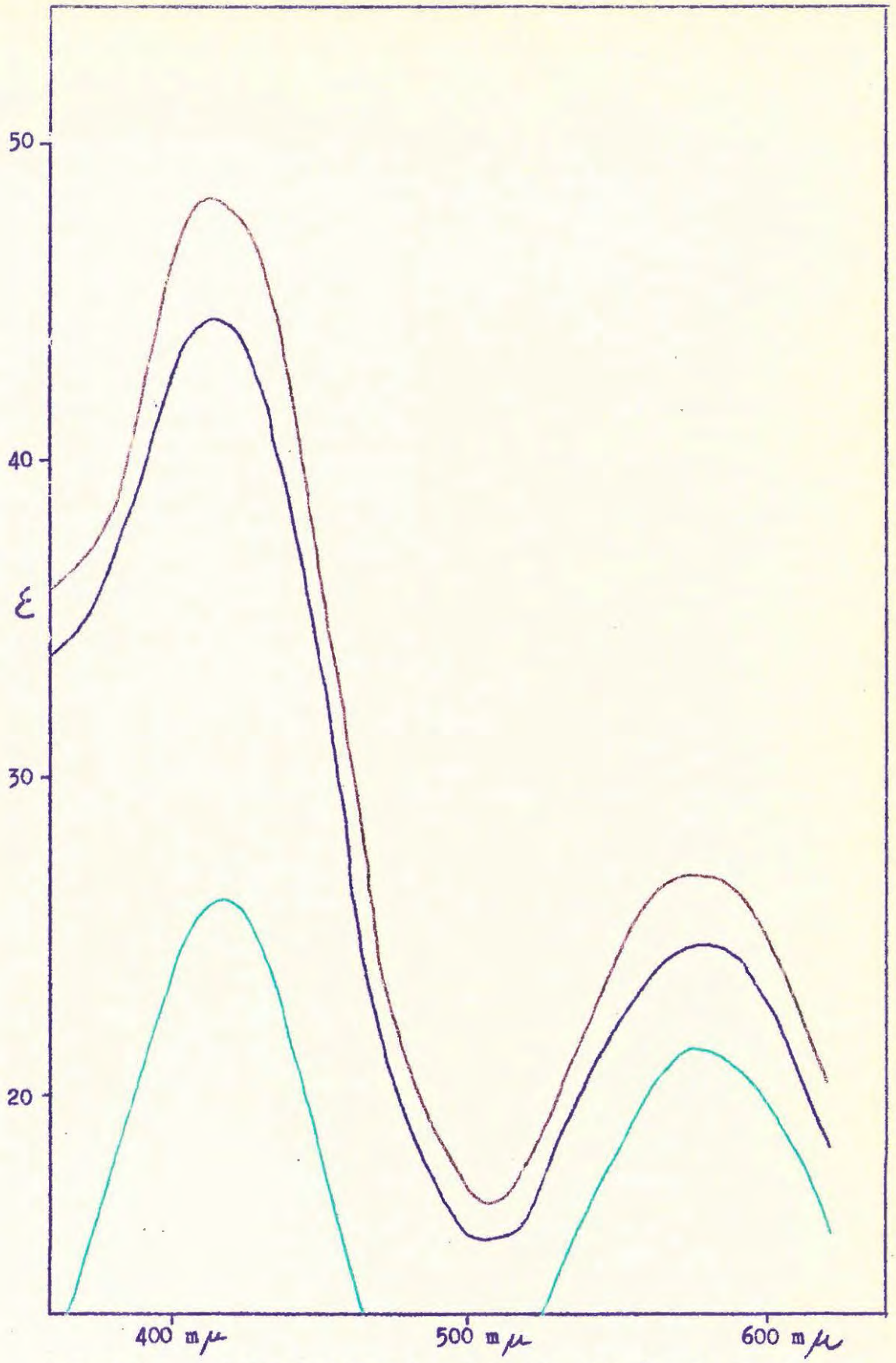

Fig. A.2. .333 molar Chromium Chloride with $\frac{1}{2}$ mole Glycine per gram atom Chromium.

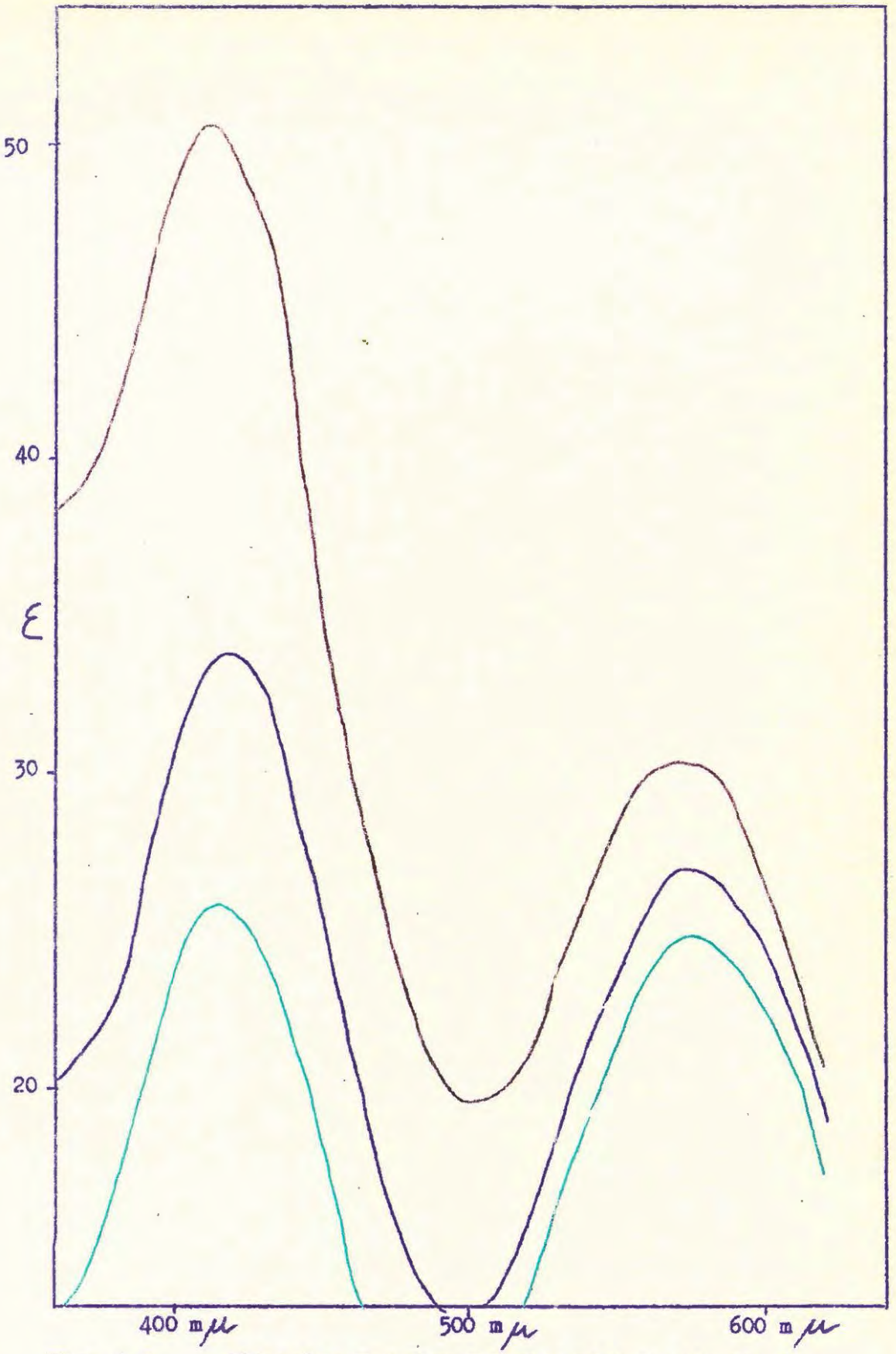

Fig. A.3. .333 molar Chromium Chloride with 1 mole Glycine per gram atom Chromium.

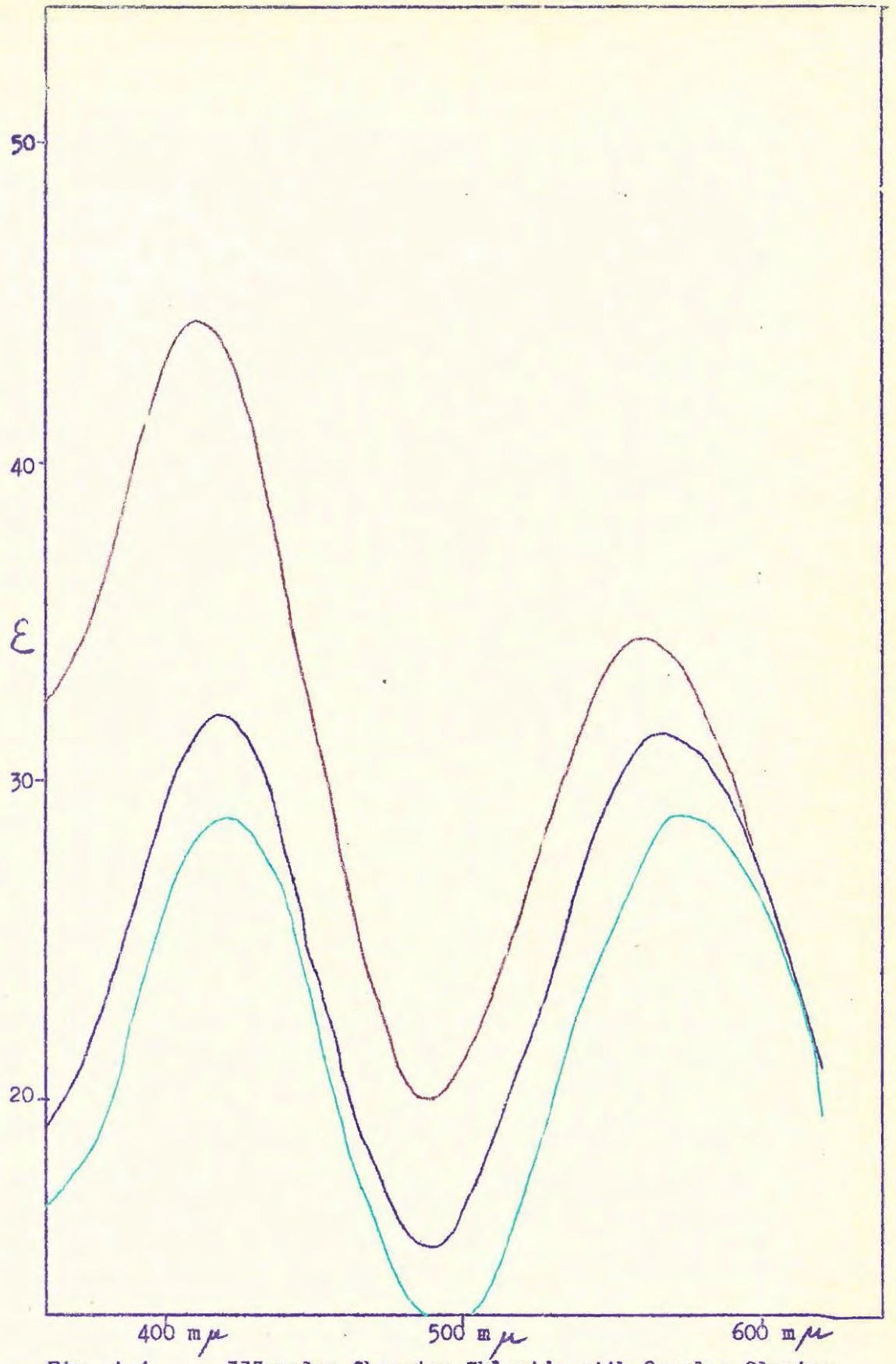

Fig. A.4. .333 molar Chromium Chloride with 2 moles Glycine per gram atom Chromium.

