SOME ASPECTS OF THE CHEMISTRY OF ZIRCONIUM COMPOUNDS RELATING TO THEIR COMBINATION WITH COLLAGEN.

by

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SUMMARY

Some properties of zirconium compounds in aqueous solution have been determined using physico-chemical techniques. Zirconium oxychloride was used as the source of zirconium in all detailed investigations; zirconium sulphate was used in a few cases for comparative purposes.

The Stokes diaphragm cell method has been used to determine the diffusion coefficient of zirconium in hydrochloric acid solution. It was found that the diffusion coefficient fell progressively with time, a limiting value being reached 4 to 5 weeks after dissolving the salt, and it was demonstrated that particles in the aged solutions were more homogeneous than in freshly prepared solutions. The limiting values were concentration dependent; dilute solutions had a lower diffusion coefficient than the more concentrated solutions when measured at the natural pH. In the presence of added acid the rate of diffusion was increased until a limiting value was reached in 0.5 M acid. The addition of alkali or complexing acids reduced the rate of diffusion.

Since the rate of diffusion is related to the size of the particle, approximate values for the radius, particle weight, and degree of polymerisation can be determined. The limiting value of 3.2 for the degree of polymerisation in 0.5 to 2 M hydrochloric acid confirms the results from ultracentrifuge and complex formation studies which indicate that the zirconium is either a trimer or tetramer. At acid concentrations below 0.2 M, zirconium is more highly polymerised, and the average degree of polymerisation in solutions of maximum basicity is about 30.

Potentiometric titration curves of zirconium in the presence of various organic reagents revealed that weak coordinate bonds are formed between carboxyl groups and zirconium oxychloride, but no coordination could be detected in sulphate solutions. There was no evidence of a coordination reaction between zirconium and amino groups.

Paper electrophoresis measurements showed that in the presence of hydroxy acids the electronegativity of the zirconium was increased and high pH conditions favoured the formation of anionic complexes.

An investigation of practical applications showed that the rate of diffusion of small particles into hide is greater than that of the large molecular weight species. A comparison of the rate of penetration of zirconium sulphate and zirconium oxychloride showed that under similar conditions of acidity and concentration zirconium sulphate always diffused more slowly into hide, but the rate of penetration was also dependent on solution conditions. It is therefore reasonable to conclude that the rate of penetration is dependent on the particle size. Application of this result enabled complete penetration of hide to be effected with smaller amounts of zirconium than has previously been possible.

Significant deductions with regard to the mechanism of the reaction between zirconium and collagen have been made from the results of potentiometry and electrophoresis measurements in the presence of model substances containing the reactive groups which are present in hide protein. It is concluded that under normal conditions of tannage no coordination reactions occur with either the carboxyl groups or the amino groups, tannage probably being effected by reactions involving residual valency forces. Since the most stable tannage is obtained with anionic zirconium, the increased hydrothermal stability using these compounds may be due to either increased stability of the zirconium to zirconium bridge by ring formation, or reinforcement due to electrovalent bonds with positively charged basic groups on the hide protein.

Since the work in this thesis required a large number of zirconium determinations to be made, a rapid accurate analytical method was developed which gave accurate and reproducible results over a wide range of zirconium concentrations and in the presence of other cations and anions.

CHAPTER 1.

INTRODUCTION

During the manufacture of leather, the fibrous skin protein, collagen, is tanned by irreversible combination with the tanning agent, which imparts certain characteristic properties to the collagen. Criteria of tannage are, for example, resistance to putrefaction, increase in hydrothermal stability, and the retention of the fibrous structure. These are discussed in detail by Lollar(1). Numerous substances of greatly differing chemical nature can function as tanning agents. Three well defined types of tanning reactions have been established: a) reactions involving coordination, e.g., chromium tannage; b) reactions involving covalent crosslinking, e.g., aldehyde tannage; and c) reactions involving linkages of a more general character, usually hydrogen bonding or van der Waals' forces, e.g., vegetable tannage. In addition a fourth type of reaction can occur involving salt links between oppositely charged groups, but no conclusive example of this type has yet been given.

The extensive use of mineral salts as tanning agents for the manufacture of leather was introduced comparatively recently,(2) although aluminium has been used as a pseudo tanning or "tawing" material for centuries(3). Of the mineral salts that are known to have tanning ability, chromium sulphate is the most extensively used, and for this reason chromium has been used in the majority of the investigations of the chemistry of mineral tanning(4-8). The other mineral tanning materials are dealt with less fully in the literature(9,10). Zirconium is the most recent of the mineral tanning materials to find commercial application, although its affinity for collagen had been discovered as early as 1907(11). The first patent for its use as a tanning agent was granted in 1933(12), and other patents followed(13-19), but it was not until the early 1940's that extensive practical use was made of this material.

The general chemistry of zirconium has been investigated fairly extensively and has recently been reviewed by Blumenthal(20), but most of the published literature relating to tanning with zirconium is of a practical nature, and this has been reviewed by Somerville(9) and Williams-Wynn(21). Several mechanisms have been proposed to explain the reaction of zirconium with collagen, and these may be divided into two groups: those that postulate that the process is one of deposition and adsorption, and those that assume chemical combination between the metal ion, usually a complex ion, and the collagen. The latter is the more generally accepted theory, but opinions differ as to the nature of the combination and the groups of collagen involved, since zirconium does not seem to fall exclusively into either of the above categories. For present ideas to be improved and extended, more fundamental knowledge of the properties of zirconium coordination compounds and the conditions of complex formation is required. Some aspects of the chemistry of zirconium compounds relating to tanning have been investigated, but before dealing with the results of the present work, a review of the chemistry of zirconium will be given.

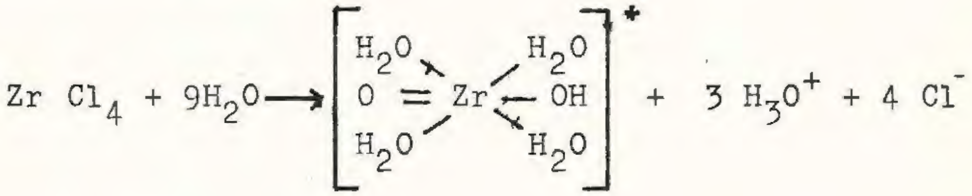
a) General Chemistry of Zirconium

The chemistry of zirconium has been investigated fairly extensively, and the work summarised by Venable(22) and by Blumenthal(20,23). Zirconium has a normal valency of 4 and may realise valencies up to 8 by coordination. Valencies of 3 and 2 are known, but zirconium occurs in its compounds almost exclusively as a quadrivalent element. It does not form the simple monatomic ion, although it may constitute part of ions or charged colloidal particles.

Hydrolysis

Although the Zr^{4+} ion has been reported(24) it is generally accepted that the quadrivalent zirconium ion does not exist in aqueous solution. Even in strongly acid solutions the zirconyl ion, ZrO^{2+}, is formed, which is very stable and remains unaltered over a wide range of solution conditions. Blumenthal(25) suggests the following mechanism: when anhydrous zirconium tetrachloride is dissolved in water, hydration and hydrolysis occur with the formation of the zirconyl ion. Hydration proceeds still further, and ultimately the zirconium atom becomes associated by covalent bonds with the maximum number of atoms or groups that the geometry of the zirconium atom and its ligands permits.

Under these conditions it is calculated that the zirconium atom attains a coordination number of 7, and the over-all reaction of zirconium tetrachloride with water can be represented by the equation:



$$\mathrm{Zr\ Cl_4} + 9\mathrm{H_2O} \longrightarrow \left[\begin{array}{ccc} \mathrm{H_2O} & & \mathrm{H_2O} \\ \mathrm{O} = & \mathrm{Zr} & \leftarrow \mathrm{OH} \\ \mathrm{H_2O} & & \mathrm{H_2O} \end{array}\right]^{+} + 3\,\mathrm{H_3O^+} + 4\,\mathrm{Cl^-}$$

X-ray analysis of solid zirconium oxychloride showed that there were no zirconium halogen bonds(26), and in aqueous solution any chlorine that was attached to zirconium is displaced by water or hydroxyl groups, and the zirconium exists in solution as a polyatomic cation. This is in direct contrast to the reaction of zirconium sulphate in water. Blumenthal(23) has suggested that whilst this salt is also hydrated, the sulphate radical is not displaced because it is bonded to zirconium through oxygen, and hydrogen ions are liberated with the formation of anionic zirconium. However, this is an over-simplification of the reaction, since cationic and nonionic complexes have been found in zirconium sulphate solution, see following section.

Ionic nature of zirconium complexes

The charge of the zirconium complex has been studied by a number of workers using ion exchange resins and electrophoresis techniques, but ion exchange methods are of doubtful accuracy because of hydrolysis effects and displacement of the equilibrium. Lasserre$^{(27)}$ noted different reactions between zirconium sulphate solutions prepared at the boil and solutions prepared at room temperature, when these were passed through ion exchange resins. She found that the zirconium was mainly cationic in solutions prepared at room temperature, but not in the solutions prepared at the boil. Using resin columns, Ranganathan and Reed$^{(28)}$ determined the relative proportions of cationic, anionic, and uncharged zirconium in solutions of zirconium sulphate complexed with varying amounts of citrate. Their results showed that an increase in the citrate concentration raised the proportion of anionic zirconium present in the solution. This was confirmed by the results of their electrophoresis experiments. In freshly prepared sulphate solutions at pH 2.07, the zirconium was mainly nonionic with a small proportion of cationic zirconium present. On the other hand, Portes$^{(29)}$ found that basic zirconium sulphate was predominantly anionic below pH 3.0 and cationic above, while zirconium oxychloride was cationic over the whole pH range 2.0 to 7.0! In the presence of acetic, formic, and lactic acids, the complexes became more electronegative, confirming the observations by Ranganathan and Reed on the effect of citrate complexing. The electronegativity of zirconium organic acid complexes is again demonstrated by one acetate compound reported by Blumenthal$^{(23)}$, formula $H_2.ZrO_2.(C_2H_3O_2)_2$, which was unaffected on passing through a cation exchanger. Lister and McDonald$^{(30)}$ came to the conclusion that in hydrochloric acid solution a complex equilibrium system exists involving cationic, anionic, and uncharged species. Electromigration experiments showed very little migration in either direction, possibly indicating that uncharged species predominated. In sulphuric acid solution, anionic zirconium complexes predominated, and in 1.5 N sulphuric acid solution, cationic species had disappeared completely.

Solution properties of zirconium complexes

The presence of organic acids affects not only the ionic nature of zirconium in solution but also the pH at which precipitation commences. However, few studies have been reported on the stability of zirconium solutions in the presence of organic reagents. In the presence of most organic acid anions, the pH of precipitation is considerably higher than in inorganic acid solutions(23,29,31-35), and an adequate quantity of some hydroxy acids may prevent precipitation altogether(23,31,36). It is apparent that only organic reagents of the polydentate type are capable of forming chelate complexes with zirconium that are stable to high concentrations of hydroxyl ion. This is illustrated in the cases of lactate, citrate, glycollate, gluconate, and tartrate, by complete resistance to precipitation in strongly alkaline solutions. Insoluble chelates are formed with some organic acid anions when the resulting complex contains no hydrophyllic groups(37). For example, some α-hydroxy acids form very sparingly soluble zirconium compounds in acid solution when a large excess of the organic acid is present(23), and some of these can be used as reagents for the quantitative precipitation of zirconium for analysis(38-40). Most dibasic organic acids which are capable of chelate formation produce insoluble compounds with zirconium(29,32,41).

The type of alkali used in basifying the zirconium solutions also affects the pH at which precipitation commences. Solutions basified with sodium carbonate precipitate at higher pH values than similar solutions to which sodium hydroxide was added. The resulting basic material differs depending on the alkali used. With 1 equivalent of –OH ions, ZrO.OH.Cl is formed, but 1 equivalent of carbonate produces $Zr_2O_3Cl_2$(23). Both basic salts are further hydrolysed because their solutions are acidic in reaction. It is stated that the polycation can form in halide solutions only in the presence of carbonic acid(23), but the presence of polymers has been established even in strongly acid CO_2-free solutions, see following section and Chap. 3a.

Polymerisation

The hypothesis that zirconium forms polymers by hydrolysis is of long standing(23,42). The formation of basic zirconium polymers by progressive hydrolysis can be inferred from visual observations on the instability of aqueous solutions of zirconium salts(43,44), but little is known of the structure of these complexes, or of the ultimate size which is attained before the polymer becomes insoluble. Blumenthal(23) has postulated various structural formulae: in the case of sulphate solutions it is suggested that the zirconium atoms are linked by sulphate groups, but this cannot explain the presence of aggregates in zirconium halide solution, although the hydrolysis and aggregation of salts of weak polyacid bases are affected in a specific manner by the anion combined with the base or hydrolysis product(45). The generally accepted theory for the mechanism of polymerisation is the aggregation of zirconium atoms by hydroxide or oxide bridges(23,46), and it has been shown that hydroxyl groups link the zirconium atoms in solid zirconium oxyhalide crystals(26).

That polymerisation takes place in aqueous solution has been deduced from studies of conductivity changes(47), potentiometric studies(33), diffusion measurements(30,45), two phase distribution equilibrium measurements(24,48), and ultracentrifuge techniques(42,49). On the other hand, the presence of monomers has been reported in moderately acid solution of extremely low zirconium concentration(24).

From the above it will be seen that some of the evidence is contradictory, and further information on the chemistry of zirconium in aqueous solution, particularly with reference to complex formation and particle size, appears to be essential for deducing the reaction mechanism of the zirconium tanning process, and to explain earlier observations which are discussed below.

b) Reaction of Zirconium With Collagen

A fundamental study of the reaction of zirconium with model substances is important, since the reaction with collagen is complicated by the physical structure of fibrous protein and may lead to erroneous conclusions. This is illustrated by the criticism of Lasserre's work(27) by Ranganathan and Reed(50). Lasserre found that normal and deaminated collagen contained similar amounts of ZrO_2, and concluded that amino groups played no part in the reaction. This incorrect inference was reached because insoluble zirconium compounds were retained by the fibrous protein. Nevertheless, results of practical tanning experiments must be taken into account when attempting to deduce the mechanisms of the reaction.

The literature relating to zirconium tannage has been reviewed in detail by Somerville(9), Williams-Wynn(21), and Ranganathan and Reed(50). The evidence indicates that the more important factors affecting fixation and tanning action are the following.

Pickling

The pretreatment of the protein, collagen, with a mixture of acid and salt, a process known as "pickling", has been shown to be important from the point of view of speed of penetration of zirconium into hide. Whilst the amount and type of acid and salt recommended by different authors varies(32,51-63), the most important factor found by most workers is the necessity for an equilibrium pickle for optimum penetration of the zirconium salt. No increase in the amount of acid compensates for a short time in pickle.

Effect of pH and basicity on the tanning action

Tanning with zirconium occurs under much the same conditions as with chromium, but the notable difference between the two mineral tanning materials is the fixation of zirconium by collagen under strongly acid conditions where chromium is not fixed(56). Despite variations in the acidity of zirconium tanning solutions, Lasserre(27) found that the zirconium complex fixed by the skin was always 35% basic, although the amount of zirconium fixed depended on the overall basicity, the greatest amount being fixed from 30% basic solutions. Different types of zirconium tannage are said to occur under varying pH conditions(58): a salt tannage at pH values below 1.0; a coordination tannage with zirconium complexes in the pH range 1.6 to 2.4; and a colloidal tannage with hydrated zirconia gel in the pH range 5.5 to 6.0. The optimum pH for zirconium tannage is between 1.0 and 3.0(52,58,64).

pH affects the extent to which various groups on the collagen are charged or uncharged, and if a chemical reaction with these groups is involved in zirconium tannage, pH might affect their reaction with zirconium. This is unlikely as it has been shown that zirconium fixation does not involve carboxyl groups(27,43,50,65-67), and all amino groups would be fully charged in the normal pH range of tannage. Ranganathan(44), however, claims that tannage is due to the entry of <u>uncharged</u> amino groups into the zirconium complex! This is highly improbable under the acid conditions of tannage.

Influence of zirconium concentration and neutral salts on penetration

The zirconium concentration has been shown to affect the rate of penetration of the tanning salts into pelt(61,66), the more concentrated solutions penetrating more rapidly than the less concentrated. The presence of neutral salt also affects the rate of penetration(32,60,61), the optimum being in the region of 8% of sodium chloride, which is superior to neutral salt sulphates(32), but the addition of neutral salts to solutions of zirconium salts reduces the uptake of zirconium by pelt(27,60). This is probably due to the inhibition of swelling of the pelt which would otherwise occur at the pH at which tannage is effected.

Effect of salts on the fixation of zirconium by collagen

Apart from the reduction of electro-osmosis as is general with salts, there is the additional influence of the anion. The type of anion in the zirconium liquor has an effect on the tanning action and the quality of the leather; leather produced from chloride and nitrate solutions are inferior to that obtained from sulphate solutions(12,14,68-71). Whilst little is known about the reactions of amino acids and proteins with zirconyl ions in aqueous solution, the differences in behaviour between sulphate and chloride solutions of zirconium toward amino acids could be explained by the formation of a pseudo-chelate structure in the case of the former, which does not occur in chloride solution(72). Different tanning action is also shown by zirconium solutions containing organic acid anions, known technically as "masked" solutions(32,44,60-63,66). Apart from raising the pH at which precipitation commences, penetration is claimed to be improved in the presence of salts of these acids(62,66), but the effect is so small as to be of negligible importance, and if used in excess of the optimum amounts(62) the rate of penetration is considerably reduced. Some organic acid anions, e.g., lactate and formate, have been found to be quite ineffective in promoting penetration of zirconium into hide(60,62,63).

The ionic nature of the zirconium tanning salt does not seem to be critical for the satisfactory tannage of pelt. Stable leathers have been produced from solutions which are claimed to be predominantly cationic(27,55,56), but equally stable leathers can be obtained from solutions containing predominantly anionic complexes(44,50,67), whilst in normal zirconium sulphate solutions a large amount of the zirconium is uncharged(28). Work on chemically modified collagen has indicated that tannage is not effected by reaction with carboxyl groups(27,43,50,65-67), and in most cases deamination had little effect on zirconium fixation, but Ranganathan and Reed(50) have shown that this observation was based on poor experimental technique and that amino groups are involved, to some extent, in the fixation of zirconium by hide protein.

Suggested mechanism of zirconium tannage

Because of the rapid fixation of zirconium at low pH, Wilson(73) advanced the hypothesis that zirconium tannage is due to salt links formed between amimo groups and anionic zirconium. Somerville, on the basis of the similarity of dyeing characteristics of zirconium and chromium tanned leather, maintained that part at least of zirconium fixation is from cationic compounds(55,56), although he does not claim that a similar mechanism is involved in each case. This is in direct contrast to results from other dyeing experiments in which acid dyes were shown to have less, and basic dyes greater affinity for zirconium tanned leather compared with chromium tanned leather(74). In this respect, zirconium tannage resembles vegetable tannage, which is the conclusion reached by Ranganathan and Reed(50), although they have shown that amino groups appear to play a large part in the fixation of zirconium to hide protein. Lasserre(75) and Schweikert(76) suggested that tannage was probably due to reaction with peptide groups, fixation through hydrogen bonds being the most likely. However, since zirconium leather can withstand hydrogen-bond-breaking reagents such as 8 M urea(67), a mechanism similar to vegetable tannage is unlikely, and the high hydrothermal stability suggests strong crosslinking bonds.

Studies of zirconium reactions, particularly with amino acids and proteins, may elucidate the mechanism of tannage, but on the evidence previously available, Somerville(9) summarised the situation as follows:-

"It is quite conceivable that the initial rapid reaction of basic zirconium sulphate with hides and skins, giving high shrinkage temperatures at low pH values, may take place between anionic zirconium and the reactive basic groups in the skin. However, in order to secure satisfactory leather quality, the character of the compound initially formed has to be modified, and in the subsequent neutralisation step may become predominantly cationic in character, while at the same time polymerisation may occur".

Fig.2a 1 General view of diffusion apparatus.

CHAPTER 2

EXPERIMENTAL METHODS.

a) Techniques used in the Present Investigation

Measurement of Diffusion Coefficients.

Apparatus

Diffusion coefficients were determined using the porous diaphragm method previously developed(77-80). The magnetically stirred diffusion cell employed in this work was similar to that described by Stokes(80), except that the pore size of the sintered glass disc was 20-40 microns instead of his recommended 5-10 microns. The larger pore size increased the effective cross-section over which diffusion took place, decreasing the time required for diffusion measurements from 4 to 5 days, to 20 to 30 hours. Streaming(81) through the relatively coarse diaphragm was avoided by careful levelling of the diaphragm, and by using the cell with the denser liquid in the lower compartment, thus using gravity as a stabilising force. Measurements of diffusion coefficients using this cell were similar to those obtained from a cell with a No. 4 sintered glass porous diaphragm, see Table 2a.I.

Table 2a.I.

Diffusion coefficients of 0.1 M zirconium oxychloride aged for 6 weeks, determined using diffusion cells with coarse and fine porous diaphragm.

$\bar{D} \times 10^6$ cm^2.sec.$^{-1}$	
Coarse diaphragm	Fine diaphragm
3.407	3.393

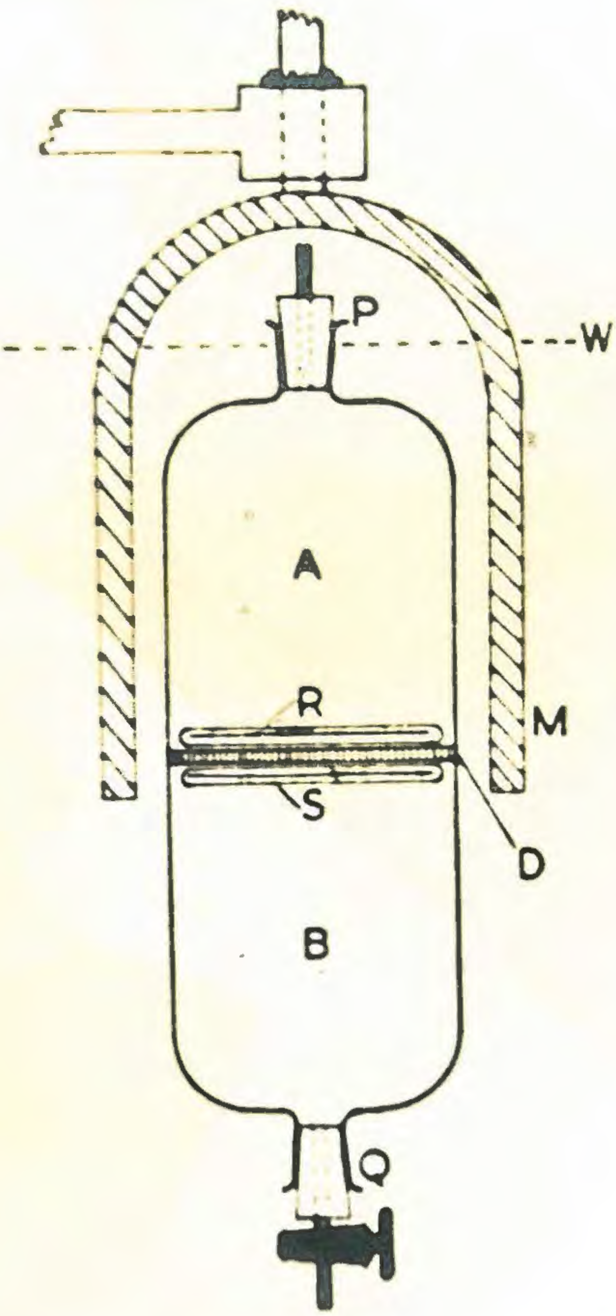


Fig.2a 2 Magnetically stirred diaphragm-cell.

A. Upper cell compartment.
B. Lower cell compartment.
D. Porous diaphragm.
M. Pulley driven magnet.
P,Q. Stoppers fitted with capillary outlets.
R,S. Glass stirrers enclosing iron wire.
W. Level of thermostat water.

The arrangement of the apparatus is shown in Fig.2a.1 and 2a.2. The cell was of resistance glass, each compartment having a volume of about 50 ml. The diaphragm was of No. 3 sintered glass, 40 mm in diameter. Each compartment contained a stirrer of glass tubing of length slightly less than the diameter of the diaphragm. A length of iron wire was sealed inside each stirrer; the thickness of the wire and the tube walls were so adjusted that the stirrer in the upper compartment sank while that in the lower compartment floated. In this position they were rotated by a pulley driven permanent magnet mounted around the cell. A rate of stirring of 50 revolutions a minute was adopted, as recommended by Stokes.

Procedure

In order to nullify the effect of the electric charge on the movement of the zirconium ion, a relatively high concentration of supporting electrolyte was used as "swamping agent"(79,82,83). In most cases 1.0 M potassium nitrate was used as supporting electrolyte because no complex nitrates of zirconium are known(84). Where the effect of acidity was investigated, the acid was used as supporting electrolyte. The solutions of zirconium oxychloride and supporting electrolyte were made up in deionised distilled water.

In all determinations the deaerated zirconium solution was introduced into the lower cell compartment while the upper compartment was filled with supporting electrolyte of the same concentration and pH. The cell was suspended in a thermostat at 25 ± 0.025°C at which temperature all determinations were made. Diffusion was permitted to proceed until 8 to 12% of the diffusing material had entered the upper compartment; each run was of between 20 and 30 hours duration. The solutions were then removed and analysed for zirconium by the Alizarin-S spectrophotometric method(85) to be described.

Calculation of the results

The integral diffusion coefficients $\bar{D}$ were calculated from the equation given by Stokes(86):

$$\bar{D} = \frac{1}{\beta t} \log \frac{c_1 - c_2}{c_3 - c_4}$$

where β is the cell constant determined from standard 0.1 N potassium chloride, the diffusion coefficient of which is 1.873 x 10^{-5} cm^2. sec.$^{-1}$(87); t is the diffusion time in seconds; c_3 and c_4 are the concentrations of the diffusing substance at the end of the run in the lower and upper cell compartments respectively, and c_1 and c_2 the initial concentrations in the two compartments.

In this work c_2 is always zero, and, since the cell was constructed in such a way that the two compartments are of equal volume, the equation becomes:

$$\bar{D} = \frac{1}{\beta t} \log \frac{c_3 + c_4}{c_3 - c_4}$$

when c_1 is expressed in terms of c_2, c_3 and c_4 according to the conservation equation of Gordon(88).

Calibration of the cell

Calibration was carried out with 0.1 N potassium chloride, for which D was taken to be 1.873 x 10^{-5} $cm^2.sec.^{-1}$. Cell constants were found to change with each successive diffusion due to wear on the sintered glass disc, and it was necessary to check the cell constant every 200 hours. The relevant cell constant for intermediate runs was determined from a graph. Values for four successive determinations of the cell constant at two different periods are given in Table 2a.II. These results indicate that reproducible measurements can be made with this type of cell.

Table 2a.II

Reproducibility of cell constant

Run	β_1x 10	β_2x 10
1	2.58	2.679
2	2.56	2.673
3	2.53	2.668
4	2.51	2.660

Measurements of the diffusion coefficients of 0.1 N hydrochloric acid and sodium chloride gave results in close agreement with published values(86), see Table 2a.III.

Table 2a. III

Comparison of diffusion coefficients for hydrochloric acid and sodium chloride with published values.

	$\bar{D}$ x 10^5 $cm^2.sec.^{-1}$	
	Found	Published
0.1 N hydrochloric acid	3.064	3.066
0.1 N sodium chloride	1.511	1.522

Fig.2a 3 General view of electrophoresis apparatus.

The figures given above indicate that streaming through the relatively coarse porous glass diaphragm is negligible. When one considers the effect of pore size on the area in porous diaphragms, surface transport effects, if present, would be altered enormously from cell to cell, but the fact that the two cells gave similar results indicates that surface transport along the walls of the pores was not a serious factor. There is no evidence from the literature which would indicate that surface transport is sufficiently serious to invalidate the method(88).

Since surface transport and streaming have been shown to be absent, and since the cell has yielded results in close agreement with published values for 0.1 N hydrochloric acid and sodium chloride, the results obtained from measurements of zirconium oxychloride are thought to be accurate within the limitations of the method.

Paper Electrophoresis

Apparatus

An apparatus essentially similar to that of Grassmann and Hanning(89) was constructed from "Perspex", and is shown in Fig. 2a.3. A cross section of the apparatus is shown in Fig. 2a.4. Strips of Whatman No. 3 M M filter paper, 2.5 cm x 40 cm were placed horizontally over a grid of five cross pieces shaped to knife edges at the points of contact with the paper. The ends of the paper were dipped into double compartment electrode vessels, the two compartments of

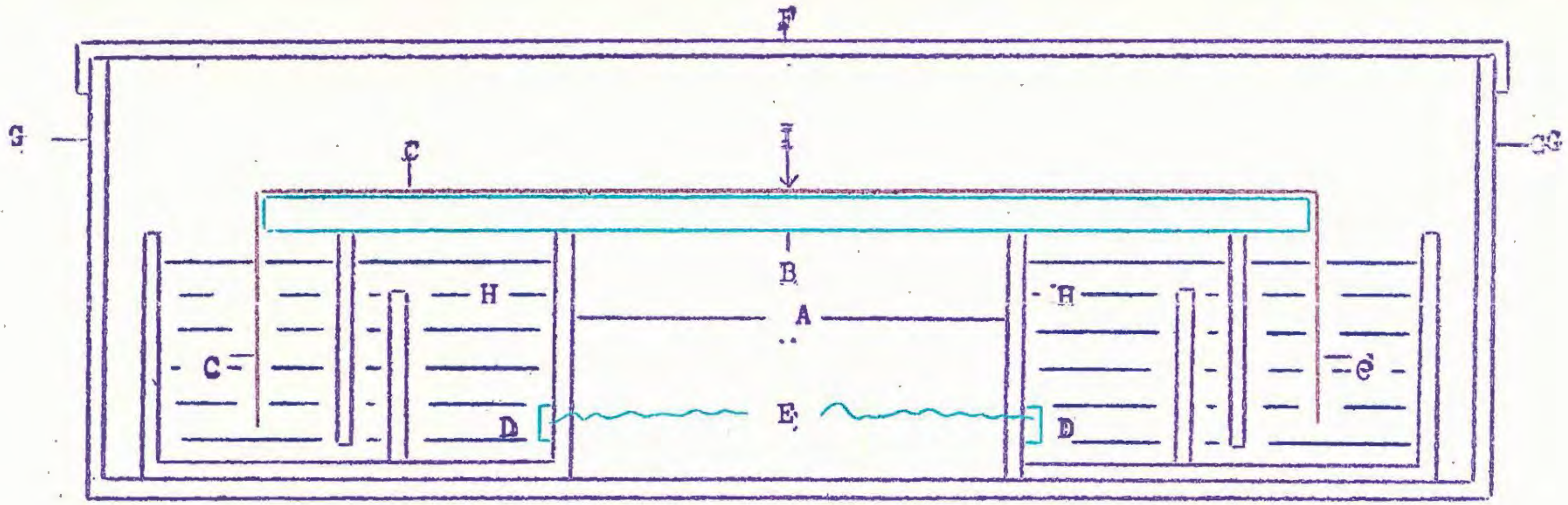


Fig. 2a.4 Paper electrophoresis apparatus.

A	Electrode vessels.	F	Perspex lid.
B	Grid to carry papers.	G	Perspex box.
C	Filter paper strips.	H	Buffer solution.
D	Platinum electrodes.	I	Point of application of zirconium solution.
E	Power supply.		

each electrode vessel being connected through a labyrinth system to eliminate contact of the paper with the products of electrolysis. The whole apparatus was enclosed in a "Perspex" box in which the atmosphere was saturated with water vapour to reduce evaporation from the paper.

The current from the stabilised power unit of a Perkin Elmer Tiselius electrophoresis apparatus was applied to platinum wire electrodes situated in the compartment of the electrode vessel remote from the compartment into which the filter paper strips dipped. The apparatus was fitted with a switch for reversing the polarity of the electrodes so that the buffer need not be replaced after each run.

Procedure

At the start of each run, the levels of the buffer in the electrode vessels were equalised by connecting them with a syphon tube for ten minutes. The paper strips, marked across their centres with a faint pencil line, were soaked in buffer solution and the excess blotted off in the region of the pencil line using dry filter paper. Six strips were placed across the grid under a slight tension, with the ends dipping into the electrode vessels. Equal volumes (0.05 ml.) of the solutions under investigation were applied along the pencil lines, the width of application being not more than 3 mm. A current of 0.8 mA per centimetre width of paper was applied at 150 V.D.C. Each run was of 6 hours duration, at the end of which time the strips were removed and air dried.

The "buffer" used was 0.05 M sodium nitrate solution adjusted to the requisite pH with nitric acid or sodium hydroxide.

The dry papers were stained with a 0.1% solution of sodium alizarin sulphonate (Alizarin-S) in N/10 hydrochloric acid. The position of the zirconium was revealed by a red coloration which is extremely sensitive(43,90) and specific for zirconium(90). The background colour is pale yellow.

0.1 M solutions of zirconium oxychloride were prepared containing equimolar amounts of twelve organic compounds as well as an unmasked zirconium solution. Each was adjusted to equilibrium to seven pH values, viz., 1,2,3,4,6,8, and 10, and aged for several weeks, after which the charge was determined using the above technique.

Potentiometry

Apparatus

The instrument employed was the "Cambridge Bench Type" pH meter with the dip-type glass calomel electrode system. A wide range glass electrode, accurate up to pH 13, was used in all pH determinations. The apparatus consisted of a 150 ml. resistance glass beaker fitted with an air driven glass stirrer. Alkali additions were made from a Grade A.NPL burette, fitted with a soda-lime tube.

The instrument was standardised using the following buffer solutions.

pH 9.2 : Cambridge buffer tablets
pH 4.16 : potassium hydrogen benzoate(91)

All measurements were made at room temperature, approximately 22°C.

Preparation of solutions and titration technique

A stock solution of 0.2 M zirconium oxychloride was prepared in deionised distilled water. Aliquots of this solution were taken, and solutions of the various organic reagents, viz., acetic, glycollic, glycine, and α-, β-, and γ-amino-n-butyric acids, were added in such quantity that the molar ratios of organic reagent to zirconium were 1, 2, and 4. Four separate aliquots were prepared at each molar ratio for all the organic acids studied, and were adjusted by the addition of $N/_1$ hydrochloric acid or $N/_1$ potassium hydroxide so that the equilibrium pH lay at one of the four predetermined values, viz., 1, 1.9, 2.8, and 3.7. Equilibrium was attained by daily pH adjustments until no further adjustment was required after seven days standing. Each masked zirconium solution as prepared was then made up to volume so that the final solution was 0.02 M with respect to zirconium. During the course of the pH adjustments the volume was increased to near the final solution volume so that the final dilution made a negligible alteration to the pH of the solution.

Titrations were carried out on 20 ml. aliquots of the zirconium solutions diluted to 50 ml. In order to minimise the effects of dilution, the titrations were performed rapidly and at approximately similar rates for comparative purposes.

Techniques for Small Scale Tannages

(i) Using electrophoresis solutions

The solutions containing equimolar amounts of organic reagent were made 0.25 M with respect to zirconium. Aliquots were taken for tanning trials before the remainder were diluted for electromigration studies. Sodium chloride was added to make the solutions 1 M. Rehydrated acetone dehydrated goatskin pieces were shaken in each of the solutions, the amount of zirconium offered being 10% ZrO_2 on pelt weight (20% moisture). After 3 days in these solutions the pieces were well washed and dried before shrinkage temperature measurements were made.

(ii) Practical application of particle size determined from diffusion measurements.

The details of the tannages linking particle size with the rate of zirconium penetration into pelt is given in Chapter 4a.

Preparation of Zirconium Salts

Purified zirconium oxychloride octahydrate

The pure zirconium oxychloride was prepared using the method described by Lasserre(43) from commercial zirconium oxychloride by repeated recrystallisation from 9 N hydrochloric acid at which concentration the zirconium salt is least soluble(92).

The commercial salt was dissolved in the smallest amount of water to give complete solution, and filtered to remove insoluble impurities. The filtrate was reduced in volume, and sufficient hot concentrated hydrochloric acid was added to make the solution 9 N. On cooling, needle-like crystals of zirconium oxychloride octahydrate separated, and were removed by filtration. The crystals were taken up in hot 9 N hydrochloric acid and recrystallised several times to ensure the removal of all impurities. Finally, the crystals were allowed to dry in air and were then analysed for zirconium, and the basicity determined, using the methods to be described.

Table 2a. IV

Composition of zirconium oxychloride

	Found	Theoretical
ZrO_2 content, %	38.25	38.23
Basicity	51.4	50.0

Purified zirconium sulphate

The pure zirconium sulphate was prepared from the purified oxychloride by heating with 60% sulphuric acid to drive off all the chloride, and then cooling to allow the zirconium sulphate to crystallise(43). The product was washed with 95% alcohol, and dried in air. The zirconium sulphate was recrystallised to ensure purity, and then analysed.

Table 2a. V

Composition of zirconium sulphate

	Found	Theoretical
ZrO_2 content, %	34.15	34.66
Basicity	-0.87	0.0

Analytical Methods

Gravimetric determination of zirconium(93)

The phosphate precipitation method was used in the analysis of all standard solutions and as a reference standard for the colorimetric method to be described.

An aliquot of the zirconium solution containing about 0.1 g of zirconium was diluted to about 100 ml. and sufficient sulphuric acid added so that the solution contained about 15% by volume. 50 ml. of a 10% solution of diammonium hydrogen phosphate was added and the resulting solution digested at 50°C for several hours and allowed to cool overnight. The precipitate was filtered into a tared ignited Gooch crucible, washed with a cold 5% solution of ammonium nitrate, ignited at 900°C, and weighed as ZrP_2O_7.

Colorimetric determination of zirconium

This method will be described in detail in Chapter 2b.

Determination of basicity

Basicity is defined as the percentage of zirconium which is combined with hydroxyl groups and not with acid. It is determined by estimating the amount of acid associated with the zirconium(94) and the zirconium concentration, calculating the amount of zirconium equivalent to the acid to make a normal salt, and applying the formula:

$$\text{Basicity} = 100 - \left(\frac{\%\ \text{Zr equivalent to the acid}}{\%\ \text{total Zr}} \times 100\right)$$

Determination of shrinkage temperature

Shrinkage temperatures were measured using the American Leather Chemists' Association apparatus(150) with water as the medium.

b) Modification of the Alizarin-S Spectrophotometric Method for the Determination of Zirconium(85)

In the course of an investigation of zirconium compounds, a rapid, accurate method for the determination of zirconium is essential. Several analytical procedures are available and are of the following types:

a) gravimetric(38,39,93,95,96) involving precipitation, filtration and ignition.
b) volumetric(97-99) involving titration using ethylenediamine tetra-acetic acid.
c) colorimetric(100-106) involving colour formation under standard conditions.

Gravimetric methods, although accurate are by their nature involved and time consuming. Moreover, many of the methods are affected by other cations in solution. The phosphate precipitation method(93) is the one generally accepted, and therefore used as standard in this work.

Volumetric methods are rapid and usually accurate, but the conditions for these methods are often difficult to maintain.

Colorimetric methods are finding wide application and are being generally accepted. In the search for suitable methods for zirconium, that of Mayer and Bradshaw(104) was selected for investigation, although other methods are promising.

The present work included an investigation of the reaction of zirconium with organic acids, amino acids, and proteins which had to be destroyed before the determination of zirconium. Earlier methods(107-109) for the determination of zirconium in leather (zirconium collagen compound) are tedious and lengthy. All these methods involve ashing of the leather sample, fusing with fusion mixture, and then dissolving in acid before determining the zirconium by gravimetric methods. The fusion method could equally well be used to obtain zirconium in solution for volumetric and colorimetric methods, but widespread acceptance of the wet oxidation method for chromium(110), i.e., treatment of the sample with a mixture of sulphuric, perchloric, and nitric acids, led to an investigation of its use for dissolving other mineral tanning materials(111). The method was found to be very satisfactory and the advantages over the above fusion methods are obvious.

Investigation of the use of Alizarin-S for the colorimetric determination of zirconium

Mayer and Bradshaw(104) measured the optical density of the coloured complex formed between zirconium and Alizarin-S in strongly acid solution, but sulphate interfered in the development of the colour, and, as sulphate was inevitably present after degradation of the zirconium complexes, a modification was sought that would eliminate the sulphate interference.

In addition, another defect which limited the direct application of the method was the intense colour produced. For this reason solutions of very high dilution had to be used if the wavelength of maximum absorption, viz., 520 mμ, was employed. Mayer and Bradshaw overcame this difficulty by working at a wavelength of 560 mμ, but at this value there is interference from other materials, e.g., trivalent chromium salts, which absorb strongly at this wavelength.

Use could be made of the differential method(112) in which the absorption density of the intensely coloured solution is measured against a standard grey solution of known absorption density(113) in place of the reagent blank usually employed.

The intensity of the colour formed by Alizarin-S with zirconium can be reduced by the addition of hydroxy acids, for example, tartaric acid, which has the added advantage of stabilising zirconium solutions to precipitation(98,114), and it was decided to investigate the use of this reagent in the above method.

Preliminary experiment to study the effect of variables on colour development and stability

The method of Mayer and Bradshaw required the aliquot of zirconium solution to be added to a 100 ml. volumetric flask containing 2.5 ml. concentrated HCl, followed by the addition of Alizarin-S solution. The flask was then immersed in boiling water for 2.5 to 3.5 minutes, cooled and made up to 100 ml. The absorption density was measured against a blank containing acid and Alizarin-S. To check on the above technique when tartrate is present, a ¼ replicate of 2^8

factorial experiment(115) was carried out in which the following factors were varied.

AB Amount of hydrochloric acid added to 100 ml. volumetric flask.
(1) 10 ml. N/$_1$ HCl
a 20 " " "
b 30 " " "
ab 40 " " "

CD Interfering anions added to 100 ml. volumetric flask
(1) None
c 0.3 g Na_2SO_4
d 0.15 g $NaClO_4$
cd 0.3 g Na_2SO_4 + 0.15 g $NaClO_4$

EF Amount of sodium tartrate added to 100 ml. volumetric flask
(1) None
e 1 ml. 10% solution
f 2 ml. " "
ef 4 ml. " "

GH Conditions for reaction after addition of reagents
(1) Prepared at room temperature
g " in boiling water for 2 minutes
h " " " " " 5 "
gh " " " " " 10 "

The above statistical design gives 64 combinations, and is arranged with defining contrasts $\overline{AB}D\overline{EF}H$ and $B\overline{CD}FG$.

Procedure

It will be noted that the method is applicable for final concentrations of 1 mg zirconium per 100 ml., and therefore a standard solution of zirconium oxychloride was made up containing 0.75 mg zirconium per 10 ml. 10 ml. aliquots were run into each of the 100 ml. volumetric flasks containing the requisite amounts of hydrochloric acid and interfering anions where necessary. The colour was developed by adding 10 ml. 0.15% Alizarin-S solution and then the tartrate where applicable. The flasks containing the solutions that had to be heated were immersed in boiling water for the required length of time, cooled and made up to volume. The absorption density at 520 mμ was read immediately and after 24 hours' standing at room temperature using as blank a solution containing the requisite amount of acid and Alizarin-S solution.

Summarised results of the preliminary experiment

The amount of tartrate added caused the most significant reduction in colour intensity and eliminated the precipitation which was apparent in most solutions containing no tartrate. It was obvious that a small amount of tartrate was sufficient to prevent precipitation and to reduce the colour, see Table 2b.I.