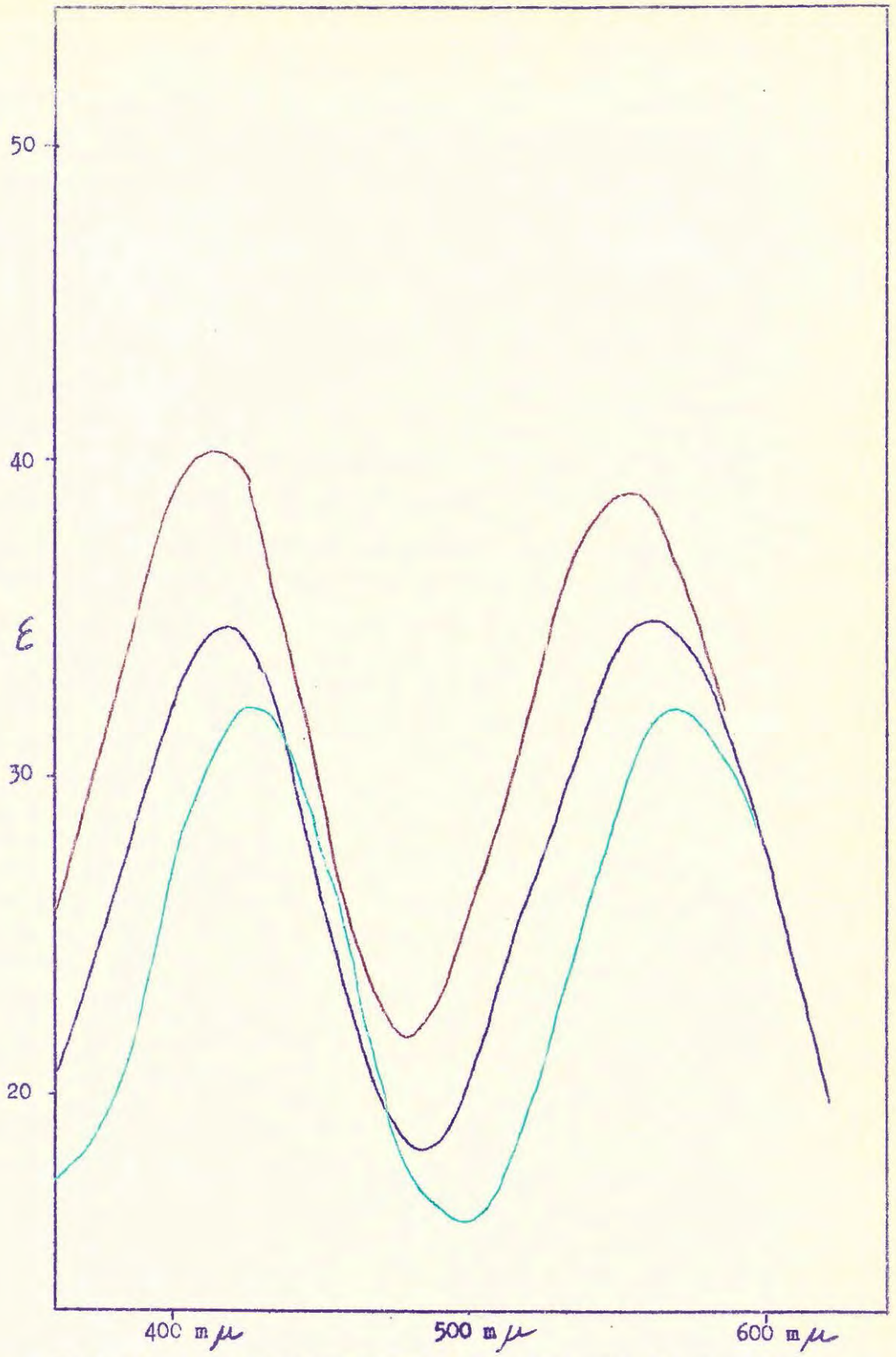

Fig. A.5. .333 molar Chromium Chloride with 3 moles Glycine per gram atom Chromium.

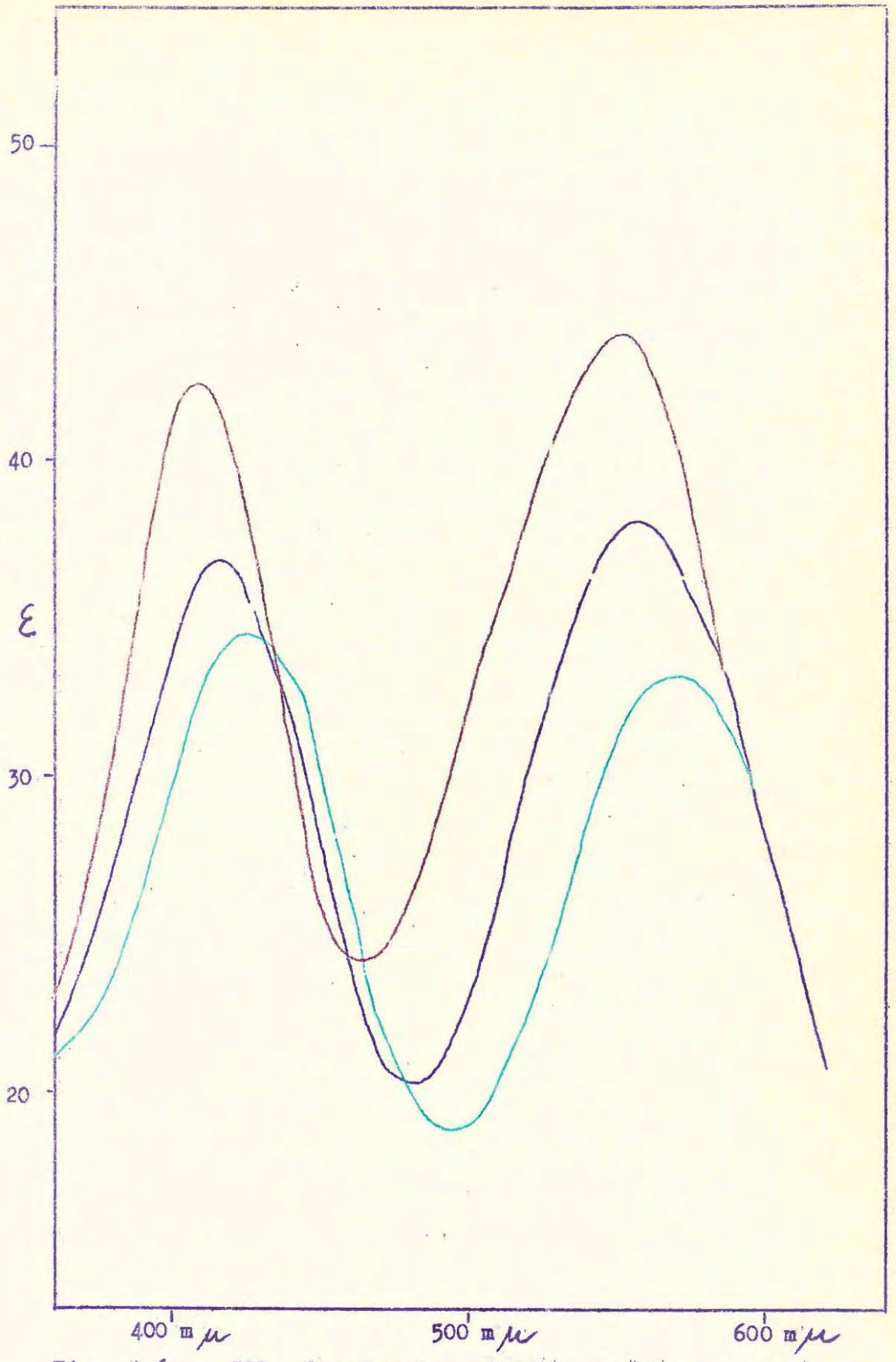

Fig. A.6. .333 molar Chromium Chloride with 4 moles Glycine per gram atom Chromium.

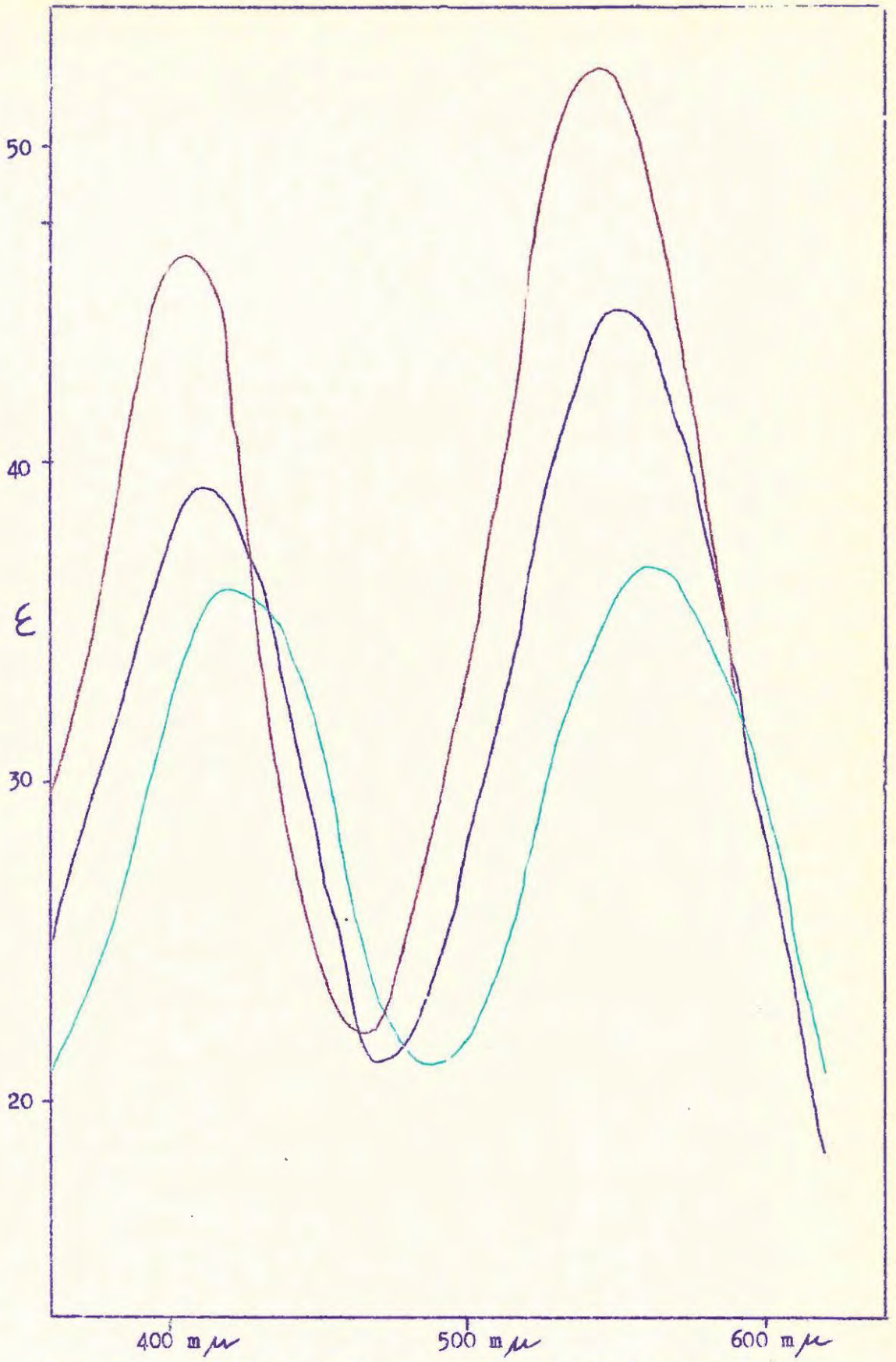

Fig. A.7. .333 molar Chromium Chloride with 6 moles Glycine per gram atom Chromium.