Table 2b.I

Tartrate Added	Absorption density	
	Initial	Aged
None	411	417
1 ml.10% solution	189	193
2 ml. " "	137	139
4 ml. " "	101	103

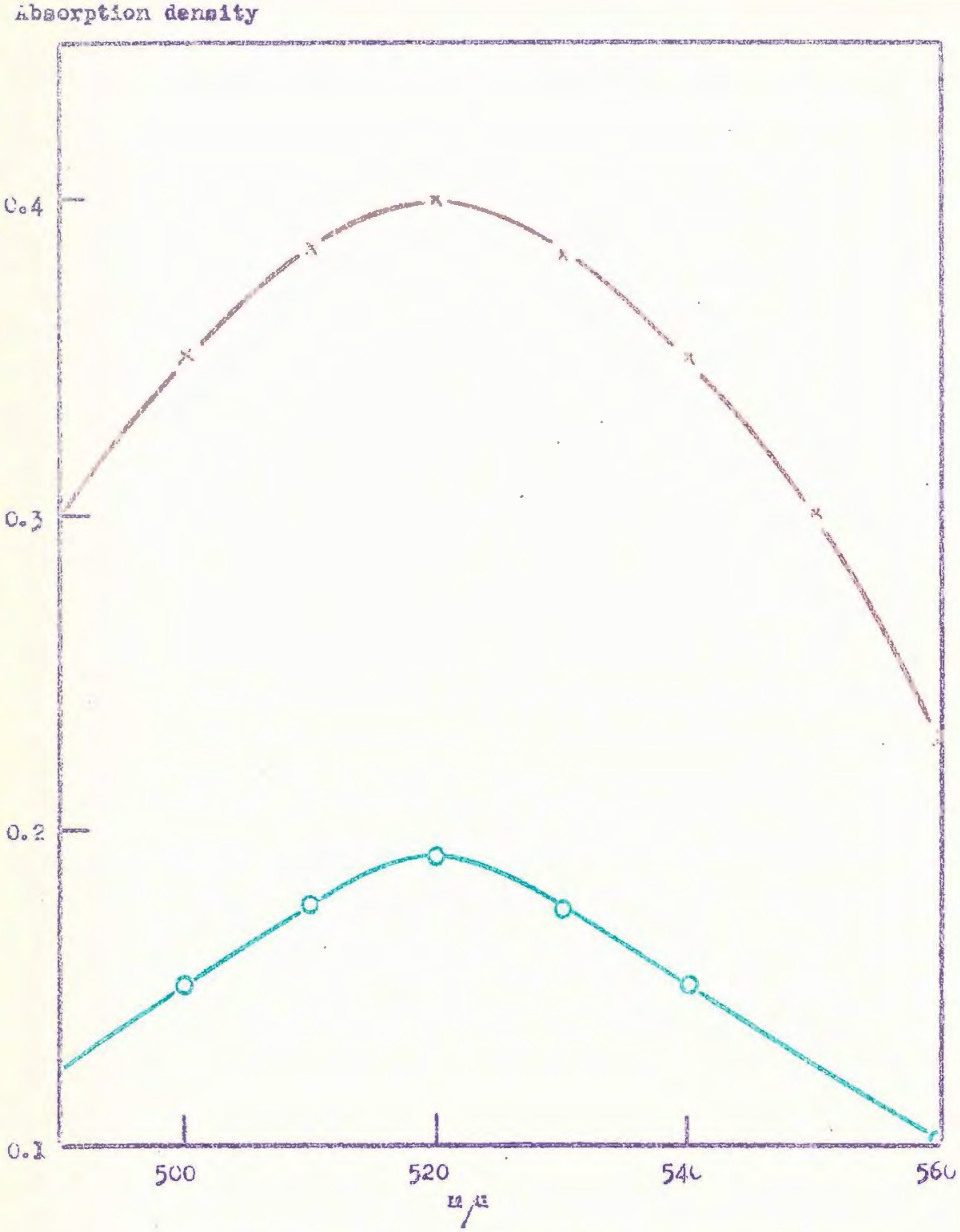


Fig. 2b.1 Wavelength of maximum absorption of zirconium/Alizarin-S compound in solution containing 0.75 mg Zr in 100 ml.

O= absorption density in the presence of tartrate.
X= absorption density in the absence of tartrate.

Ageing had little effect, although the solutions without tartrate were affected more than those with tartrate. The presence of tartrate did not alter the wavelength of maximum absorption, see Fig. 2b.1.

The amount of acid added was unimportant, see Table 2b.II, but the lower amounts of acid gave solutions which were not optically clear after standing, although the change in absorption density was not affected.

Table 2b.II

HCl added	Absorption density	
	Initial	Aged
10 ml. N/1 solution	208	211
20 " " "	211	214
30 " " "	209	213
40 " " "	211	215

As expected, sulphate interfered, but where tartrate was present, the interference was reduced. Perchlorate was completely without effect. The interaction between tartrate and the interfering anion on absorption density is given in Table 2b.III.

Table 2b.III

Tartrate added	Interfering anion			
	None	SO_4	ClO_4	SO_4+ ClO_4
None	466	380	442	378
1 ml. 10% solution	202	178	200	177
2 ml. " "	146	129	144	129
4 ml. " "	107	96	106	95

Heating the solution did not affect the absorption density, but all the solutions prepared cold or heated for only 2 minutes were not optically clear.

The effect of small variations in the amount of added tartrate

From the previous experiment it is seen that large variations in the amount of tartrate added made large differences in the absorption density. It was decided, therefore, to test the effect of small variations of tartrate of the order of ± 10%, in order to determine the care needed in the preparation of the tartrate solution.

The colour was developed in 100 ml. volumetric flasks containing 25 ml. $N/_1$ hydrochloric acid solution and 10 ml. standard zirconium solution, by the addition of 10 or 15 ml. 0.15% Alizarin-S solution, the variable amounts of tartrate being added before heating for 5 minutes in boiling water. No significant difference was found in the absorption density as determined by an analysis of variance(116), see Table 2b.IV.

Table 2b.IV

Alizarin-S added	Tartrate added, 1% solution			
	9 ml.	10 ml.	11 ml.	MEAN
10 ml. 0.15% solution	203	201	200	201
15 ml. " "	201	200	200	200
MEAN	202	201	200	201

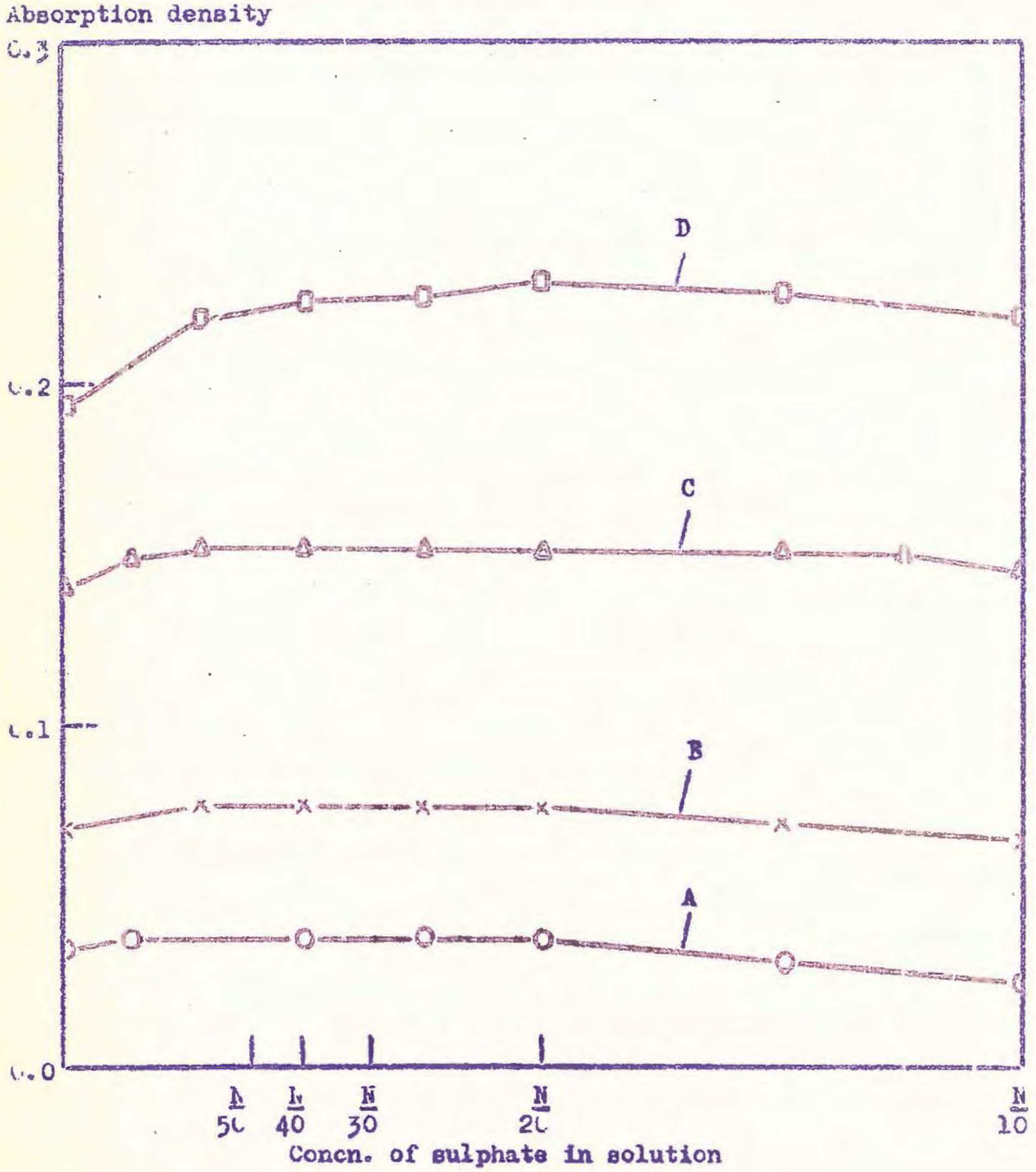


Fig. 2b.2 Effect of sulphate concentration on the absorption density of the zirconium/Alizarin-S compound.

A = absorption density of 0.15 mg Zr in 100 ml.
B = absorption density of 0.30 mg Zr in 100 ml.
C = absorption density of 0.60 mg Zr in 100 ml.
D = absorption density of 1.20 mg Zr in 100 ml.

Effect of sulphate concentration

Chloride and perchlorate are without effect, but sulphate has been shown to interfere. In order to study the effect of the sulphate in detail, four series containing 2,4,8, and 12 ml. aliquots of the standard zirconium solution were prepared, and to each of these varying amounts of sulphate were added. The result was that the absorption density increased with increasing sulphate content until the solution was N/50 with respect to sulphate. With further addition of sulphate, the absorption density of each series was constant until the sulphate concentration reached N/20, and then decreased slowly, see Fig. 2b.2. It will be seen that curve D is erratic, confirming earlier observations that the method is applicable to a maximum of 1 mg zirconium in the reaction flask.

Recommended Method

From the above it is seen that fairly wide conditions exist for the reproducible development of a colour with zirconium and Alizarin-S, and this property can be used for the determination of zirconium, and the following reagents and procedure have been found most suitable.

Reagents

Perchloric/sulphuric acid digestion mixture(110):-

mix 200 ml. 70% $HClO_4$ and 77 ml. conc.H_2SO_4.

Sodium alizarin sulphonate/sodium tartrate reagent:-

dissolve 1 g Alizarin-S and 5 g sodium tartrate in about 500 ml. of hot water, acidify with a few drops of concentrated HCl, filter through Whatman No.42 filter paper and dilute to 1 litre.

Procedure

Weigh into a 100 ml. Kjeldahl digestion flask approximately 0.3 g of the zirconium compound (leather) of about 10% ZrO_2 content, or an aliquot of the solution containing an equivalent amount of zirconium. Add 10 to 15 ml. perchloric/sulphuric acid digestion mixture and 15 ml. concentrated nitric acid. Heat gently to digest organic matter, then heat strongly until fumes of perchloric acid are given off. Cool, dilute with about 50 ml. N/1 hydrochloric acid and boil for 5 minutes. Transfer to a 500 ml. volumetric flask and make up to the mark with distilled water.

Run a 10 ml. aliquot into a 100 ml. volumetric flask containing 25 ml. N/1 hydrochloric acid. Add 20 ml. of the sodium alizarin sulphonate/sodium tartrate reagent and heat in boiling water for 5 minutes. Allow to cool amd make up to 100 ml. with water. Measure the absorption density at 520 mμ using a solution of 25 ml. N/1 hydrochloric acid and 20 ml. Alizarin-S/tartrate reagent made up to 100 ml. as blank.

Note. Where sulphate is present potassium must be avoided because sparingly soluble double sulphates are formed with zirconium(117). This means that Rochelle salt must not be used for the preparation of the Alizarin-S/tartrate reagent.

Table 2b.V

Comparison between spectrophotometric and gravimetric methods

	Spectrophorometric method, X1 mg ZrO_2	Phosphate gravimetric method, X2 mg ZrO_2	Difference (X1 - X2) mg ZrO_2
1	26.1	25.8	+0.3
2	42.6	42.4	+0.2
3	30.1	30.1	0.0
4	45.8	46.0	-0.2
5	35.6	35.6	0.0
6	32.4	32.2	+0.2
7	51.9	51.8	+0.1
8	40.7	41.0	-0.3
9	27.6	27.4	+0.2
10	41.3	41.2	+0.1
11	44.1	44.3	-0.2
12	41.9	42.1	-0.2
13	35.6	35.5	+0.1
14	35.2	35.3	-0.1
15	41.9	41.7	+0.2
16	42.4	42.4	0.0
17	26.7	26.5	+0.2
18	33.8	34.3	-0.5
TOTAL	675.7	675.6	+0.1
MEAN	37.54	37.53	+0.00556

A t-test(118) gave a value of $t = 0.109$, $\phi = 17$, which indicates a completely insignificant difference between the two methods.

Preparation of standard graph

Dissolve 8 g zirconium oxychloride octahydrate in water, and make up to 250 ml. Standardise the solution gravimetrically with phosphate(93); 1 ml. of this solution should contain about 10 mg of zirconium. Dilute this solution 100 times, and use aliquots of up to 10 ml. in 100 ml. volumetric flasks containing 25 ml. N/1 hydrochloric acid and 5 ml. N/2 sulphuric acid. Develop the colour as recommended, and measure the absorption density at 520 mμ in a 1 cm cell.

Comparison of results by gravimetric and spectrophotometric methods.

Eighteen experimentally prepared leathers were analysed by the above methods. In order to avoid sampling errors, aliquots for the two determinations were taken from the same diluted digestion solution. The results quoted in Table 2b.V are calculated back to the original amount of ZrO_2 taken.

Interference from other cations

Mayer and Bradshaw(104) have shown that a number of cations do not interfere, but, in leather, chromium, iron, aluminium, and titanium may be present. To test the effect of these cations, the equivalent of 5% of Fe_2O_3, Cr_2O_3, and Al_2O_3, and 10% TiO_2 on leather weight, the maximum normally found in leather, was added. The effect of these additions are given in Table 2b.VI. Titanium, aluminium, and iron do not interfere, but hexavalent chromium seriously increases

Table 2b. VI

Absorption densities of zirconium solutions in the presence of interfering cations

	ml.standard zirconium solution		
	2	4	8
Zirconium only	41	81	163
Zirconium + titanium	40	80	161
Zirconium + aluminium	41	82	163
Zirconium + iron	41	82	163
Zirconium + chromium$^{(VI)}$	117	158	239
Zirconium + chromium$^{(III)}$	42	84	166

the absorption density. This interference can be overcome by reducing the chromium with sodium sulphite, boiling, and making up to volume before taking aliquots for colour development. It is seen that trivalent chromium gives a small but negligible increase in absorption density.

Composition of the zirconium-Alizarin-S compound

The composition of chelate compounds in solution can be determined by the method of continuous variation(119). For a constant total concentration of metal and chelating agent, the concentration of chelate is greatest when the metal and chelating agent are brought together in the same ratio in which they exist in the chelate. In the case of zirconium the intense red colour formed with Alizarin-S enables a simple colorimetric method to be used to detect the equivalence point.

0.005 M solutions of zirconium oxychloride and Alizarin-S were prepared, and aliquots of each to a total of 10 ml. were run into 100 ml. volumetric flasks containing 25 ml. N/1 hydrochloric acid. After heating in boiling water for 5 minutes and cooling, they were made up to the mark and the absorption density measured against the appropriate blank containing an equal concentration of Alizarin-S. The absorption densities for each ratio of zirconium to Alizarin-S are plotted in Fig. 2b.3 as curve A. Curve B was obtained in an exactly similar manner, but the 100 ml. volumetric flasks contained 10 ml. 1% sodium tartrate

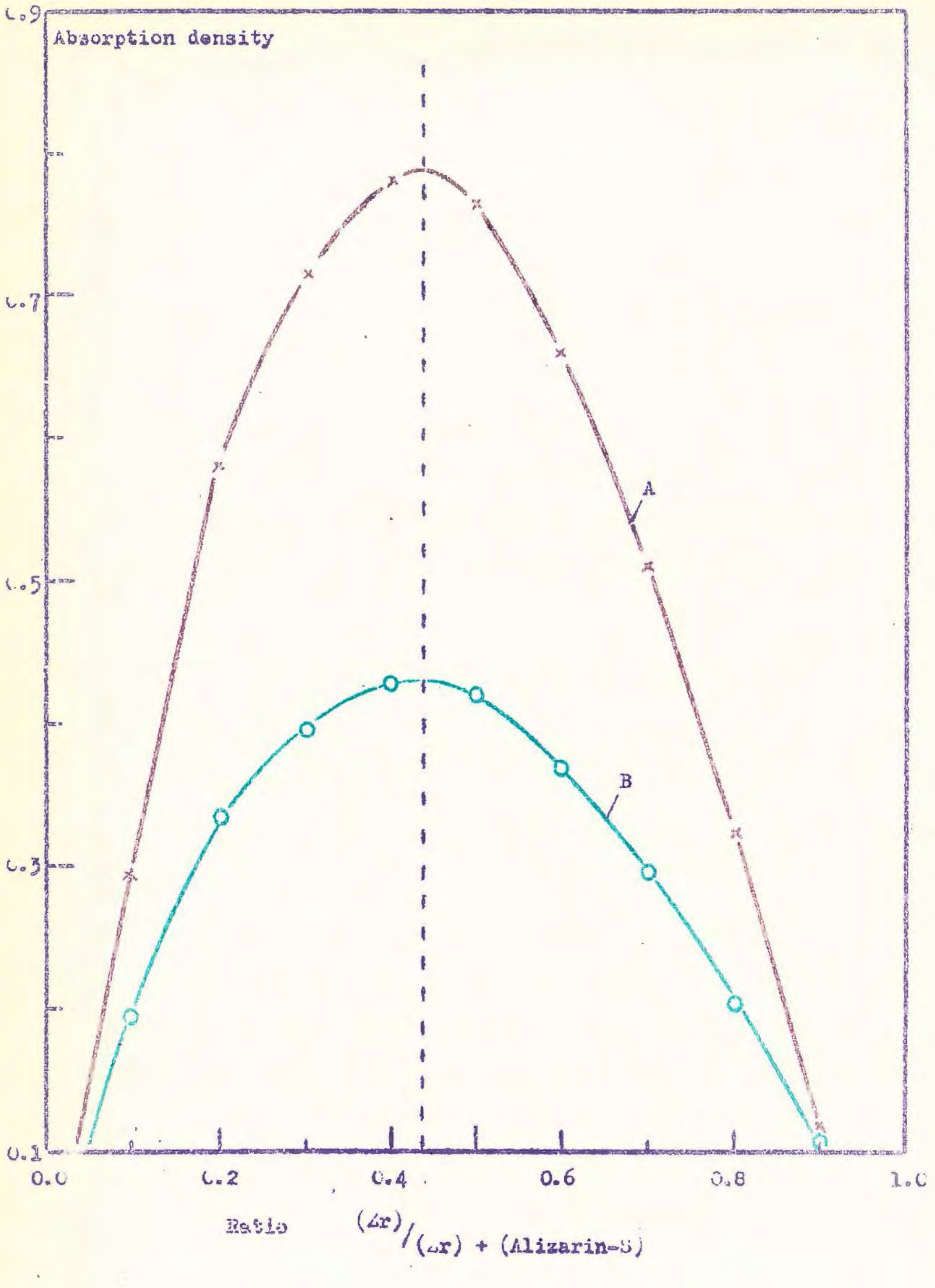


Fig. 2b.3 Composition of the zirconium/Alizarin-S compound determined by the method of continuous variation.

A in the absence of tartrate.
B in the presence of tartrate.

in addition to the hydrochloric acid. It will be seen that the presence of tartrate, whilst reducing the absorption density, has no effect on the amount of Alizarin-S reacting with the zirconium. The peaks occur at a point corresponding to 5.59 ml. of Alizarin-S solution and 4.41 ml. of zirconium solution, i.e., 1.28 moles of Alizarin-S per mole of zirconium. These results appear to correspond with those obtained by other workers. Mayer and Bradshaw, using a slightly different technique, arrived at a ratio of 1.26(104), and a value of 1.24 can be calculated from the data given by Green(101).

Conclusions

Although this method was intended primarily for the determination of zirconium in leather, or in solutions containing organic reagents, it can be adapted for most zirconium determinations; the conditions to be used are similar to those used in the preparation of the standard graph. This method has been used for the determination of zirconium in solutions from the diffusion experiment, see Chapter 3a. In dealing with solutions of zirconium, it is necessary to depolymerise the zirconium in order to obtain the stoichiometric relationship between zirconium and Alizarin-S. This was discovered when a solution of standard zirconium oxychloride was used to check on the standard graph. The only modification to the above method was the replacement of the 25 ml. N/1 hydrochloric acid with 2.5 ml. concentrated hydrochloric acid in the 100 ml. volumetric reaction flask. Solutions obtained from the digestion of leather should, therefore, be analysed immediately, or given the above modified treatment.

CHAPTER 3

SOME EXPERIMENTALLY DETERMINED PROPERTIES OF ZIRCONIUM COMPOUNDS IN AQUEOUS MEDIA

a. Diffusion Coefficients and Particle Weights of Zirconium Oxychloride Determined at $25^{\circ}C$

Details of the apparatus and procedure used in this study are given in Chapter 2a. The measurement of diffusion coefficients is one method which allows the size of a component in solution to be estimated. The initial aim was to compare the particle size of zirconium tanning complexes in masked and unmasked solutions to determine whether observed differences in tanning behaviour and ability are purely chemical, or if changes in physical properties are also involved, i.e., the inability of some zirconium complexes to penetrate may be due to large particle size.

During preliminary work, zirconium sulphate was found to precipitate in the cell, and so, for basic information, zirconium oxychloride was used. Exploratory determinations indicated that many factors, e.g., concentration, age of solution, and acidity, influenced the diffusion coefficient, and to a large extent the work has been limited to a detailed investigation of these factors.

Limits of conditions for the measurement of diffusion coefficients

Following preliminary trials, the first series of

Table 3a. I

Variations with Age of Solution in the Diffusion Coefficient, Radius, Particle Weight, and Degree of Polymerisation of Zirconium Oxychloride. Supporting electrolyte 1.0 M potassium nitrate, $\eta = 8.93 \times 10^{-3}$ poise.

($\bar{D}$ in $cm^2 . sec^{-1} \times 10^{-6}$, r in $cm \times 10^{-8}$)

Zirconium concn.	Age of soln. days	Measured Diffusion coeff. $\bar{D}$	Computed		
			Radius r	Particle weight	Degree of polymerisation
ca.0.5M	1.5	4.30	5.69	800	4.1
"	4	3.96	6.17	1020	5.2
"	8	3.86	6.34	1110	5.6
"	16	3.85	6.36	1110	5.7
"	24	3.85	6.36	1110	5.7
"	28	3.84	6.37	1120	5.7
"	40	3.78	6.47	1180	6.0
"	56	3.81	6.42	1150	5.9
"	84	3.80	6.44	1160	5.9
ca.0.1M	1.5	4.70	5.21	610	3.1
"	2.5	4.55	5.38	670	3.4
"	4	4.39	5.58	750	3.8
"	5	4.30	5.70	800	4.1
"	6	4.11	5.94	910	4.6
"	14	3.65	6.71	1300	6.7
"	21	3.54	6.89	1420	7.2
"	28	3.47	7.05	1520	7.8
"	35	3.42	7.16	1590	8.1
"	42	3.40	7.20	1620	8.2
"	56	3.40	7.20	1620	8.2
"	84	3.40	7.20	1620	8.2
Calculated monomer		6.87	3.56	196.2	1.00
Calculated dimer		5.45	4.49	392.4	2.00

measurements of the diffusion coefficient was made at varying time intervals. 0.5 and 0.1 M solutions of zirconium oxychloride were prepared in 1.0 M potassium nitrate solution and diffusion measurements were made eight hours after preparation, and then at intervals up to twelve weeks. The solutions were prepared and stored at 21 ± 1^{o}C.

The second series was an investigation of the effect of concentration of the zirconium on the rate of diffusion. The solutions, ranging in concentration from 0.05 to 0.85 M, were prepared in 1.0 M potassium nitrate solution without pH adjustment, and aged for 5 to 6 weeks before diffusion measurements were made.

The effect of acidity on the diffusion coefficient was investigated in the third series of measurements. 0.05 M solutions of zirconium oxychloride were prepared in hydrochloric acid solution up to a concentration of 5 M. In this series, acid was used as the supporting electrolyte, but when the concentration of the acid was less than 1 M, additional supporting electrolyte (potassium nitrate) was added to bring the total molar concentration to 1 M.

In the fourth series, diffusion coefficients of basified zirconium solutions were measured over a range of zirconium concentrations. Two alkalies, sodium carbonate and sodium hydroxide, were used to basify the solutions. The zirconium concentration varied between 0.05 and 0.5 M; the basicity varied between 50 and 75% for the solutions basified with sodium carbonate, and between 50 and 70% for

Table 3a. II

Distribution of Particle Size in Fresh and Aged 0.1 M Zirconium Oxychloride Solution. Supporting electrolyte 1.0 M potassium nitrate, $\eta = 8.93 \times 10^{-3}$ poise.

($\bar{D}$ in $cm^2 . sec^{-1} \times 10^{-6}$, r in cm $\times 10^{-8}$)

Age of soln.	% diffused	Measured Diffusion coeff. $\bar{D}$	Computed Radius r		
			Radius r	Particle weight	Degree of Poly-merisation
5 days	2.8	4.85	5.05	560	2.6
	5.4	4.72	5.19	610	3.1
	10.6	4.44	5.51	730	3.7
	18.0	4.25	5.76	830	4.2
5 weeks	2.0	3.40	7.20	1620	8.3
	4.0	3.46	7.07	1530	7.8
	6.8	3.44	7.11	1560	7.9
	14.0	3.41	7.18	1600	8.1

those basified with sodium hydroxide. The upper limits of the basicity were the maximum that could conveniently be attained without precipitation. The solutions were aged for 8 weeks before measurements were made.

In the final series, diffusion coefficients of solutions of zirconium were measured in the presence of organic reagents. Four organic reagents, acetic, gluconic and citric acids, and urea, were used at a 1 to 1 molar ratio. Two zirconium concentrations, 0.1 and 0.5, were used and the pH was adjusted to match that of the unmasked zirconium solution of the same concentration. The solutions were aged for 10 weeks before diffusion measurements were made.

Results

Diffusion coefficient as a function of time

The diffusion coefficient decreased with increasing time, and reached a limiting value after 4 to 5 weeks. These results are given in Table 3a.I from which it will also be seen that the more concentrated solution, (0.5M), attains equilibrium more rapidly than the dilute solution (0.1M). Furthermore, the equilibrium diffusion coefficient was not the same in each case and was a point requiring further study; this factor was subsequently examined in greater detail.

Another factor of importance was the homogeneity of the particles in solution. Fresh solutions are likely to be polydisperse and this was confirmed in an experiment where runs were for short successive periods. Since the smaller particles diffused more rapidly, diffusion of a solution

Table 3a.III

Variations with Concentration of Solution in the Diffusion Coefficient, Radius, Particle Weight and Degree of Polymerisation of Zirconium Oxychloride. Supporting electrolyte 1.0 M potassium nitrate $\eta = 8.93 \times 10^{-3}$ poise; solutions aged 5 - 6 weeks.
(c in moles/litre, $\bar{D}$ in $cm^2. sec.^{-1} \times 10^{-6}$, r in cm $\times 10^{-8}$)

$ZrOCl_2$ solution		Measured Diffusion Coeff.	Computed		
C	pH	$\bar{D}$	Radius r	Particle weight	Degree of polymerisation
0.856	0.38	3.86	6.34	1100	5.6
0.564	0.47	3.86	6.34	1100	5.6
0.558	0.47	3.84	6.37	1120	5.7
0.494	0.50	3.84	6.37	1120	5.7
0.281	0.65	3.71	6.60	1250	6.4
0.280	0.65	3.71	6.60	1250	6.4
0.236	0.72	3.65	6.71	1320	6.7
0.185	0.86	3.69	6.63	1260	6.4
0.110	1.00	3.47	7.05	1520	7.8
0.097	1.08	3.48	7.03	1510	7.7
0.052	1.32	3.27	7.48	1810	9.3
0.856	0.38	3.86	6.34	1100	5.6
0.200	0.38	4.01	6.10	980	5.0
0.110	0.38	4.17	5.87	880	4.5
0.055	0.38	4.49	5.45	700	3.6

containing a range of sizes led to a concentration of the larger particles in the original solution, and the value of the diffusion coefficient fell with each successive diffusion. After ageing for 5 weeks, at which time apparent equilibrium had been reached as shown above, the particles were less heterogeneous, which is additional confirmation of the attainment of equilibrium. Detailed results are given in Table 3a.II.

Diffusion coefficient as a function of concentration

The first experiment indicated that the equilibrium diffusion coefficients were concentration dependent, and the second series of measurements was made to investigate the effect of concentration on the diffusion coefficient in greater detail. The results are given in the upper part of Table 3a.III. Dilute solutions were shown to have a lower diffusion coefficient than the more concentrated solutions when measured at the natural pH after ageing for 5 to 6 weeks. It was thought that the higher pH might be responsible for greater hydrolysis and increase in particle size in the more dilute solutions. Solutions of 0.05, 0.1, and 0.2 M zirconium were therefore prepared while maintaining the pH at the value of the 0.856 M solution (pH 0.38), by the addition of hydrochloric acid. The results of diffusion measurements on these solutions are given in the lower part of Table 3a.III. Under these conditions it was shown that dilute solutions had a greater rate of diffusion than the more concentrated solutions, i.e., hydrolytic polymerisation was

Table 3a.IV

Variations with Acidity of Solution in the Diffusion Coefficient, Radius, Particle Weight and Degree of Polymerisation of 0.05 M Zirconium Oxychloride. Solutions aged 8 weeks.
(c in moles/litre, $\bar{D}$ in cm^2. sec^{-1}x 10^{-6}, η in poises x 10^{-3}, r in cm x 10^{-8})

		Measured		Computed		
Acid c	Added KNO_3 c	Diffusion Coeff. $\bar{D}$	Viscosity, η	Radius, r	Particle weight	Degree of Polymerisation
5.0	-	4.63	10.9	4.33	350	1.8
2.0	-	4.64	9.4	5.11	580	2.9
1.0	-	4.59	8.9	5.33	660	3.3
0.5	0.5	4.57	8.9	5.36	670	3.4
0.37	0.63	4.49	8.9	5.45	700	3.6
0.2	0.8	4.46	8.9	5.49	720	3.7
0.1	0.9	4.30	8.9	5.69	800	4.1
0.0	1.0	3.27	8.9	7.48	1810	9.3
Alkali c						
0.02	1.0	2.75	8.9	8.90	3060	15.6
0.04	1.0	2.44	8.9	10.03	4370	22.3
0.05	1.0	2.21	8.9	11.07	5880	30.0

repressed by the presence of acid.

Diffusion coefficient as a function of acidity

Since the results given in the previous section indicate that there is an interaction between the effects of concentration and acidity, a further series was run to determine the effect of acidity on the diffusion coefficient measured in 0.05 M solutions of zirconium oxychloride. The results are given in Table 3a.IV. Results for solutions of decreased acidity brought about by basification are also included.

The presence of acid increased the diffusion coefficient of zirconium, but a limiting value was attained when the acid concentration was 0.5 M or greater. Lister and McDonald(30) found no limiting value in nitric acid solution of comparable concentration, a difference that may be due to the lower coordination potential of the nitrate compared with the chloride.

The addition of alkali, on the other hand, rapidly reduced the rate of diffusion, and substantiates the view(45) that highly aggregated hydrolysis products are formed.

Diffusion coefficient as a function of basicity

Since the results of the basified solutions described in the previous section showed a reduction in the diffusion coefficient of zirconium in 0.05 M solutions, and, since concentration has been shown to affect the diffusion coefficient, the effect of basicity on solutions of varying

Table 3a.V (contd.)

$ZrOCl_2$ soln. basified with NaOH			Measured Diffusion Coeff.	Computed		
c	Basicity	pH	$\bar{D}$	Radius r	Particle Weight	Degree of polymer - isation
ca.0.50	50	0.50	3.84	6.37	1120	5.7
"	60	1.07	3.67	6.67	1290	6.5
"	70	1.27	3.27	7.48	1810	9.2
ca.0.25	50	0.71	3.65	6.71	1320	6.7
"	60	1.21	3.51	6.97	1470	7.5
"	70	1.50	3.27	7.48	1810	9.2
a.0.10	50	1.00	3.48	7.03	1510	7.7
"	60	1.48	3.22	7.60	1900	9.7
"	70	1.77	-	-	-	-
ca.0.05	50	1.32	3.27	7.48	1810	9.2
"	60	1.80	2.83	8.65	2810	14.3
"	70	2.07	2.45	9.99	4320	22.0

Table 3a.V

Variations with Basicity of Solution at Four Concentrations in the Diffusion Coefficient, Radius, Particle Weight and Degree of Polymerisation of Zirconium Oxychloride

Supporting electrolyte 1.0 M potassium nitrate, η = 8.93 x 10^{-3} poise; solutions aged 8 weeks.
(c in moles/litre, $\bar{D}$ in cm^2 x sec^{-1} x 10^{-6}, r in cm x 10^{-8})

$ZrOCl_2$ soln. basified with Na_2CO_3			Measured	Computed		
			Diffusion Coeff.	Radius	Particle weight	Degree of polymerisation
c	Basicity	pH	$\bar{D}$	r		
ca.0.50	50	0.50	3.84	6.37	1120	5.7
"	60	-	3.52	6.95	1460	7.4
"	70	1.08	3.06	8.00	2220	11.3
"	75	1.28	2.94	8.32	2490	12.7
ca.0.25	50	0.71	3.65	6.71	1320	6.7
"	60	-	3.33	7.35	1720	8.8
"	70	1.30	2.98	8.21	2400	12.2
"	75	1.63	2.62	9.34	3530	18.0
ca.0.10	50	1.00	3.48	7.03	1510	7.7
"	60	1.15	3.09	7.92	2150	11.0
"	70	1.63	2.73	8.96	3120	15.9
"	75	1.91	2.66	9.20	3380	17.2
ca.0.05	50	1.32	3.27	7.48	1810	9.3
"	60	-	2.75	8.90	3060	15.6
"	70	1.89	2.42	10.11	4480	22.8
"	75	2.22	2.21	11.07	5880	30.0

(see over for continuation of table)

concentration was investigated. Two alkalies, sodium carbonate and sodium hydroxide, were used for preparing the basified solutions, as these are claimed to yield basic compounds of different compositions(23). The results are presented in Table 3a.V.

The diffusion coefficient increased with increasing concentration at all basicities, and increase in basicity resulted in a lower rate of diffusion. The nature of the alkali used also affected the rate of diffusion in the resulting basic solution. Solutions basified with sodium hydroxide had larger diffusion coefficients and hence smaller particles than the equivalent solutions basified with sodium carbonate. Nevertheless, when using sodium carbonate it was possible to obtain clear solutions of higher basicity than when sodium hydroxide was used. The maximum basicities that could conveniently be obtained with sodium carbonate and sodium hydroxide were 75 and 70% respectively.

The highly basic solutions, particularly those that were faintly opalescent, contained particles that were probably markedly asymmetric and of high molecular weight, in which case the calibration of the cell by low molecular weight substances was not strictly valid(120). Diffusion coefficients of particles in solutions of this kind can therefore be regarded as only approximate when measured in this type of apparatus, but the results are at least qualitatively correct.

Table 3a.VI

Variations in the Diffusion Coefficient, Radius, and Particle Weight of Zirconium Oxychloride masked with Equimolar Amounts of Organic Reagents. Supporting electrolyte 1.0 M potassium nitrate, $\eta = 8.93 \times 10^{-3}$ poise; solutions aged 10 weeks; pH adjusted to 0.50 for 0.5 M, and 1.00 for 0.1 M solutions.

(c in moles/litre; $\bar{D}$ in $cm^2.sec^{-1} \times 10^{-6}$; r in cm $\times 10^{-8}$)

Masking Agent	Zirconium c	Diffusion Coeff. $\bar{D}$	Radius r	Particle Weight
None	0.5	3.81	6.42	1150
	0.1	3.40	7.20	1620
Acetic	0.5	1.52	16,10	-
	0.1	2.02	12.12	-
Gluconic	0.5	1.21	20.23	-
	0.1	1.98	12.36	-
Citric	0.5	1.68	14.57	-
	0.1	2.40	10.20	-
Urea	0.5	3.69	6.63	-
	0.1	3.20	7.65	-

Diffusion of masked zirconium solutions

The addition of organic reagents to zirconium solutions to increase the rate of penetration into hide has been advocated by a number of workers. The effect on the rate of penetration of these masked solutions is small when compared with the enormous effect of masking of chromium solutions on the rate of penetration. In addition, an optimum amount of masking agent for zirconium was noted(62), above which the rate of penetration was actually reduced. To investigate the effect of masking on the rate of diffusion, four organic reagents, acetic, gluconic, and citric acids, and urea, were added to solutions of zirconium oxychloride in equimolar proportions which is an excess by practical standards. The concentrations were adjusted to 0.5 and 0.1 M and the pH was brought to the same value as unmasked solutions of the same concentration. Potassium nitrate was added to make the solutions 1.0 M with respect to this reagent. Diffusion measurements were carried out after 10 weeks' ageing, and the results are given in Table 3a.VI.

The most obvious effect was the very appreciable reduction in the rate of diffusion in the presence of the organic acids. In the presence of urea, the diffusion was virtually unchanged, and the small differences could be due to experimental error. Contrary to unmasked solutions of zirconium oxychloride, the diffusion coefficients of zirconium in the presence of organic acids were greater in the more dilute solutions.

In connection with the marked differences in the diffusion coefficient between masked and unmasked zirconium solutions, the possibility of acceleration or retardation of ions in the presence of other ionic species during diffusion measurements must be considered(121). This effect would lead to erroneous results, and is a point requiring further investigation.

General Discussion

Advantages and limitations of the method

The porous diaphragm cell as used above for the determination of diffusion coefficients has several advantages and limitations compared with other methods(120). The main advantages of the method are:

a) The cell is simple and inexpensive to construct, and manipulation and calibration are comparatively easy.

b) The relative insensitivity to convectional and vibrational disturbances due to the stability of the concentration gradient in the pores of the sintered glass disc.

Against these advantages must be set several limitations to which this method is subject.

a) The calibration of the cell by low molecular weight substances is not necessarily valid for high molecular weight substances, especially if the molecules of the latter are markedly asymmetric. The use of a known substance of high molecular weight for purposes of calibration would be more satisfactory, but even so, molecular shape effects might cause difficulty.

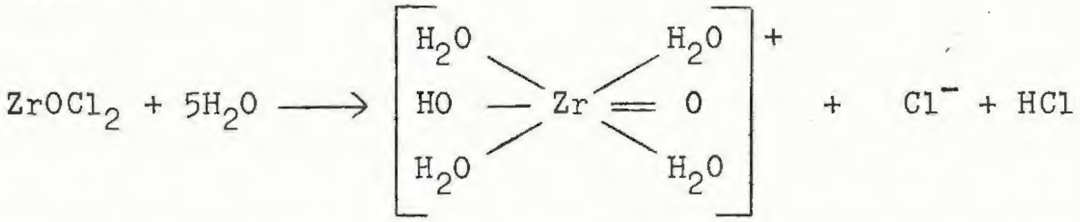
Assuming the particle is spherical, from this radius it is possible to calculate its volume and, if the density is known, its weight.

$$\text{Particle Weight} = \frac{4}{3}\pi\left(\frac{RT}{6\pi\eta DN}\right)^3 N\rho$$

where ρ is the density of the particle in the liquid. (In this work the density is taken to be 1.72 g per c.c., see following section). The particle weights calculated from the diffusion data are neither weight nor number averages, but are usually intermediate values$^{(124)}$.

The density of the diffusing species

When zirconium oxychloride is dissolved in water, hydration occurs, and ultimately the zirconium atom becomes associated by covalent bonds with the maximum number of atoms or groups that the geometry of the zirconium atom and its ligands permits. Although the maximum covalency of zirconium is 8, this is not achieved due to steric effects, and only 7 positions are filled$^{(25)}$. The over-all reaction of zirconium oxychloride with water may be represented by the following equation.



The ionic volume of the hydrated zirconyl ion can be calculated from the volumes of the constituent groups and atoms using Kopps conclusions regarding the approximate additivity of molecular volume(125). From Mellor(126), the molecular or atomic volume of H_2O is given as 18.8, - OH as 13.3, and =O as 12.2. The atomic volume of zirconium calculated from its atomic radius of 1.48 Å(127) is 13.5, which is in close agreement with the volume calculated from the atomic weight and density of the element. Thus the ionic volume of the zirconyl ion is 114.2.

The density, ρ , of the ion is given by the ratio:

$$\frac{\text{Ionic weight}}{\text{Ionic volume}} = \frac{196.2}{114.2} = 1.72$$

which can be compared with 1.8 for the hydrated salt.