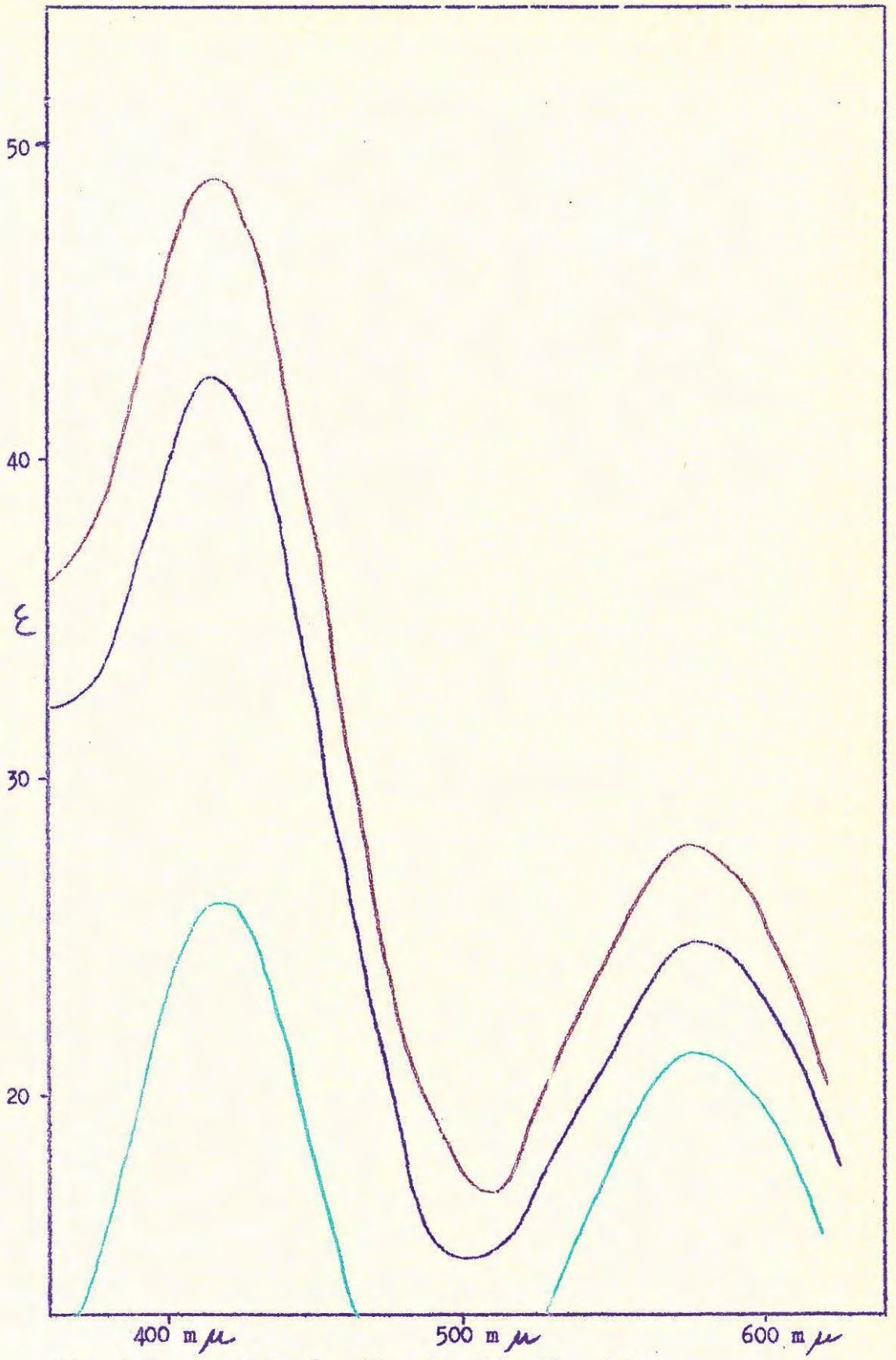

Fig. A.8. .333 molar Chromium Chloride with $\frac{1}{3}$ mole α-amino-n-Butyric Acid per gram atom Chromium.

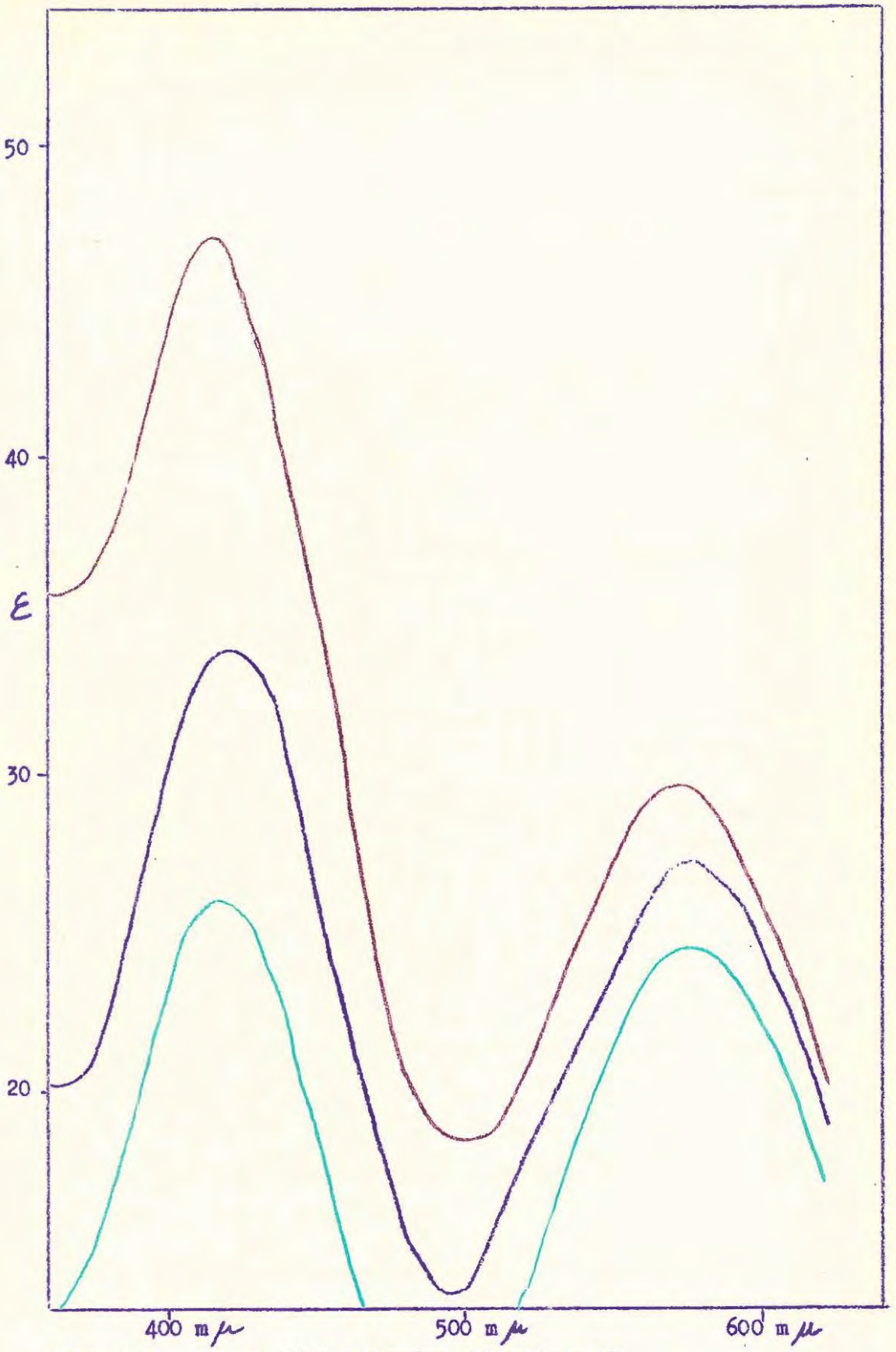

Fig. A.9. .333 molar Chromium Chloride with
1 mole α-amino-n-Butyric Acid per gram atom Chromium.

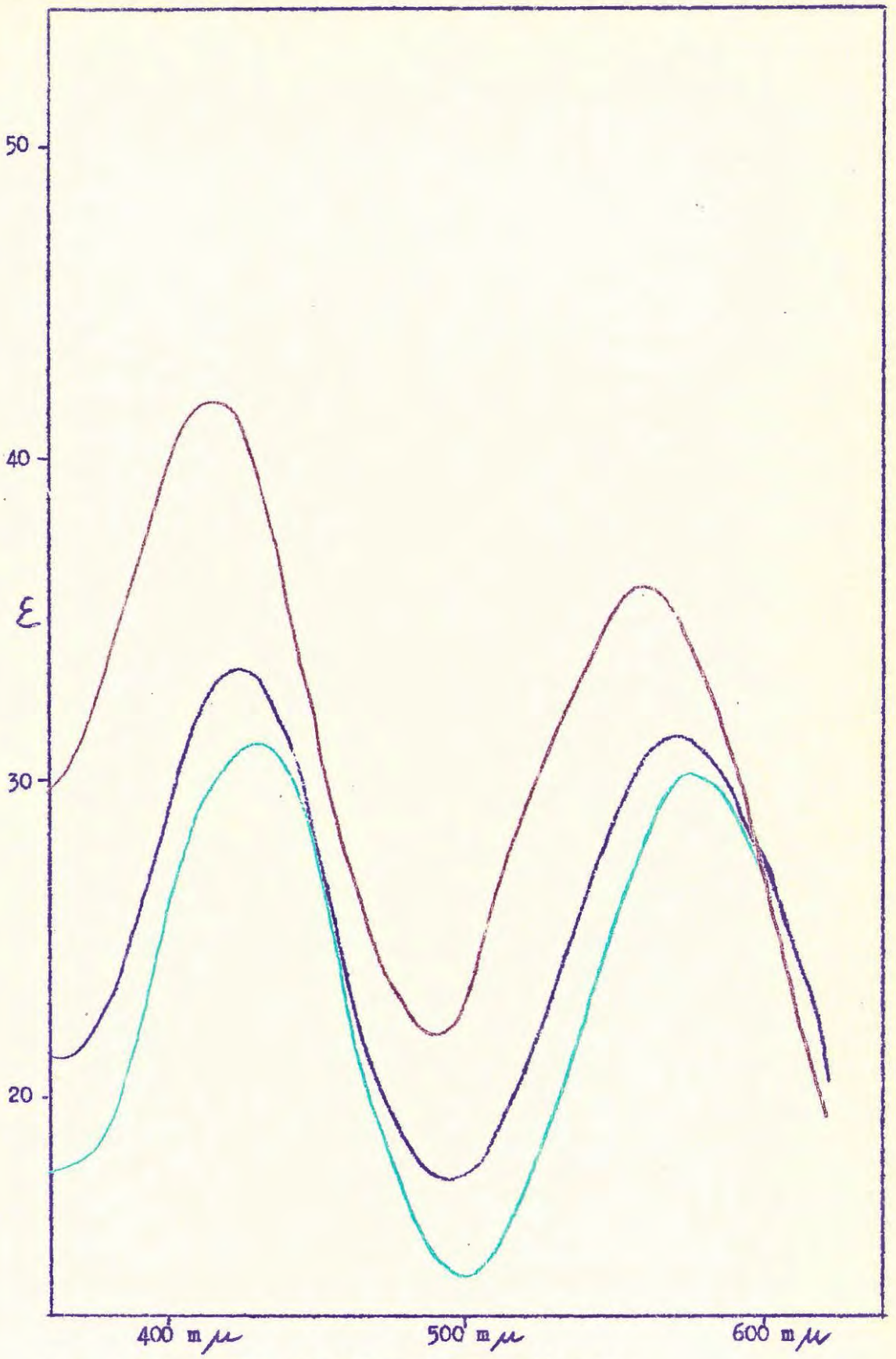

Fig. A.10. .333 molar Chromium Chloride with
2 moles α-amino-n-Butyric Acid per gram atom Chromium.