Validity of derived radii and particle weights

In view of the absence of complete theoretical treatment, there is some limitation of the absolute accuracy of the calculated values. The following are the more important limitations:

a) The relationship between diffusion coefficient and radius as given by the Sutherland-Einstein equation is valid only in the case of spherical particles, but it has been stated that small deviations from spherical shape can be ignored(83). For example, in the case of two particles of the same volume, one spherical and the other a spheroid of axial ratio 2 to 1, the value of the diffusion coefficient will differ by only 4%.

b) In calculating particle weight, D enters the expression as the 3rd power. Hence it is desirable to achieve the best possible accuracy, since an error in D will be

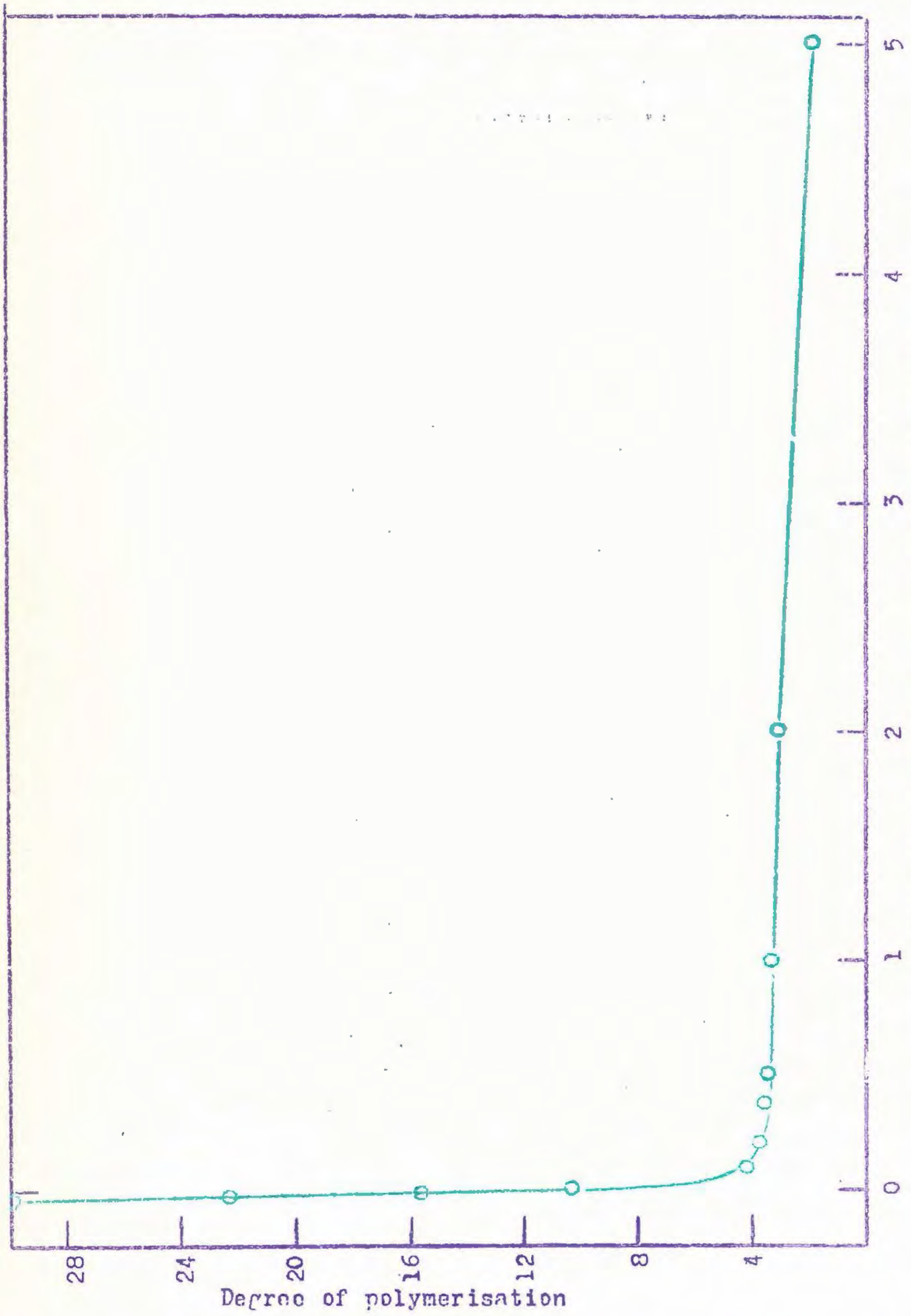


Fig.3a.3 Degree of polymerisation computed as a function of acidity. Concentration of zirconium solutions ca. 0.05M

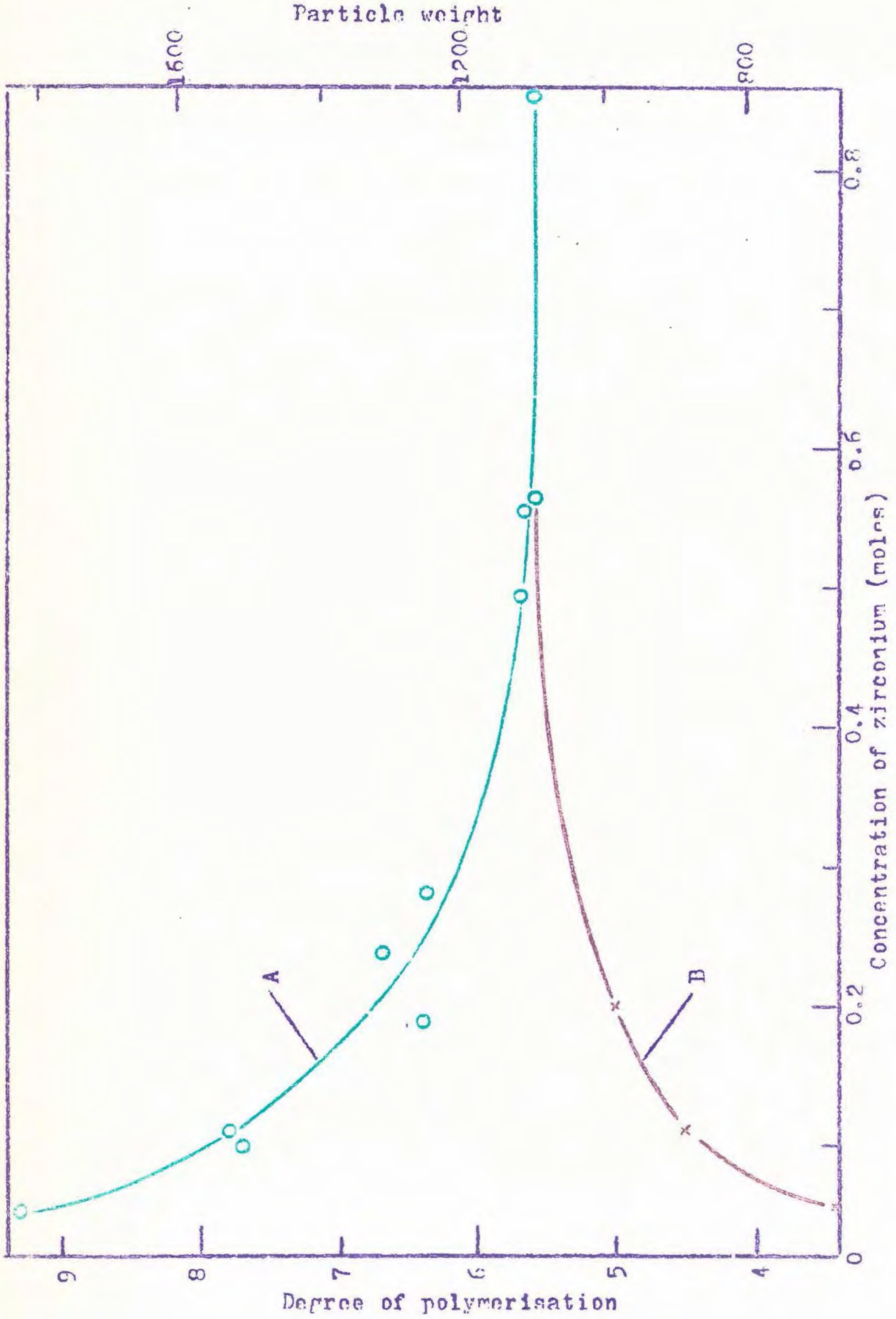


Fig. 3a.2 Particle weight and degree of polymerisation of zirconium computed as a function of concentration.
A. zirconium solution at its natural pH.
B. zirconium solution adjusted to pH 0.38.

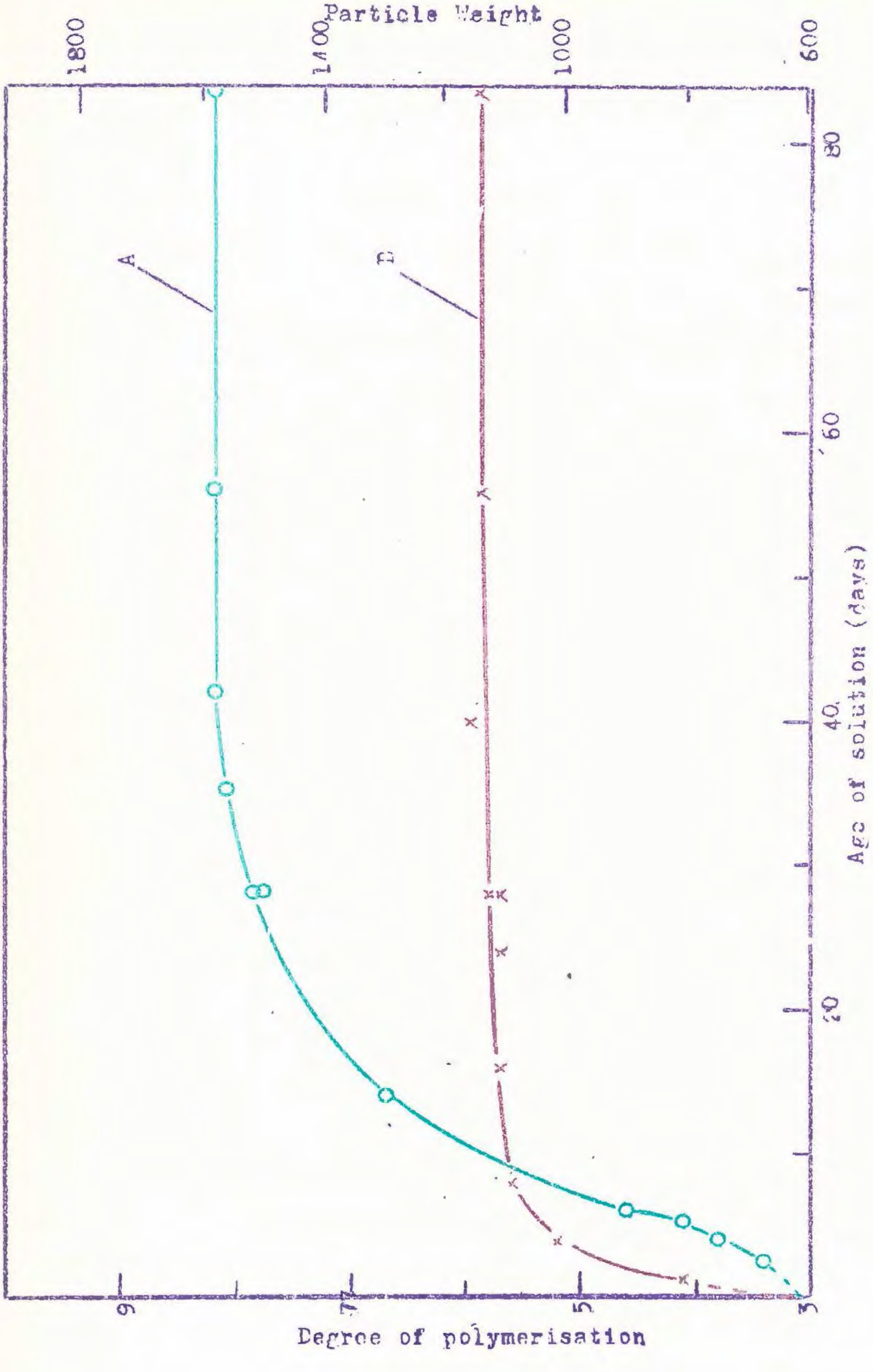


Fig.3a.1 Particle weight and degree of polymerisation of zirconium computed as a function of time.

A. 0.1 M zirconium oxychloride at natural pH

B. 0.5 M zirconium oxychloride at natural pH.

considerably magnified when expressed in terms of particle weight.

c) In calculating the particle weight, the density of the diffusing particle must be used. Obviously, the density to be used is not that of the solid salt, but of the hydrated zirconyl ion, and this can only be estimated from atomic and molecular volumes of the hypothetical zirconyl ion.

Calculation of the degree of polymerisation of the zirconium ion

From the above density calculation it will readily be seen that the monomer is the hydrated zirconyl ion with an ionic weight, calculated from atomic weights, of 196.2. This figure affords the basis for the calculation of the degree of polymerisation from the particle weights determined from the diffusion data. The degree of polymerisation is the average number of hydrated zirconium ions forming a complex. In strongly acid solution, hydrolysis will probably be reduced, and the degree of polymerisation calculated on the basis of fully hydrated ions will be too low.

Results of computations of radius, particle weight and degree of polymerisation

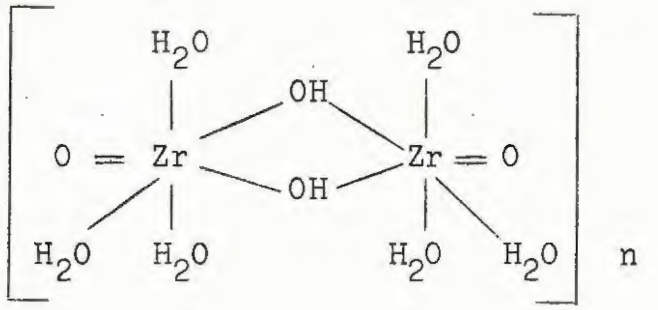
The calculated results are included with the diffusion data in Tables 3a.I - 3a.VI, and some of the results are also recorded graphically in Figs. 3a.1 - 3a.3. The trends are the obverse of those previously described for the changes in the diffusion coefficient.

Extrapolation to zero time of the curves in Fig. 3a.1 indicates a degree of polymerisation of 3.1. At this point hydrolysis and polymerisation could not have commenced, and the value of 3.1 represents the average number of zirconium atoms in a complex. A similar value of 3.2 is the limiting value in hydrochloric acid solution of concentration between 0.5 and 2.0 M, see Fig. 3a.3. This suggests that, under these conditions, hydrolysis and polymerisation are suppressed, and the zirconium complex has a form similar to that in freshly prepared solution. In these solutions it would appear that zirconium exists predominantly as trimers and tetramers, confirming results from studies under similar acid conditions using ultracentrifuge(42,49) and complex formation(24) methods, and implies a special structure for zirconium. In this connection, however, the finding of Clearfield and Vaughan(26) from an X-ray analysis of solid zirconium oxychloride, that the zirconyl group appears as the tetramer in the form of a square, does not quite substantiate the above results. It is possible that the average value of 3.1 results from the opening of some tetranuclear rings to form dimers.

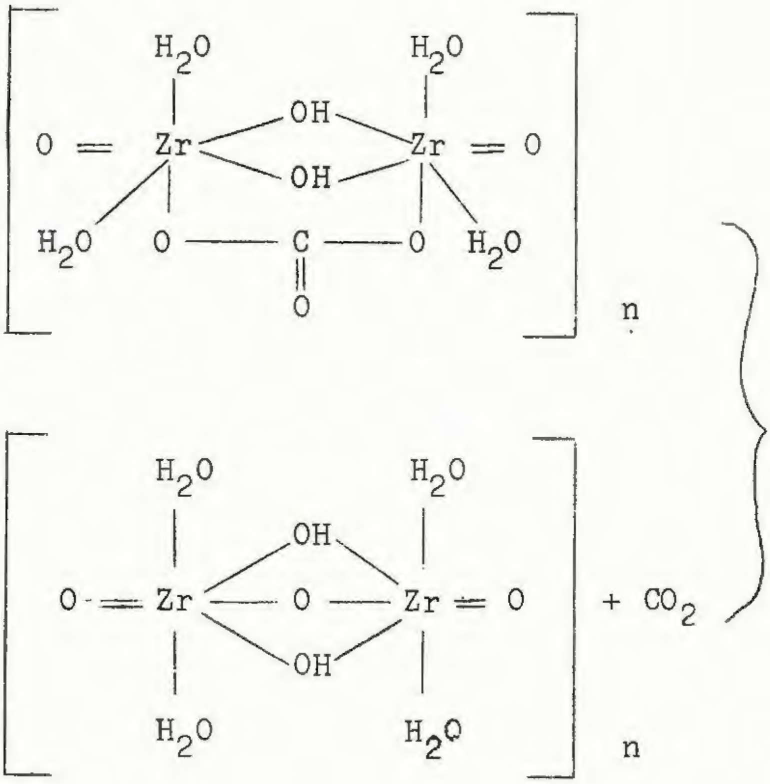
The degree of polymerisation in 5 M hydrochloric acid is apparently lower than the limiting value, but the hydration of the zirconium ion may be reduced in acid of this concentration, resulting in a low particle weight, and thus giving a fictitiously low value for the degree of polymerisation.

The apparent degree of polymerisation in the highly basic solutions lies between 20 and 30, see Fig. 3a.3, but the results obtained from diffusion data are likely to be inexact since zirconium is very sensitive to precipitation and polymeric reactions are complicated at low acidities due not only to the formation of high molecular weight products but also to the slow attainment of equilibrium(46). It was noted that in solutions which had initially been turbid after the addition of the alkali, but cleared on ageing, the degree of polymerisation was not more than 30 with a particle weight of about 6000, even though the addition of further small amounts of alkali caused immediate irreversible precipitation. It would seem, therefore, that this is the maximum particle size prior to precipitation.

The type of alkali used for basifying the solutions also results in differences in particle size. The particle size of zirconium in solutions basified with sodium carbonate is greater than that in solutions of equivalent basicity obtained by the addition of sodium hydroxide, see Table 3a.V. The basic salts obtained from the two alkalies differ in their composition(23), but when sodium carbonate is used it is uncertain whether the radical produced is the basic zirconyl cation, $Zr_2O_3^{2+}$, or whether a compound containing carbonate is obtained. This uncertainty arises because larger particles were found in these solutions than in solutions basified with sodium hydroxide, which would not be the case if carbon dioxide were eliminated from the radical as is indicated by the structures below.



possible basic material formed on addition of sodium hydroxide.

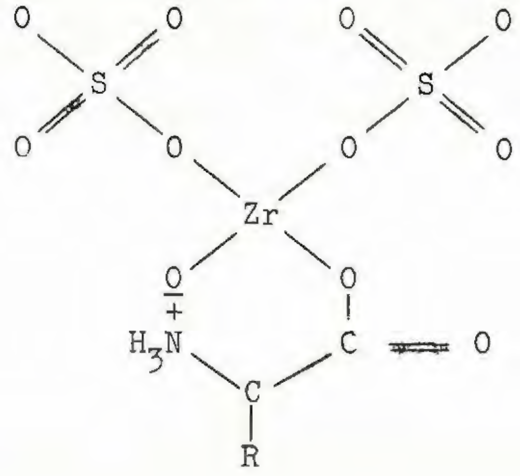


possible basic material formed on addition of sodium carbonate.

Calculation of the particle size from the diffusion measurements of masked zirconium solutions reveals that in many cases the radius is more than doubled in the presence of organic reagents, see Table 3a.VI, and may account for the reduced rate of penetration of acetate and lactate masked solutions into hide(62). The small effect of urea would tend to indicate absence of reaction between this reagent and zirconium, and this view is substantiated in the chapters on potentiometry and electrophoresis.

b. Ionic Nature of Zirconium Determined from Electrophoretic Measurements on Solutions of Zirconium Oxychloride in the Presence of Some Organic Reagents.

Knowledge of the charge on the zirconium complex may be of assistance in determining the mechanism of the reaction between zirconium and collagen, since it is claimed that only specific ionic species are effective tanning agents. Somerville(55,56), for example, maintained that cationic zirconium is responsible for the tanning action, whilst Wilson(73) and Gustavson(67) consider that most of the tannage is accomplished by fixation of anionic complexes. Ranganathan and Reed(28,50) have found that anionic zirconium combines readily with collagen, but they do not preclude the tanning action of complexes of a different charge, whilst Lasserre(75) has found that zirconium fixation is independent of the charge on the complex. Blumenthal(72) suggests that the carboxyl groups of amino acids and proteins tend to become bonded to the zirconium atom in solution, and that in sulphate solutions, which are excellent tanning agents, a pseudo-chelate structure may be formed.



The ionic nature of zirconium complexes has not previously been investigated in great detail, so the charge of zirconium oxychloride was determined at a range of pH values alone and in the presence of a number of organic reagents using the apparatus and technique described in Chapter 2a. The solutions used were 0.1 M with respect to zirconium, and contained the added organic reagents at a 1 to 1 molar ratio. The organic reagents used were acetic, glutaric, glycollic, tartaric, gluconic acids, glycine, α-,β-,γ-amino-n-butyric acids, methylamine, ethylenediamine, and urea. An aliquot of each of the solutions was aged to equilibrium at one of the pH levels 1,2,3,4,6,8, and 10 before electrophoretic measurements were made.

The results and photographic reproductions of the electrograms are given overleaf.

Results

Zirconium oxychloride

At pH 1, the zirconium was predominantly cationic. There were no bands of varying mobility, the area between the front and the origin being uniformly stained. There was a slight indication of migration towards the anode. At pH 2, the result was similar. At all other pH values the zirconium was insoluble and no movement from the original area of application could be detected.

FIG 3b 1

Zirconium oxychloride in the presence of acetic acid

Fig 3 b 2

In the presence of acetic acid at pH 1 there was no evidence of anionic zirconium. The solution was shown to be predominantly cationic. At pH 2, the cationic character of the zirconium was reduced, and anionic zirconium was shown to be present. At pH 3, the migration in the direction of the anode had increased, whilst cationic zirconium had almost entirely disappeared. At higher pH values, the zirconium was insoluble and no migration took place in either direction.

Zirconium oxychloride in the presence of glutaric acid

At pH 1, the greater proportion of the zirconium remained at the origin, but a small amount migrated in the direction of the cathode. At all the other pH values there was no migration, presumably because of the insolubility of the zirconium/glutaric acid complex.

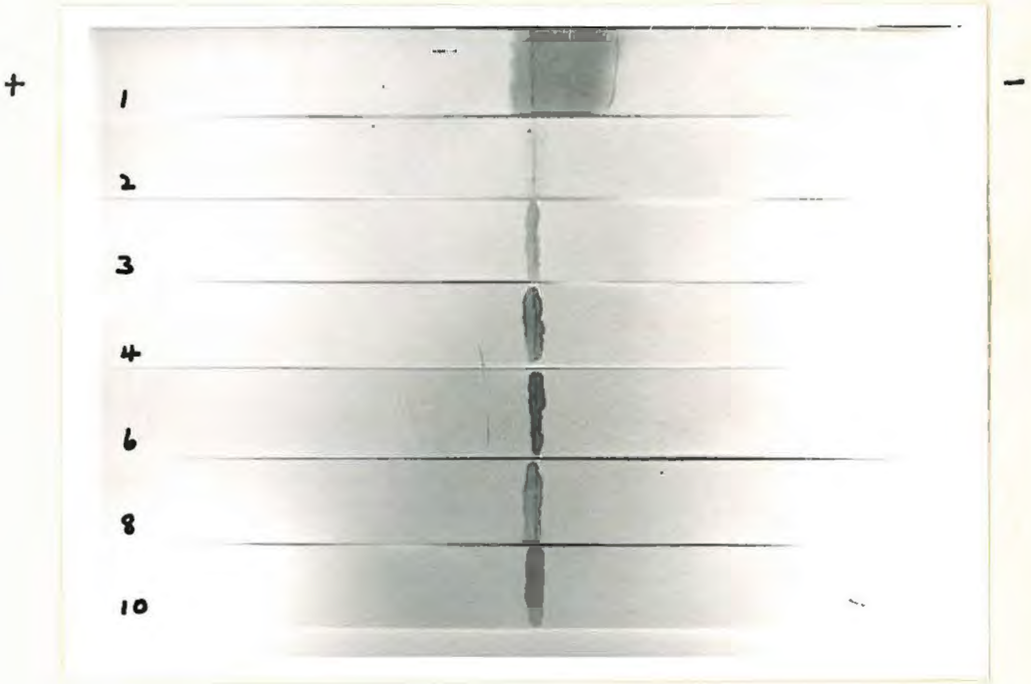


FIG 3b 3

Zirconium oxychloride in the presence of glycollic acid

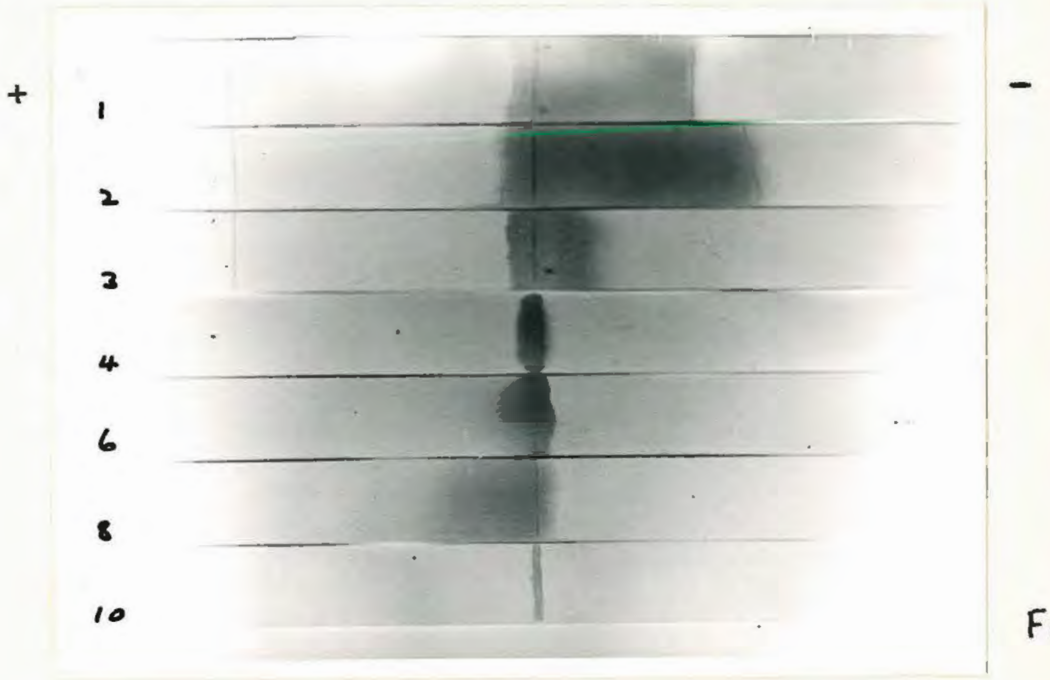


Fig 3b 4

Glycollic acid formed cationic complexes with zirconium at pH values lower than 4. At pH 4, there was little migration in either direction, and the solution applied to the paper was cloudy. At this pH the over-all charge on the zirconium complex was zero, and it can be regarded as a nonionic complex. At pH values of 6 and 8 the complex was anionic, the electronegativity of the zirconium increasing with pH. At pH 10, all the zirconium had precipitated and there was no migration from the origin.

Zirconium oxychloride in the presence of tartaric acid

In the case of the zirconium solution complexed with tartrate, at pH 1 the zirconium was predominantly anionic, although there was a small proportion of cationic forms present. With increase in pH, more and more material travelled towards the anode, and no cationic forms could be detected above pH 2. Although the zirconium became more electronegative with increase in pH, the area between the front of the migrating zirconium and the origin was uniformly stained, indicating a range of mobilities with no definite compounds present. The amount of zirconium remaining at the origin was small at high pH values, but nevertheless was an indication of soluble nonionic complexes under these conditions. The zirconium remained soluble over the whole pH range studied.

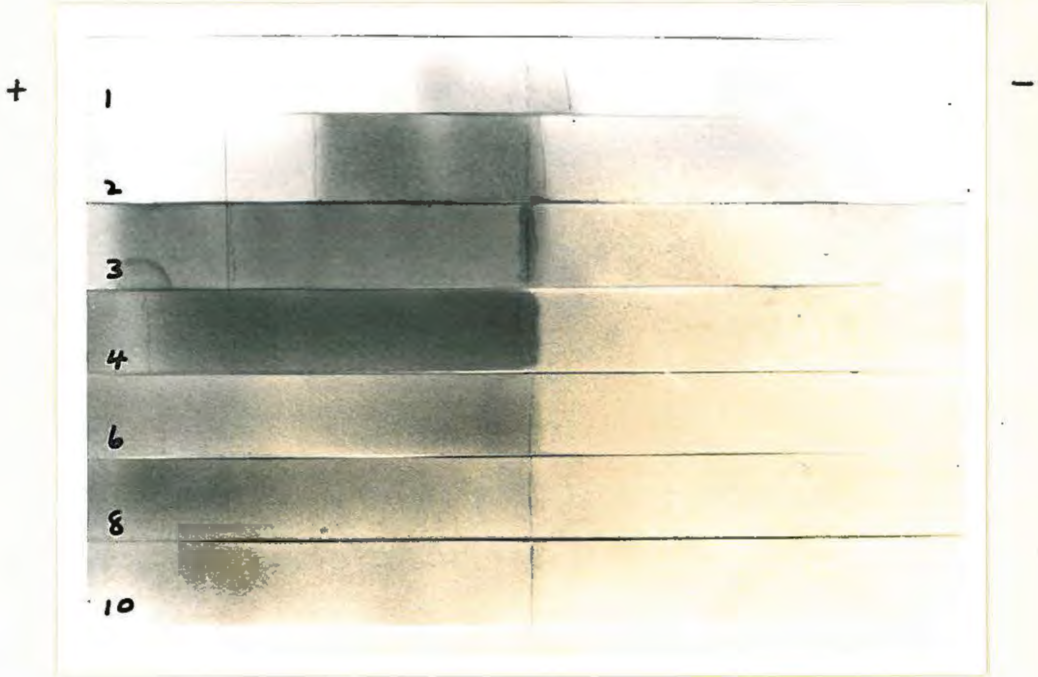


FIG 36 5

Zirconium oxychloride in the presence of gluconic acid

Fig 3b 6

Gluconic acid forms predominantly cationic complexes with zirconium in solutions at pH 1 and pH 2, but a small proportion of anionic material was also present. At pH 3, a precipitate formed, but most of the zirconium remained in solution mainly in the anionic form; a very small amount travelled in the direction of the cathode. At pH 4 and higher, no cationic forms existed, and at the high pH values, viz., 8 and 10, the zirconium was present entirely in the anionic state, no zirconium being left at the origin of the electrogram.

Zirconium oxychloride in the presence of amino acids

Four amino acids, glycine, α-, β-, and γ-amino-n-butyric acids were used, but the reactions in each case were so similar that they can be considered together. Only at pH 4 could minor differences be detected and this will be discussed later. The over-all picture is that at pH values up to 3, the mobile zirconium is mainly cationic with a very small proportion moving towards the anode. At pH values of 6, 8, and 10, all the zirconium had precipitated, and there was no evidence of soluble ionic forms. No soluble zirconium was found in the presence of glycine at pH 4, whilst only a very small proportion was soluble in the presence of α-amino-n-butyric acid and this did not migrate. A much greater proportion of the zirconium was soluble in the presence of β-amino-n-butyric acid and still more was soluble in the presence of the γ isomer. This can probably be explained by the increase of the pH of precipitation with increase of the pK value of the four acids (see section on potentiometry) with the resulting increase in the amount of unprecipitated zirconium at pH 4 in the presence of the respective amino acid. In the case of β-and γ-amino-n-butyric acids the soluble zirconium migrated mainly in the direction of the cathode, although a small proportion of anionic complexes were present.

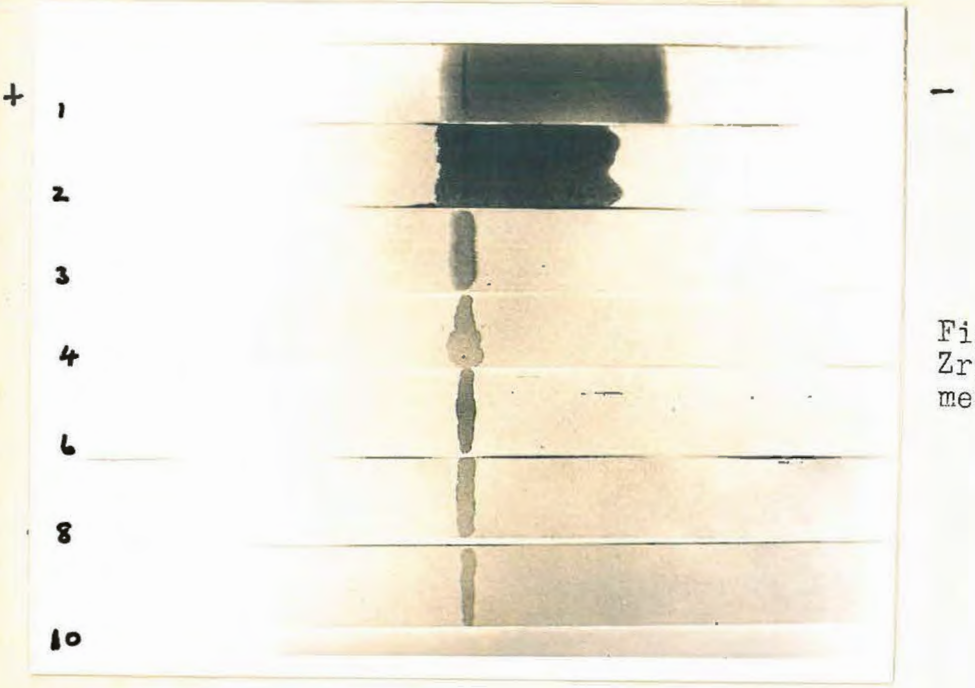


Fig.3b 11
$ZrOCl_2$ +
methylamine

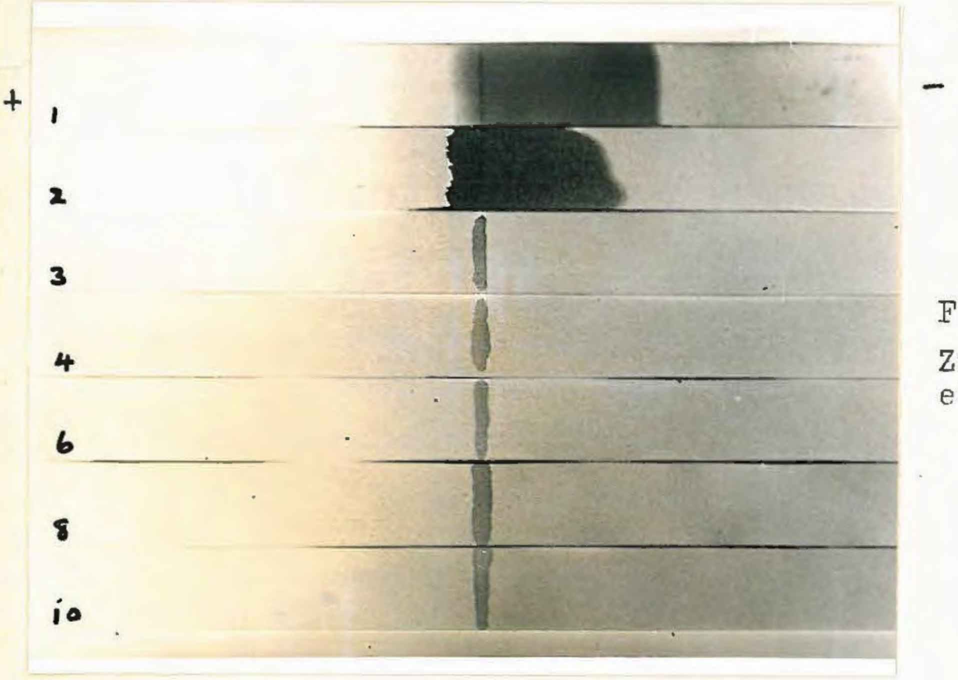


Fig.3b 12
$ZrOCl_2$ +
ethylenediamine

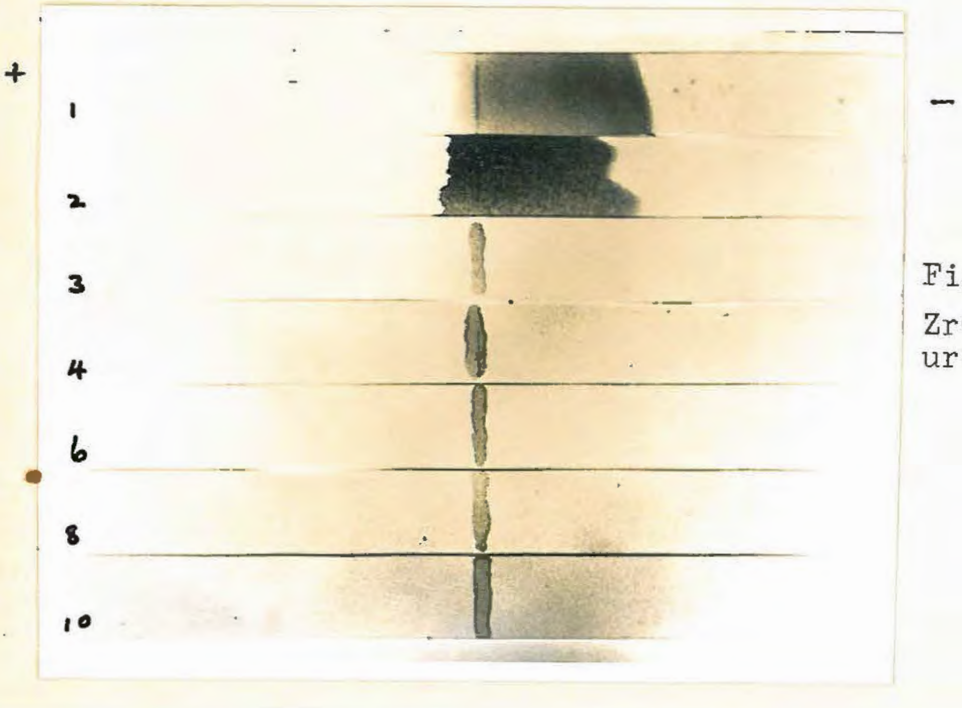


Fig.3b 13
$ZrOCl_2$ +
urea

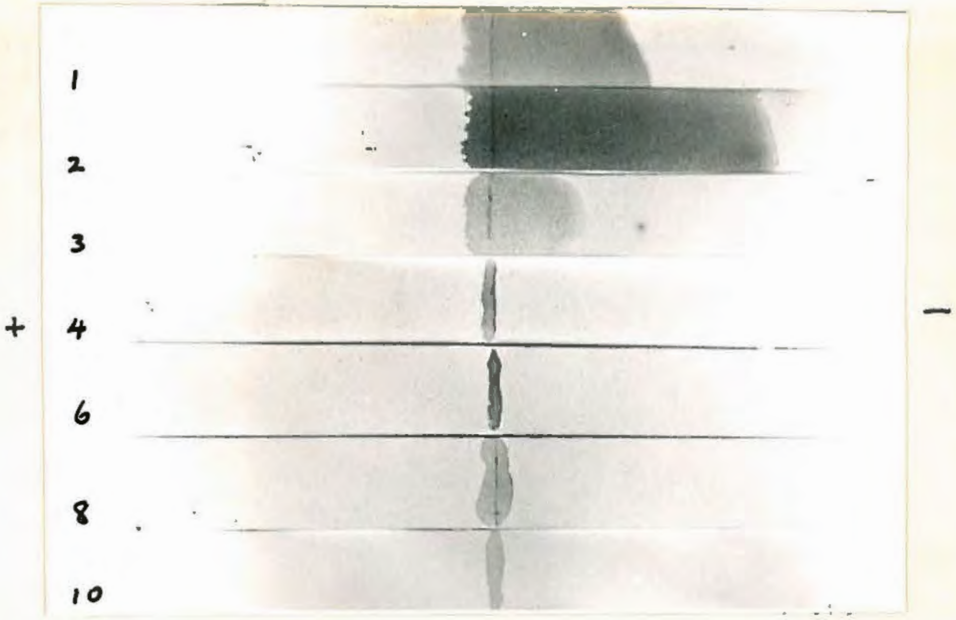


Fig.3b 7
glycine
⟶

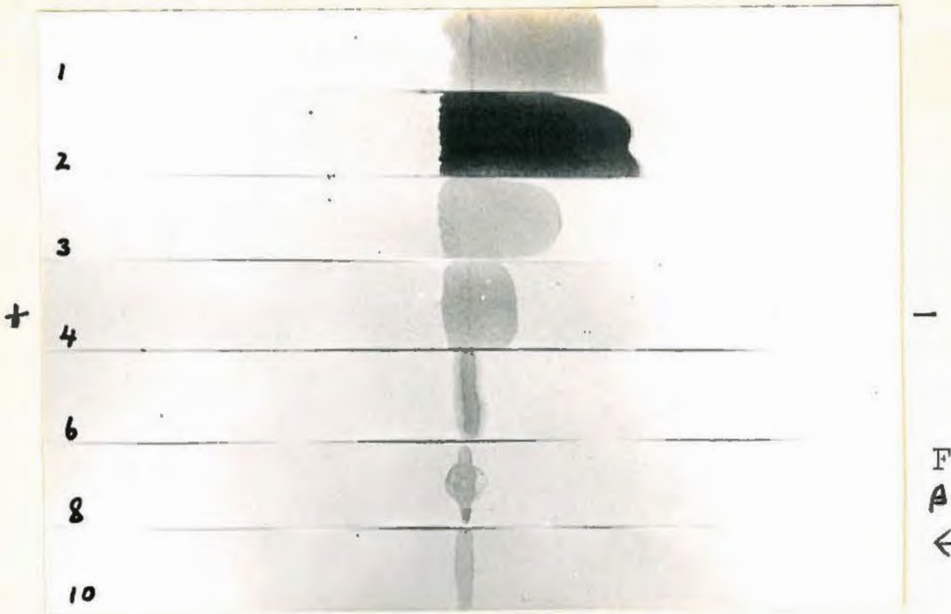


Fig3b 9
β-NH_2 butyric
⟵

Fig.3b 8
α-NH_2 butyric
⟶

Fig.3b 10
γ-NH_2 butyric
⟵

Zirconium oxychloride in the presence of methylamine and ethylenediamine

Methylamine and ethylenediamine did not confer any increased resistance to precipitation on solutions of zirconium oxychloride, and there was no evidence of soluble ionic complexes formed at pH values of 3 and above. At pH values 1 and 2, the solutions behaved in exactly the same manner as unmasked zirconium oxychloride solution.

Zirconium oxychloride in the presence of urea

No reaction with urea could be detected. The solutions were similar to unmasked zirconium oxychloride solutions in every respect. This similarity extends also to the potentiometric titration of solutions of zirconium in the presence of urea, see Chapter 3c. In addition, urea has little effect on the particle size of zirconium in solutions (see section on diffusion measurements, Chapter 3a).

Discussion

Although the zirconium salt used in this work was the oxychloride, the results bear out the findings of Ranganathan and Reed(28) in most respects where the work overlaps, but do not agree with the results of Portes(29). Ranganathan and Reed, using zirconium sulphate, found increased electronegativity of the zirconium with increased masking with citrate. In the present work it was also found that in the presence of hydroxy acids the anionic nature of the zirconium was increased, (Fig.3b.4 to 3b.6), and at higher pH levels cationic species were nonexistent. In the case of glycollic acid, Fig. 3b.4, anionic complexes did not form until a pH of 4 had been reached.

Portes found that zirconium oxychloride became more predominantly cationic with increase of pH up to pH 7, the amount of migration being quite considerable at this pH! This seems unlikely since zirconium oxychloride is insoluble at pH values above 3. The electrolyte used by Portes was a 2% solution of hydrochloric acid and it seems probable that small amounts of zirconium were redissolved during the course of the experiment, giving an erroneous impression.

In the presence of the amino acids, Figs. 3b.7 to 3b.10, zirconium did not behave in the same way as it did in the presence of acetic acid, Fig. 3b.2. The resulting complexes were all positively charged, whereas the zirconium in the presence of acetic acid became more anionic in character, thus indicating that the amino groups of the acids had not been involved in the reaction with zirconium. The amines, Figs. 3b.11 and 3b.12, and urea, Fig. 3b.13, caused no change over the whole pH range, and it seems that under these conditions nitrogen is not coordinated to zirconium.

Table 3c.I

The pH values at which precipitation occurred in 0.05 M solutions of zirconium oxychloride and zirconium sulphate in the presence of organic reagents on titration with sodium hydroxide and sodium carbonate.

	Molar Ratio of Organic Reagent to Zirconium							
	1 : 1		2 : 1		4 : 1		8 : 1	
	NaOH	Na_2CO_3	NaOH	Na_2CO_3	NaOH	Na_2CO_3	NaOH	Na_2CO_3
Zirconium oxychloride	2.27	3.16						
$ZrOCl_2$ + acetate	3.34	-	4.47	5.00	5.02	5.00	5.13	5.17
" + tartrate	ppt in orig	ppt in orig	no pptn.	no pptn	no pptn	no pptn	no pptn	no pptn
" + lactate	10.81	no pptn	11.82	no pptn	12.16	no pptn	12.31	no pptn
" + gluconate	no pptn	no pptn	no pptn	no pptn	no pptn	no pptn	no pptn	no pptn
" + urea	2.30	3.36	2.47	3.63	2.52	3.65	2.90	4.00
" + glycine	2.88	-	2.82	4.09	2.90	4.38	-	4.60
" + methylamine	4.1	5.3	4.2	5.0	4.3	5 2	-	-
" + ethylenediamine	3.6	4.6	3.8	4.4	4.5	4.5	-	-
Zirconium sulphate	1.4	2.6						
$Zr(SO_4)_2$ + acetate	2.4	3.4	3.2	5.0	4.3	5.2	4.9	5.5
" + tartrate	ppt in orig	ppt in orig	no pptn	no pptn	no pptn	no pptn	no pptn	no pptn
" + lactate	5.5	-	6 7	no pptn	8.2	no pptn	11.7	no pptn
" + gluconate	no pptn	no pptn	no pptn	no pptn	no pptn	no pptn	no pptn	no pptn
" + methylamine	crystals of basic zirconium sulphate formed							
" + ethylenediamine	" " " " " "							

c. Potentiometric Titration Studies on Solutions of Zirconium Oxychloride and Zirconium Sulphate in the Presence of Some Organic Reagents

Potentiometric measurements provide evidence, which cannot always be obtained by other means, concerning the nature of acidic and basic groups present in complex ions. Potentiometry also affords the means of determining which groups are involved in reactions between organic reagents and metal ions.