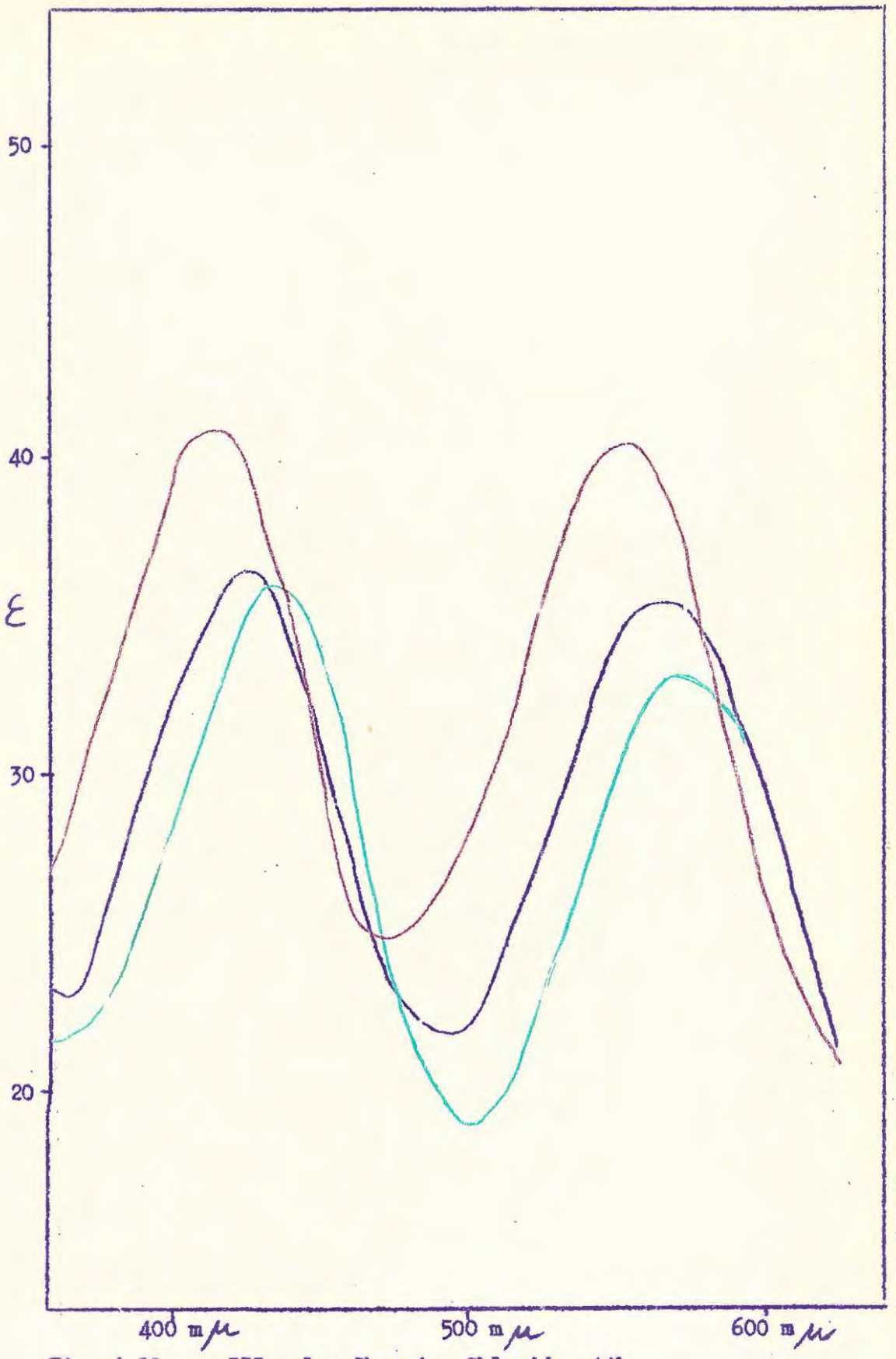

Fig. A.11. .333 molar Chromium Chloride with 3 moles α-amino-n-Butyric Acid per gram atom Chromium.

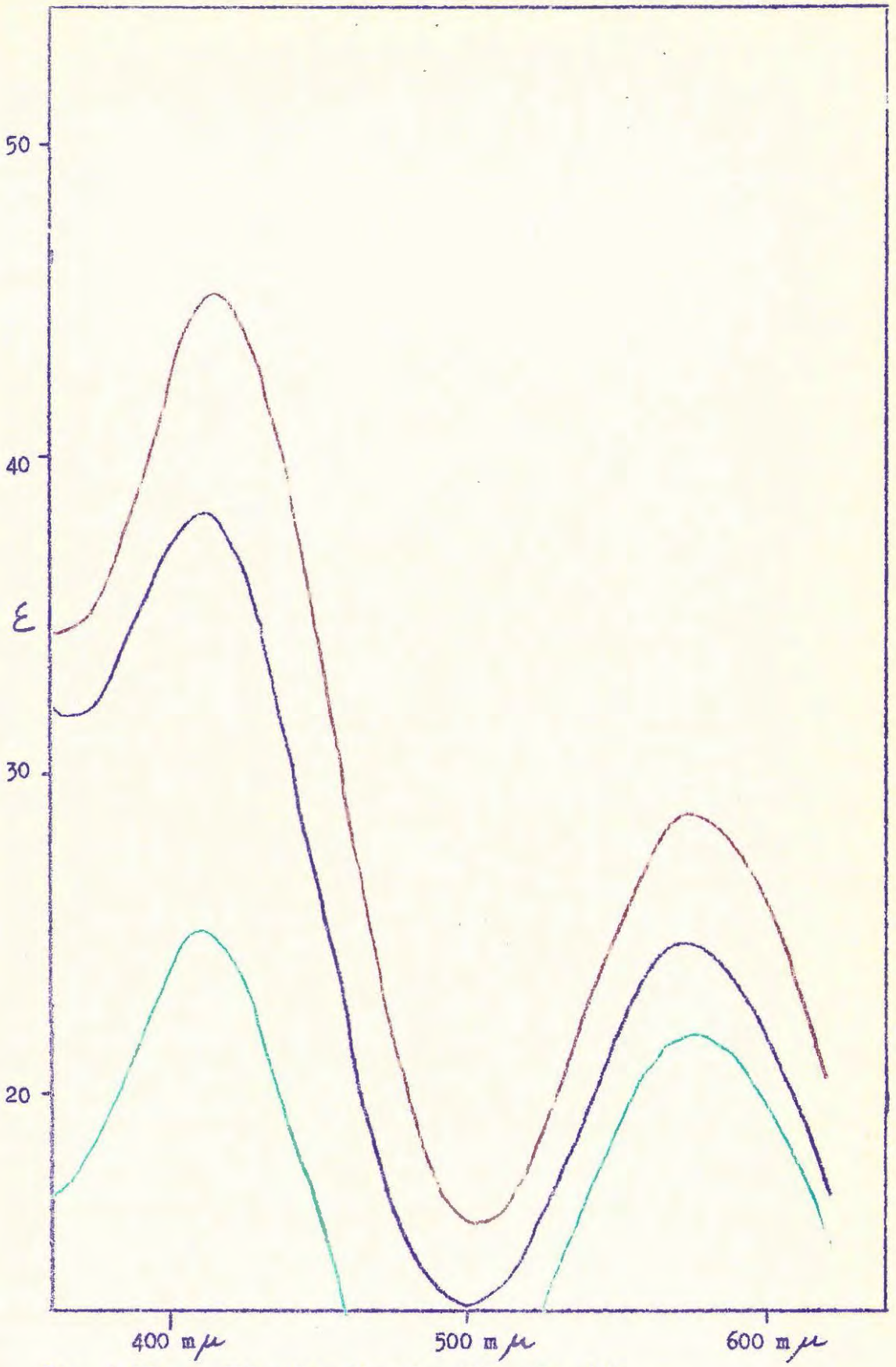

Fig. A.12. .333 molar Chromium Chloride with $\frac{1}{2}$ mole β-amino-n-Butyric Acid per gram atom Chromium.

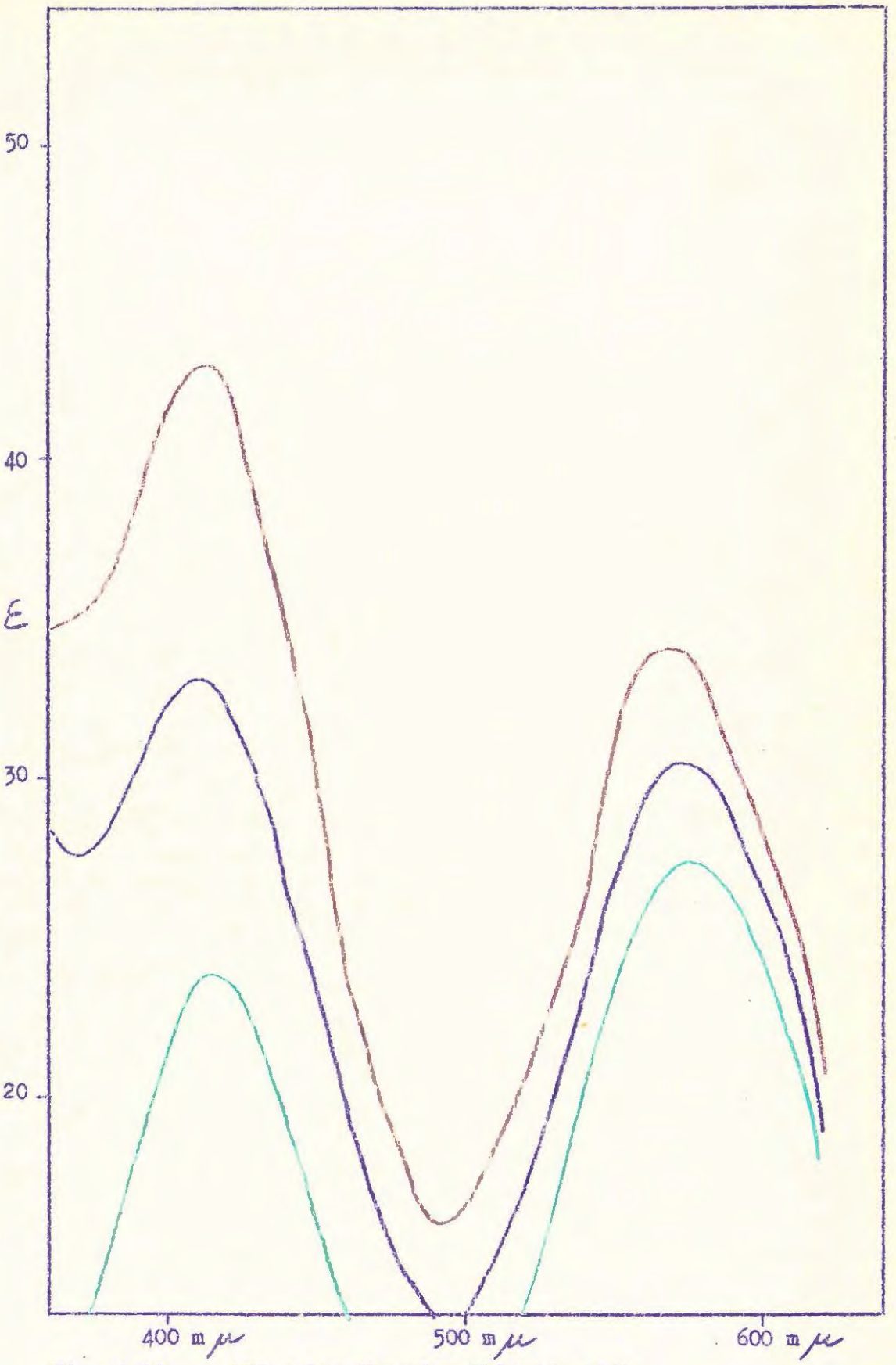

Fig. A.13. .333 molar Chromium Chloride with
1 mole β-amino-n-Butyric Acid per gram atom Chromium.