The potentiometric method has been employed by a number of workers in measuring the stability of metal complexes with organic acids, amino acids, and peptides(29,31,128-138) and to study the hydrolysis and polymerisation of zirconium salts(30,33,139).

Qualitative potentiometric studies

The relative stabilities of solutions of zirconium oxychloride or sulphate in the presence of various molar ratios of several organic reagents containing the reactive groups found in hide protein, viz., carboxyl, amino, hydroxyl etc., were determined by measuring the pH of precipitation when solutions 0.05 M with respect to zirconium were titrated with $N/_5$ sodium hydroxide or sodium carbonate. The results are given in Table 3c.I.

It is interesting to note that zirconium precipitated from oxychloride solutions at a higher pH value than it did from sulphate solutions. If the pH of precipitation is taken as a measure of the stability of the complexes formed, high pH of precipitation indicating strong complex formation, the above results appear to indicate that chloride formed stronger complexes than sulphate. However, since zirconium sulphate solutions are known to be unstable due to the formation of insoluble basic compounds containing sulphate(44,75), the above results cannot necessarily be taken as evidence that chloride is a stronger complexing agent than sulphate. The published precipitation points of pH 2.40 and 3.50(21) are for 50% basic zirconium sulphate solutions titrated with sodium hydroxide and sodium carbonate respectively, and are more likely to be comparable with the oxychloride results.

In general, the greater the amount of organic reagent present, the higher was the pH at which the zirconium was precipitated, but the protection afforded the zirconium varied considerably with the organic reagent. Of the organic reagents listed in Table 3c.I, only gluconate afforded complete protection over the pH range 1 to 13, with as little as 1 mole per mole of zirconium. Tartrate also prevented precipitation at high pH values at a ratio of 1 mole per mole, but in acid solution a precipitate occurred which was dissolved on addition of a further mole or more of tartrate. Lactate, the other hydroxy acid ligand investigated, imparted much increased stability to zirconium solutions, but precipitation was not entirely prevented even when it was present in a large excess. The difference between zirconium oxychloride and sulphate solutions in the presence of lactate was very marked, the zirconium precipitating from sulphate solutions at a much lower pH value even in the presence of

8 moles of lactate per mole of zirconium.

Glycine which also has two reactive groups, actually imparts less stability than acetate to zirconium solutions. Chelation greatly increases stability as illustrated by the reaction between glycine and copper(130), thus the above results indicate that chelation between glycine and zirconium does not occur under the conditions studied, and that the relative stabilities may be a function of the acid dissociation constants. The addition of glycine to zirconium sulphate solutions resulted in immediate precipitation.

Urea has very little effect on the pH of precipitation of zirconium. The small increase in stability in the presence of a large excess of urea may be due to some slight protection in the same way that neutral salts increase the pH of precipitation(32). Urea complexes with zirconium are stable only under anhydrous conditions, and they decompose in water due to the greater affinity of zirconium for the oxygen atoms of the water than for the nitrogen atoms of urea(140,141).

The addition of methylamine hydrochloride and ethylenediamine hydrochloride imparted some stability to solutions of zirconium oxychloride, although there is no evidence of the combination of organic amines with zirconium in aqueous solution(140). In zirconium sulphate solutions containing the amines, crystals of a basic zirconium salt which contained no nitrogen are formed after standing for 24 hours. On titration with alkali these crystals decomposed at an indeterminate pH with the formation of a gelatinous precipitate. Crystals of basic zirconium sulphate are not formed in sulphate solution under similar conditions of pH and concentration, on ageing for the same length of time. The above results indicate that only hydroxy acids are effective complexing agents, and this agrees with previous work(31).

Potentiometric titration curves

Potentiometric methods appear to be of value in determining the reaction mechanism of zirconium with collagen. Unfortunately the equilibrium time necessary and steric hindrance effects produce difficulties, so a study of the reaction between zirconium and amino acids was undertaken. Since amino groups α to the carboxyl groups are not present in collagen, a series of α-, β -, and γ -amino acids was used, as the last named is more likely to reflect the relative positions of the reactive groups in fibrous protein.

A series of aqueous solutions of zirconium oxychloride was made up 0.02 M with respect to zirconium containing the organic acids acetic, glycollic, glycine, α -, β -, and γ -amino-n-butyric in 1, 2, or 4 to 1 molar ratios. Each series was adjusted to equilibrium pH values of 1.0, 1.9, 2.8, or 3.7 with hydrochloric acid or sodium hydroxide respectively, and aged before titrating with $N/_5$ sodium hydroxide using the technique described in Chapter 2a. pH measurements were made with a wide range glass electrode and a complete titration curve plotted for each solution. pH values at which the solutions became opalescent, and at

Table 3c.II

pH values at which opalescence and coagulation were noted in 0.02 M solutions of zirconium oxychloride in the presence of organic and amino acids on titration with N/$_5$ sodium hydroxide.

Equilibrium pH of Aged Solutions

	1 . 0		1 . 9		2 . 8		3 . 7	
	Opal.	Coag.	Opal.	Coag.	Opal.	Coag.	Opal.	Coag.
Zirconium oxychloride	3.1	3.9	3.4	4.7	4.2	5.5	4.9	5.8
$ZrOCl_2$ + 1 mole acetate	3.5	4.4	4.0	4.9	3.8	5.1	Opal. orig.	-
" + 2 " "	4.4	5.0	4.3	5.2	3.6	5.1	4.6	5.3
" + 4 " "	4.9	5.8	-	-	4.3	5.2	4.5	6.2
" + 1 " glycine	2.8	4.9	2.9	5.3	2.8	5.3	opal. orig.	4.8
" + 2 " "	2.8	4.7	3.1	5.5	3.5	5.4	3.7	5.4
" + 4 " "	2.9	5.0	3.9	5.4	4.0	5.6	4.2	5.9
" + 1 " α NH_2 butyric	2.8	4.6	2.9	5.0	-	4.7	opal. orig.	4.5
" + 2 " "	2.7	4.2	3.4	5.3	3.7	5.2	3.7	5.4
" + 4 " "	2.9	4.2	3.3	5.2	3.9	5.3	4.2	6.0
" + 1 " β NH_2 butyric	3.5	5.7	3.3	5.6	4.3	5.5	opal. orig.	5.0
" + 2 " "	3.5	5.8	3.5	5.7	3.8	5.6	3.9	5.8
" + 4 " "	3.2	5.6	3.5	5.7	4.1	6.0	4.3	6.2
" + 1 " γ NH_2 butyric	3.5	6.0	3.6	-	4.1	5.7	4.0	5.8
" + 2 " "	4.2	6.2	4.1	6.3	4.3	6.1	4.1	5.9
" + 4 " "	4.0	7.5	4.2	6.1	4.5	6.2	4.5	6.6
" + 1 " glycollate	no pptn.	no pptn.	no pptn.	no pptn.	no pptn.	no pptn.	no pptn.	no pptn.
" + 2 " "	ppt.orig.	clear 6.3	ppt.orig.	clear 4.7	ppt.orig.	clear 3.9	"	"
" + 4 " "	"	clear 6.2	"	clear 4.0	"	clear 2.9	"	"

which the precipitate coagulated, were noted and are recorded in Table 3c.II.

The most obvious difference in the behaviour of the organic acids investigated was that of glycollic. At low pH values and at a 1 to 1 molar ratio the solutions were clear, but, when the pH was raised, insoluble non-gelatinous compounds were precipitated which dissolved when more alkali was added. In solutions containing 2 and 4 moles of ligand per mole of zirconium, at low pH, precipitates formed which redissolved on raising the pH. This agrees with Blumenthal's statement on the reaction of α-hydroxy acids with zirconium(23).

No great differences between the remaining acids were apparent. All solutions yielded a gelatinous precipitate when sufficient alkali was added to raise the pH above 7.0, but minor differences in the pH of incipient precipitation were noted. At first sight these pH values seemed to be related to the acid dissociation constants of the acids, but a plot of the pH of precipitation against pK_1, see Fig. 3c.1, shows that acetic acid with the highest pK_1 value was no better than glycine with the lowest pK_1 value. This could be explained by Monk's observation(130) that the introduction of an amino group increases chelation tendency with consequent increase in stability, although the dissociation constant is reduced. No linear or curvolinear relationship exists between the stability and the pK_1 values of these acids, see Fig. 3c.1, but this is hardly to be expected since the relationship between stability and the dissociation

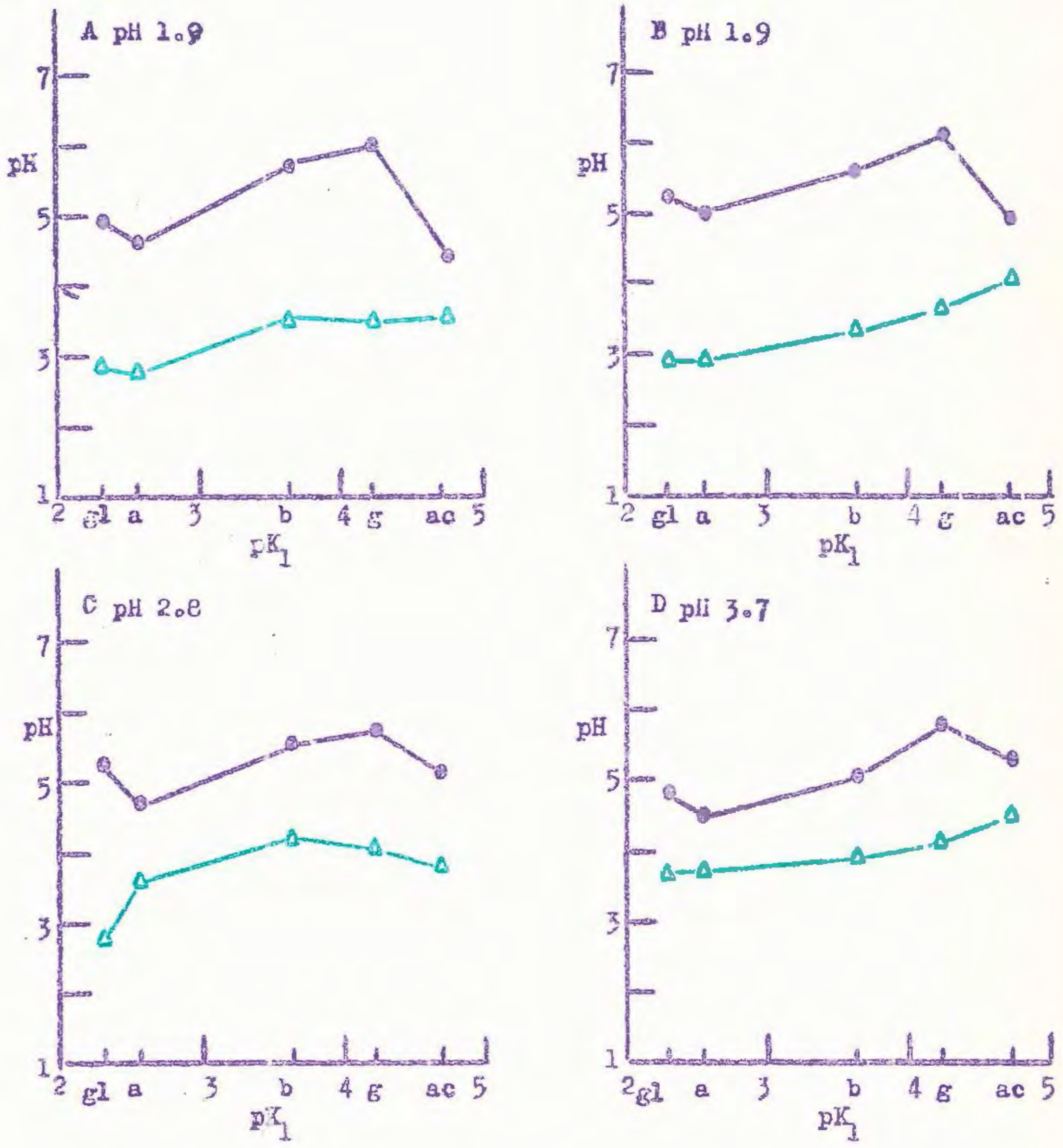


Fig. 3c.1 Relationship between pH ofopalesence and coagulation, and the pK$_1$ values of the organic acids.

a=α-amino-n-butyric acid
b=β-amino-n-butyric acid
g=γ-amino-n-butyric acid
ac= acetic acid
gl= glycine

Δ= pH of opalesence 1 mole ligand / mole zirconium
●= pH of coagulation 1 mole ligand / mole zirconium

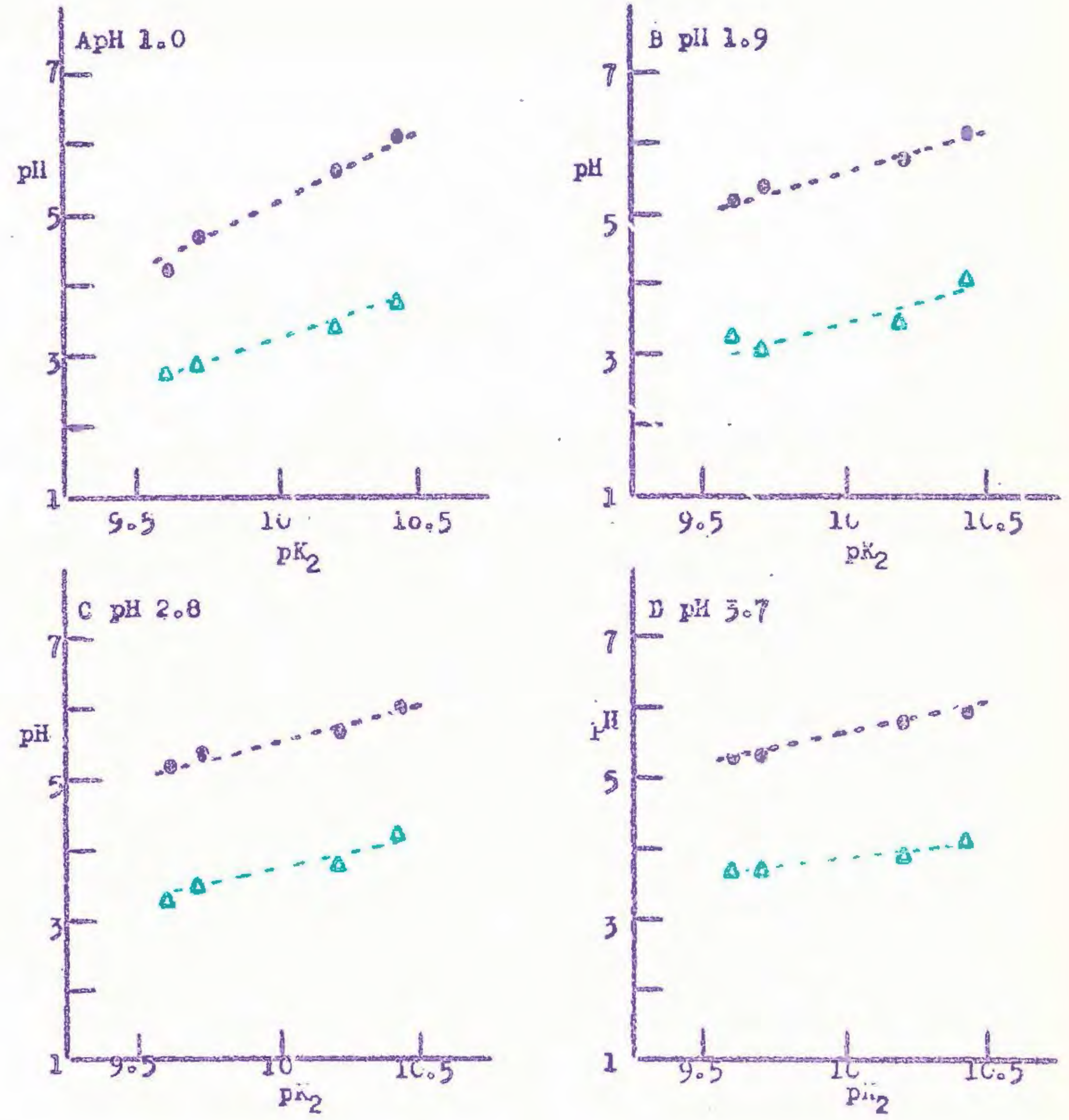


Fig. 3c.2 Relationship between pH of opalescence and coagulation, and the pK_2 values of the organic acids.

Δ = pH of opalescence 1 mole ligand / mole zirconium
θ = pH of coagulation 1 mole ligand / mole zirconium

constants has been shown to be more complicated than had hitherto been assumed$^{(142)}$. The same relationship does not hold for the same substituents on complexing agents of different nature. Hence in this investigation it is permissible to compare only the amino acids or more strictly the isomeric amino-n-butyric acids. If this is done, a linear relationship is found between the stabilities and the pK_1 values, see Fig. 3c.1. If the pH of precipitation is plotted against the pK_2 values, which are related to the pK_1 values, a similar result is found, see Fig. 3c.2.

Since the pH of precipitation is difficult to determine with any degree of accuracy, too much reliance cannot be placed on these results. The determination of stability constants would be more accurate if suitable methods were available. The titration curves plotted in this work do not permit the calculation of stability constants, but it is possible to determine that complex formation has taken place$^{(128)}$. When a mixture of two substances which do not mutually form a complex is titrated with alkali, the curve obtained reproduces the component curves, i.e., the titration effect is additive when no complex formation takes place. When, however, the two substances form a complex, an entirely different picture is seen. The new curve no longer traverses the component curves but follows an independent path. The extent of the displacement forms a measure of the stability of the complex.

A detailed investigation of the titrations

Table 3c III

Approximate pK Values of Organic Acids(143)

	pK_1	pK_2
Acetic acid	4.70	-
Glycollic	$(3.83)^{++}$	-
Glycine	2.31	9.72
α-NH_2-n-butyric acid	2.55	9.60
β-NH_2-n-butyric acid	3.63	$(10.20)^{+}$
γ-NH_2-n-butyric acid	4.23	10.43

(+ Estimated value ++ Calculated from the dissociation constant(144)) performed on solutions equilibrated at pH 1.0 will not be made because of the inaccuracy of pH as a measure of hydrogen ion concentration at this level. The complete range of titration curves on solutions aged to equilibrium at the other pH values is given in Figs. A1 to A45 in the appendix. These curves are for zirconium oxychloride in the presence of acetic acid, glycine, and α-, β-, and γ-amino-n-butyric acids aged to equilibrium at pH values of 1.9, 2.8, and 3.7 using 1, 2 and 4 moles ligand per mole of zirconium when titrated with $N/_5$ sodium hydroxide.

From the titration curves of zirconium oxychloride in admixture with the organic ligands, Figs. A1-A45, it will be seen that there is considerable displacement from the blank curve, which is a composite curve derived from the addition of the titration curves of the components performed independently. Since all the solutions were adjusted to one of three predetermined pH values, the displacements read from the titration curves for equimolar amounts of the various ligands are not strictly comparable because of the different pK_1 values of the acids used, see Table 3c. III. Thus at any of the chosen pH values, a greater proportion of the carboxyl groups of acids with low pK_1 values will have been titrated, than the carboxyl groups of acids with high pK_1 values. For example, at pH 2.8 the greater portion of the carboxyl groups of glycine and α-amino-n-butyric acid will have been titrated, whereas the carboxyl groups of the remaining acids will not have reached the half-neutralisation point. This will have to be taken into account when the relative displacement of the curves of the different ligands are considered. The displacements were measured at pH values between 7.0 and 8.0 at which point the carboxyl groups of all the organic acids had been titrated.

Consideration of Fig. 3c.3 (Fig. A1) shows that the displacement of the titration curve of zirconium oxychloride in the presence of 1 mole of acetate per mole of zirconium is equivalent to approximately 1 mole of alkali, read at the endpoint of the titration. This means that 1 mole of acetate ligand is no longer available for titration and has been coordinated to the zirconium. This displacement is slightly increased with increasing molar ratios of organic ligand, see Figs. 3c.4 and 3c.5. (Figs. A2, A3).

In the presence of the amino acid ligands, see for example Figs. 3c.6 to 3c.9 (Figs. A10, A19, A28, A37), similar displacements are noted, but there is no evidence that the amino groups have been involved in the reaction with the zirconium. The amino groups are free to titrate, and the portion of the curve at pH values in the region of the pK_2 values follows parallel to the blank.

Interpretation of the titration curves of the solutions equilibrated at higher pH values, viz., 2.8 and 3.7, is more difficult, because some of the carboxyl groups of the organic acid ligands have been titrated. However, as the titration curves of the zirconium solutions containing equimolar amounts of the complexing agents, but aged to

Table 3c.IV

Moles of Organic Acid Coordinated per Mole of Zirconium

	Moles Added								
	1:1			2:1			4:1		
	pH 1.9	pH 2.8	pH 3.7	pH 1.9	pH 2.8	pH 3.7	pH 1.9	pH 2.8	pH 3.7
Acetic acid	1.0	1.0	0.9	1.1	1.1	1.2	1.8	1.7	1.8
Glycine	1.0	1.0	0.9	1.4	1.2	1.1	2.4	1.8	1.7
α -amino-n-butyric	0.6	0.6	0.6	0.6	0.6	0.7	0.6	0.5	0.4
β " "	0.7	0.7	0.7	0.7	0.7	0.7	0.8	0.7	0.7
γ " "	0.8	0.5	0.8	1.0	0.8	0.8	1.3	0.9	0.7

equilibrium at different pH values, are almost superimposable, allowance can be made for the amount of organic acid already titrated at the equilibrium pH. From this, the amount of organic acid that has been complexed at each pH can be calculated, and these results are given in Table 3c.IV. Particularly striking is the low amount of coordination of α-, β - and γ-amino-n-butyric acid compared with acetic acid and glycine, which may be due to steric hindrance.

The results of these titrations indicate that carboxyl groups coordinate directly with the zirconium, and there is no evidence of reaction with amino groups. This is contrary to what has been found in previous work, viz., that carboxyl groups play no part in the reaction between zirconium and collagen, and that amino groups are responsible for at least a portion of the zirconium fixation(50). Thus the differences must lie in the type of zirconium salt used in the various investigations. Ranganathan and Reed(50) used zirconium sulphate in the study of the reaction mechanism employing small scale tannages, so this salt was investigated potentiometrically in the presence of the organic acid ligands used above at pH 1.9 and at 1 to 1 molar ratio with zirconium. The results of these titrations are given in Figs. 3c.10 to 3c.14.

It is interesting to note that in the acid range these curves almost exactly duplicate the blank curve, indicating that there is no appreciable coordination of the carboxyl groups to the zirconium under the condition studied.

This is quite different from the curves derived from zirconium oxychloride under similar conditions of concentration and pH. At higher pH values some displacement does occur with a reduction in buffering capacity. This does not prove that amino groups have been coordinated, because a similar trend is found in the presence of acetate where there are no amino groups to take part in the reaction.

Discussion

The difference in behaviour of the two zirconium salts investigated above may explain the different reactions of the salts with collagen. Coordination to carboxyl groups is claimed to be the main reaction in chromium tanning(4); whilst similar co-ordination has been shown with zirconium oxychloride, leathers of poor stability are produced even though the zirconium content is quite high. This can only mean either that the chloride tanning complexes are not big enough to form crosslinking bonds, which is most unlikely in view of the findings on particle size, see Chapter 3a, or that the polymers are held together by weak bonds which are unable to impart high hydrothermal stability. Zirconium sulphate on the other hand forms large aggregates but does not react with collagen through the carboxyl groups, and there is little evidence for the reaction with amino groups. The combination of zirconium sulphate with collagen must therefore be by some as yet undetermined means.

The over-all reaction of zirconium oxychloride with carboxyl groups is similar to that of chromium, but minor differences in detail occur. The potentiometric evidence is not conclusive, but if the extent of the displacement of the titration curve from the composite blank is an indication of the extent of coordination of the organic acid ligand, then solutions aged to equilibrium at pH 1.9 show a greater number of coordinated carboxyl groups than carboxyl groups in similar solutions aged at higher pH values, see Table 3c.IV. Thus the reaction, in the case of the chloride, appears to involve uncharged carboxyl groups, but this is not likely because no reactions of a similar kind have been reported and it would mean that the small number of hydroxyl groups from the carboxyl of the organic ligand had successfully competed with the very large excess of water in the system. The reaction of chromium and organic acids has been shown to involve the charged carboxyl groups(4,145-148), and it is probable that a similar reaction occurs with zirconium oxychloride. The most likely explanation of the reduced coordination of carboxyl groups to zirconium at the higher pH values is that, at these pH values, competition from hydroxyl groups, for which zirconium has great affinity, has become considerably greater, and the resulting olation makes reaction with carboxyl groups more difficult due to steric effects.

This work has shown that approximate estimations can be made of the amounts of organic acids coordinated to zirconium oxychloride from potentiometric studies. It is also apparent from the results in Table 3c.IV that there is no indication of definite combining proportions; the pattern is typical of a mass-action relationship, but the relative amounts bound bear no simple relationship to the pK_1 or pK_2 values of the acids employed. Zirconium sulphate appears to react quite differently with the organic acids, presumably because of competition from the sulphate radical and the attendant increase in olation with the formation of a stable six membered ring, if the reaction is analogous to chromium(149). This explains the absence of coordinated carboxyl groups in systems of this kind.

Fig. 30.3 Titration of zirconium oxychloride in the presence of 1 mole of acetic acid, equilibrated to pH 1.9 before titration.

Curve A. Titration of mixture.
B. Blank.

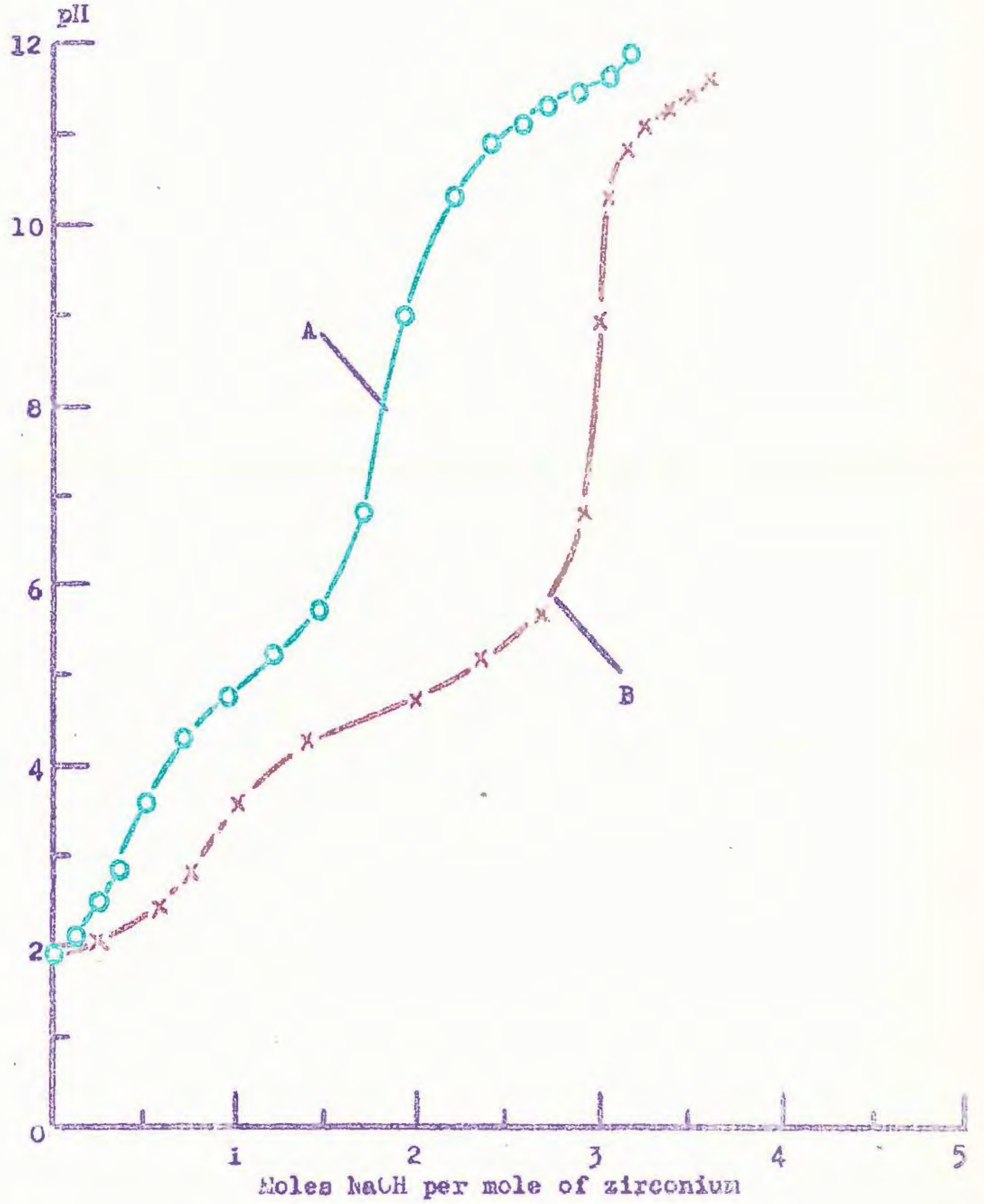


Fig. 3c.4 Titration of zirconium oxychloride in the presence of 2 moles of acetic acid, equilibrated to pH 1.9 before titration.

Curve A. Titration of mixture.
B. Blank.

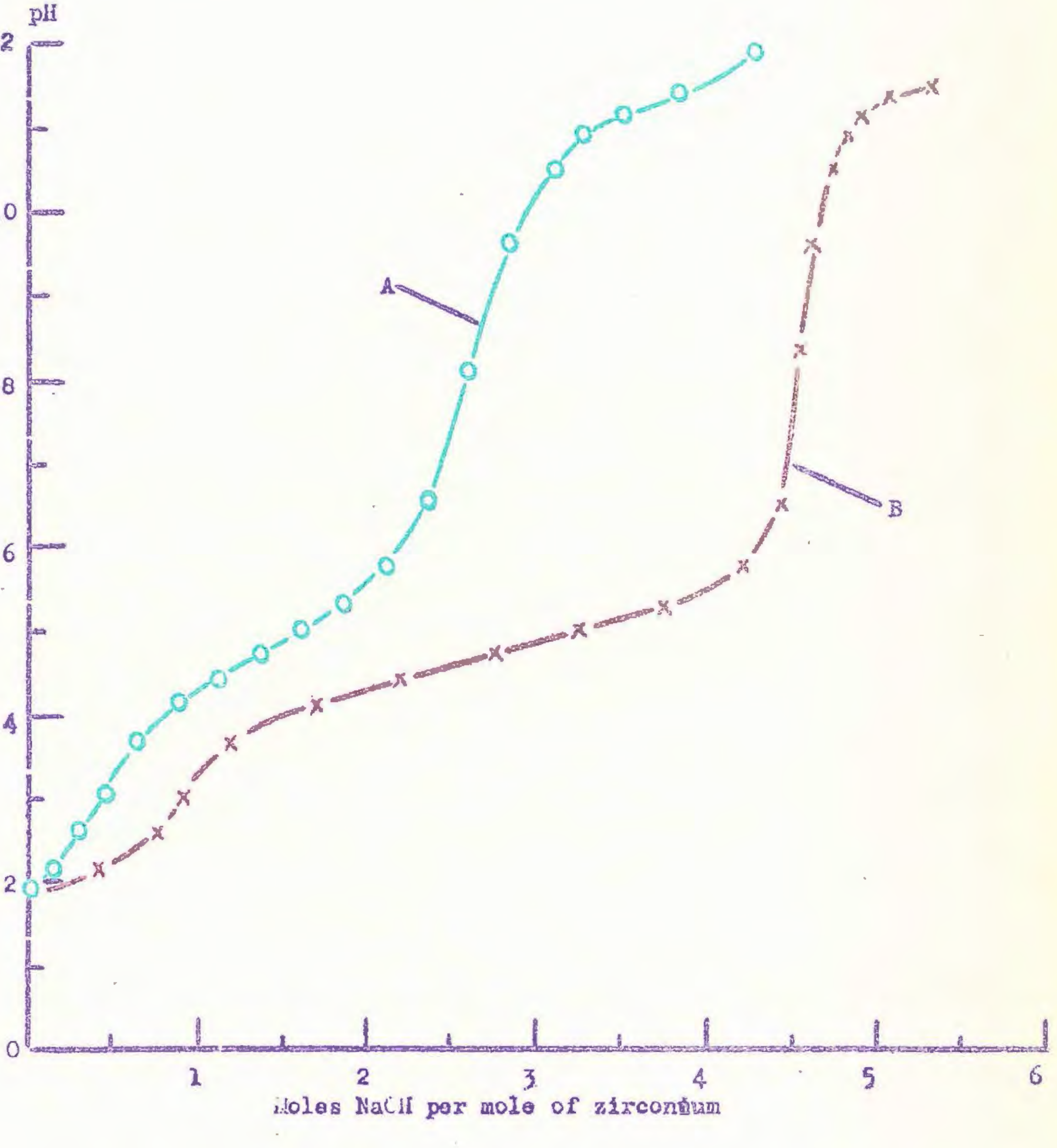


Fig. 3c.5 Titration of zirconium oxychloride in the presence of 4 moles of acetic acid, equilibrated to pH 1.9 before titration.

Curve A. Titration of mixture.
B. Blank.

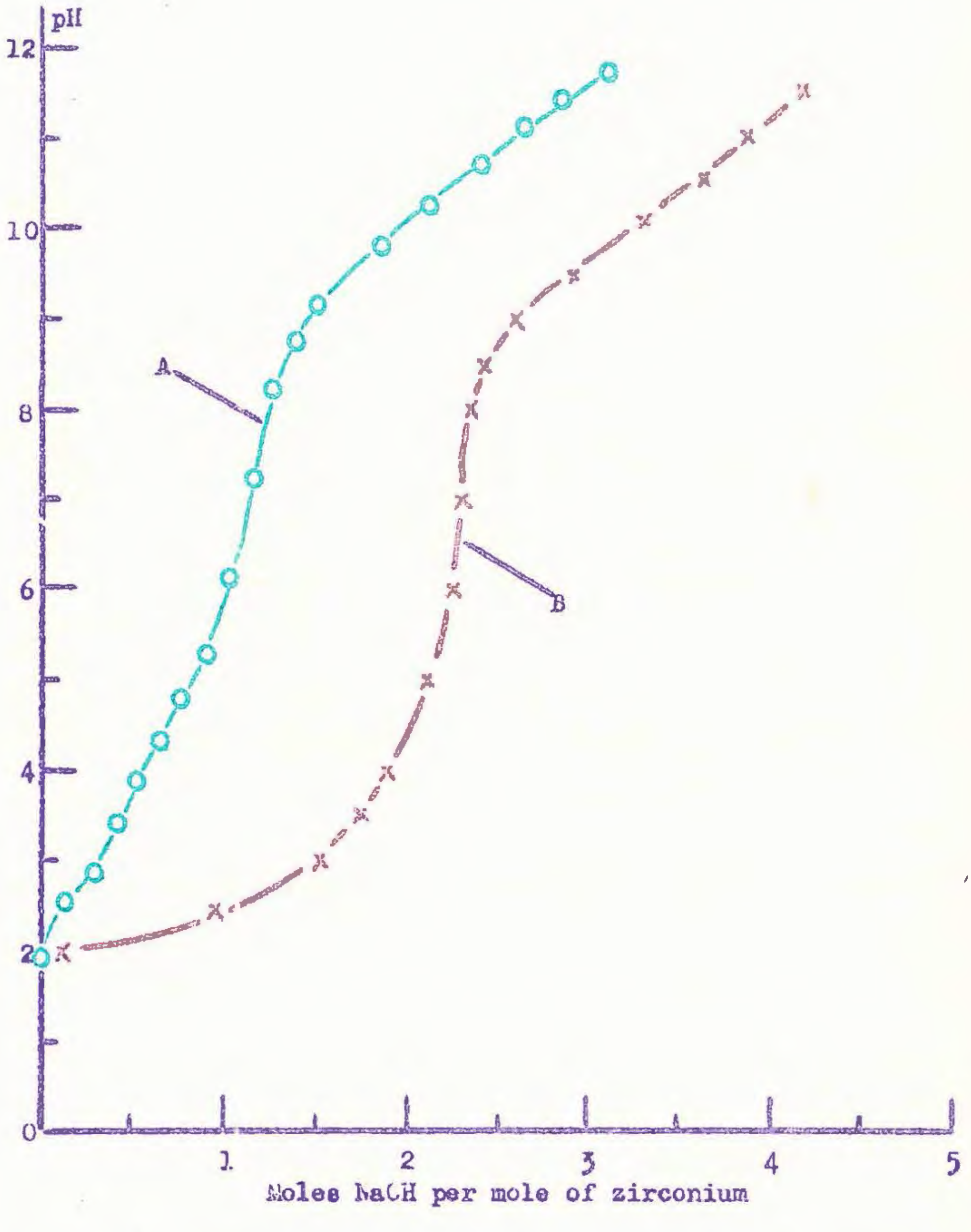


Fig. 3c.6 Titration of zirconium oxychloride in the presence of

1 mole of glycine, equilibrated to pH 1.9 before

titration.

Curve A. Titration of mixture.

B. Blank.

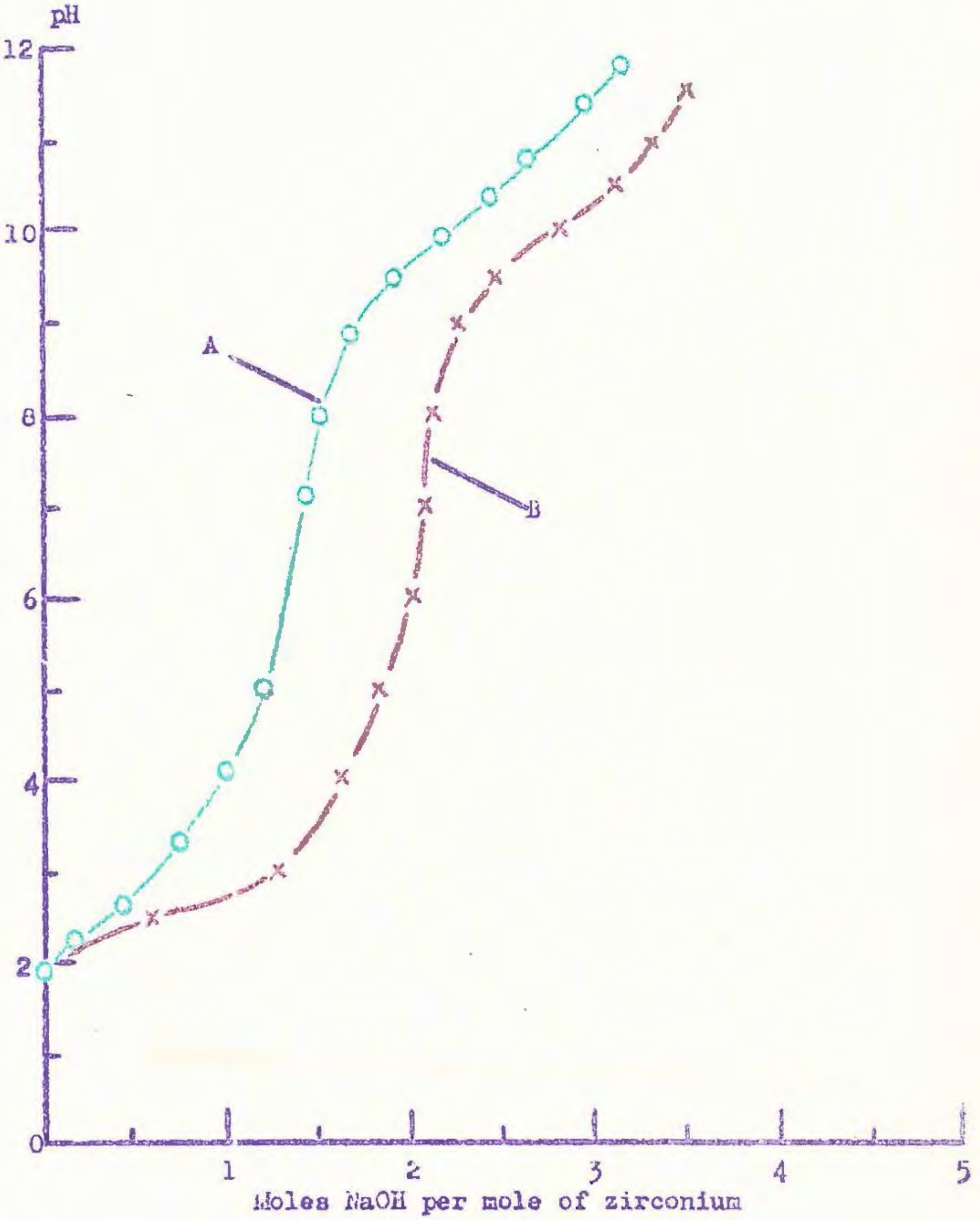


Fig. 3c.7 Titration of zirconium oxychloride in the presence of 1 mole of α-amino-n-butyric acid, equilibrated to pH 1.9 before titration.

Curve A. Titration of mixture.
B. Blank.

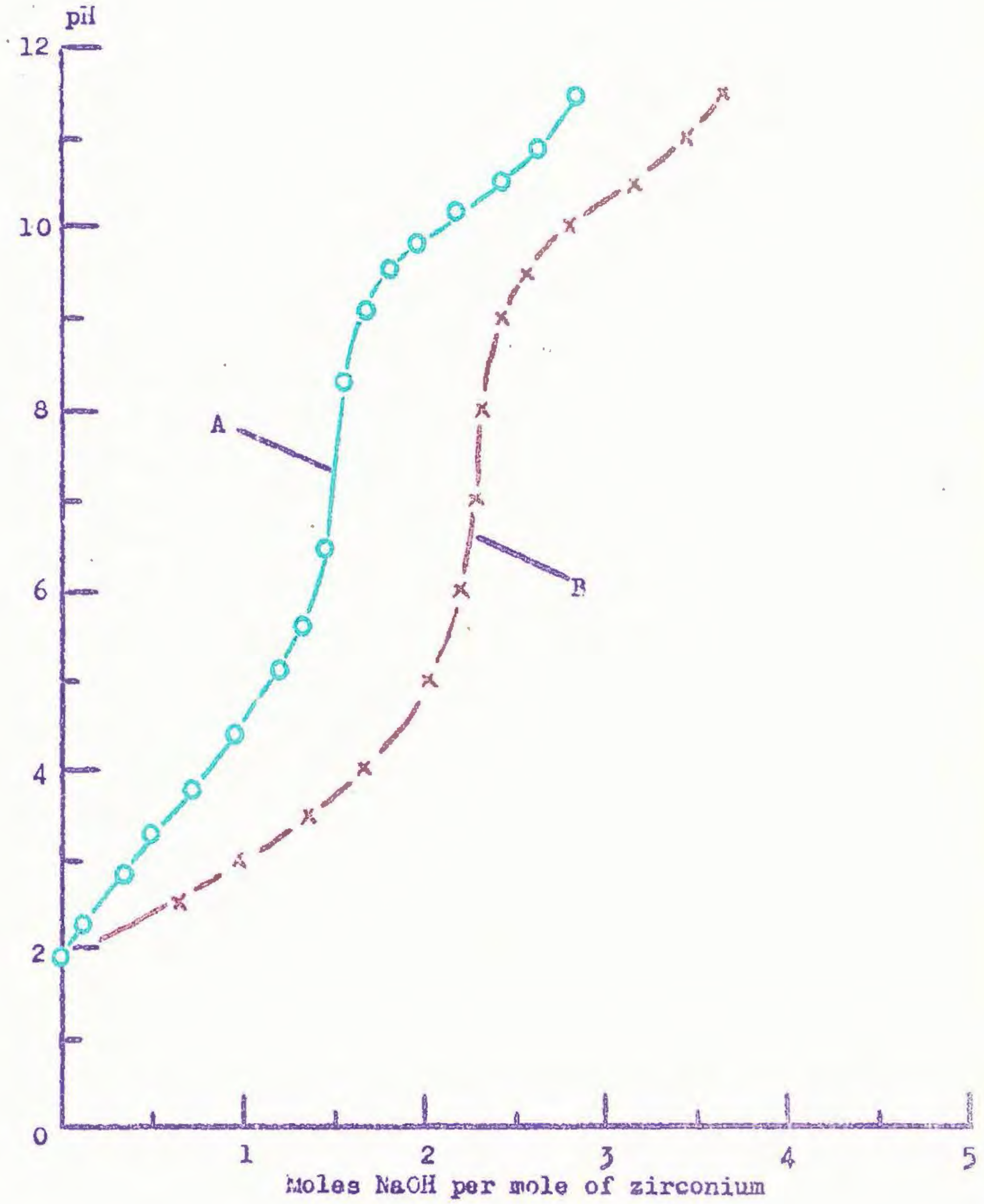


Fig. 3c.8 Titration of zirconium oxychloride in the presence of 1 mole of β-amino-n-butyric acid, equilibrated to pH 1.9 before titration.

Curve A. Titration of mixture.
B. Blank.

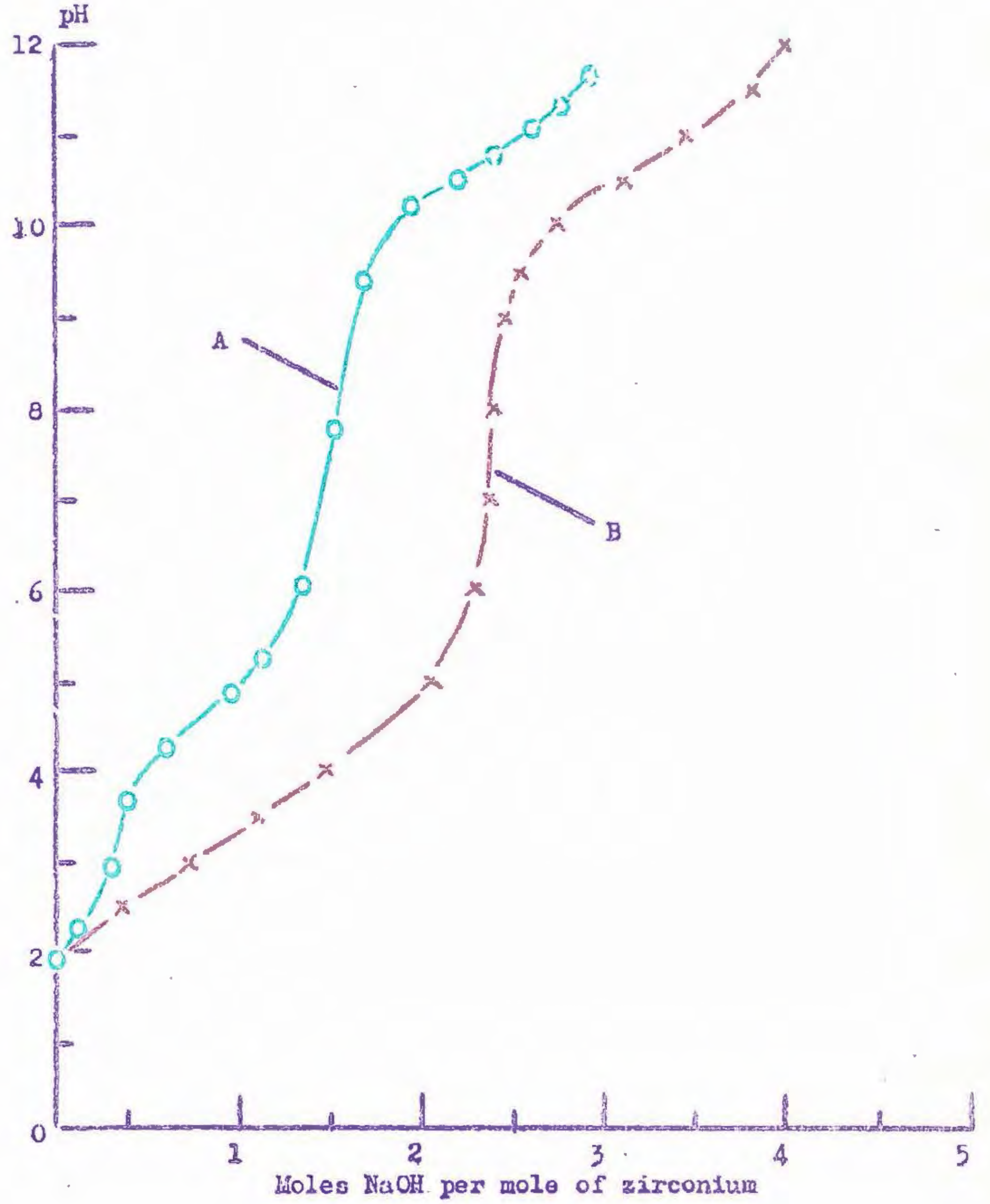


Fig. 3c.9 Titration of zirconium oxychloride in the presence of 1 mole of γ-amino-n-butyric acid, equilibrated to pH 1.9 before titration.

Curve A. Titrationoof mixture.
B. Blank.

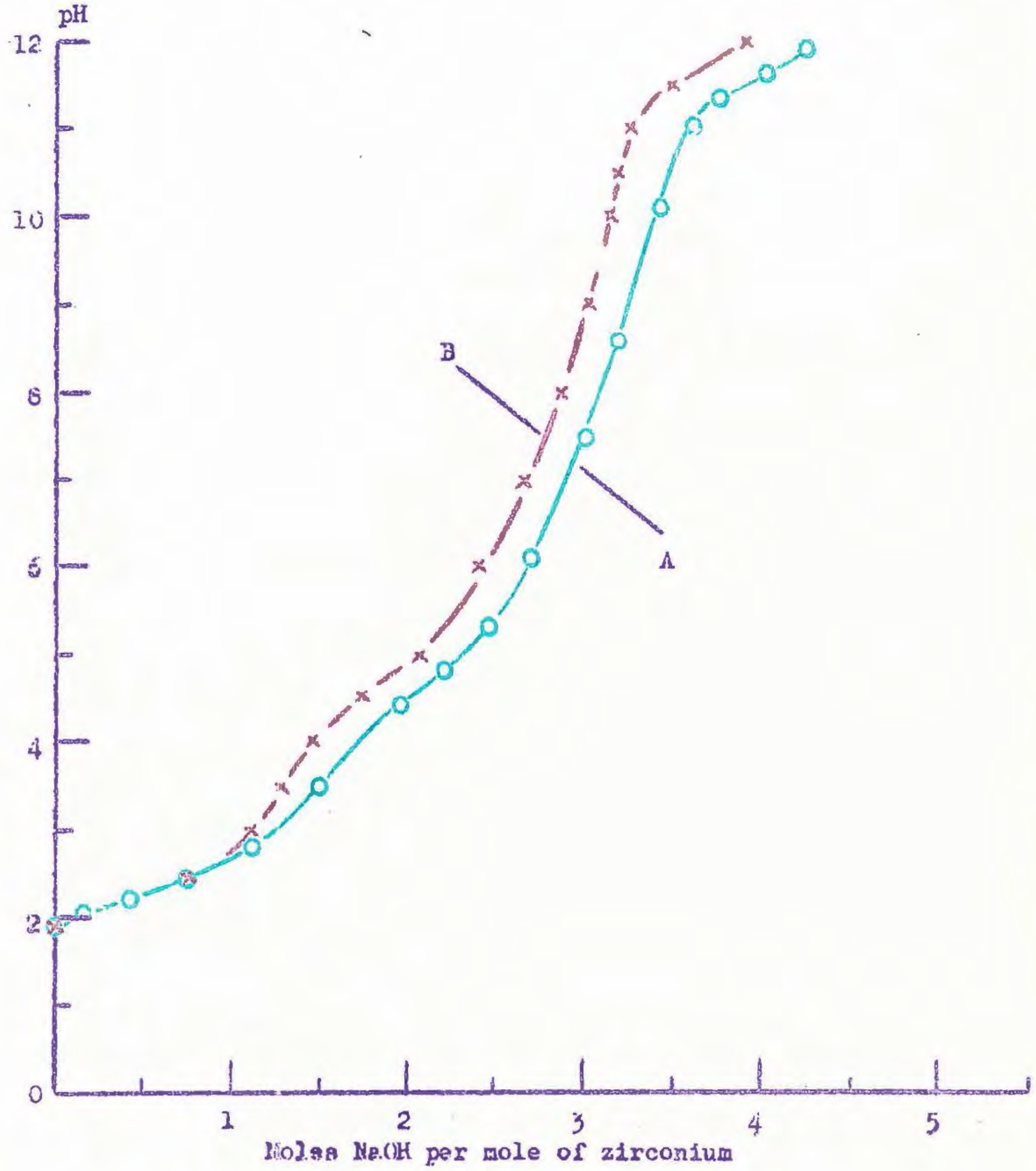


Fig. 3c.10 Titration of zirconium sulphate in the presence of 1 mole of acetic acid, equilibrated to pH 1.9 before titration.

Curve A. Titration of mixture.
B. Blank.

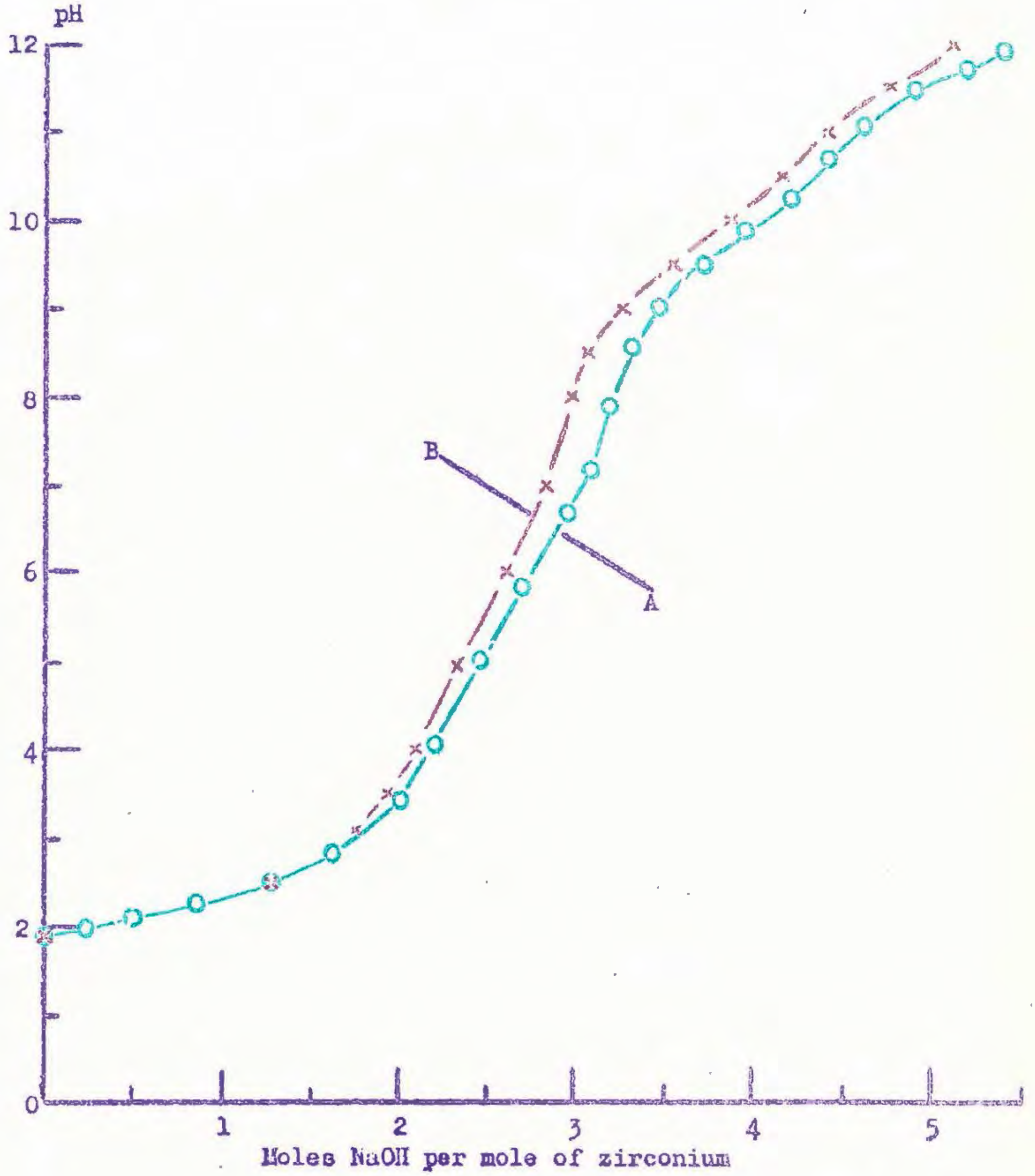


Fig. 3c.11 Titration of zirconium sulphate in the presence of 1 mole of glycine, equilibrated to pH 1.9 before titration.

Curve A. Titration of mixture.
B. Blank.

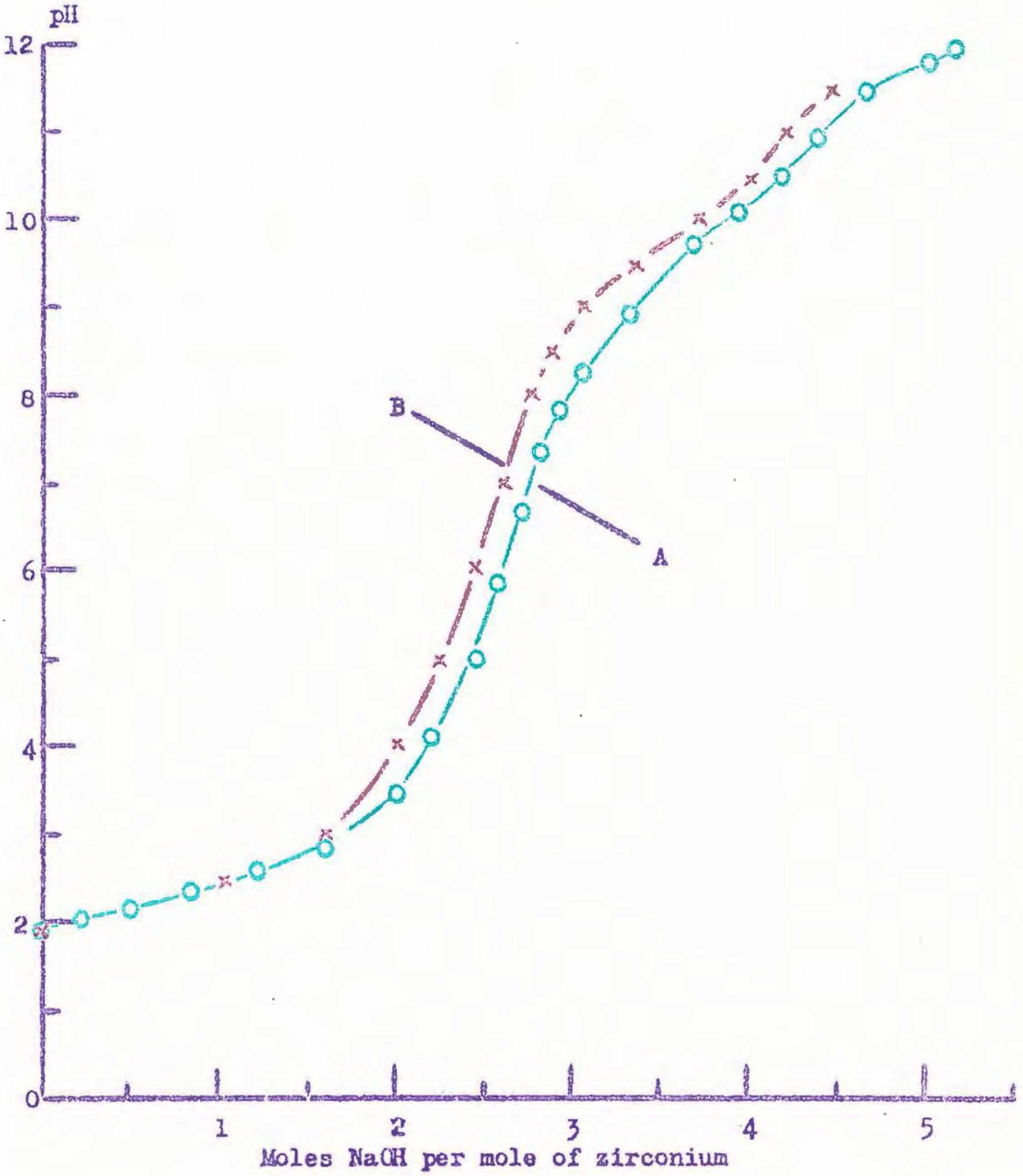


Fig. 3c.12 Titration of zirconium sulphate in the presence of 1 mole of α-amino-n-butyric acid, equilibrated to pH 1.9 before titration.

Curve A. Titration of mixture.
B. Blank.

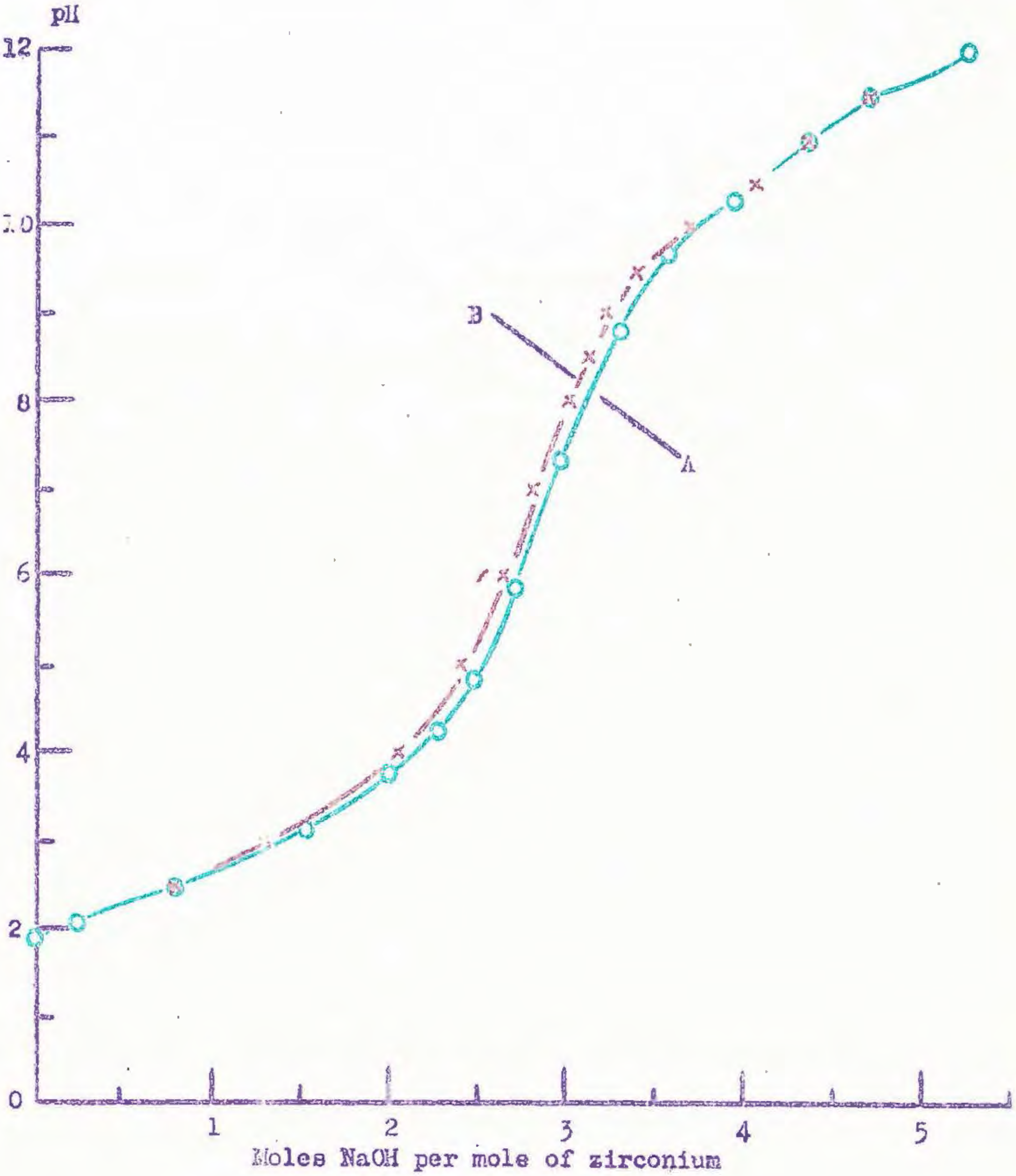


Fig. 3c.13 Titration of zirconium sulphate in the presence of 1 mole of β-amino-n-butyric acid, equilibrated to pH 1.9 before titration.

Curve A. Titration of mixture.
B. Blank.

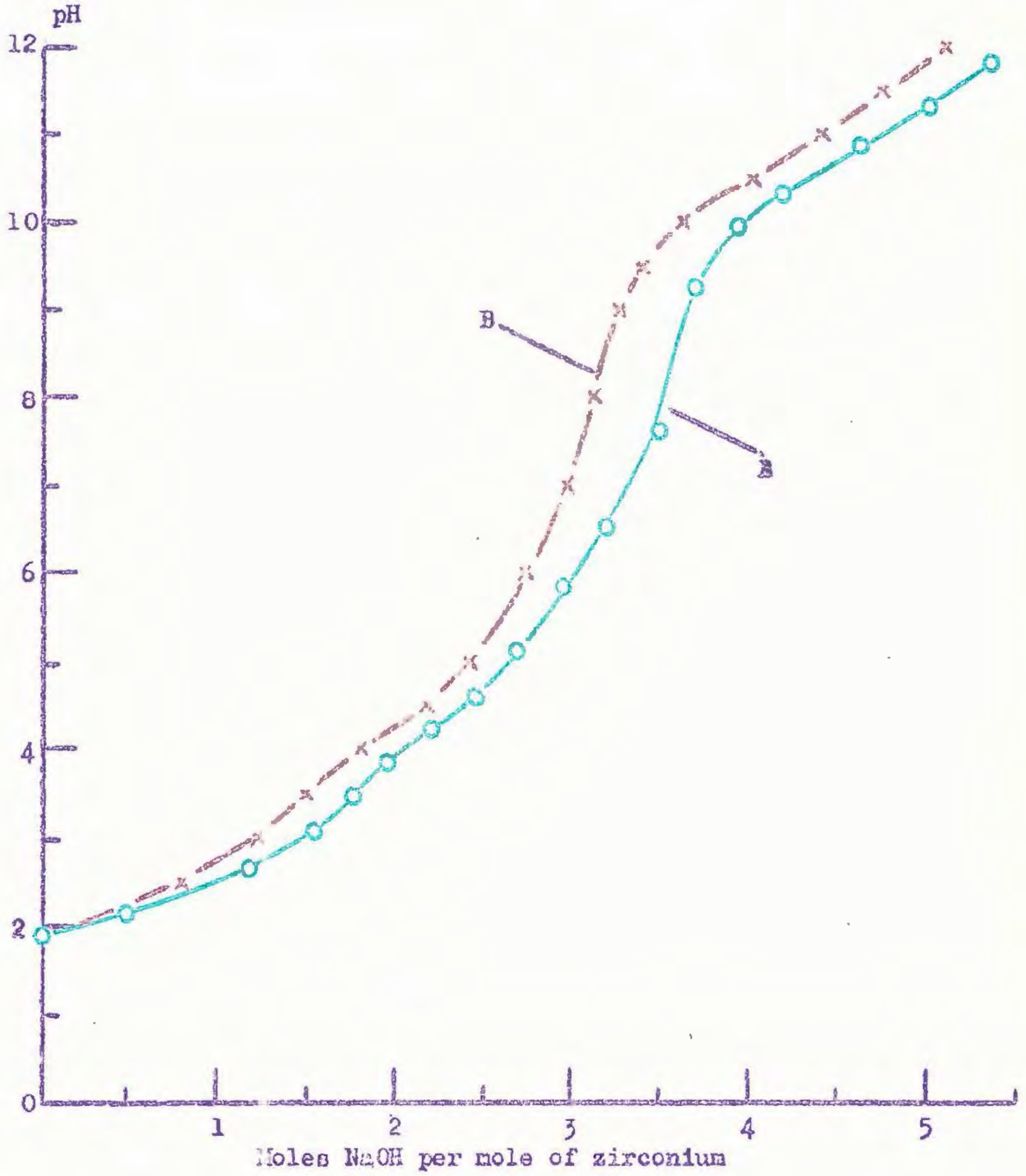


Fig. 3c.14 Titration of zirconium sulphate in the presence of 1 mole of γ-amino-n-butyric acid, equilibrated to pH 1.9 before titration.

Curve A. Titration of mixture.
B. Blank.

CHAPTER 4.

PRACTICAL APPLICATIONS

a. The Effect of Particle Size on the Penetration of Zirconium into Hide

The particle size of zirconium compounds determined from diffusion measurements (see Chap. 3a) indicated that certain solution conditions resulted in a small particle size, and it was decided to determine whether the size of the zirconium complex had any effect on the rate of penetration of zirconium tanning salts into hide. Hitherto, suitable conditions for zirconium tannage had been determined by purely empirical methods, and it was often found that complete penetration of zirconium tanning materials into heavy hide was difficult to achieve. Certain factors which were thought to affect penetration have been studied by a number of workers and the results of these investigations have been reviewed$^{(21)}$, and it is possible to reconcile some of these findings with the results from the investigation of particle size. From the published work the following conclusions were drawn for the optimum rate of penetration:

a) an equilibrium pickle, but not necessarily at low pH.

b) the addition of 7 to 8% of neutral salt to the tan liquor to repress the swelling, sodium chloride being the most effective for the purpose.

c) a minimum of 4 to 5% ZrO_2 on pelt weight.

d) sufficient mechanical action to squeeze tan liquor between the fibres before it has become exhausted of zirconium.

Further, various masking agents, e.g., formate, acetate, lactate, and citrate, have been suggested as suitable additives to tanning liquors not only to assist during pH adjustments, but also to increase the rate of penetration into hide. However, the effect of these masking agents on the speed of penetration of zirconium into hide is small, and it is doubtful whether there is any real benefit to be derived from their use, although they may be of value because of the increased resistance to precipitation and added buffering which may prevent accidental losses during pH adjustments.

In most tanning formulae, the zirconium salt is added to the drum as a dry powder. It has been found empirically that it is bad practice to dissolve the tanning salt beforehand, particularly if heat is used to aid solution, because there is danger of losses occurring from the precipitation of insoluble basic compounds which are valueless for leather manufacture. This property of zirconium salts in solution led to the investigation of particle size of zirconium under various conditions from measurements of the diffusion coefficient.

The results of these diffusion studies indicate that there is a sound reason for adding the dry zirconium tanning salt to the drum, because of the smaller and hence more mobile particle obtained in fresh solutions compared with aged solutions. . Also, tannages conducted in a normal tannery float, 120 to 150% have been found to require a minimum of 5% ZrO_2, which approximately corresponds to a 0.3M solution. It will be remembered that in Chapter 3a, it was found that a 0.3 M solution has a fairly small particle, and that in more dilute solutions the particle size is considerably increased. This probably explains why attempts at obtaining penetration with smaller amounts, and hence more dilute solutions of zirconium, have failed in normal tannery floats, possibly due to the large particle size obtained at lower concentrations. The addition of acid also has a marked effect, and the amount normally added in pickle liquors is thought to be sufficient to ensure a relatively small zirconium particle in solution.

As was mentioned above, zirconium sulphate solutions are much less stable than the chloride solutions, and, although measurements of diffusion data of zirconium sulphate are impracticable, it is possible to compare the effects of various factors on the rates of penetration of zirconium sulphate and chloride in small scale tannages. In this way the expected changes in particle size of zirconium in sulphate solution can be deduced from the reactions of zirconium in chloride solution.

Small scale laboratory tannages

A small scale factorially planned tanning experiment was carried out in glass bottles in a shaker to determine the similarities between zirconium salts. The following factors were varied:

A. Amount of zirconium offered.

(1) 4% ZrO_2)
) on delimed weight
a 2% ZrO_2)

B. Concentration of zirconium solution.

(1) 0.5 M solution
b 0.1 M solution

C. Type of zirconium tanning salt.

(1) 50% basic zirconium sulphate
c 50% basic zirconium chloride

D. Addition of acid (type depends on tanning salt)

(1) None
d enough to make final solution 0.5 N.

E. Type of neutral salt present in tan liquor.

(1) sodium chloride
e sodium nitrate

Details of treatments

The butt area of a heavy hide was soaked and depilated for 5 days with $1\frac{1}{2}$% sodium sulphide and 4% lime in 400% water, all based on hide weight. Pieces 6 inches by $1\frac{1}{2}$ inches were cut from the limed pelt and thoroughly delimed with 2% ammonium chloride and $\frac{1}{2}$% hydrochloric acid prior to the removal of soluble salts by exhaustive washing. The pieces were freeze dried to prevent collapse of the structure and denaturing of the protein, and grain and flesh layers were split off to give a thickness of 4 mm composed entirely of corium. At the beginning of the experiment, the pelt pieces were rehydrated under vacuum, and allowed to soak in water for 24 hours, after which their weights were adjusted to 10 g. The pelt was pickled in 100% water, 10% sodium chloride and 1% sulphuric acid for 24 hours, when the liquid was drained off. Meanwhile the tanning solutions were prepared according to the experimental plan given above, and immediately after solution of the zirconium salt the pelt was added. The bottles were shaken continuously, and depth of penetration into the pelt was checked 1½ and 4 hours after commencement of the tannage, by staining a freshly cut edge with an acid solution of Alizarin-S.

Results of laboratory experiment

The most significant effect was due to the concentration of the zirconium salt in the solution. After 1½ hours the dilute solution (0.1 M) had penetrated only 20% of the thickness, whereas the concentrated solution (0.5 M) had penetrated 29.5%. After 4 hours the penetration was 26% and 36.5% respectively. The amount of zirconium offered had no significant effect on the rate of penetration. The results are given in Table 4a.I.

The only other factor which had a significant effect was the type of neutral salt used in the tan liquor. The presence of sodium nitrate caused a higher rate of penetration than sodium chloride. This may be due to the smaller tendency to coordination shown by nitrate(4) and the fact that no complex nitrates of zirconium are known(84). Penetration of zirconium chloride was somewhat faster than zirconium sulphate, 26.9% and 22.5% after 1½ hours, and 34.4% and 28.1% respectively after 4 hours, but this difference is not statistically significant at the 1% level.

Table 4a.I

Effect of amount of zirconium offered and concentration of zirconium solution on rate of penetration into hide. Penetration after 1½ h; per cent of total thickness penetrated.

	Concentration of zirconium soln.		
Amount of zirconium offered	0.5 M	0.1 M	Mean
2% on soaked pelt wt.	28	21	24.5
4% on soaked pelt wt.	31	19	25.0
Mean	29.5	20.0	

Complete penetration was not achieved under any of the conditions studied even after prolonged shaking, because of the inadequacy of the mechanical action. These results were, however, used as a guide for an experiment on a larger scale.

b) Pilot plant experiment

Details of treatments

The pieces used in this experiment were cut from the butt area of heavy hides. After soaking they were pulp unhaired in a drum using a calcium hydroxide/sodium sulphide paste followed by 24 hours in a calcium hydroxide suspension(151).

After scudding and fleshing, they were washed in running water for 30 minutes, then delimed with 2% ammonium chloride, and ½% hydrochloric acid added after 2 hours. The pelt pieces were left in this liquor overnight, by which time they were completely delimed. The delimed pelt varied between 6 and 7 mm in thickness.

Tannages were carried out in either 150% or 75% or 0% float, and the amount of zirconium offered was either 2% or 4% on limed weight. Tannage was effected by the addition of dry zirconium tanning salt (Zircotan N) to the exhausted pickle liquor, viz., 1% sulphuric acid and the requisite float of 8% salt solution, for 24 hours except for the pieces which received a dry tannage. The latter were pickled in a 100% float of 8% salt solution with 1% sulphuric acid for 24 hours, then drained prior to the addition of the zirconium salt.

After 4, 8, 24, and 36 hours tannage, and then at daily intervals the extent of the penetration into all 24 pieces in each drum was assessed by staining a freshly cut edge with Alizarin-S solution. When penetration was complete, or after 8 days tannage, the leathers were thoroughly washed and dried out in such a way that collapse of the untanned portions was prevented (freeze-dried). The dried leather was split into 3 layers for stratigraphic analysis.

Results of pilot plant experiment

The percentage penetration is given in Table 4a.II and 4a.III for tanning periods of 4 and 8 hours respectively, and the time required for complete penetration is given in Table 4a.IV.

Table 4a.II

Average percent penetration after 4 hours drumming

Amount of zirconium	Length of tanning float			Mean
	150%	75%	0%	
2% on limed wt.	13	23	82	39
4% on limed wt.	25	50	100	58
Mean	19	36	91	

Table 4a.III

Average percent penetration after 8 hours drumming

Amount of zirconium	Length of tanning float			Mean
	150%	75%	0%	
2% on limed wt.	37	44	94	58
4% on limed wt.	61	80	100	80
Mean	49	62	97	

Table 4a.IV

Time in hours required for complete penetration

Amount of zirconium	Length of tanning float		
	150%	75%	0%
2% on limed wt.	>200	>200	8-24
4% on limed wt.	>200	24-36	< 4

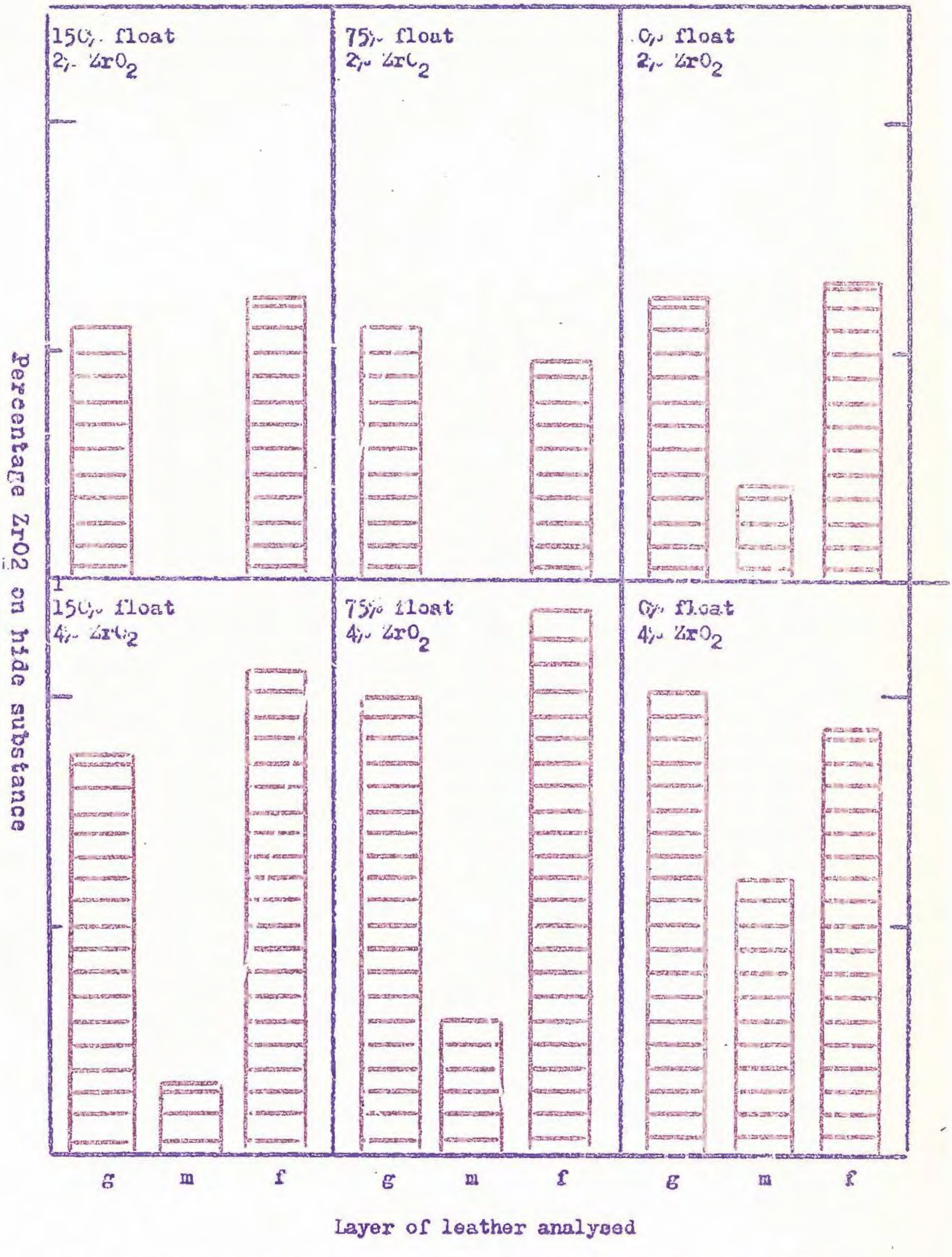


Fig. 4a.1 Layerwise analysis of zirconium tanned leathers. Average percentage ZrO_2 on hide substance of the grain, middle, and flesh layers of leather from each of the six tannages. (See text for details of the tannages.)

The results show that the dry tannage, i.e., very concentrated tanning liquor, gives extremely rapid penetration, and it is possible to obtain complete penetration on thick pelt with as little as 2% ZrO_2 by this means. Penetration is progressively slower with the longer floats, and was not complete in the 150% float even after drumming for 8 days.

The results of the analysis of the centre layers are given in Table 4a.V as percentage of ZrO_2 on hide substance. The relative percentages of ZrO_2 on hide substance in the three layers are given in Fig. 4a.1, for each of the six tannages.

Table 4a.V

Percentage ZrO_2 on hide substance in the middle 2 mm layers

Amount of zirconium	Length of tanning float		
	150%	75%	0%
2% on limed wt.	0	0	4.3
4% on limed wt.	3.1	6.0	12.0

These results clearly indicate that penetration is more rapid with the dry tannage than with the other tannages, and it is possible to obtain complete penetration of heavy hide (6 mm thick) with as little as 2% ZrO_2 on limed weight.

The average increase in shrinkage temperature for the three layers of the pieces which had been given the dry tannages, see Table 4a.VI, shows that, although the amount of ZrO_2 in the centre is relatively small, the centre layers of pieces from both tannages have a reasonably high shrinkage temperature.

Table 4a.VI

Average increase in shrinkage temperature, °C, for the three layers of the pieces from the dry tannages

Amount of zirconium	Grain	Middle	Flesh
2%	34	22	27
4%	38	38	37

Discussion

Results of the practical tanning trials bear out the findings of the experiment on particle size. Whilst factors other than particle size undoubtedly influence the rate of penetration of zirconium into pelt, the results indicate that particle size is one of the major factors controlling penetration.

A particularly important observation to be made from the laboratory experiment is the essential similarity with regard to penetration between tannages with 50% basic zirconium sulphate and zirconium chloride. Although the chloride penetrated more rapidly than the sulphate, a difference which was increased with time of tannage, the effects of all the other factors were similar in each case. Therefore, it seems reasonable to conclude that factors such as concentration, acidity, and time, which, through diffusion measurements, have been shown to affect the particle size of zirconium chloride, affect zirconium sulphate in a similar manner.

b. Tannages with Solutions of Zirconium Oxychloride in the Presence of Some Organic Reagents

The technique used in the small scale tannages has been described in Chapter 2a. The solutions were 0.25 M with respect to zirconium and contained the added organic reagents at a 1 to 1 molar ratio. The organic reagents used were acetic, glutaric, glycollic, tartaric, gluconic acids, glycine, α-, β-, and γ-amino-n-butyric acids, methylamine, ethylenediamine, and urea. An aliquot of each solution was adjusted to equilibrium to one of the pH levels 1, 2, 3, 4, 6, 8, or 10 before tanning strips of pelt. After washing, many of the pieces tanned at pH 1 were decidedly swollen and tended to dry out rather hard. On the whole the "leatheriness" of the pieces was fairly good, those tanned at high pH being somewhat softer and more flexible than the others, which indicated that leathering was rather more effective at pH 6 and above, than at lower values. This is substantiated by the shrinkage temperatures of leathers tanned in these solutions compared with those tanned at lower pH values, see Table 4b.I. The table records differences in shrinkage temperature, ΔTs, between leather from the masked and unmasked zirconium solutions.

Treatment of pelt with zirconium, either masked or unmasked, increased the shrinkage temperature above that of the control pieces of pelt treated for the same length of time in salt solution of the same concentration and pH but without zirconium salts. The shrinkage temperatures are in most cases fairly low, thus confirming the relatively poor tanning ability of zirconium oxychloride. It is interesting to note that in unmasked solutions at high pH, where zirconium is known to be quantitatively precipitated, hydrothermal stability is imparted to the pelt. This may be due to the supposed colloidal tannage suggested by Paquet(58) and by Schachowskoy and Frohlich(64).

The shrinkage temperature of the leather obtained from the zirconium solutions within the pH range 1 to 4 to which equimolar amounts of the masking agents had been added was lower than the shrinkage temperature of the leather tanned in the unmasked zirconium oxychloride solutions within the same pH range. At the higher pH values, there was little difference between the shrinkage temperatures of leathers tanned in any of the solutions except those masked with hydroxy acids. The hydroxy acids, glycollic, tartaric, and gluconic, gave clear zirconium solutions at pH values of 6, 8, and 10, andpelt tanned in these solutions had a somewhat higher shrinkage temperature than leather obtained from the other zirconium solutions of corresponding pH.

In the presence of the hydroxy acids at high pH values, zirconium was predominantly anionic, — in the presence of tartaric and gluconic acids no other ionic species were found, see Chapter 3b —,and it was under these conditions that leather with the highest shrinkage temperature was produced. This suggests that the reaction might be between the anionic zirconium and uncharged amino groups on the protein which are likely to exist at these pH values, but not under the conditions at which Ranganathan(44) worked. The charge on

Table 4b.I

Difference in Shrinkage Temperature, ΔTs, of Pelt Tanned in Solutions of Zirconium Oxychloride in the Presence of Some Organic Reagents. (+, Ts greater than, -, Ts less than that of pelt tanned in Zirconium Oxychloride only).

	pH 1	pH 2	pH 3	pH 4	pH 6	pH 8	pH 10
Raw pelt Ts	-	45	47	50	50	51	48
Pelt tanned in $ZrOCl_2$	clear 69	clear 69	clear 73	opal. 74	ppt. 68	ppt. 70	ppt. 70
" " + acetic	clear -11	clear - 6	opal. - 9	ppt. -16	ppt. + 7	ppt. + 2	ppt. + 8
" " + glutaric	ppt. -12	ppt. -15	ppt. -16	ppt. -19	ppt. - 6	ppt. -10	ppt. - 9
" " + glycollic	clear -15	ppt. - 3	ppt. -17	ppt. -14	opal.+ 9	clear+ 5	clear+10 gel
" " + tartaric	ppt. - 5	ppt. -13	ppt. -17	ppt. + 6	clear+ 8	clear+ 5	clear+ 9
" " + gluconic	ppt. -10	clear -18	clear -22	clear+14	clear+12	clear+ 4	clear 0
" " + glycine	clear - 9	clear -11	opal. -11	ppt. + 4	ppt. + 1	ppt. + 3	ppt + 3
" " + α-NH_2-butyric	clear -14	clear -12	opal. -18	ppt. - 8	ppt + 3	ppt. + 2	ppt. + 2
" " + β-" "	clear -13	clear -15	opal. -19	ppt. -15	ppt. 0	ppt. + 3	ppt - 2
" " + γ-" "	clear -13	clear -14	opal. -13	ppt. - 6	ppt. + 9	ppt. 0	ppt. + 3
" " + methylamine	clear -15	clear -14	ppt. -15	ppt. + 1	ppt. + 3	ppt. + 1	ppt. + 3
" " + ethylene-diamine	clear -17	clear -14	ppt. -15	ppt. - 6	ppt. + 3	ppt. 0	ppt. 0
" " + urea	clear -14	clear -13	ppt. -10	ppt. + 4	ppt. + 6	ppt. + 3	ppt. + 4

the zirconium complex may have no bearing on the reaction; the role of the organic ligand for the production of leathers with high hydrothermal stability may not be in modifying the charge of the zirconium complex, but in retaining the zirconium in solution so that it is more readily available for reaction with the pelt, because the organic acids which, with zirconium, gave clear solutions at high pH values also produced the most stable leather, see Table 4b.I.