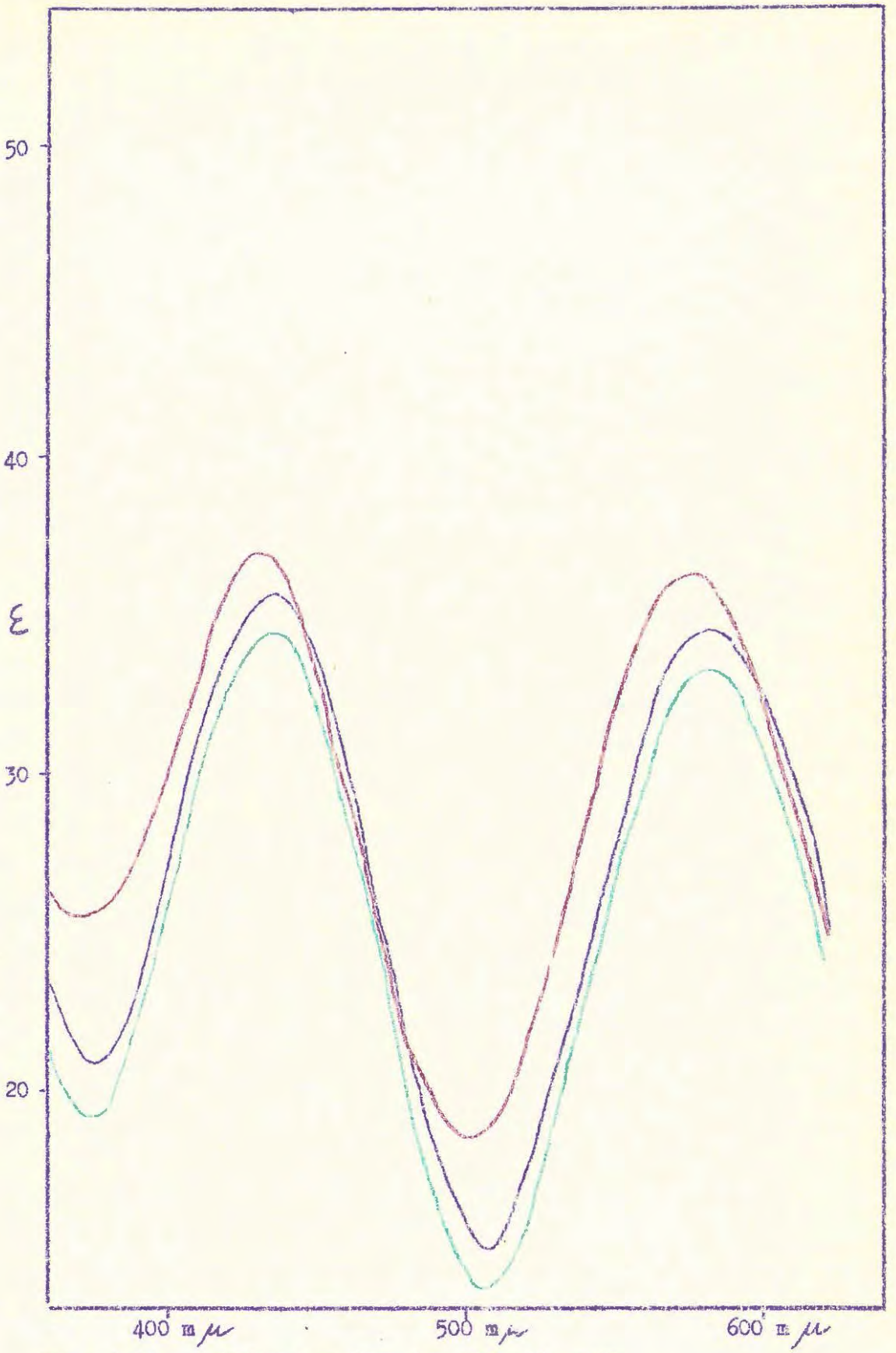

Fig. A.14. .333 molar Chromium Chloride with 2 moles β-amino-n-Butyric Acid per gram atom Chromium.

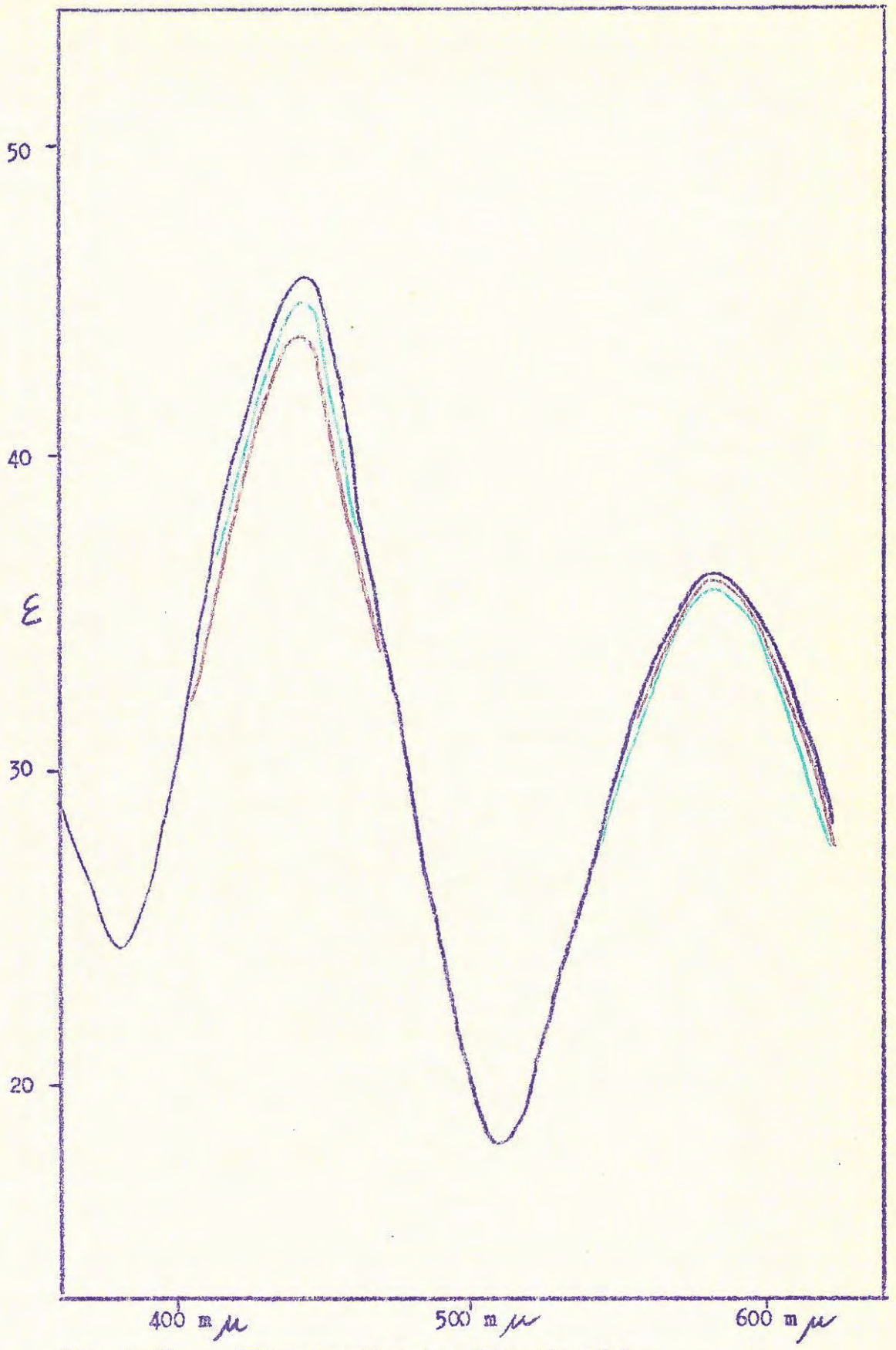

Fig. A.15. .333 molar Chromium Chloride with 3 moles β-amino-n-Butyric Acid per gram atom Chromium.

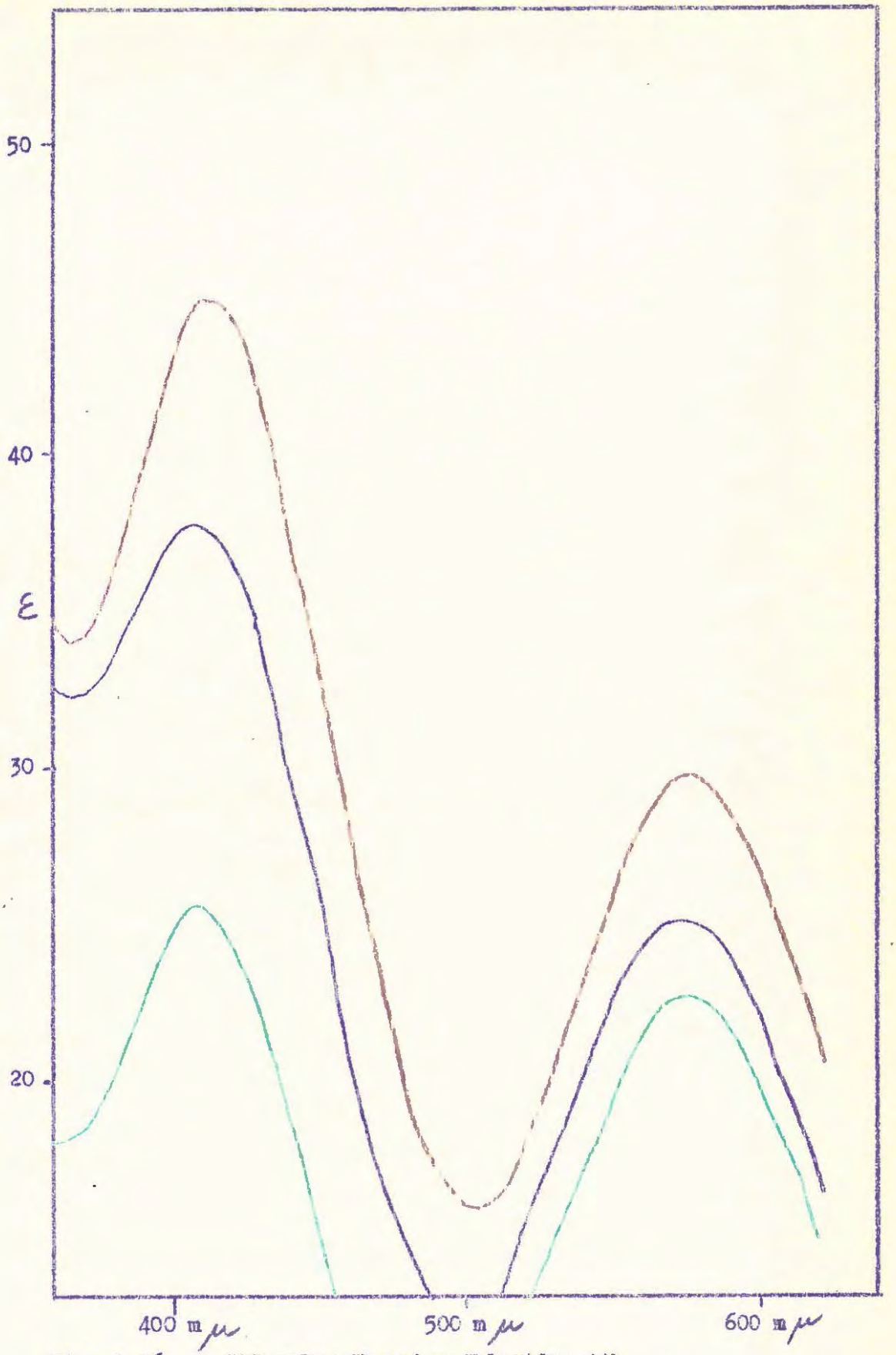

Fig. A.16. .333 molar Chromium Chloride with
½ mole γ -amino-n-Butyric Acid per gram atom Chromium.