Reaction of zirconium with amino groups in aqueous solution seems unlikely in view of the poor stability of solutions containing the amines, and treatment of pelt with these solutions resulted in leather with shrinkage temperatures virtually unchanged from that of the blank, i.e., leather tanned in unmasked zirconium oxychloride.

It seems that in the presence of carboxylic acids tanning action of zirconium oxychloride is impaired due to the competition with carboxyl groups in the collagen. Coordination of amino groups appears to be unlikely whereas reaction of pelt with anionic zircomium yields leather with a relatively high shrinkage temperature.

CHAPTER 5

DISCUSSION AND CONCLUSIONS

An investigation into certain aspects of the combination of zirconium compounds with collagen was undertaken because of the present considerable, and potentially extensive importance, of this reaction in leather manufacture. Tanning agents do not form a distinct group of compounds chemically, but they may conveniently be divided into two main classes: mineral tanning agents, and tanning agents of organic composition. It is generally accepted that tanning involves the formation of cross-links between adjacent polypeptide chains in the collagen fibres with increase in resistance to putrefaction and enhanced hydrothermal stability(1), and irrespective of the type of tanning material used the mechanism of the reaction may involve one or more of the following bonds:

(i) Electrovalent or salt links.
(ii) Non-polar adsorption.
(iii) Residual valency forces; van der Waals' forces or hydrogen bonds.
(iv) Coordinate bonds.
(v) Covalent bonds.

Hitherto, all mineral tanning agents have been considered as one group and reference was made to the properties of mineral salts in so far as it was relevant to formulating a common theory of mineral tanning(4); this was based mainly on the observed behaviour of chromium. McLaughlin and Theis(152) questioned the inclusion of zirconium in this group, and more recently the individuality of zirconium was recognised(9,153). This arose from the observations that although zirconium tannage is metallic in character, it appears to have more in common with vegetable tannage than with chromium tannage(50).

Some experiments have been performed to investigate which reactive groups in the collagen are involved in zirconium tannage, but since much of the evidence presented in the literature is apparently contradictory, the present work was undertaken to gain further information on the chemistry of zirconium salts in aqueous solution. In the experimental work which has been described in this thesis, the approach to the subject comprised an investigation of both physical and chemical properties of zirconium salts. It is proposed to discuss this work with a view to determining possible mechanisms of reaction between zirconium and collagen, and to try to reconcile some facts that have been determined empirically with observed properties of the zirconium salts.

During practical tanning trials it had been found that penetration of zirconium salts was often difficult to achieve, and, since zirconium was considered to be a mineral tanning material, the problem of obtaining satisfactory rapid and complete penetration was investigated by means which are known to be effective with chromium tanning salts. In chromium tanning, rapid penetration of small amounts of chromium can be obtained by working at pH values in the region of 2 at which pH hydrolysis of the chromium is prevented, or by masking the chromium salt by the addition of organic complexing acids. These measures were singularly ineffective when applied to zirconium, and the effective tanning of collagen with small amounts of zirconium remained a problem.

Chemical means having apparently failed to overcome the difficulty, it was thought that physical properties of the zirconium tanning salt were responsible for the slow penetration of this material into hide. The molecular weight of vegetable tanning materials has been shown to influence the rate of penetration into hide(154), and it seemed possible that the size of the zirconium particle in the tanning solution has an effect on the rate of penetration. The normal methods of molecular weight determination (e.g., elevation of the boiling points, etc.) were impracticable for measuring the particle size of zirconium complexes, because not only would these methods yield a mean value for all the molecules or ions in solution, but also the elevated temperature would modify the complexes, and in many cases would result in the formation of insoluble compounds. One method which allows the size of an isolated component in solution to be estimated is the measurement of its diffusion coefficient.

Zirconium sulphate is the salt usually used in tanning because solutions of this salt have been shown to yield better quality leather than other salts(12,14,68-71). Unfortunately, zirconium sulphate is relatively unstable in aqueous solution, and basic salts precipitate after a relatively short ageing period. On the other hand, solutions of zirconium chloride are stable except in very dilute or highly basic solutions. For this reason, the diffusion measurements reported in this thesis were performed on solutions of the latter salt to obtain general information of the behaviour of zirconium in aqueous solution. From this work it was found that zirconium particles diffused most rapidly a) when the solutions were freshly prepared, b) in concentrated solution, c) in strongly acid solution, and d) in the absence of complexing agents. Since the rate of diffusion is related to particle size, the bigger the particle the slower the rate of diffusion, solutions that had the highest diffusion coefficients contained the smallest particles.

A comparison of the rate of penetration of 50% basic zirconium sulphate and zirconium oxychloride into hide has shown that a number of factors, e.g, acidity, concentration, etc., affected the two salts in a similar manner, but under similar conditions zirconium sulphate always diffused into hide more slowly than the oxychloride. Thus it seems reasonable to conclude that differences in the rate of penetration of zirconium sulphate can be ascribed to particle size, since rapid penetration was obtained under solution conditions which in the case of oxychloride have been found to give particles of small size.

The alteration of physical properties of zirconium compounds caused by chemical changes in the tanning solutions, e.g., increase in the degree of polymerisation with increase in basicity, or the larger particle size of zirconium in sulphate solution compared with that in chloride solution, may also affect the reactivity of the zirconium tanning salt to collagen if the mechanism of the reaction is multipoint attachment of the tanning material by residual valency forces. These results emphasise that the physical properties of zirconium particles in solution play an important role in the tanning process.

Some of the conditions which have been found empirically to be the optimum for penetration of zirconium into hide have sound scientific reasons for their effectiveness, based on the particle size of the tanning material in solution, if zirconium sulphate behaves in a similar manner to zirconium oxychloride as is indicated in the small scale tanning experiments. For example, it is often recommended that the dry zirconium tanning salt be added to the drum containing the pickled pelt. Under these conditions the solution of the zirconium salt is as fresh as possible, and it has been shown that particles in fresh solutions are small compared with those in aged solutions. Similarly, the necessity for an equilibrium pickle can be explained. During an equilibrium pickle the acid binding capacity of the collagen is completely satisfied and zirconium solutions are less likely to be affected by changes in degree of hydrolysis on coming into contact with the skin. However, if the collagen has not taken up all the acid of which it is capable, some of the hydrolised acid from the zirconium salt may be absorbed in the surface layers of the pelt causing more basic and hence larger particles to be formed which then diffuse more slowly into the centre of the hide.

The importance of particle size on the rate of penetration can also be shown to account for the inability of complete penetration to be achieved with amounts of zirconium tanning salt equivalent to less than 4% ZrO_2, based on limed hide weight(61,66). As the normal volume of tanning solution is in the region of 100 to 120% of pelt weight the concentration of zirconium in solution when 4% ZrO_2 is offered is about 0.3 M. Consideration of Fig. 3a.2 shows that at concentrations somewhat less than this, the size of the zirconium complex was considerably greater than the particles in 0.3 M solution. However, when the solution concentration was increased by reduction of the volume of the tanning solution, complete penetration was obtained with smaller amounts of zirconium, indicating that the small particles in the more concentrated solutions diffused more rapidly into hide.

The diffusion measurements have also explained why the use of complexing agents in zirconium tanning solutions has been ineffective in promoting penetration. Mitton and Wyatt(62) have shown that there is an optimum amount of complexing agent (about 0.3 mole of acetate per mole of zirconium) which should be used for the greatest rate of penetration, although this effect is so small as to be of negligible practical importance. At molar ratios of 1 to 1 they showed that penetration was less than with unmasked solution. The present work has shown that zirconium, in the presence of complexing salts at a molar ratio of 1 to 1, has a very much slower rate of diffusion than in unmasked solutions of the same concentration and pH, which is attributed to a larger particle size. It has been made clear in the text that these are relative rather than absolute values for particle size, but values for the diffusion coefficients are fairly accurate.

Regardless of the mechanism of zirconium tannage, the particle size of the tanning complex is of paramount importance because, if the particles are so large that penetration into the fibrous protein is restricted or prevented, reinforcement of the bonds holding the polypeptide chains together cannot be effected. On the other hand, effective tanning can occur only when the particle of the tanning material is large enough to form cross-linking bonds, the more bonds that are formed the higher the hydrothermal stability imparted to the collagen. Since zirconium has been shown to polymerise even under highly acid conditions, it is unlikely that zirconium complexes will at any stage be too small to form effective cross-linking bonds.

Of all the possible mineral tanning materials, chromium alone is able to impart greatly increased hydrothermal stability to collagen, so that the shrinkage temperature is over 100°C, and it is generally accepted that the mechanism of that reaction is the formation of directional coordinate links between polynuclear chromium complexes and ionised carboxyl groups of the protein(145-148). Since all other mineral tanning agents produce very much less hydrothermally stable compounds with collagen than are formed with chromium and collagen, reasons for this lower stability must be sought. Four possible reasons for the lower stability are apparent. Firstly, the metal to metal links in the tanning complex may be weaker, secondly, the coordination bond between the metal tanning agent and reactive groups on the protein may be less stable, thirdly, the tanning reaction may involve a completely different mechanism from that obtaining in chromium tanning, or fourthly, fewer cross-links may be formed; this latter reason is unlikely.

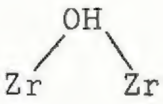
Considering zirconium in connection with the above possibilities, it has been shown from potentiometric studies that no coordination with carboxyl groups occurred in the case of zirconium sulphate, whereas coordination did occur with zirconium oxychloride, but the number of coordinated carboxyl groups were reduced with increase in solution pH, and the complex is probably not very stable since the pH of precipitation is raised only slightly in the presence of carboxylic acids. This confirms previously published work which showed that carboxyl groups played no part in the reaction between collagen and zirconium sulphate(27,43,50,65-67).

The potentiometric studies also give no evidence of a coordination reaction between zirconium and amino groups, a reaction which is suggested by Ranganathan and Reed(50) to account for at least part of the fixation of zirconium to hide protein. Ranganathan's proposal(44) that "it is probable that fixation occurs mainly by the entry of uncharged amino groups into such complexes (anionic) of zirconium", is highly improbable since, at the low pH values at which the experiments were performed, viz., pH 1.0 and 3.0, the amino groups would all be fully charged. Reference to the chemical literature(140) reveals that zirconium in aqueous solution is not bound to organic radicals through nitrogen, and it seems conclusive that coordination of amino groups is not involved in zirconium tannage.

Since directional coordination bonds do not occur, and covalent bonds can be ruled out in the case of mineral tannages, the increase in hydrothermal stability may be due to multipoint attachment involving residual valency forces. However, the rise in shrinkage temperature varies with the type of zirconium complex, and, generally, the greatest rise in shrinkage temperature occurs with anionic complexes. This is illustrated by the higher shrinkage temperature of leather tanned in zirconium sulphate solutions of high acidity(56), under which conditions the zirconium is predominantly anionic(30), compared with leather tanned in normal zirconium sulphate solutions in which the proportion of anionic zirconium is much lower. The greater shrinkage temperature with the anionic complexes can be explained in two ways:

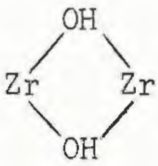
(i) Reinforcement of the zirconium to zirconium bridge by ring formation with sulphate or organic acid anions, see structures III and IV, since the diol bridge, structure II, if formed, may be unstable due to the large size of the zirconium atoms and the strain imposed on the bonds by an element with a coordination number of 8, and the mono-ol bridge, structure I, is weak. The change in the ionic nature of the zirconium may be purely incidental.

I



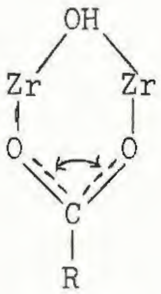
very weak.

II



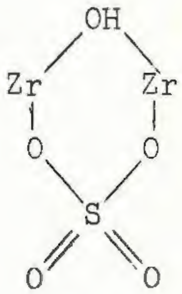
weak

III



fairly stable

IV



stable

(ii) The ionic nature may be of importance because it has been observed from the work on electrophoresis and the small scale tannages that the maximum increase in shrinkage temperature was obtained when the zirconium oxychloride complexes became predominantly anionic, and hence reinforcement could come from salt links between anionic zirconium and charged basic groups. Although generally discredited in the case of chromium tanning, the evidence for salt links is stronger in the case of zirconium tannage, since higher shrinkage temperatures were obtained with anionic zirconium complexes, and the shrinkage temperature was reduced when the number of basic groups were reduced(50). Some evidence for the formation of salt links is given by the lower shrinkage temperature of zirconium leather determined in M/2 sodium chloride and calcium chloride which would be expected to break reinforcing salt links. Zirconium leather shrank in water at 83°C, in sodium chloride and calcium chloride at 72°C.

Whilst significant deductions can be made with regard to the reaction between zirconium and collagen from the results reported in this work, the mechanism is still not fully understood, and further extensive investigations seem to be required for its elucidation, particularly the extension of particle size studies to zirconium sulphate solutions and the determination of bond strengths which it has been suggested are of importance in the process.

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APPENDIX

Potentiometric Data

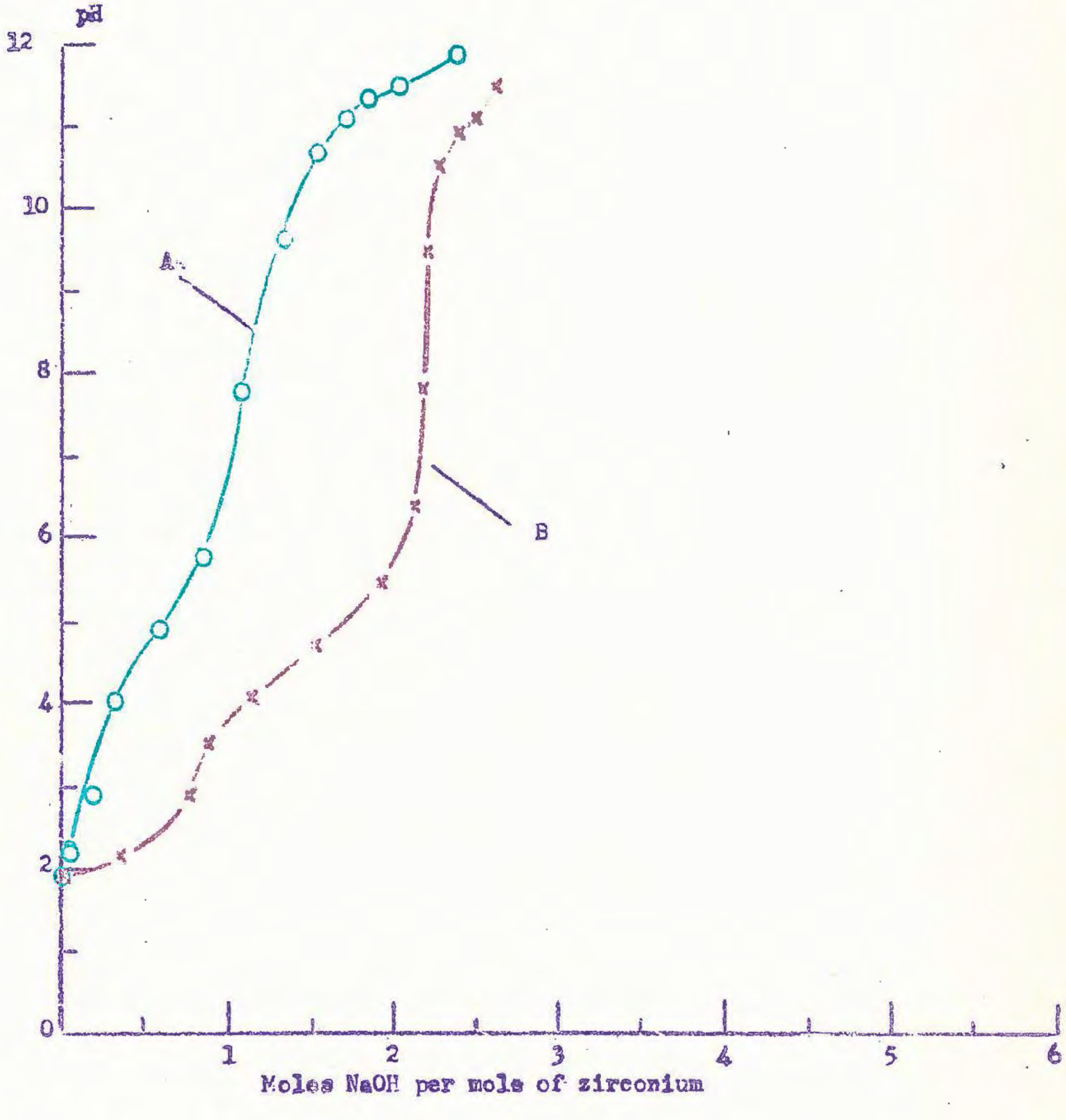

Fig. A1 Titration of zirconium oxychloride in the presence of 1 mole of acetic acid, equilibrated to pH 1.9 before titration.

Curve A. Titration of mixture.
B. Blank.

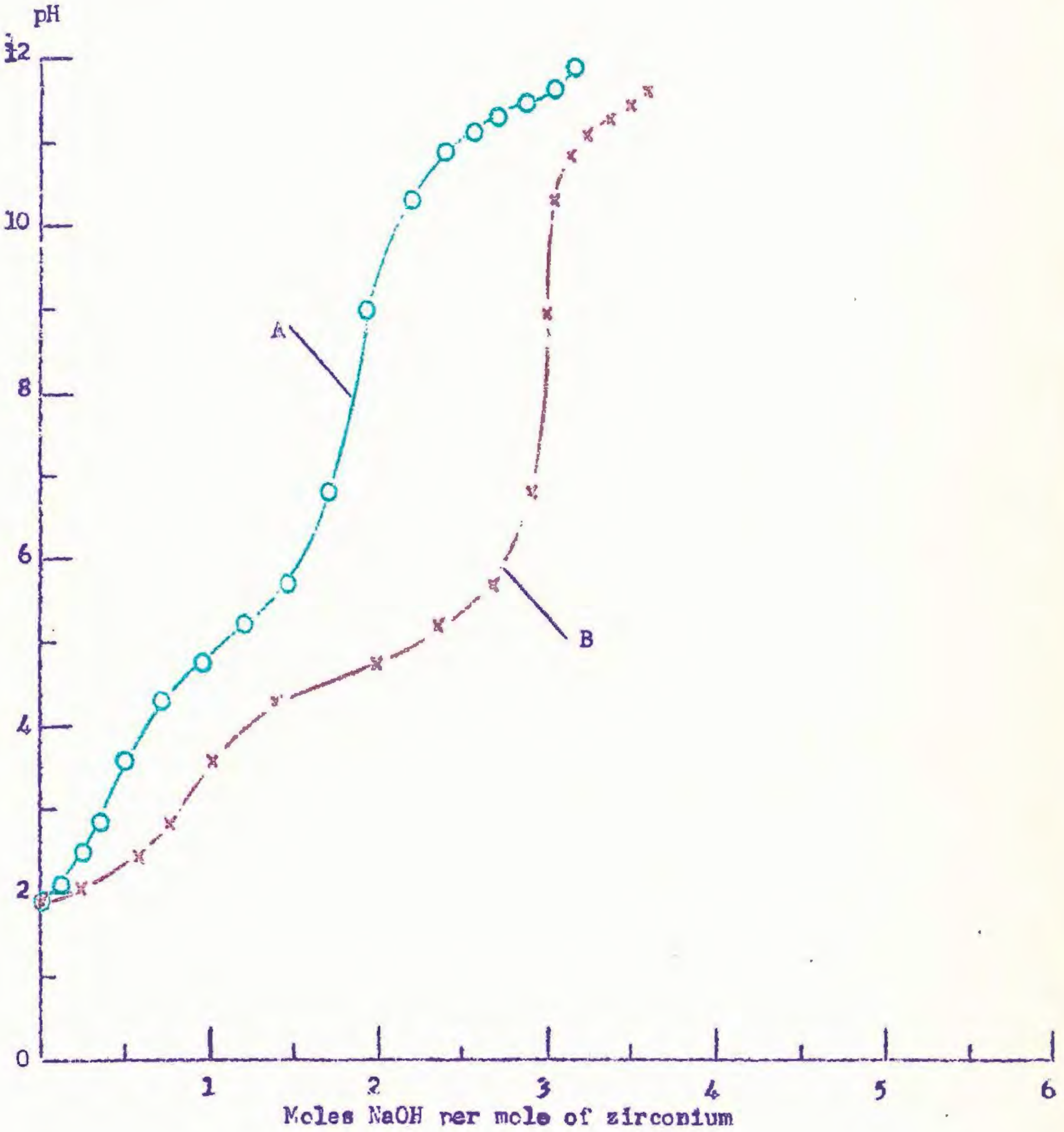

Fig. A2 Titration of zirconium oxychloride in the presence of 2 moles of acetic acid, equilibrated to pH 1.9 before titration.

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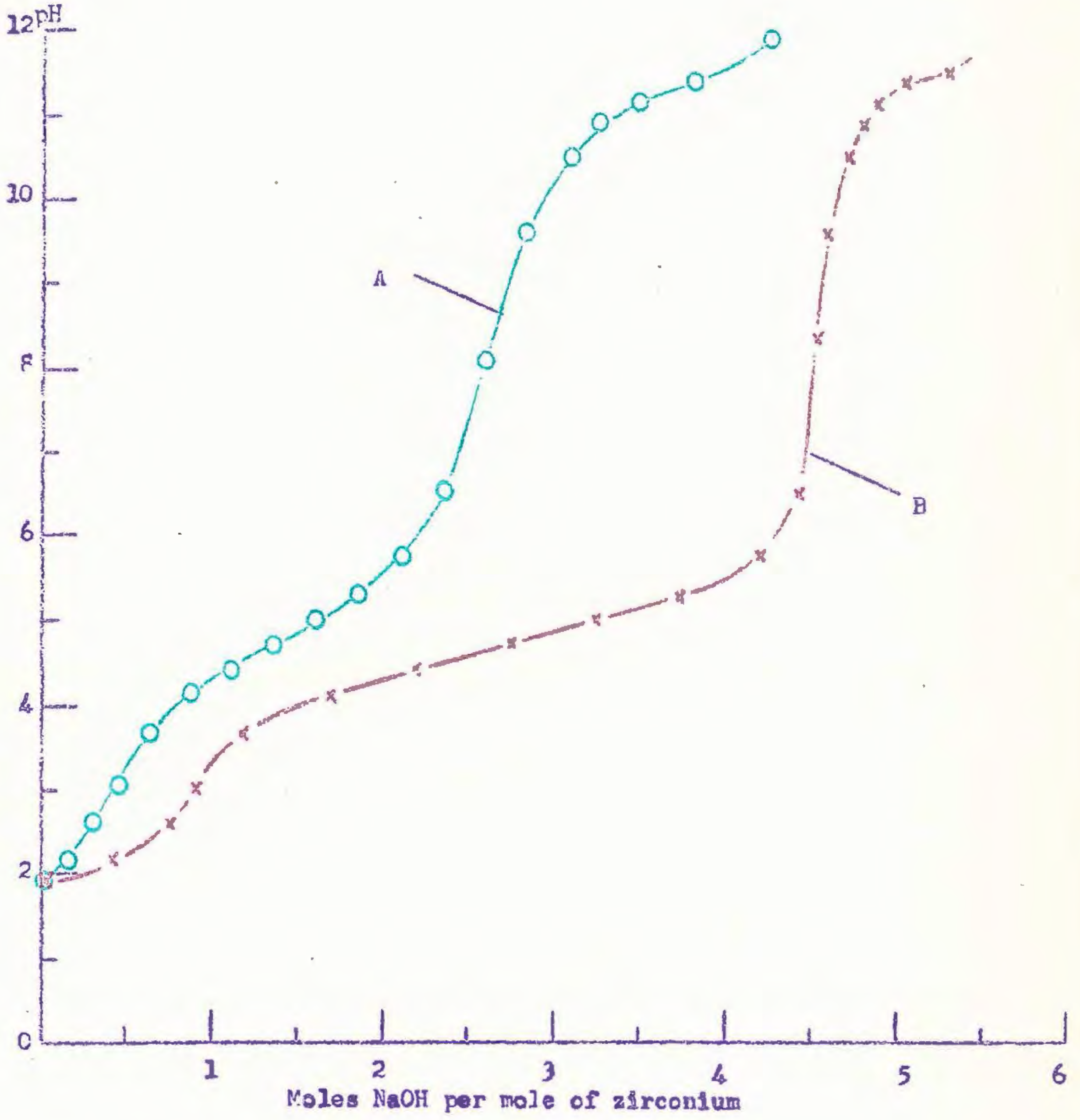

Fig A3 Titration of zirconium oxychloride in the presence of 4 moles of acetic acid, equilibrated to pH 1.9 before titration.

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B. Blank.

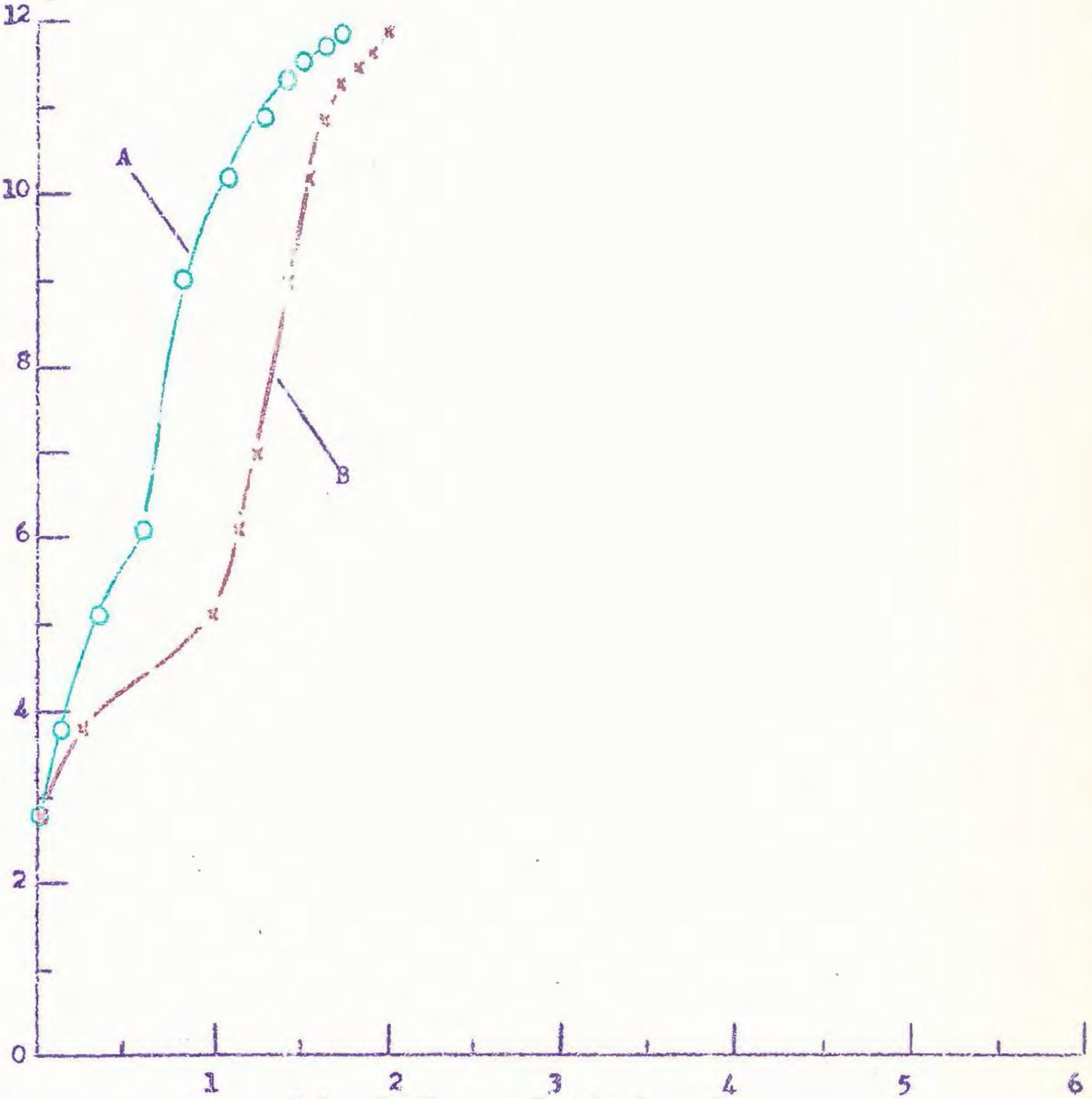

Fig A4 Titration of zirconium oxychloride in the presence of 1 mole of acetic acid, equilibrated to pH 2.8 before titration.

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B. Blank.

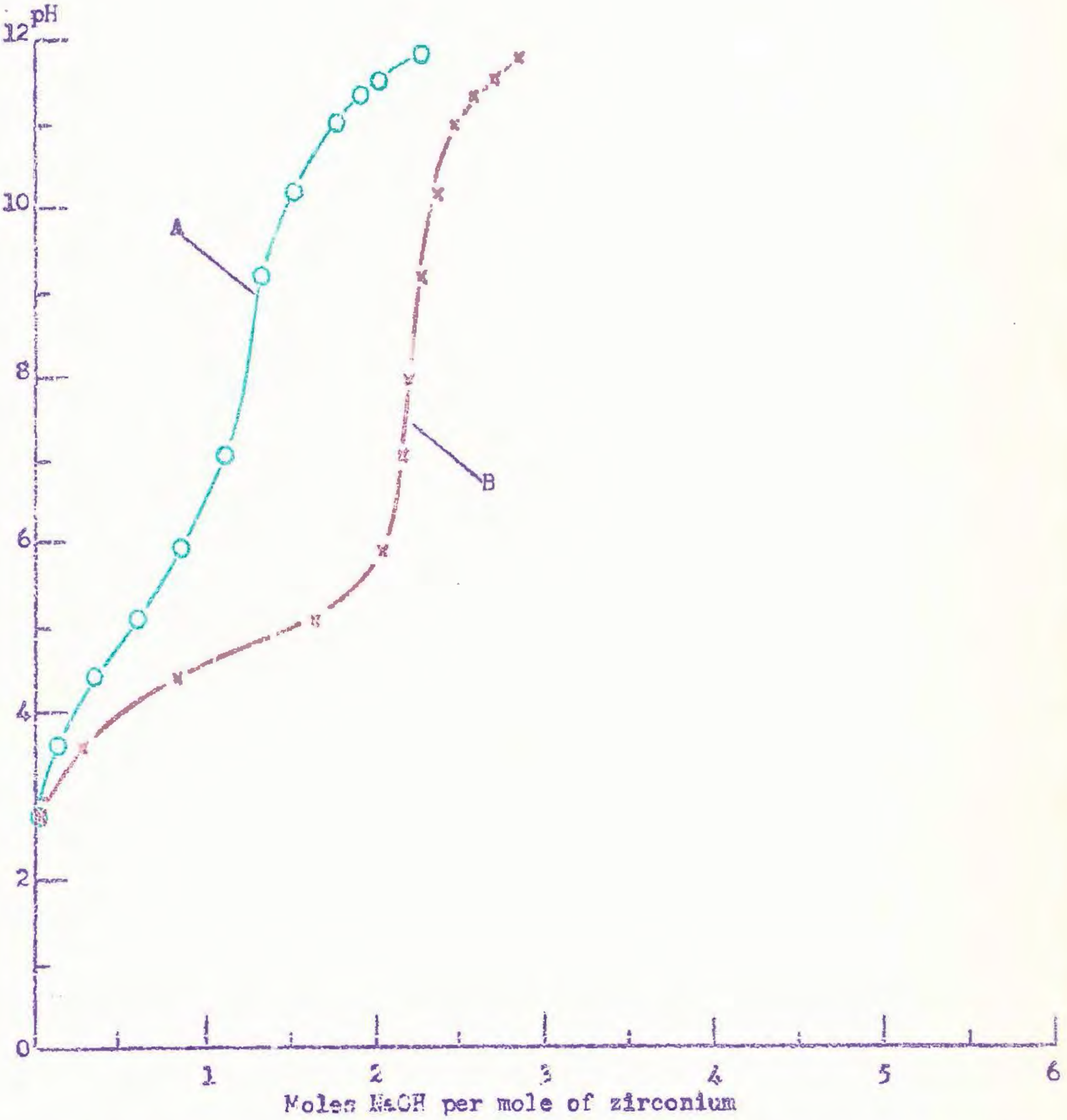

Fig. A5 Titration of zirconium oxychloride in the presence of 2 moles of acetic acid, equilibrated to pH2.8 before titration.

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B. Blank.

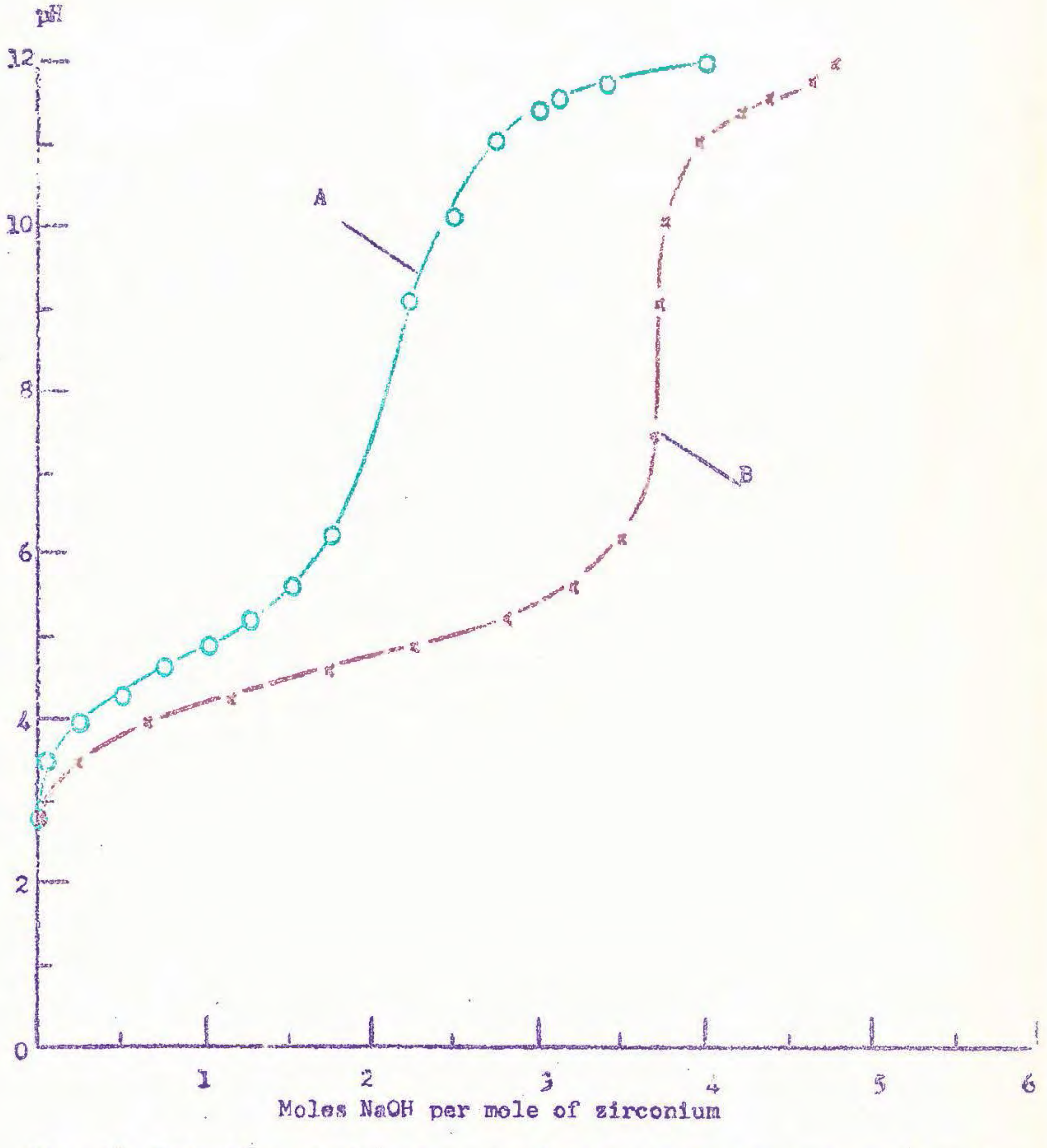


Fig. A6 Titration of zirconium oxychloride in the presence of 4 moles of acetic acid, equilibrated to pH 2.8 before titration.

Curve A. Titration of mixture.
B. Blank.

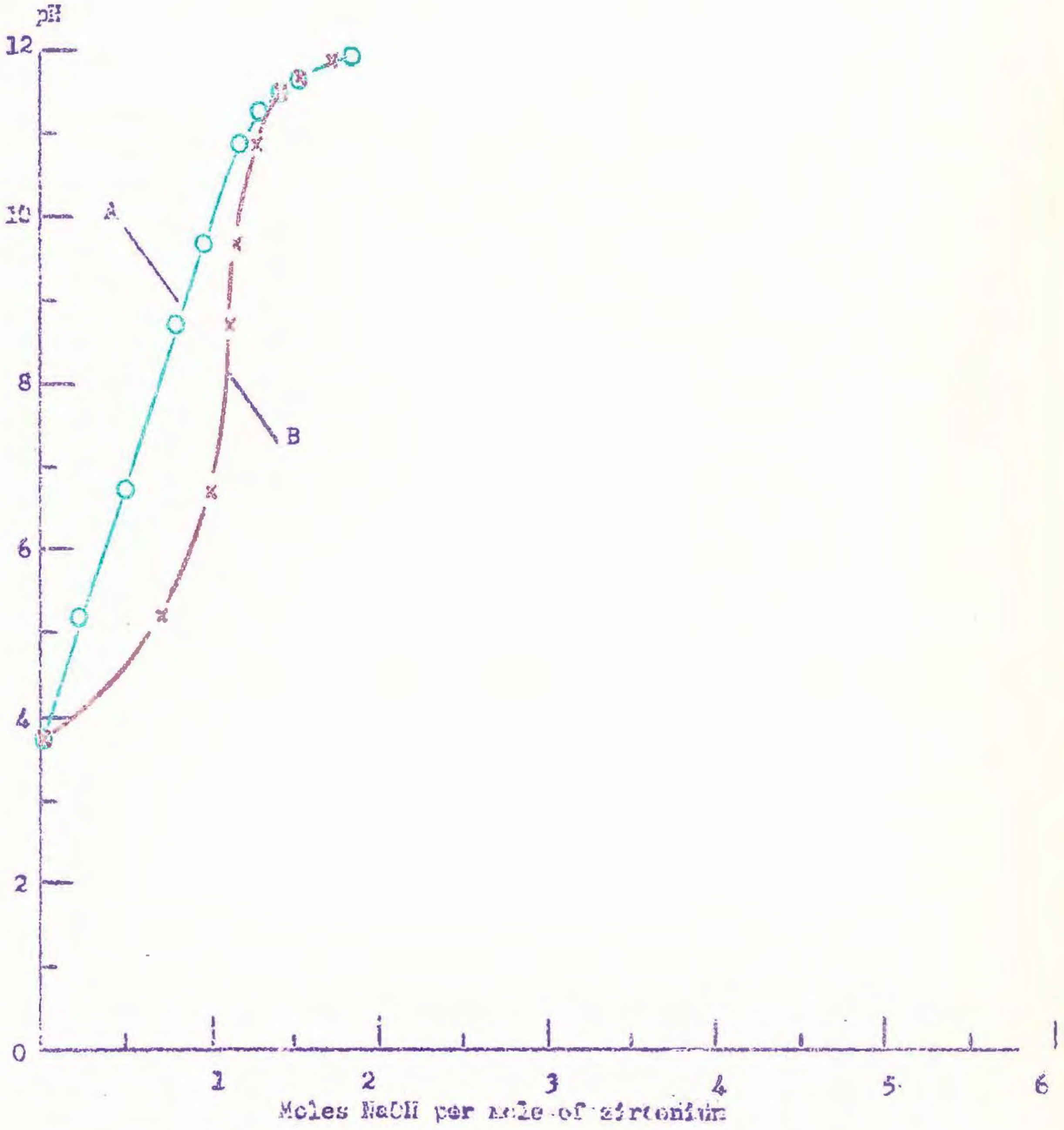


Fig. A7 Titration of zirconium oxychloride in the presence of 1 mole of acetic acid, equilibrated to pH 3.7 before titration.

Curve A. Titration of mixture.
B. Blank.

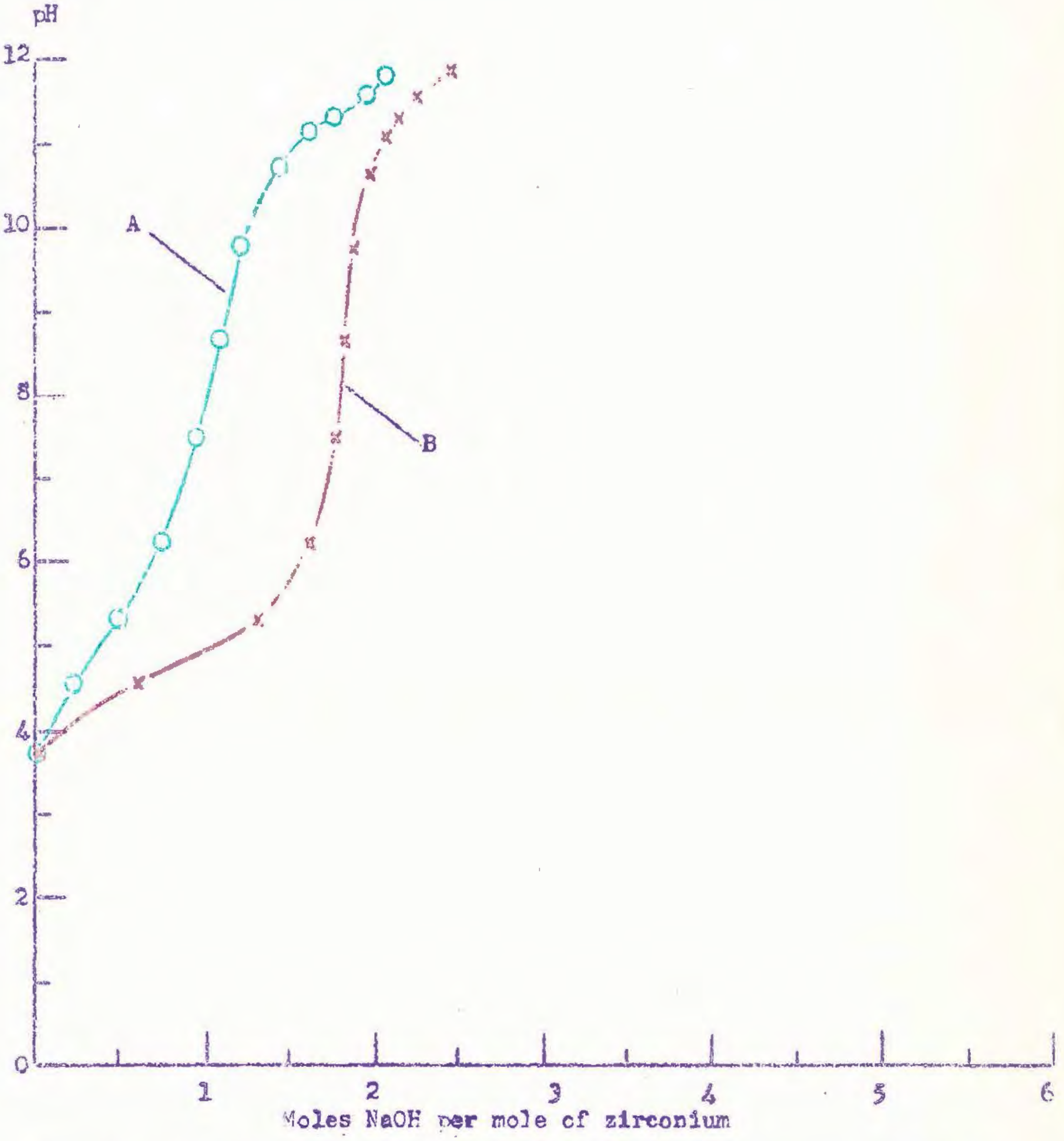


Fig. A8 Titration of zirconium oxychloride in the presence of 2 moles of acetic acid, equilibrated to pH 3.7 before titration.

Curve A. Titration ofmixture.
B. Blank.

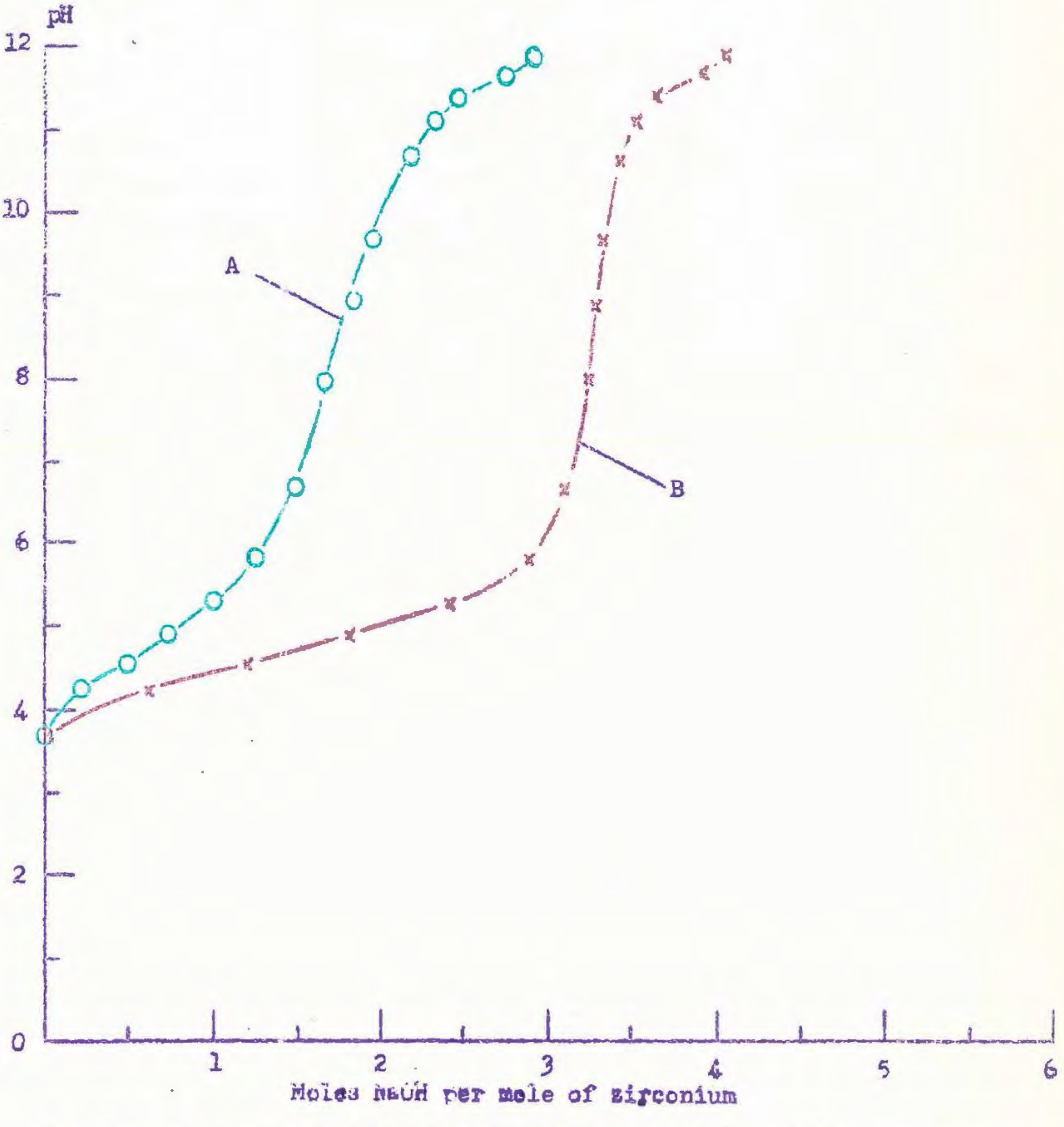


Fig. A9 Titration of zirconium oxychloride in the presence of 4 moles of acetic acid, equilibrated to pH 3.7 before titration.

Curve A. Titration of mixture.
B. Blank.

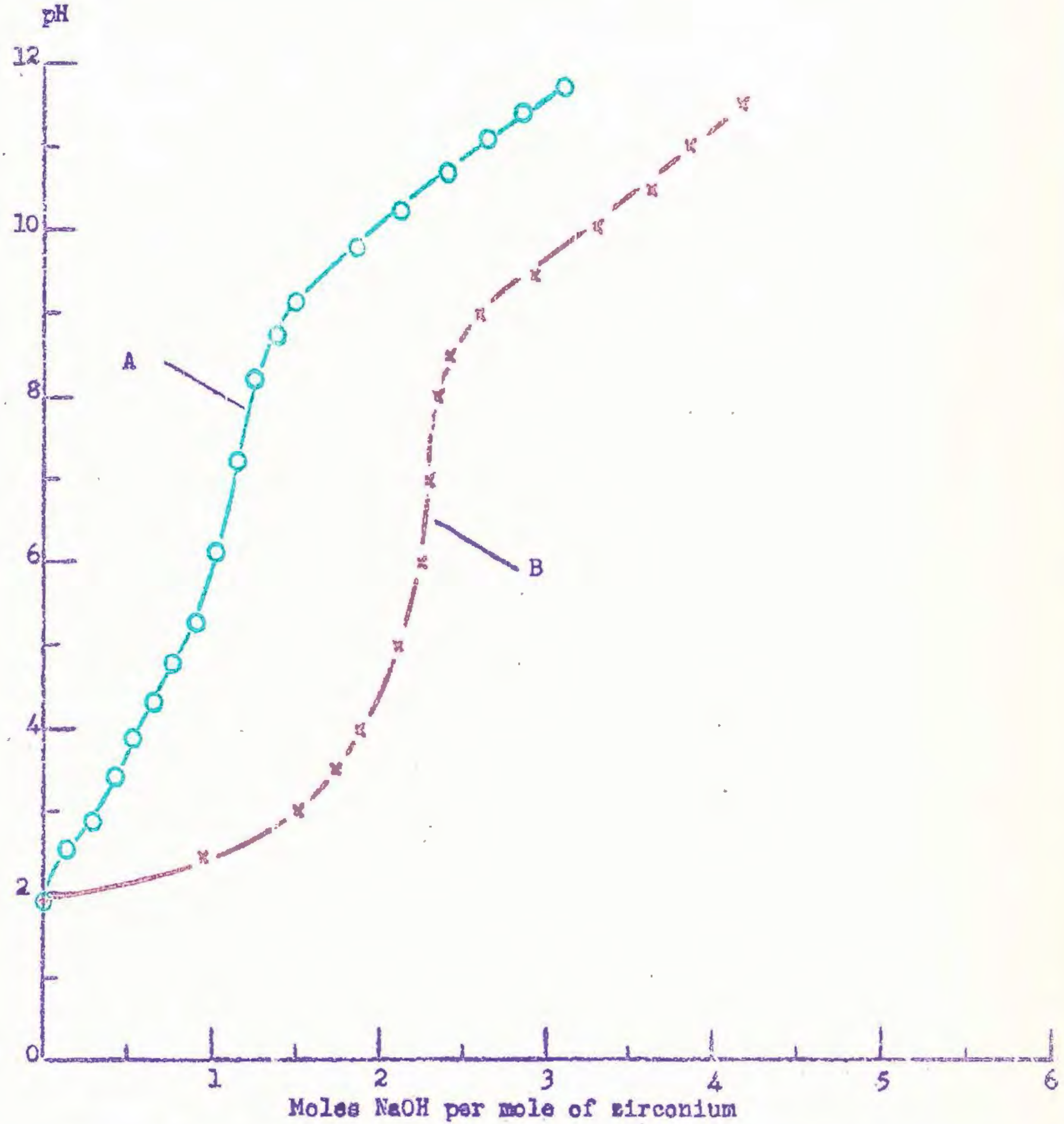


Fig. A10 Titration of zirconium oxychloride in the presence of 1 mole of glycine, equilibrated to pH 1.9 before titration.

Curve A. Titration of mixture.
B. Blank.

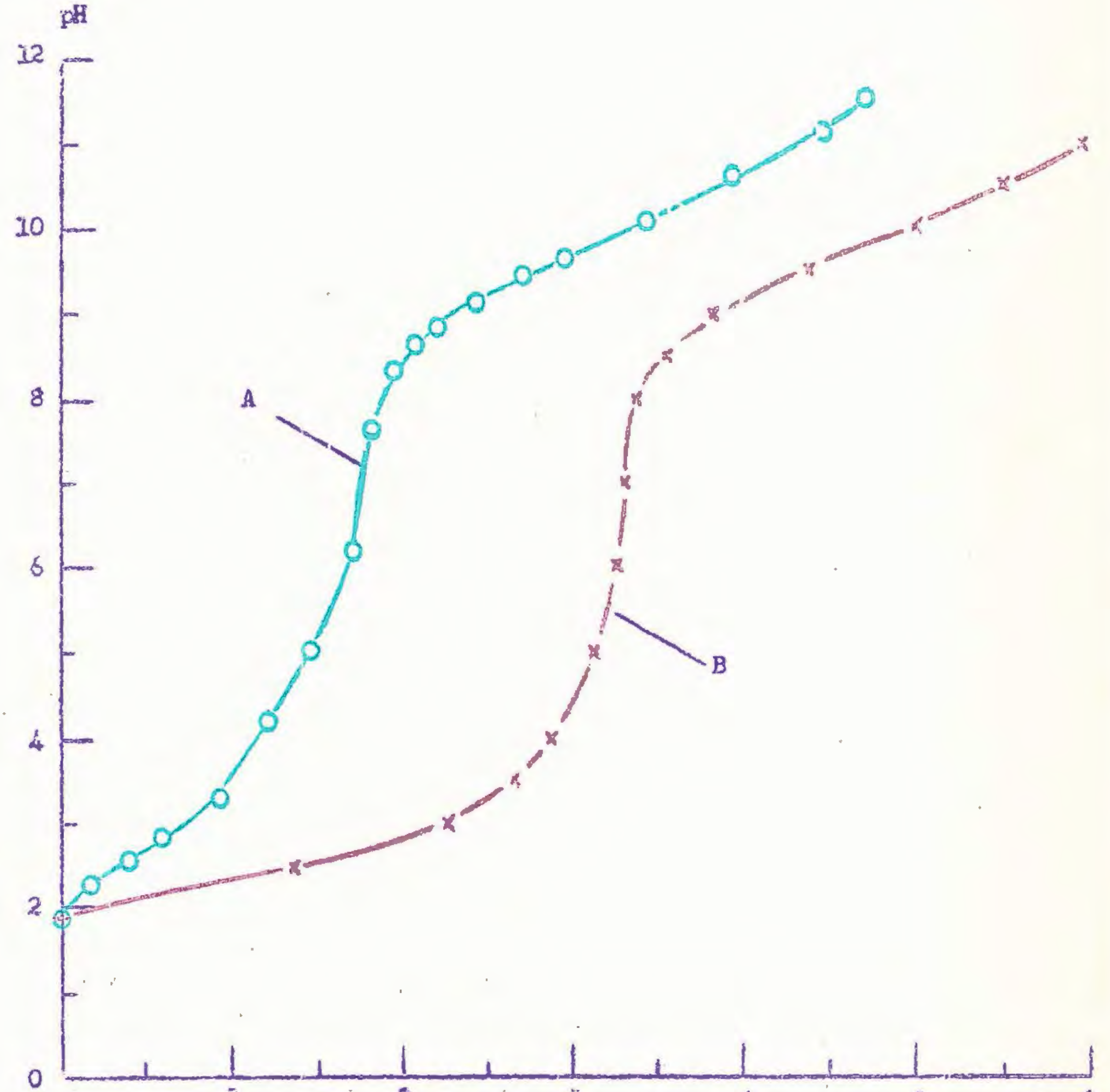


Fig. A11 Titration of zirconium oxychloride in the presence of 2 moles of glycine, equilibrated to pH 1.9 before titration.

Curve A. Titration of mixture.
B. Blank.

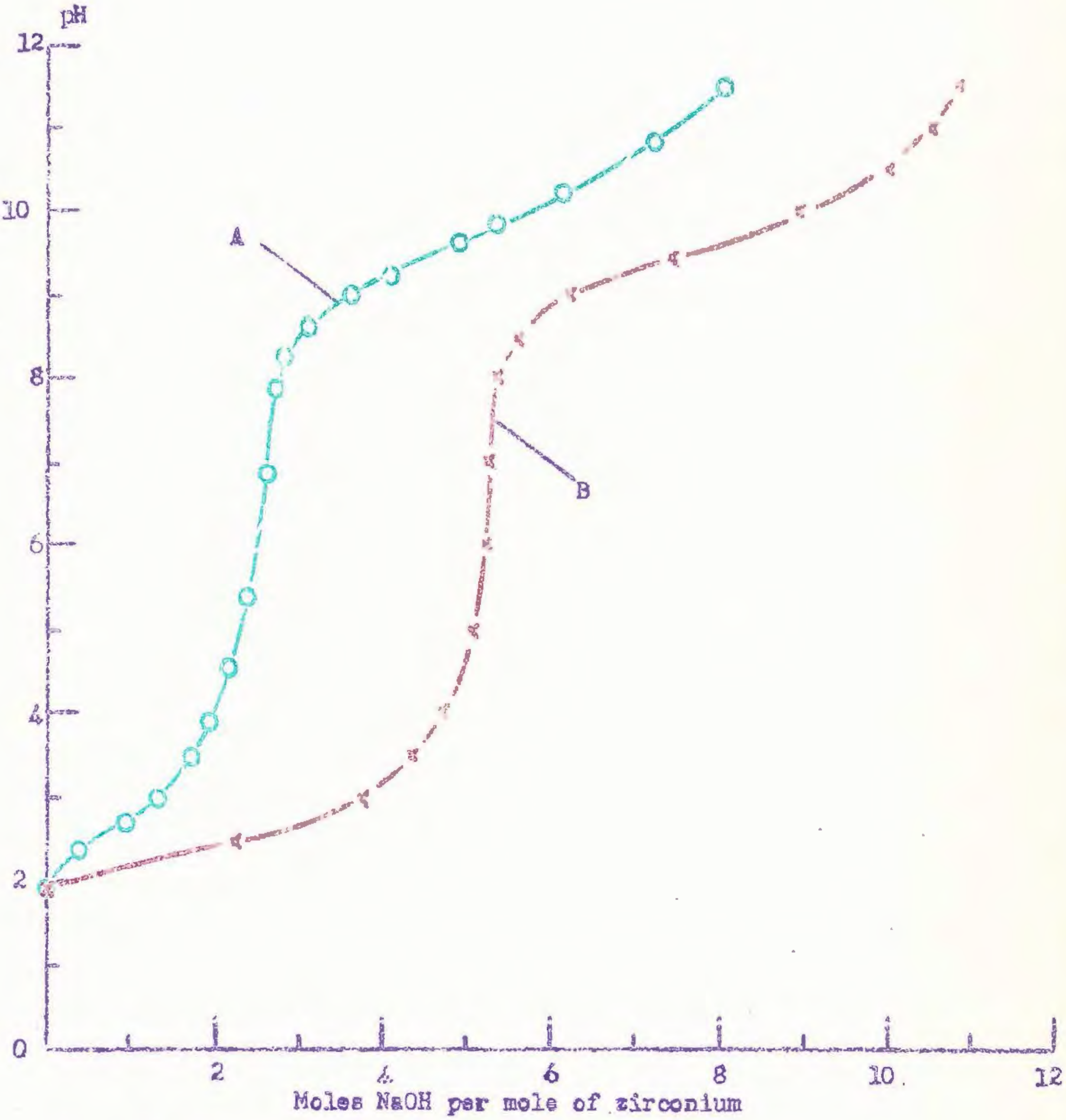


Fig. A12 Titration of zirconium oxychloride in the presence of 4 moles of glycine, equilibrated to pH 1.9 before titration.

Curve A. Titration of mixture.
B. Blank.

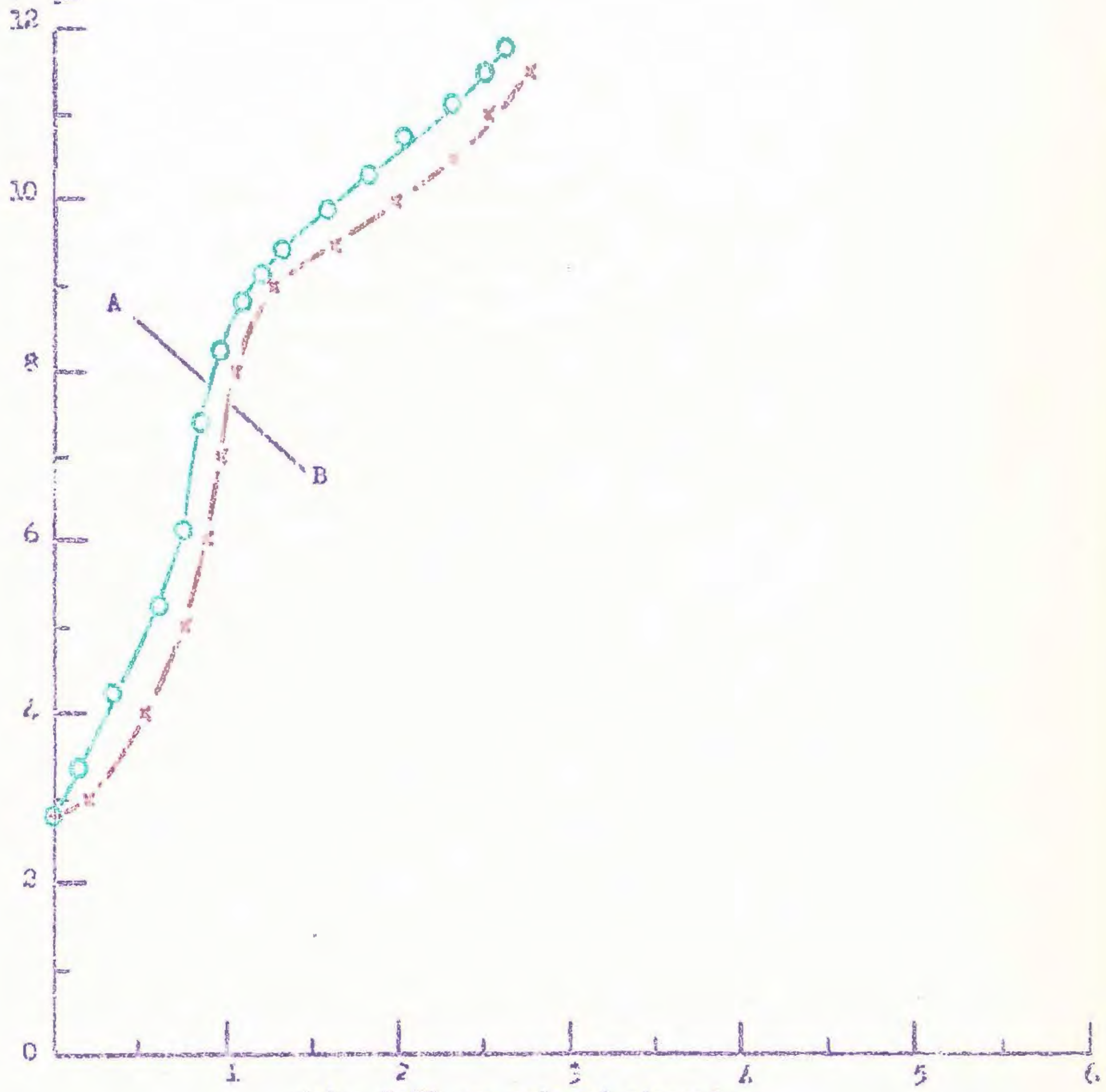


Fig. A12 Titration of zirconium oxychloride in the presence of 1 mole of glycine, equilibrated to pH 2.8 before titration.

Curve A. Titration of mixture.
B. Blank.

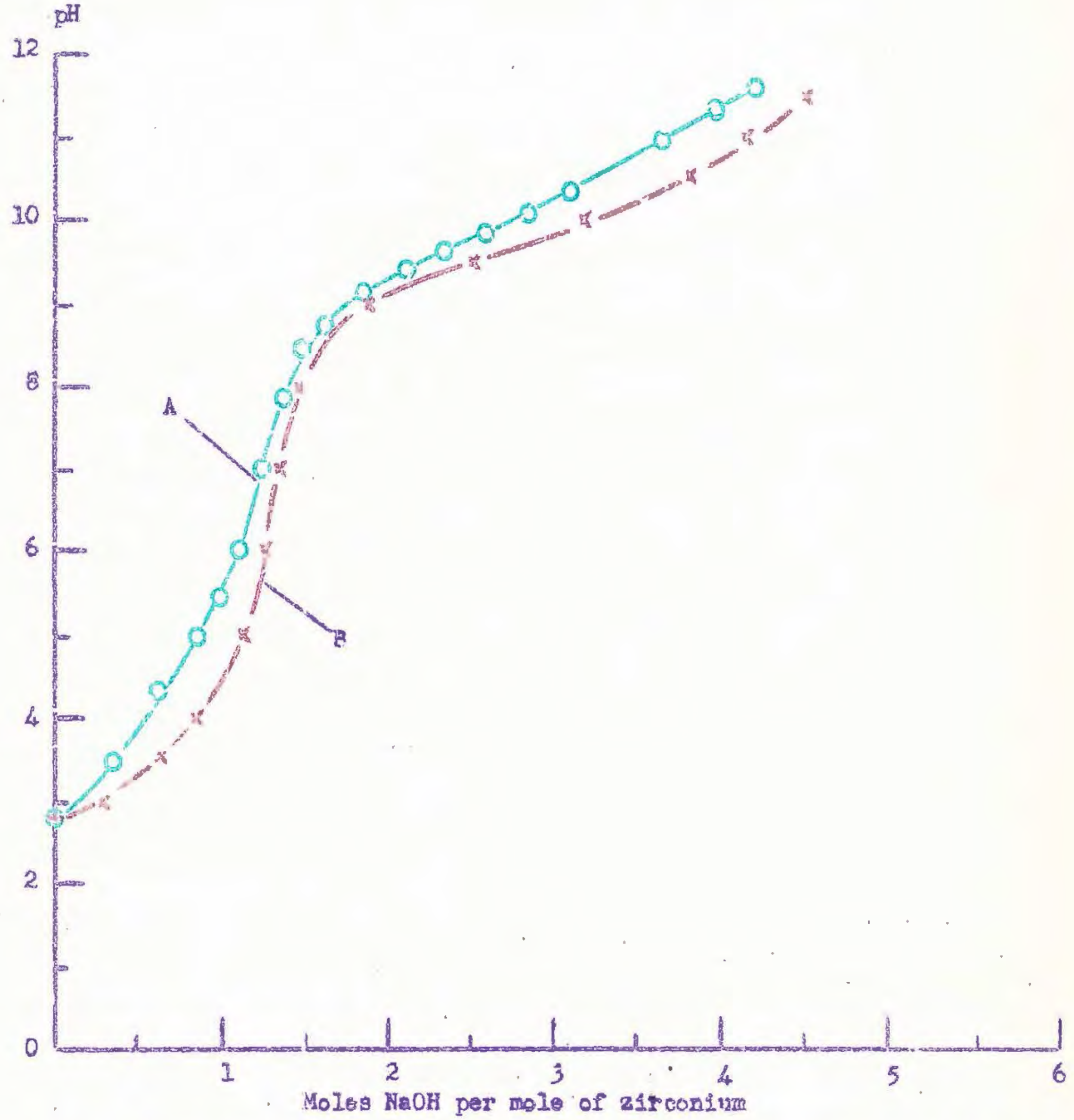


Fig. A14 Titration of zirconium oxychloride in the presence of 2 moles of glycine, equilibrated to pH 2.8 before titration.

Curve A. Titration of mixture.
B. Blank.

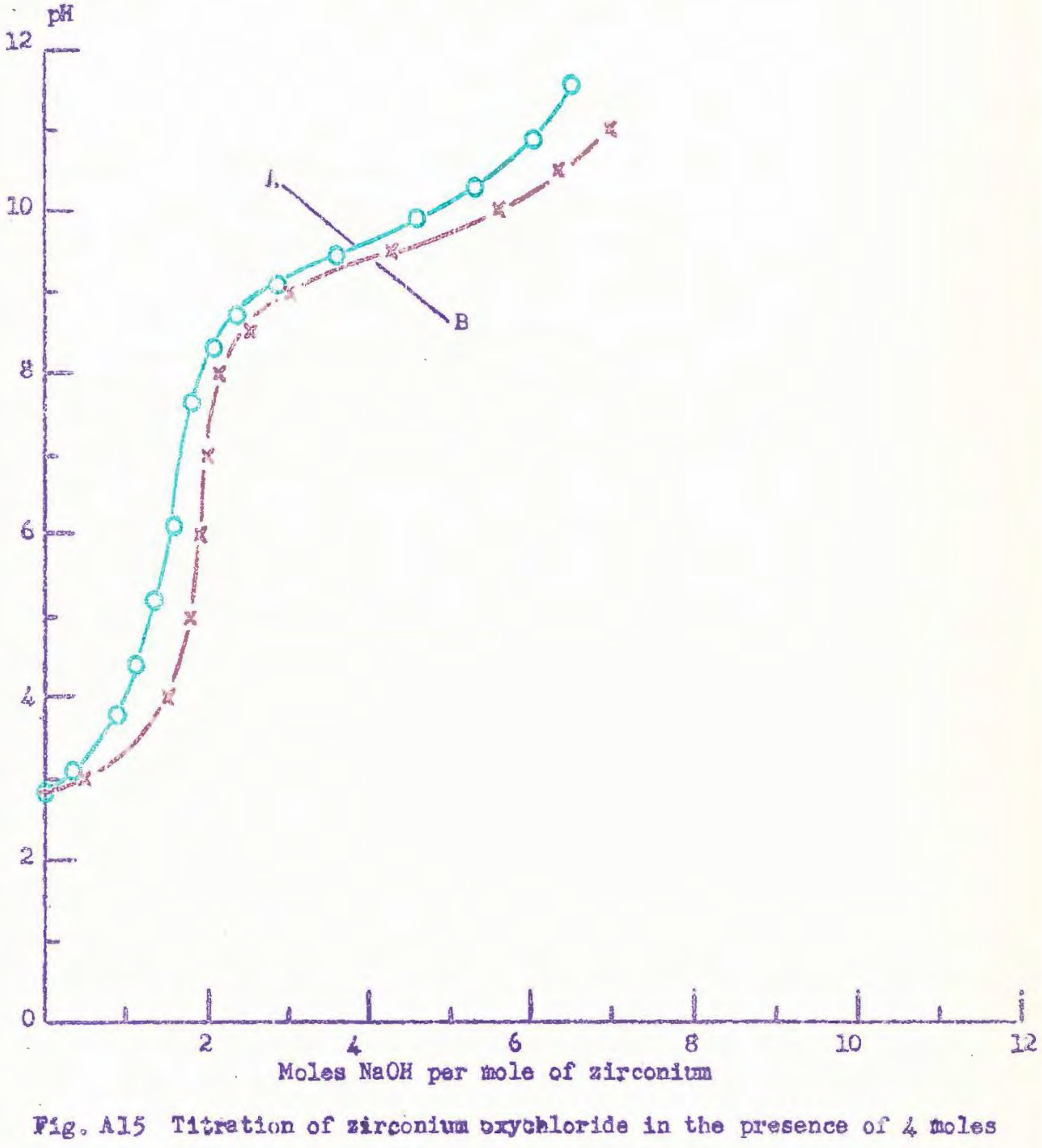


Fig. A15 Titration of zirconium oxychloride in the presence of 4 moles of glycine, equilibrated to pH 2.8 before titration.

Curve A. Titration of mixture.
B. Blank.

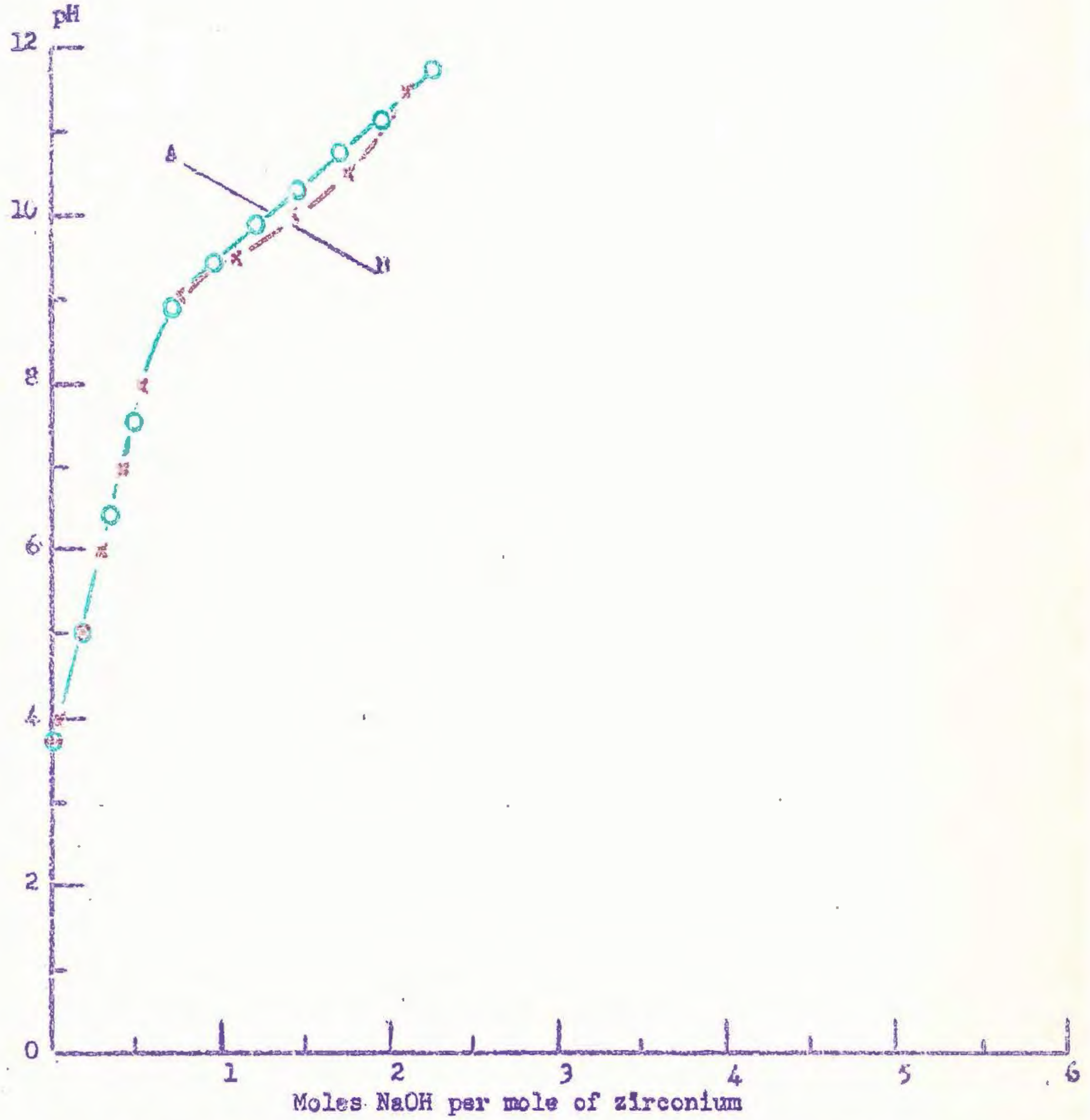


Fig. A16 Titration of zirconium oxychloride in the presence of 1 mole of glycine, equilibrated to pH 3.7 before titration.

Curve A. Titration of mixture.
B. Blank.

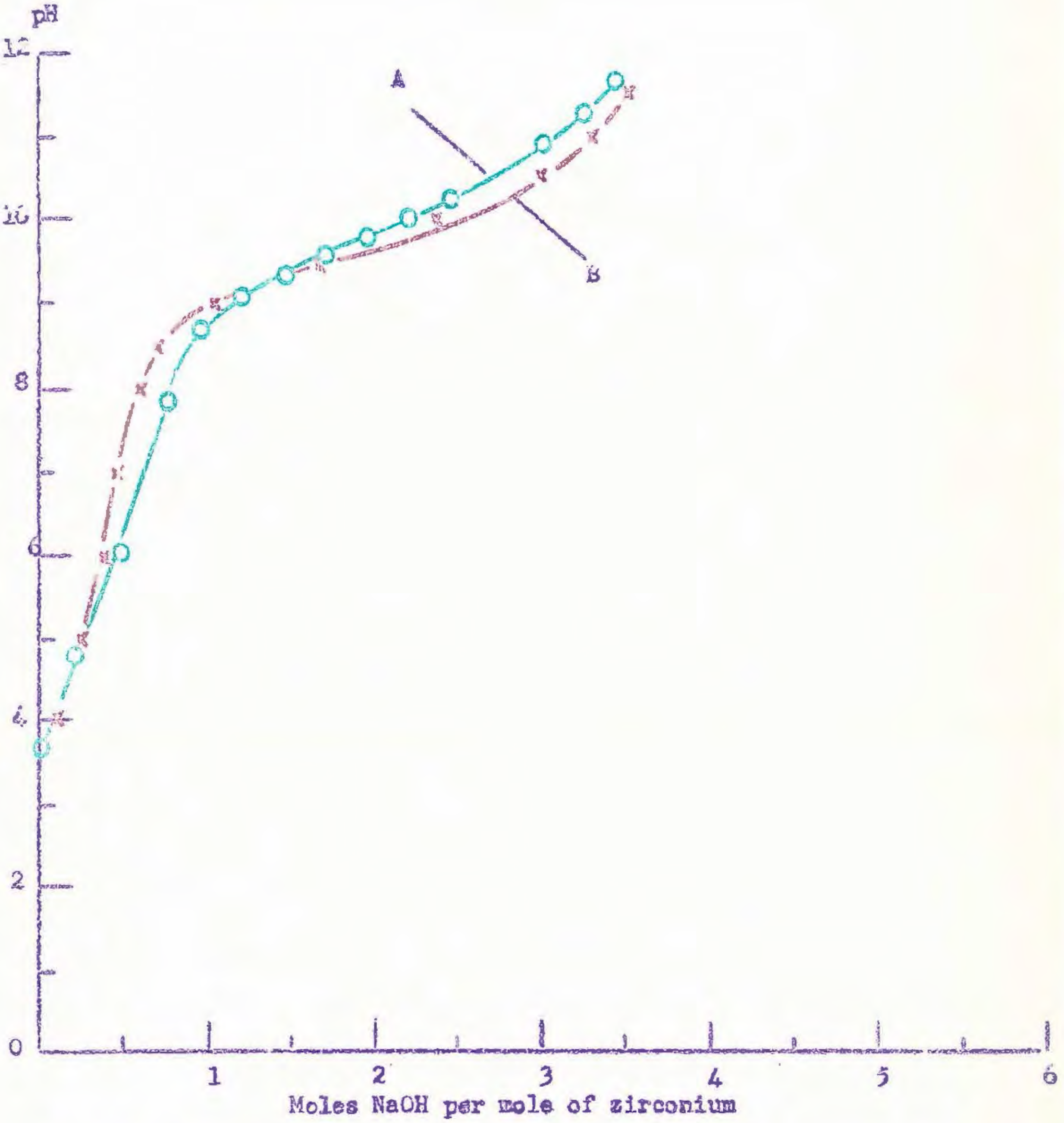


Fig. A17 Titration of zirconium oxychloride in the presence of 2 moles of glycine, equilibrated to pH 3.7 before titration.

Curve A. Titration of mixture.
B. Blank.

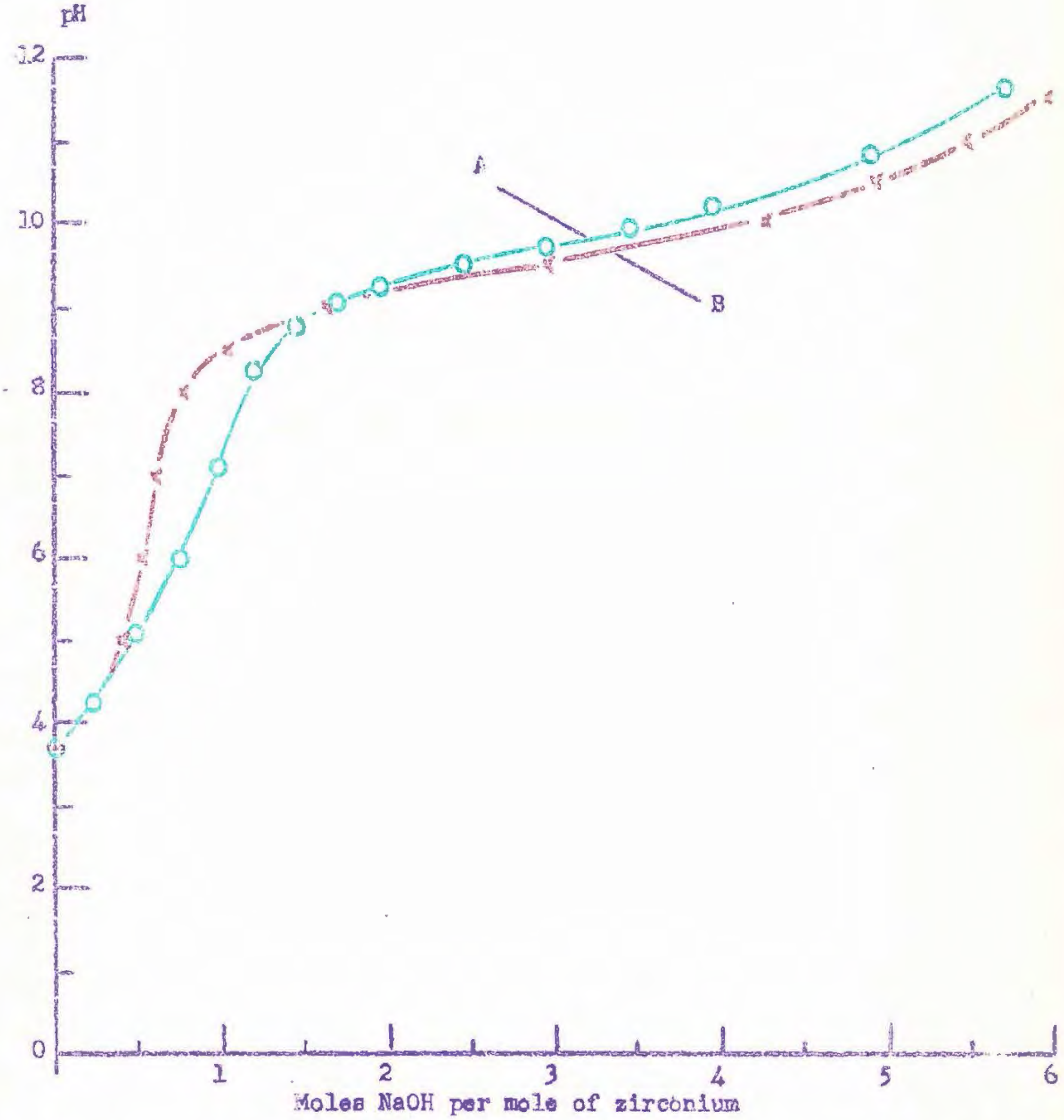


Fig. A18 Titration of zirconium oxychloride in the presence of 4 moles of glycine, equilibrated to pH 3.7 before titration.

Curve A. Titration of mixture.
B. Blank.

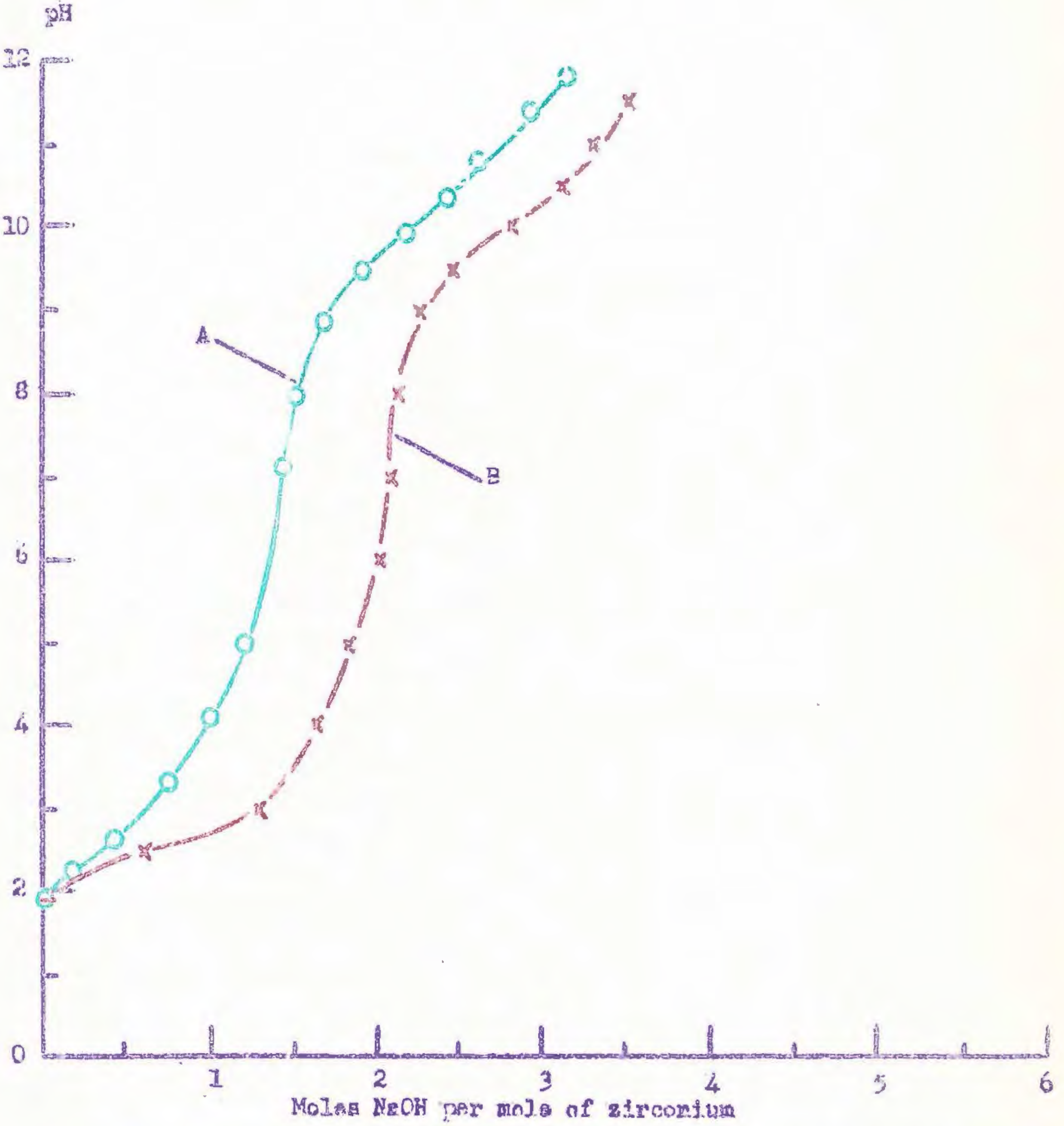


Fig. A19 Titration of zirconium oxychloride in the presence of 1 mole of α-amino-n-butyric acid, equilibrated to pH 1.9 before titration.