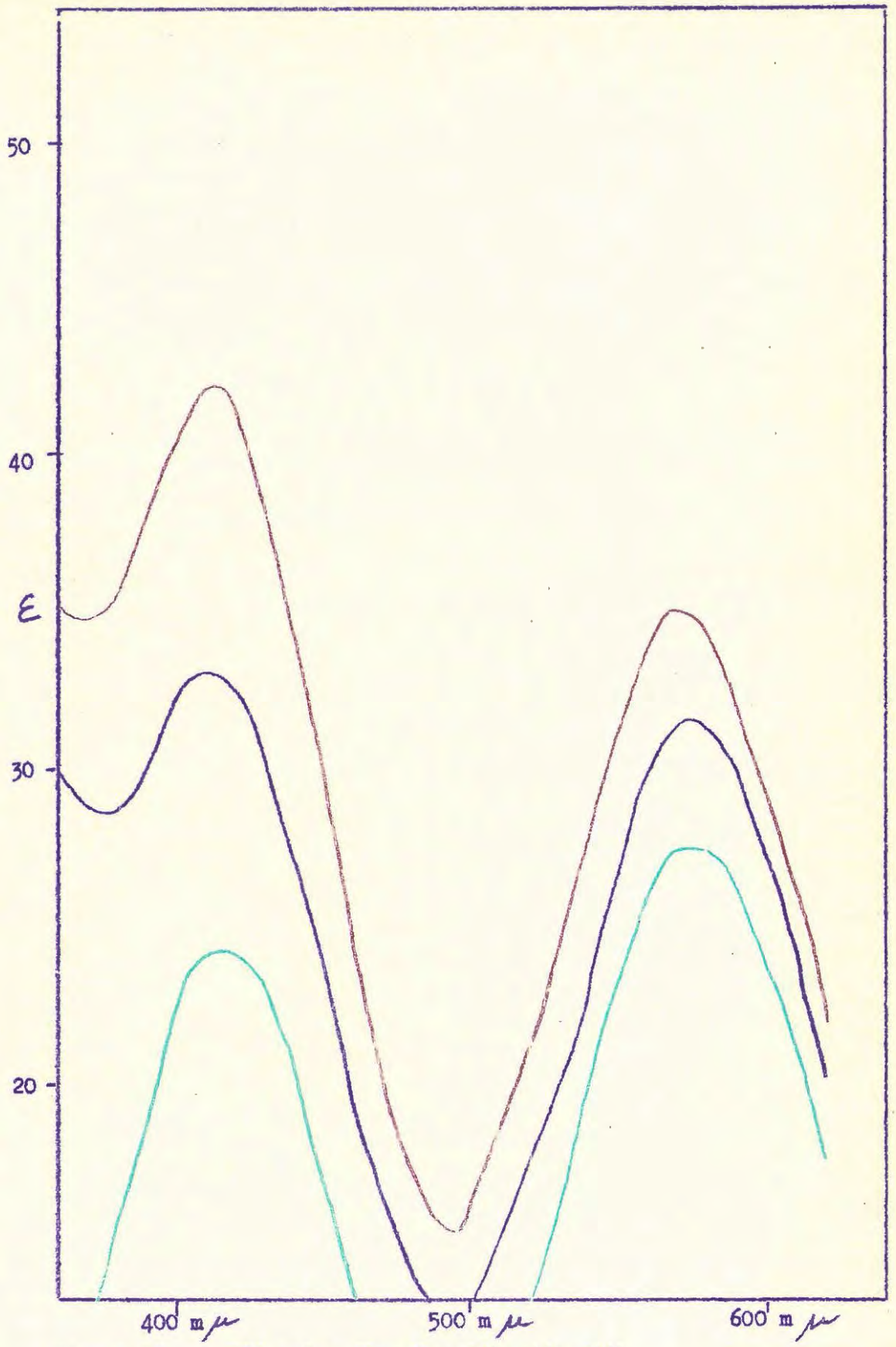

Fig. A.17. .333 molar Chromium Chloride with 1 mole γ-amino-n-Butyric Acid per gram atom Chromium.

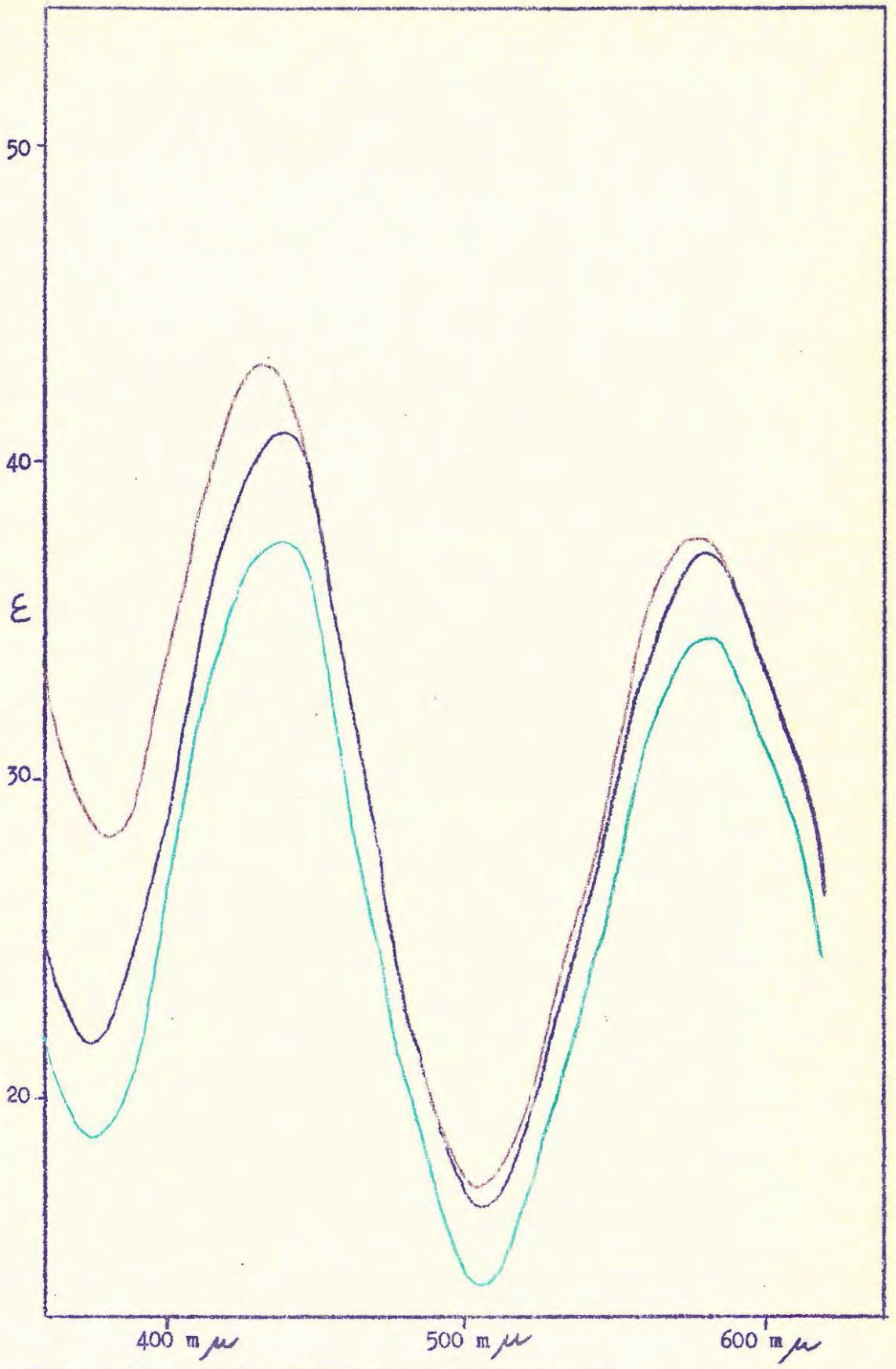

Fig. A.18. .333 molar Chromium Chloride with
2 moles γ-amino-n-Butyric Acid per gram atom Chromium.

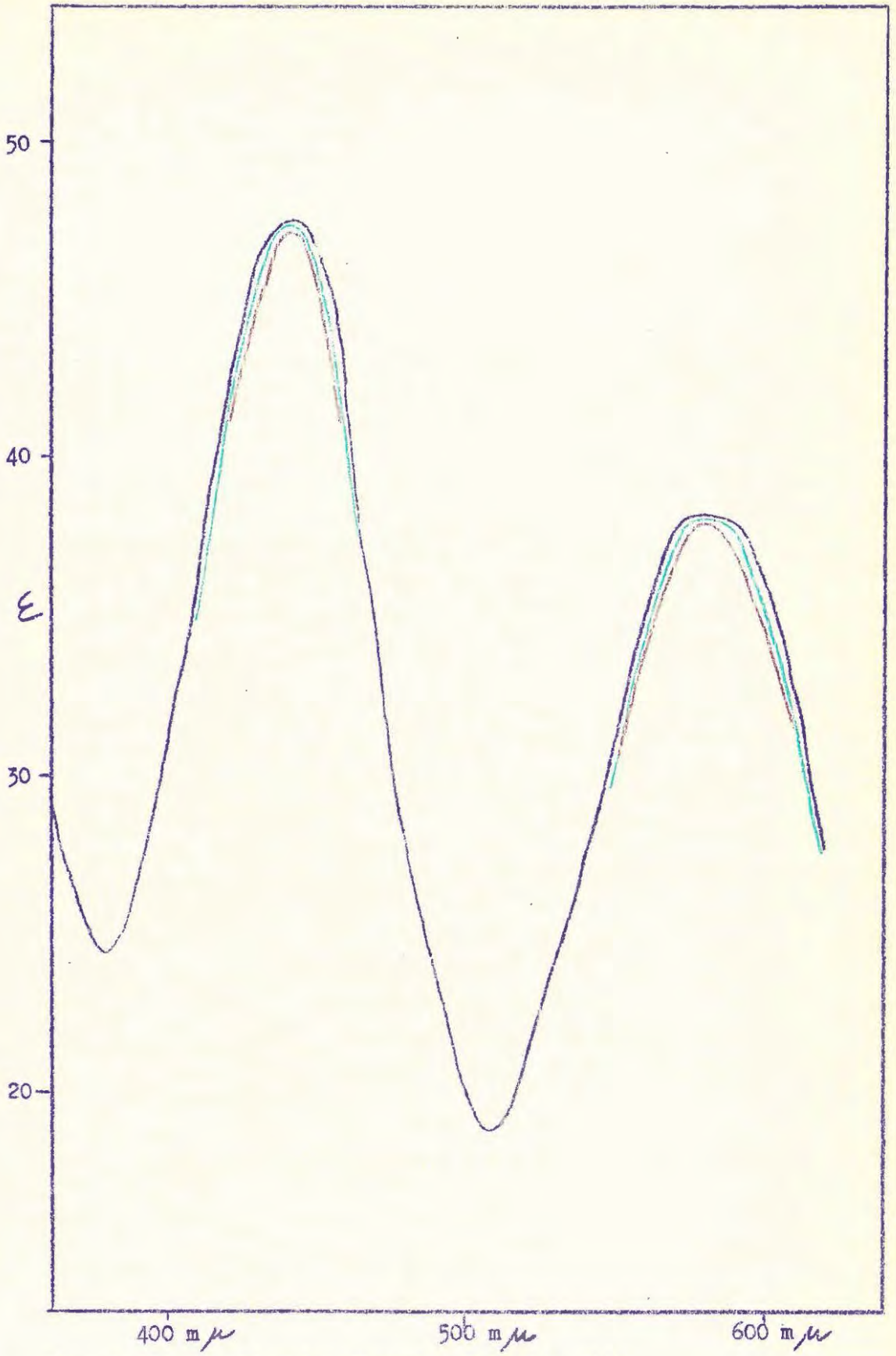

Fig. A.19. .333 molar Chromium Chloride with 3 moles γ-amino-n-Butyric Acid per gram atom Chromium.

APPENDIX B.

Tables B.1 - B.15 give the properties of complexes prepared from chromium chloride and chromium sulphate by adding known quantities of alkali to solutions containing 3 moles of ligand per gram atom of chromium. The final concentration of chromium was 0.333 gram atom per litre.

The following properties are tabulated:

Column 1. Equivalents of KOH added per gram atom of chromium. Zero represents the equivalent of the carboxylic acid salt: negative quantities, a mixture of carboxylic acid and carboxylic acid salt; positive quantities, salt plus added alkali.

2. The pH values of the solutions.

3,4. The wavelength of maximum absorption (λ max), in mμ , and the maximum molar extinction coefficient (ε max) at the blue peak (420 mμ region).

5,6. The corresponding properties of the complexes at the yellow peak (580 mμ region).

7,8. Properties of skin tanned with the complexes: chromium fixation (m.moles of chromium per gram of leather); and increase in shrinkage temperature (Δ Ts^{o}C).

Table T.1.

No Ligand.

24 hours cold reaction.

moles KOH per gram atom Cr.	pH	Blue Peak λ max mμ	Blue Peak ε max	Yellow Peak λ max mμ	Yellow Peak ε max	m.moles Cr per gm leather	ΔTs °C
Chromium Chloride.							
0	2.12	417	18.1	586	14.2	.25	24
.17	3.14	415	18.1	583	14.5	.55	38
.33	3.23	417	19.1	580	15.4	.65	38
.5	3.16	416	20.3	579	16.1	.74	50
.67	3.13	418	21.6	580	16.9	.79	55
.83	3.21	420	23.2	578	18.0	.77	55
1	3.21	422	23.9	580	18.5	.91	52
1.17	3.15	423	25.3	580	19.1	.92	53
1.33	3.18	420	26.5	584	20.0	1.00	54
1.5	3.27	424	27.5	587	20.5	1.04	53
1.67	3.36	424	28.8	587	21.3	1.06	52
1.83	3.75	425	29.0	585	21.5	1.10	52
2	3.61	423	29.3	585	22.6	1.19	51
2.16	4.03	425	30.4	585	24.0	1.42	51
2.33	4.35	420	38.0	584	28.7	1.42	51
Chromium Sulphate.							
0	1.38	410	18.1	581	16.9	.14	12
.17	2.34	415	18.5	582	16.8	.27	20
.33	2.57	413	18.7	583	16.9	.42	30
.5	2.99	413	19.0	580	16.9	.63	36
.67	3.32	414	19.8	580	17.5	.78	48
.83	2.98	420	20.8	582	18.2	.86	50
1	3.21	418	22.1	584	18.7	.93	52
1.17	3.30	422	24.1	585	19.6	1.04	50
1.33	3.38	425	25.1	580	20.6	1.06	51
1.5	3.54	422	26.8	584	20.6	1.16	56
1.67	3.46	423	28.6	585	21.2	1.23	51
1.83	3.56					1.31	52
2	3.70					1.42	52
2.17	3.78					1.44	50
2.33	3.94					1.43	52

Table B.2.

No Ligand.

20 hours heating.

moles KOH per gram atom Cr.	pH	Blue Peak λmax mμ	Blue Peak εmax	Yellow Peak λmax mμ	Yellow Peak εmax	m.moles Cr per gm leather	ΔT_s °C
Chromium Chloride.							
0	1.22	418	18.2	587	14.3	.14	12
.17	1.40	420	19.7	584	15.3	.36	27
.33	1.52	422	20.9	587	15.6	.22	32
.5	1.62	419	21.7	585	16.3	.62	45
.67	1.86	424	23.8	585	17.5	.71	50
.83	1.97	423	25.0	581	18.5	.78	51
1	2.34	424	25.9	586	18.7	.87	51
1.17	2.51	427	26.4	584	18.7	.88	52
1.33	2.61	425	27.6	584	19.6	.74	55
1.5	2.69	425	27.3	588	20.4	.95	54
1.67	2.70	428	27.4	586	20.5	.99	50
1.83	2.74	427	28.7	587	21.6	1.06	51
2	2.46	425	27.1	585	20.8	.99	53
2.17	2.50	425	29.8	584	22.9	1.08	48
2.33	2.62	precipitated.				1.07	49
2.5	2.96						
Chromium Sulphate.							
0	1.04	421	20.1	590	20.5	.24	20
.17	.96	423	20.6	590	21.1	.32	26
.33	1.10	424	20.8	590	21.1	.43	31
.5	1.30	425	20.5	590	21.0	.54	34
.67	1.55	423	21.2	590	21.3	.74	51
.83	1.75	424	21.4	590	21.7	-	-
1	2.16	424	22.0	592	21.6	.91	54
1.17	2.49	426	23.7	591	21.3	1.00	59
1.33	2.66	427	26.1	586	21.6	1.07	53
1.5	2.69	small precipitate.				1.10	52
1.67	2.62					1.02	51
1.83	2.60					1.45	55

Table B.3.

3 moles Acetate per gram atom Chromium.

20 hours heating.

moles KOH per gram atom Cr.	pH	Blue Peak		Yellow Peak		m.moles Cr per gm leather	$\Delta Ts^{0}C$
		λ max mμ	ε max	λ max mμ	ε max		
Chromium Chloride.							
-3.	.62	415	18.7	579	18.7	.05	5
-2.67	.70	414	19.5	577	20.0	.06	10
-2.33	.88	414	19.6	576	21.1	.07	12
-2	1.03	414	20.5	576	22.6	.11	15
-1.67	1.26	417	21.4	576	24.7	.16	21
-1.33	1.50	422	23.6	576	26.7	.20	25
-1	1.78	428	26.6	580	28.2	.23	28
- .67	2.28	436	32.8	583	31.0	.23	31
- .33	3.30	438	38.6	584	32.6	.16	25
0	4.02	430	35.5	575	37.1	.16	22
.33	4.44	421	34.3	570	44.1	.13	19
.67	4.72	416	33.6	568	45.5	.20	18
Chromium Sulphate.							
-3	.87	420	20.8	584	23.2	.13	16
-2.67	.98	421	21.7	585	24.8	.17	17
-2.33	1.16	423	22.1	583	25.7	.22	22
-2	1.33	424	23.3	584	26.8	.27	27
-1.67	1.50	429	25.3	584	28.5	.29	26
-1.33	1.77	430	26.8	584	29.2	.32	30
-1	1.96	436	29.7	584	29.9	.33	35
- .67	2.35	438	33.1	584	31.4	.32	34
- .33	2.82	440	35.0	586	32.3	.32	35
0	3.48	436	36.2	576	34.5	.29	32
.33	3.87	precipitated.				.22	27
.67	4.12					.19	25

Table B.4.

3 moles amino-Acetate per gram atom chromium.

20 hours heating.

moles KOH per gram atom Cr.	pH	Blue Peak		Yellow Peak		m.moles Cr per gm leather	$\Delta Ts^{o}C$
		λmax mμ	εmax	λmax mμ	εmax		
Chromium Chloride.							
0	1.95	415	27.6	568	32.1	.12	18
.33	2.26	414	28.6	568	33.6	.18	23
.67	2.54	413	30.1	562	35.8	.27	26
1	2.85	411	32.2	555	38.3	.32	30
1.33	3.24	409	34.3	554	40.7	.40	31
1.67	3.85	408	37.5	551	43.3	.53	35
2	4.35	405	40.0	547	44.0	.63	36
2.33	4.74	405	41.3	547	43.0	.62	35
2.67	5.13	precipitated.					
3	8.61						
3.33	9.13						
3.67	9.63						
Chromium Sulphate.							
0	2.13	424	28.3	573	31.5	.16	19
.33	2.37	421	29.3	572	33.1	.13	21
.67	2.64	418	30.7	565	35.4	.23	27
1	2.90	416	32.1	560	37.5	.28	28
1.33	3.27	412	34.1	555	40.1	.36	38
1.67	3.66	412	36.2	552	42.9	.35	48
2	4.09	408	39.9	551	44.0	.43	35
2.33	4.62)					.41	32
2.67	5.00)	ppt. on dilution				.64	30
3	5.53	precipitated.					
3.33	5.73						
3.67	9.06						

Table B.6.

3 moles amino-Acetate per gram atom chromium.

1 hour heating.

moles KOH per gram atom Cr.	pH	Blue Peak		Yellow Peak	
		λ max mμ	ε max	λ max mμ	ε max
Chromium Chloride.					
0	1.90	416	27.4	568	31.9
.33	2.21	416	28.7	566	33.6
.67	2.27	416	29.0	565	34.0
1	2.83	413	31.7	557	37.5
1.33	3.30	410	34.0	553	40.2
1.67	3.84	406	37.4	548	42.8
2	4.51	405	41.9	546	45.0
2.33	4.96	404	45.9	547	46.5
2.67	5.54	401	50.3	544	48.7
3	6.56	precipitated.			
3.33	8.97				
3.67	9.32				

Table B.7.

3 moles hydroxy-Acetate per gram atom chromium.

20 hours heating.

moles KOH per gram atom Cr.	pH	Blue Peak λmax mμ	Blue Peak εmax	Yellow Peak λmax mμ	Yellow Peak εmax	m.moles Cr per gm leather	ΔTs°C
Chromium Chloride.							
0	3.94	430	25.4	578	22.7	.24	25
.33	4.23	432	26.4	580	23.0	.19	24
.67	4.76	434	26.4	586	22.6	.13	20
1	6.88	436	26.7	590	22.0	.05	6
1.33	8.60	428	26.9	594	17.2	.04	2
1.67	10.80	Gelled					
2	12.59						
2.33	12.43						
2.67	12.71						
3	12.06						
3.33	12.38						
3.67	12.29						
Chromium Sulphate.							
0	2.70	420	42.0	570	43.2	.39	38
.33	2.90	423	44.2	570	44.6	.44	44
.67	3.15	428	45.6	572	44.6	.44	46
1	3.38	426	47.2	577	44.4	.43	47
1.33	3.68	427	50.0	580	44.8	.38	39
1.67	4.06	429	52.5	585	44.8	.46	37
2	4.62	429	53.2	589	44.3	.42	32
2.33	5.92	430	55.3	592	44.3	.21	19
2.67	6.70	429	55.7	593	43.7	.07	9
3	7.64	426	49.3	590	38.7	.11	6
3.37	9.94	precipitated					
3.67	11.78						

Table B.8.

3 moles chloro-Acetate per gram atom chromium.

24 hours cold reaction.

moles KOH per gram atom Cr.	pH	Blue Peak		Yellow Peak		m.moles Cr per gm leather	$\Delta Ts^{o}C$
		λmax mμ	εmax	λmax mμ	εmax		
Chromium Chloride.							
-3	.87	415	17.4	584	15.1	.04	1
-2.67	1.13	416	17.6	584	15.4	.04	5
-2.33	1.49	415	18.0	582	16.1	.07	7
-2	1.72	413	18.5	580	16.9	.09	15
-1.67	1.98	416	18.9	584	17.9	.15	23
-1.33	2.19	415	19.4	580	18.7	.19	29
-1	2.40	417	20.0	575	19.6	.25	31
- .67	2.66	417	20.7	575	21.2	.36	41
- .33	2.86	416	21.8	574	23.6	.44	49
0	3.05	415	24.1	571	28.1	.68	54
.33	3.13	415	26.1	574	32.8	.69	51
.67	3.40	417	27.4	572	35.6	.90	47
1	3.67	417	27.9	570	36.2	1.09	52
Chromium Sulphate.							
-3	.98	412	17.8	580	17.3	.06	3
-2.67	1.20	412	18.4	577	17.9	-	2
-2.33	1.46	412	18.6	577	18.4	.09	12
-2	1.68	412	19.3	577	19.1	.15	15
-1.67	1.96	413	19.1	576	19.0	.19	24
-1.33	2.14	412	19.7	575	19.9	.26	27
-1	2.32	412	20.3	576	20.6	.35	31
- .67	2.55	412	21.7	574	23.0	.43	37
- .33	2.74	412	22.2	572	24.1	.53	51
0	2.95	414	22.9	575	25.9	.64	53
.33	3.12	415	23.8	573	27.8	.72	54
.67	3.34	415	25.1	573	30.8	.94	53
1	3.51	417	30.8	573	38.9	.98	50

Table B.9.

3 moles Bromo-Acetate per gram atom chromium.

24 hours cold reaction.

moles KOH per gram atom Cr.	pH	Blue Peak		Yellow Peak		m.moles Cr per gm leather	$\Delta Ts^{o}C$
		λmax mμ	εmax	λmax mμ	εmax		
Chromium Chloride.							
-3	.98	417	17.4	583	14.9	.04	2
-2.67	1.22	417	17.6	584	15.4	.06	1
-2.33	1.52	416	17.9	585	16.1	.08	10
-2	1.77	416	18.4	584	16.8	-	14
-1.67	2.01	416	19.0	580	17.8	.26	24
-1.33	2.22	415	19.5	579	18.8	.33	31
-1	2.44	414	20.3	577	20.3	.47	34
- .67	2.66	414	21.1	576	21.7	.56	37
- .33	2.86	small precipitate				.68	46
0	3.04					.77	54
.33	3.18					.90	50
.67	3.44					.95	55
1	3.76					1.10	56
Chromium Sulphate.							
-3	1.01	412	18.4	579	17.7		
-2.67	1.25	412	18.6	578	18.1		
-2.33	1.50	412	19.1	578	18.9		
-2	1.73	412	19.8	577	19.7		
-1.67	1.98	413	20.4	574	20.3		
-1.33	2.21	413	20.9	573	21.5		
-1	2.39	412	21.6	575	22.9		
- .67	2.62	412	22.2	574	23.6		
- .33	2.81	413	22.3	572	24.2		
0	3.07	precipitated					
.33	3.24						
.67	3.40						
1	3.61						

Table B.10.

3 moles Propionate per gram atom chromium.

20 hours heating.

moles KOH per gram atom Cr.	pH	Blue Peak		Yellow Peak		m.moles Cr per gm leather	$\Delta Ts^{o}C$
		λmax mμ	εmax	λmax mμ	εmax		
Chromium Chloride.							
-3	.63	416	19.9	576	19.7	.04	3
-2.67	.67	416	20.6	580	21.4	.05	3
-2.33	.82	416	21.4	574	22.4	.05	5
-2	.98	416	22.0	574	24.0	.09	12
-1.67	1.28	418	23.3	576	25.9	.14	16
-1.33	1.52	422	26.0	580	28.1	.13	20
-1	1.75	430	29.4	580	30.4	.22	22
- .67	2.05	434	34.3	584	32.7	.23	27
- .33	2.42	precipitated					
0	3.98						
.33	4.67						
.67	5.18						
1	5.57						
Chromium Sulphate.							
-3	.78	420	22.0	580	24.1	.10	11
-2.67	1.05	422	22.4	584	25.1	.11	16
-2.33	1.16	422	24.0	584	27.8	.14	22
-2	1.25	424	24.4	580	28.1	.19	23
-1.67	1.47	428	26.1	582	29.3	.25	27
-1.33	1.67	430	28.1	584	31.6	.25	33
-1	1.94	436	30.6	584	30.7	.26	33
- .67	2.32	436	33.6	584	32.6	.29	35
- .33	3.00	436	37.2	584	34.1	.31	36
0	3.50	precipitated					
.33	3.92						
.67	4.76						
1	5.10						

Table B.11.

3 moles α -amino - propionate

20 hours heating.

moles KOH per gram atom Cr.	pH	Blue Peak λmax mμ	Blue Peak εmax	Yellow Peak λmax mμ	Yellow Peak εmax	m.moles Cr per gm leather	ΔTs °C
Chromium Chloride.							
0	1.83	420	27.8	572	30.7	.16	16
.33	2.07	420	30.1	568	33.7	.21	22
.67	2.51	416	31.5	564	36.0	.28	24
1	2.79	412	32.4	556	37.6	.36	30
1.33	3.32	410	35.9	551	41.3	.60	31
1.67	3.93	406	39.0	548	43.6	.52	33
2	4.59	402	43.5	544	45.4	.75	35
2.33	5.06	402	45.8	542	45.6	.69	35
2.67	5.52	precipitated					
3	7.64						
3.33	10.00						
3.67	10.08						
4	10.42						
Chromium Sulphate.							
0	2.14	430	33.9	576	34.6	.13	17
.33	2.44	428	31.4	570	33.1	.17	13
.67	2.70	420	32.4	568	35.3	.23	23
1	2.94	416	33.7	560	37.9	.31	31
1.33	3.23	414	35.2	554	40.7	.38	30
1.67	3.56	412	37.9	552	44.4	.44	44
2	4.14	408	41.0	546	46.0	.47	37
2.33	4.59	404	46.5	544	47.3	.47	36
2.67	4.98	404	48.5	540	46.7	.42	31
3	5.58	400	50.8	540	45.8	.38	29
3.33	6.10	precipitated					
3.67	8.33						
4	9.68						

Table B.12.

3 moles β - amino - propionate per gram atom chromium.

20 hours heating.

moles KOH per gram atom Cr.	pH	Blue Peak		Yellow Peak		m.moles Cr per gm leather	ΔTs °C
		λ max mμ	ε max	λ max mμ	ε max		
Chromium Chloride.							
0	3.06	436	33.8	582	33.7	.13	18
.33	3.34	434	32.3	578	34.9	.18	22
.67	3.76	430	31.5	578	37.9	.17	24
1	3.97	420	30.0	568	38.8	-	23
1.33	4.32	416	30.0	566	40.7	.18	21
1.67	4.77	414	30.3	564	40.5	.16	20
2	5.01	416	30.0	568	36.6	.15	19
2.33	5.28	416	30.4	568	34.5	.16	15
2.67	5.96	418	31.5	576	33.6	.13	13
3	8.52	precipitated					
3.33	9.38						
3.67	9.90						
4	10.20						
Chromium Sulphate.							
0	3.06	440	38.7	590	35.6	.15	18
.33	3.30	440	34.4	584	33.7	.19	24
.67	3.66	436	33.7	580	35.6	.23	26
1	3.96	430	32.5	576	37.9	.26	26
1.33	4.26	424	32.3	568	40.6	.30	25
1.67	4.50	416	33.1	568	42.8	.35	24
2	4.76	416	34.3	566	42.7	.48	24
2.33	4.95	416	34.5	566	38.8	.63	21
2.67	5.25	420	35.1	570	34.5	.80	15
3	5.64	precipitated					
3.33	7.18						
3.67	9.21						
4	10.04						

Table B.13.

3 moles α-hydroxy - Propionate per gram atom chromium.

20 hours heating.

moles KOH per gram atom Cr.	pH	Blue Peak λmax mμ	Blue Peak εmax	Yellow Peak λmax mμ	Yellow Peak εmax	m.moles Cr per gm leather	Δ Ts°C
Chromium Chloride.							
-1	1.19	428	38.2	576	33.5	.08	9
- .67	1.47	430	40.5	576	34.9	.07	10
- .33	1.84	434	43.0	582	36.6	.09	7
0	2.60	430	44.6	576	39.8	.12	14
.33	3.07	428	47.9	570	45.2	.17	20
.67	3.33	426	51.1	568	50.1	.18	24
1	3.67	424	51.4	566	51.7	.23	23
1.33	4.18	424	51.2	560	51.4	.23	29
1.67	4.67	426	52.9	568	53.2	.25	26
2	4.90	428	55.5	570	55.1	.26	28
2.33	5.89	430	50.4	576	51.3	.24	27
2.67	6.78	432	50.7	584	53.2	.16	14
3	6.86	430	44.3	588	46.4	.09	8
Chromium Sulphate.							
-1	1.62	428	38.4	576	33.8	.10	11
- .67	1.92	428	39.8	576	35.3	.10	14
- .33	2.18	428	42.1	576	37.8	.13	15
0	2.50	428	44.4	574	40.7	.14	17
.33	2.82	426	46.5	570	43.6	.17	19
.67	3.10	424	49.2	580	47.3	.20	23
1	3.36	422	51.6	568	50.2	.25	26
1.33	3.80	422	53.2	570	52.7	.27	27
1.67	4.04	424	54.1	568	54.0	.27	30
2	4.26	424	55.8	568	54.0	precipitated	
2.33	4.84	426	56.2	570	55.4		
2.67	5.35	428	56.3	576	58.4		
3	6.16	432	54.0	584	53.6		

Table B.14.

3 moles α-Bromo - propionate per gram atom of chromium.

20 hours heating.

moles KOH per gram atom Cr.	pH	Blue Peak λmax mμ	Blue Peak εmax	Yellow Peak λmax mμ	Yellow Peak εmax	m.moles Cr per gm leather	$\Delta Ts^{o}C$
Chromium Chloride.							
0	.54	420	28.8	568	24.6	—	—
.33	.62	420	30.4	566	26.4		
.67	.76	420	31.1	568	27.8		
1	.92	424	32.3	568	29.2		
1.33	1.11	424	34.2	568	30.8		
1.67	1.33	428	36.0	574	32.5		
2	1.65	432	38.4	576	34.0		
2.33	2.09	434	41.0	580	35.7		
2.67	2.81	429	43.6	576	40.2		
3	3.61	424	49.4	568	50.8		
3.33	3.24	426	49.5	574	48.7		
3.67	4.10	426	49.7	572	51.8		
4	4.73	428	50.5	574	51.4		

Table B.15.

3 moles β-Bromo - propionate per gram atom of chromium.

20 hours heating.

moles KOH per gram atom Cr.	pH	Blue Peak		Yellow Peak		m.moles Cr per gm leather	$\Delta Ts^{o}C$
		λ max mμ	ε max	λ max mμ	ε max		
Chromium Chloride.							
0	.49	416	20.6	578	20.4	—	—
.33	.21	416	21.1	578	21.7		
.67	.72	416	22.0	574	23.3		
1	.88	416	22.7	575	24.7		
1.33	.82	418	23.9	574	26.6		
1.67	1.08	424	26.3	576	28.9		
2	1.45	428	29.3	576	30.7		
2.33	1.98	434	33.8	580	32.9		
2.67	3.28	438	39.8	582	35.3		
3	4.04	432	35.5	576	38.2		
3.33	4.38	426	33.7	568	41.9		
3.67	4.79	422	33.0	566	44.6		
4	5.45	424	33.1	568	43.4		