Curve A. Titration of mixture.
B. Blank.

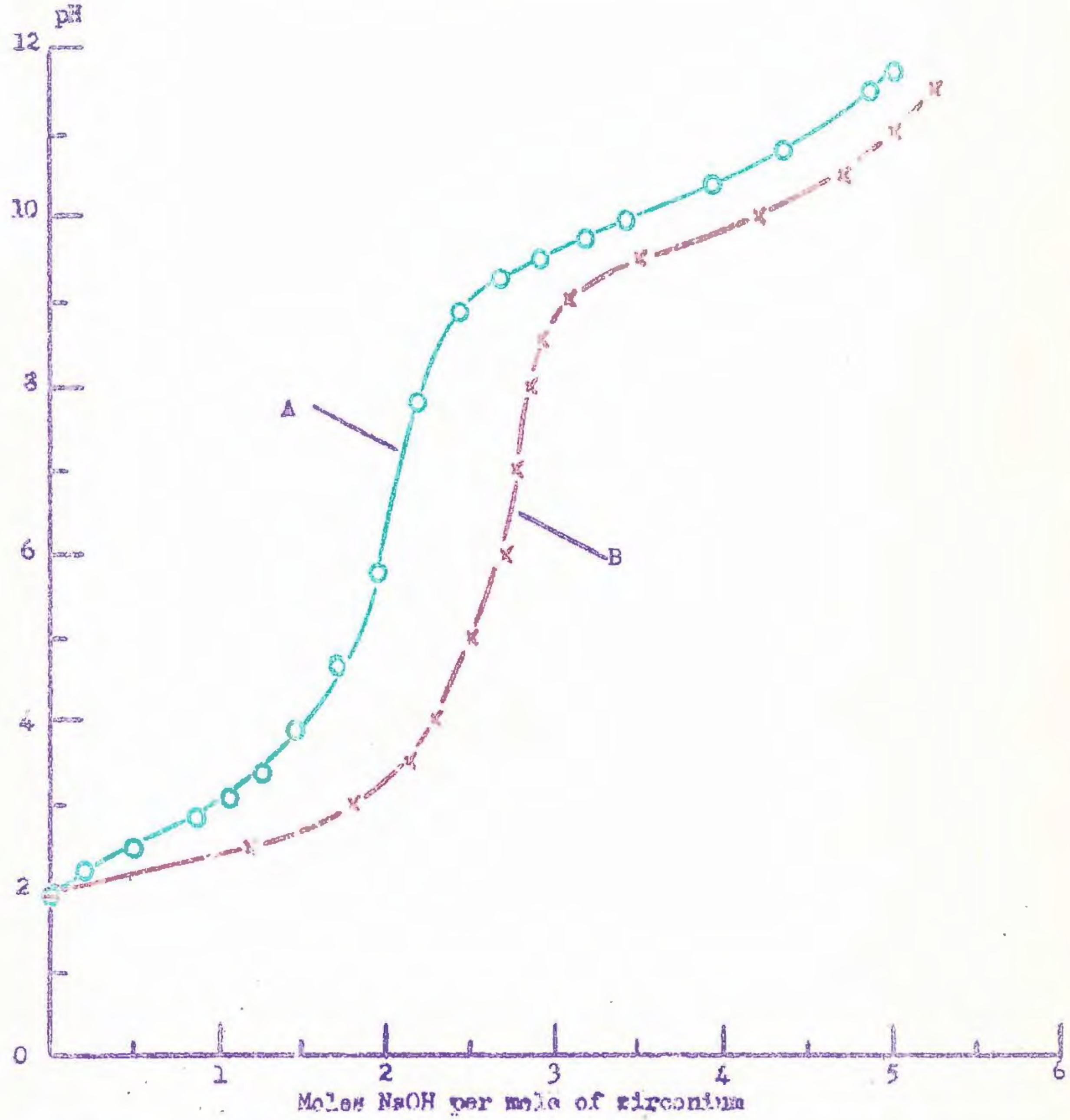


Fig. A20 Titration of zirconium oxychloride in the presence of 2 moles of α-amino-n-butyric acid, equilibrated to pH 1.9 before titration

Curve A. Titration of mixture.
B. Blank.

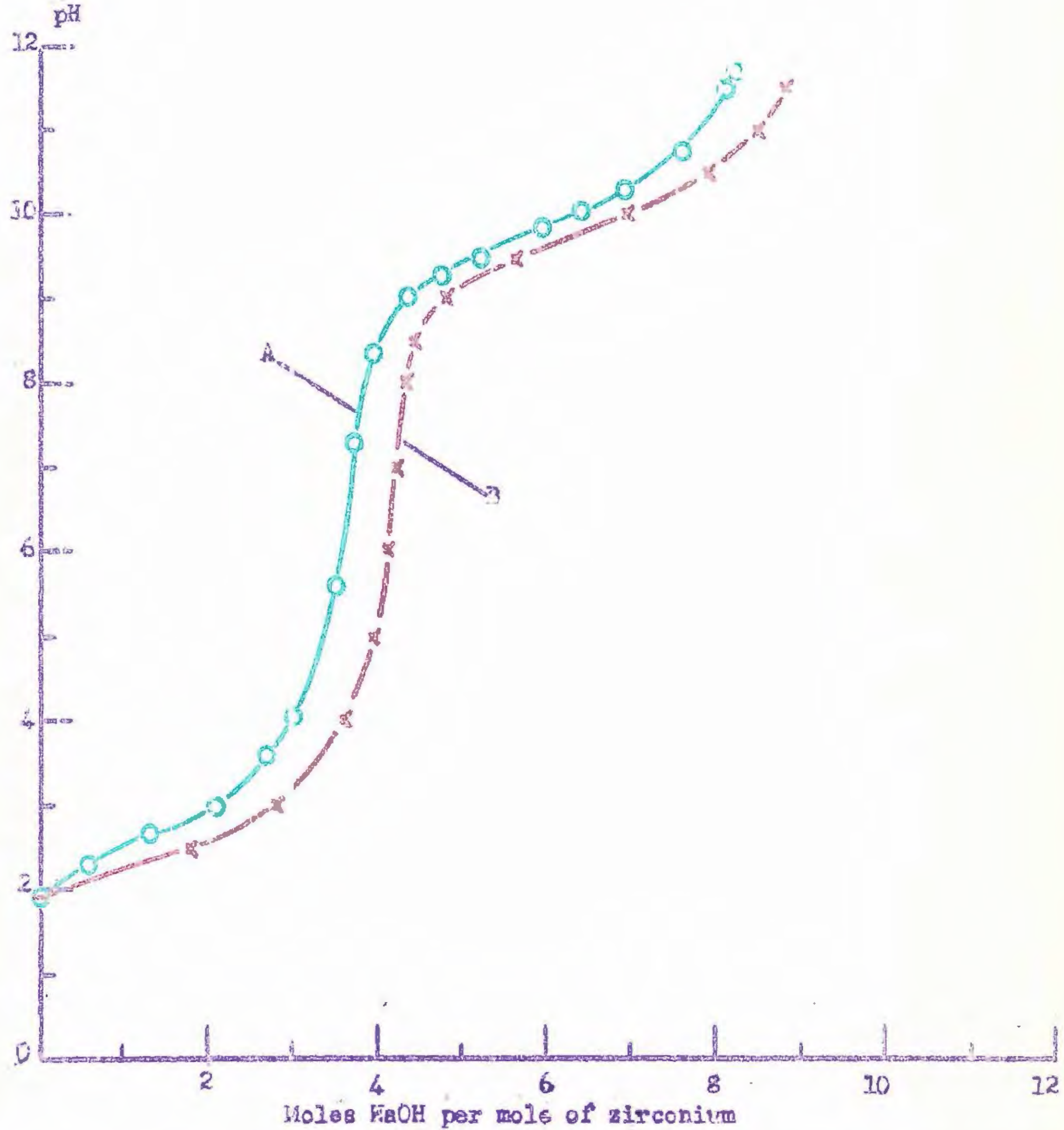


Fig. A21 Titration of zirconium oxychloride in the presence of 4 moles of α-amino-n-butyric acid, equilibrated to pH 1.9 before titration.

Curve A. Titration of mixture.
B. Blank.

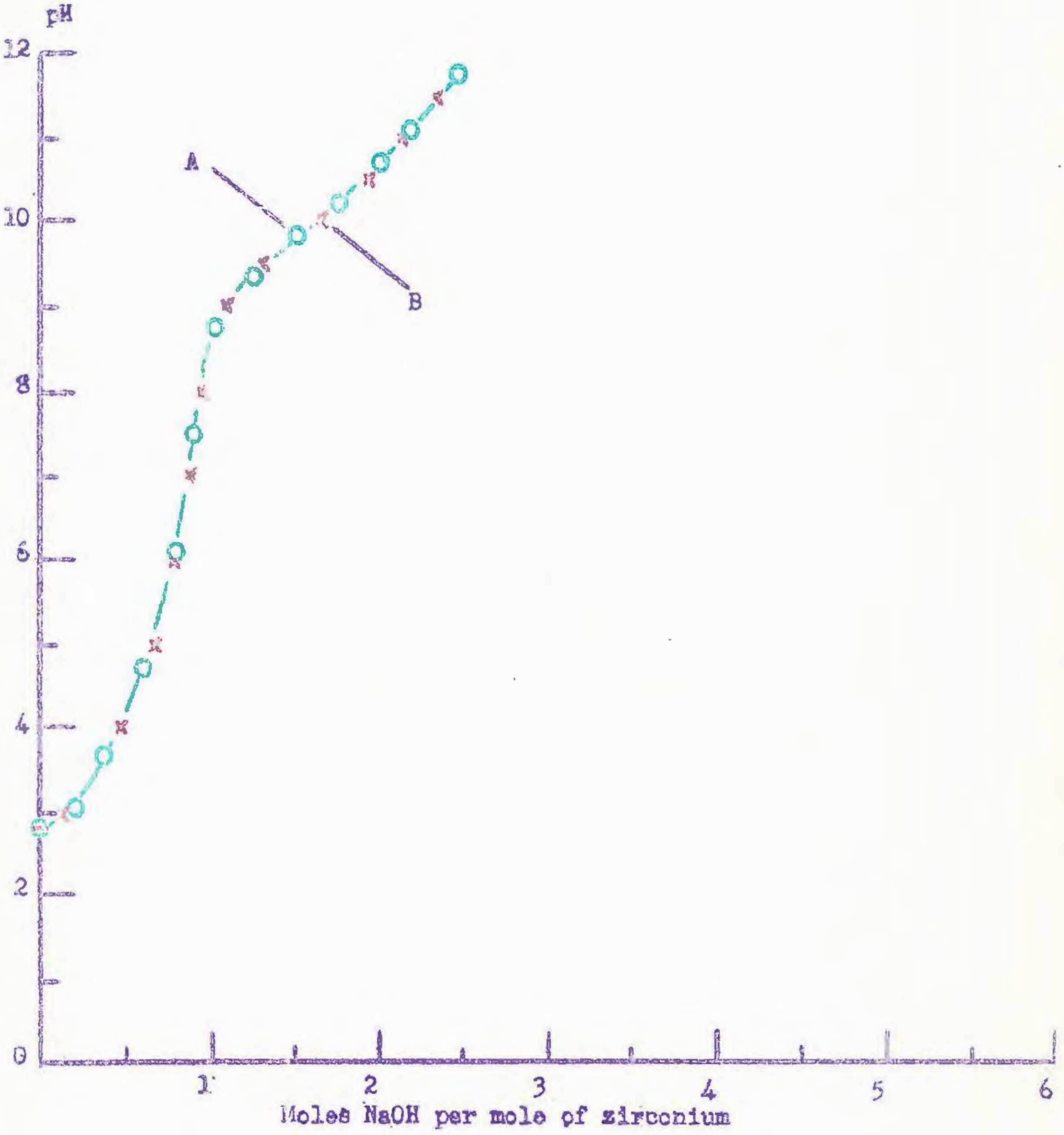


Fig. A22 Titration of zirconium oxychloride in the presence of 1 mole of α-amino-n-butyric acid, equilibrated to pH 2.8 before titration.

Curve A. Titrationnof mixture.
B. Blank.

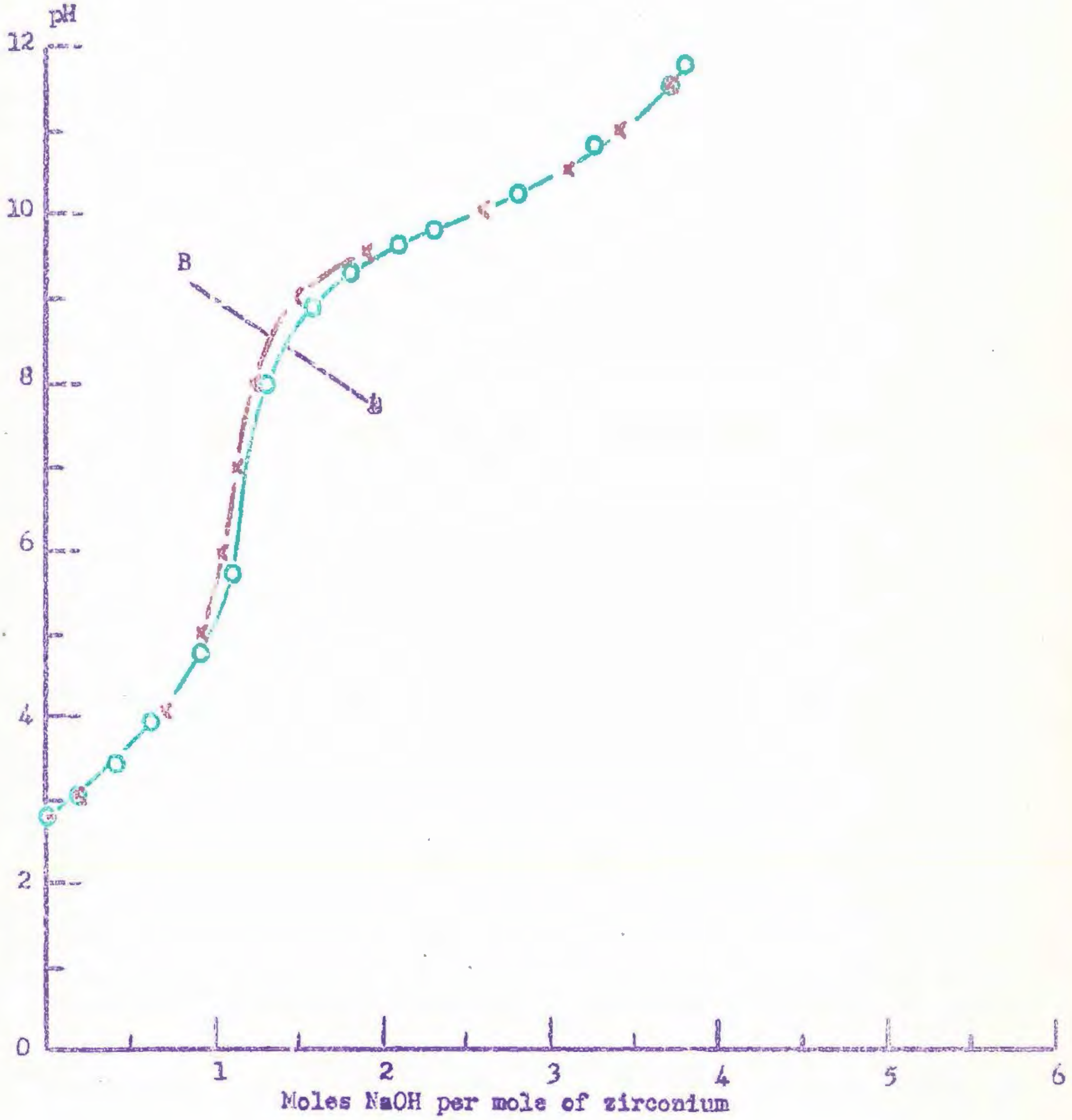
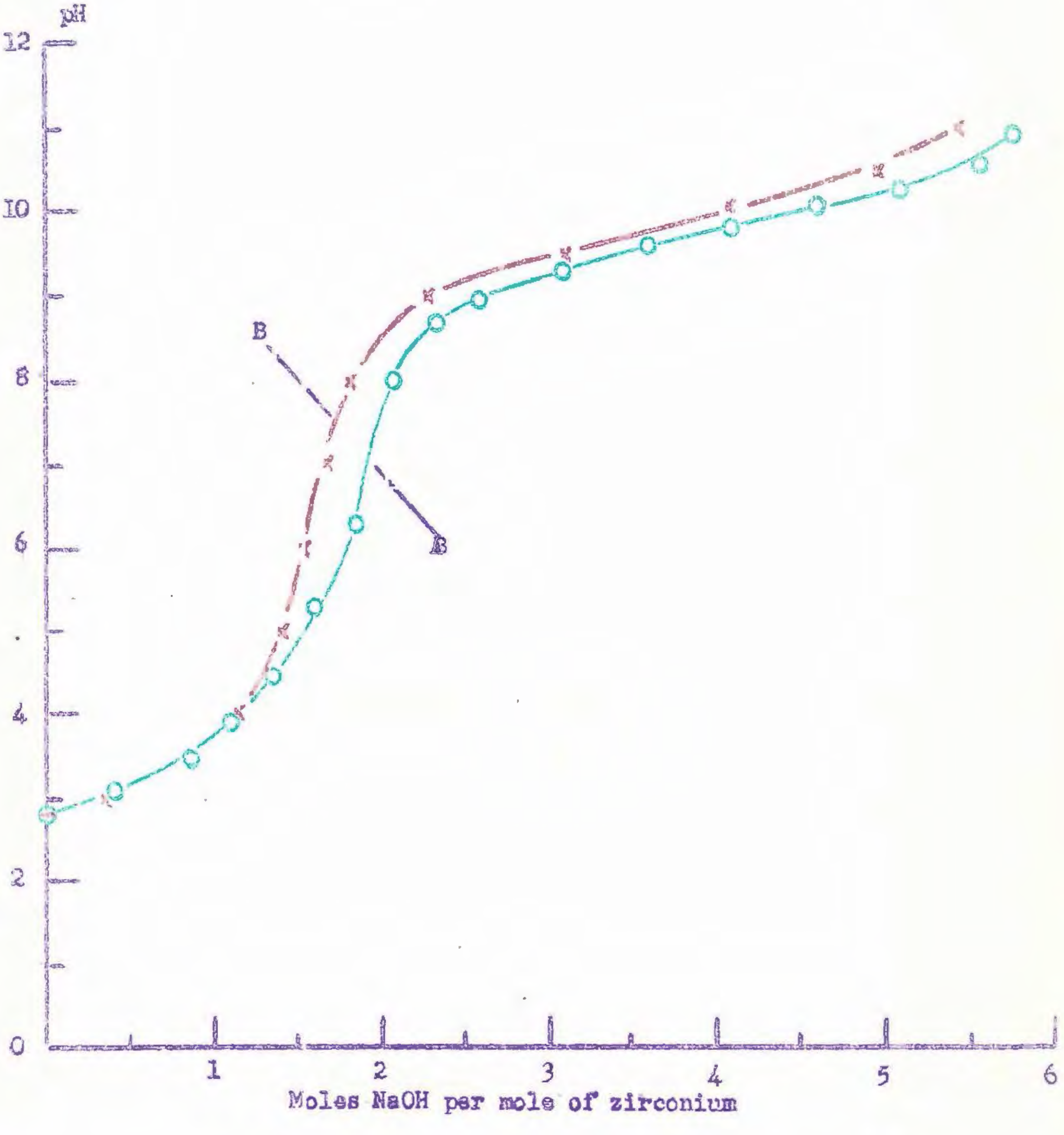


Fig. A23 Titration of zirconium oxychloride in the presence of 2 moles of α-amino-n-butyric acid, equilibrated to pH 2.8 before titration.

Curve A. Titration of mixture.
B. Blank.



Fig, A24 Titration of zirconium oxychloride in the presence of 4 moles of α-amino-n-butyric acid, equilibrated to pH 2.8 before titration.

Curve A. Titration of mixture.
B. Blank.

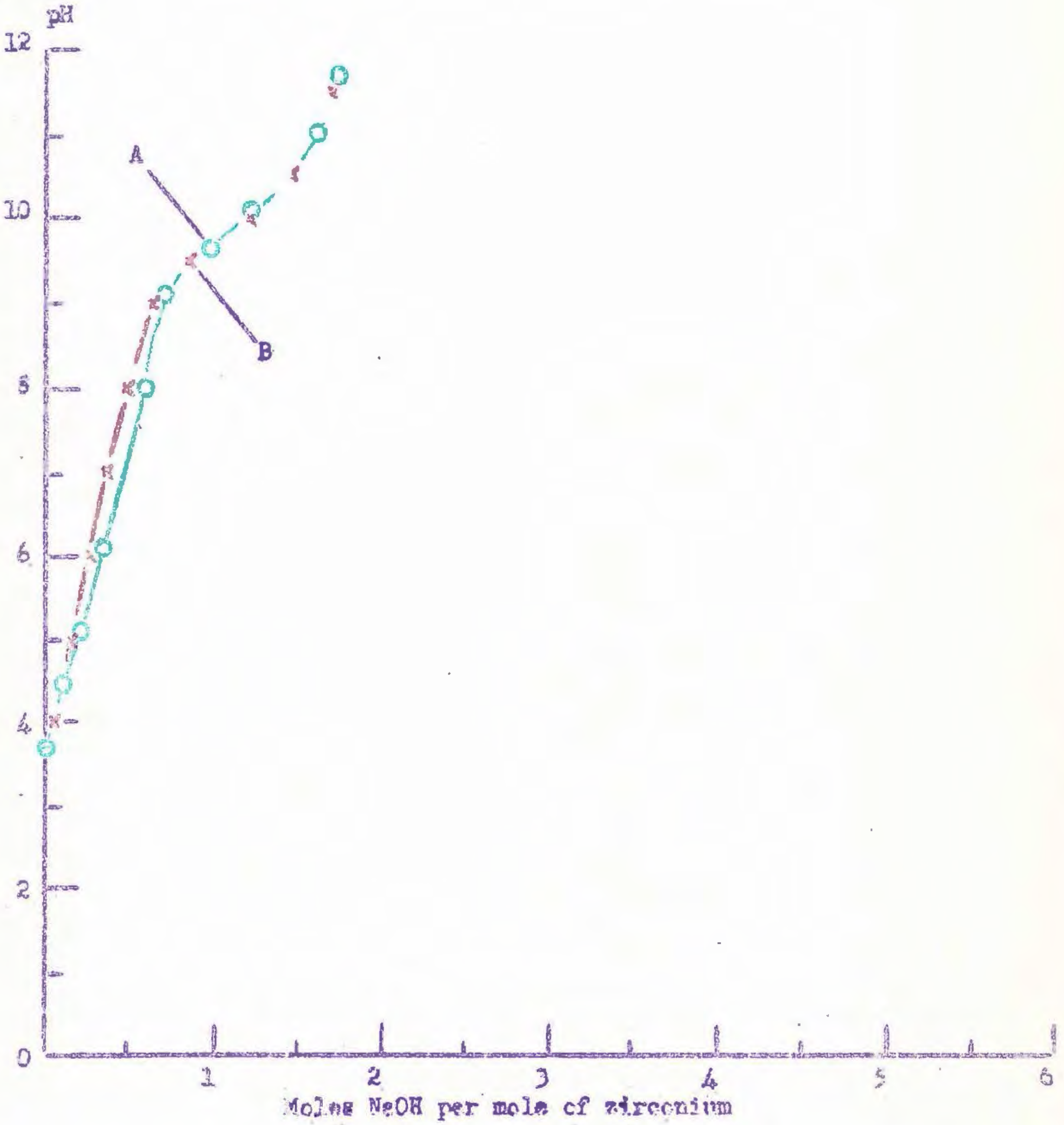


Fig. A25 Titration of zirconium oxychloride in the presence of 1 mole of α-amino-n-butyric acid, equilibrated to pH 3.7 before titration.

Curve A. Titration of mixture.
B. Blank.

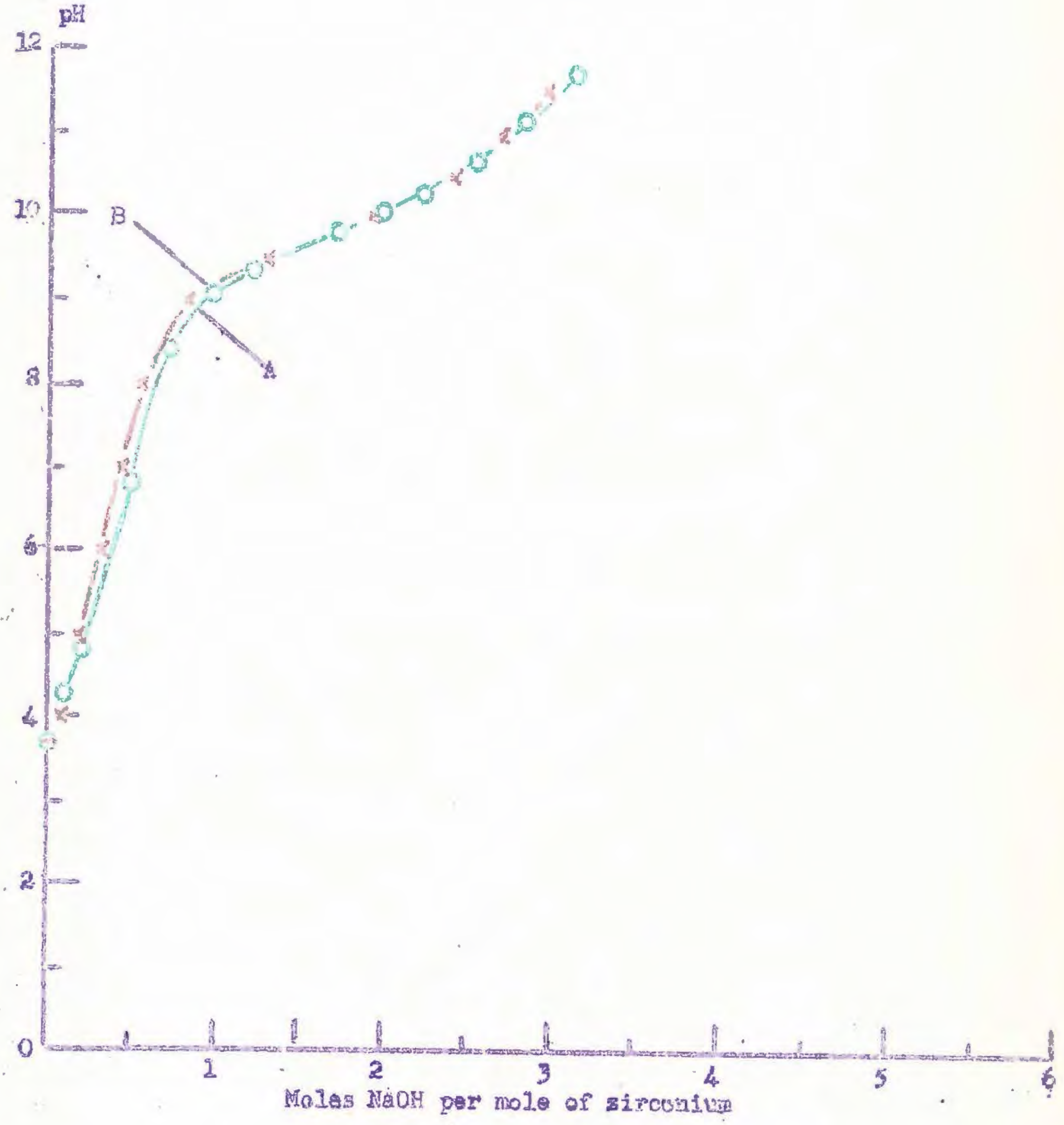


Fig. A26 Titration of zirconium oxychloride in the presence of 2 moles of α-amino-n-butyric acid, equilibrated to pH 3.7 before titration.

Curve A, Titration of mixture.
B, Blank.

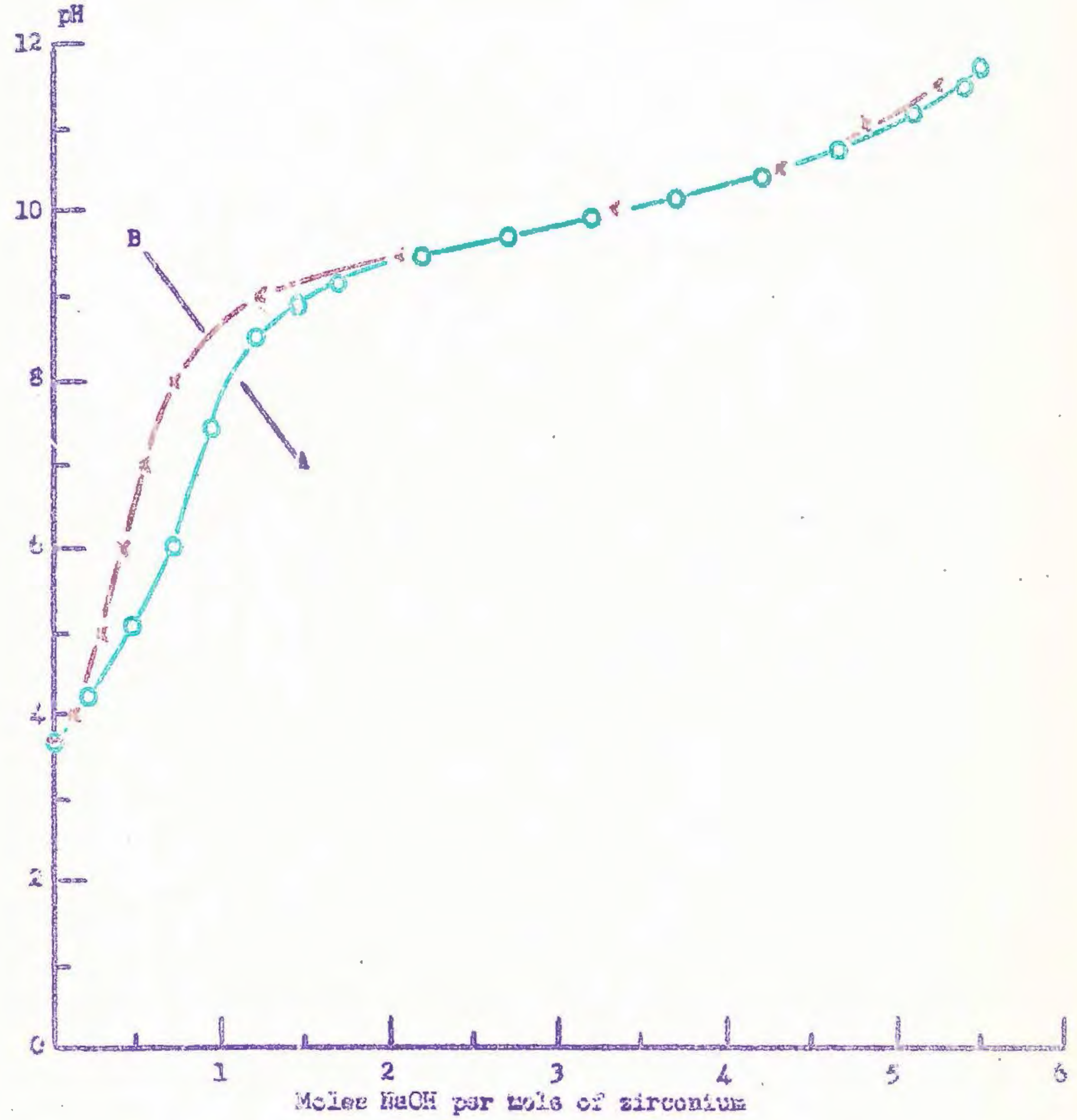


Fig. A27 Titration of zirconium oxychloride in the presence of 4 moles of α-amino-n-butyric acid, equilibrated to pH 3.7 before titration.

Curve A. Titration of mixture.
B. Blank.

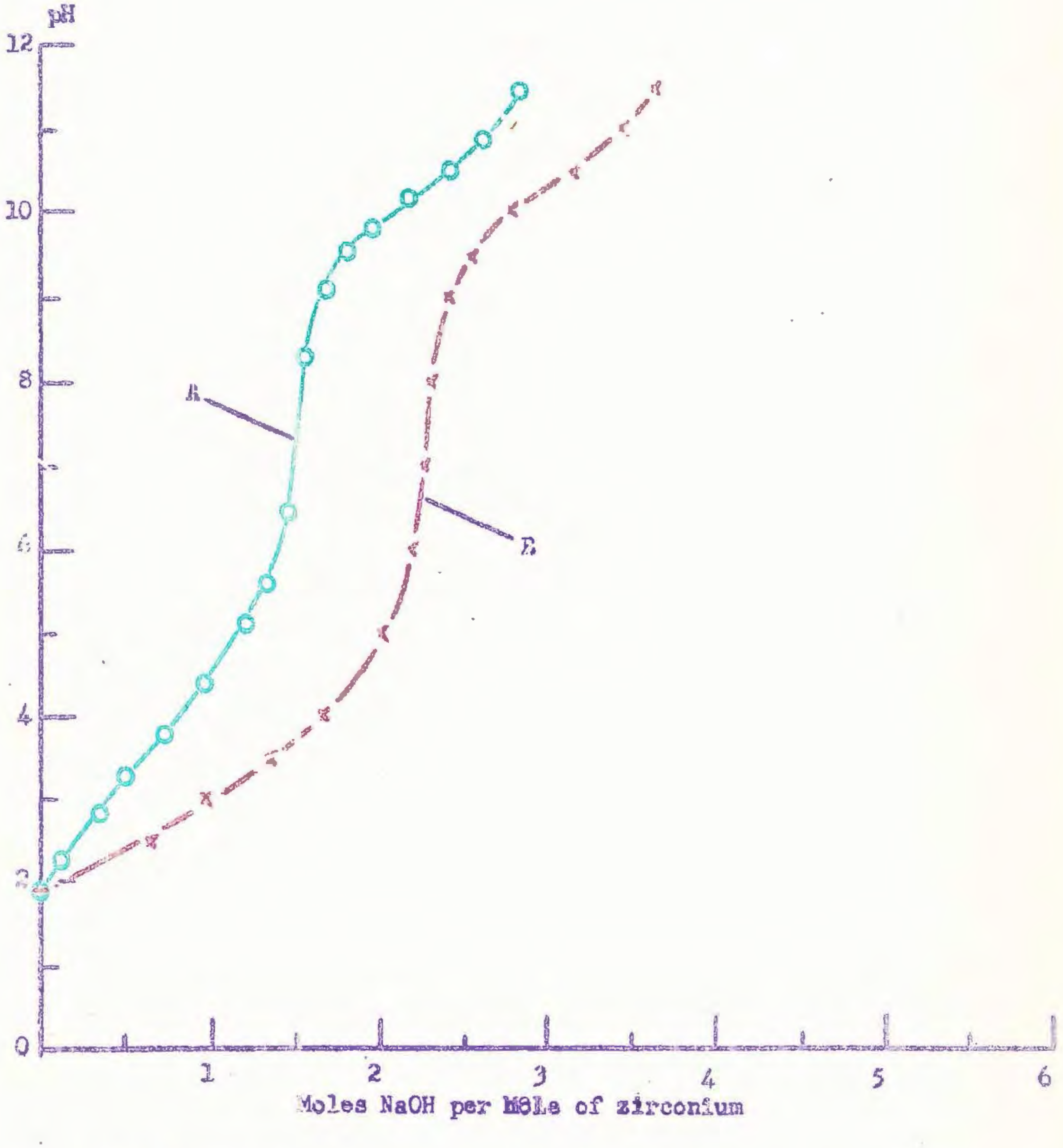


Fig. A28 Titration of zirconium oxychloride in the presence of 1 mole of β-amino-n-butyric acid, equilibrated to pH 1.9 before titration.

Curve A, Titration of mixture.
B, Blank.

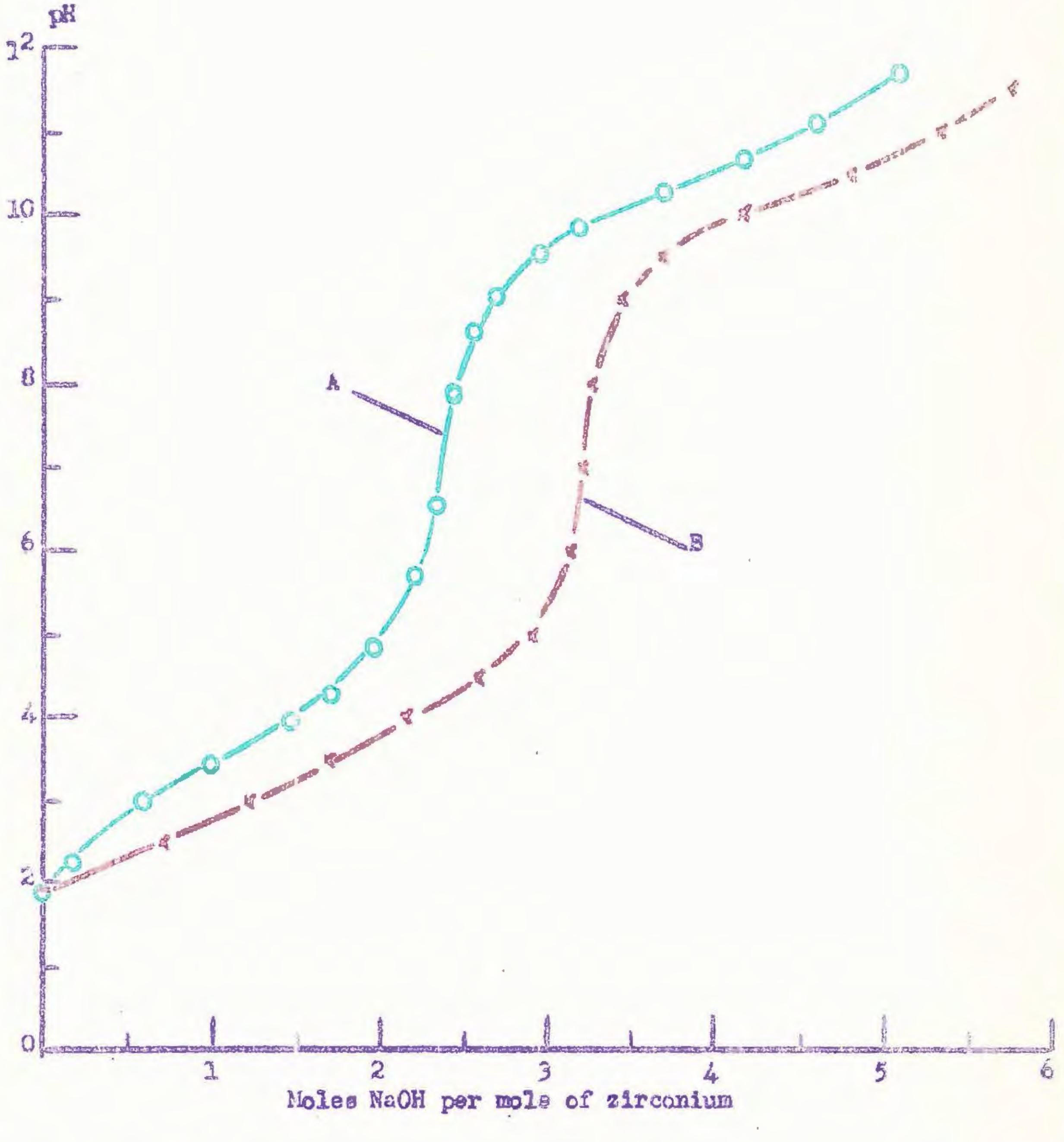


Fig. A29 Titration of zirconium oxychloride in the presence of 2 moles of β-amino-n-butyric acid, equilibrated to pH 1.9 before titration.

Curve A Titration of mixture.
B Blank.

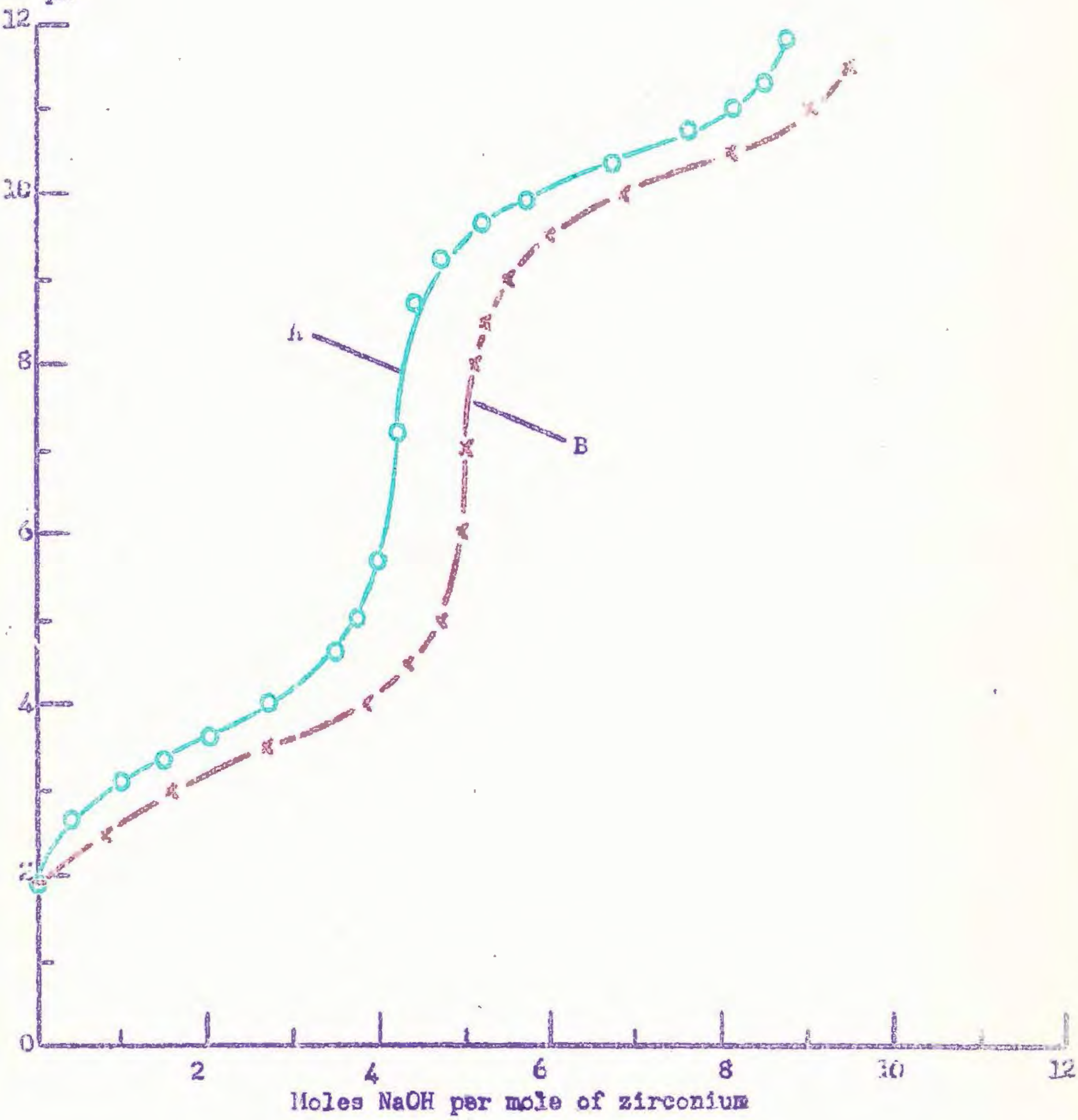


Fig. A30 Titration of zirconium oxychloride in the presence of 4 moles of β-amino-n-butyric acid, equilibrated to pH 1.9 before titration.

Curve A Titration of mixture.
B Blank.

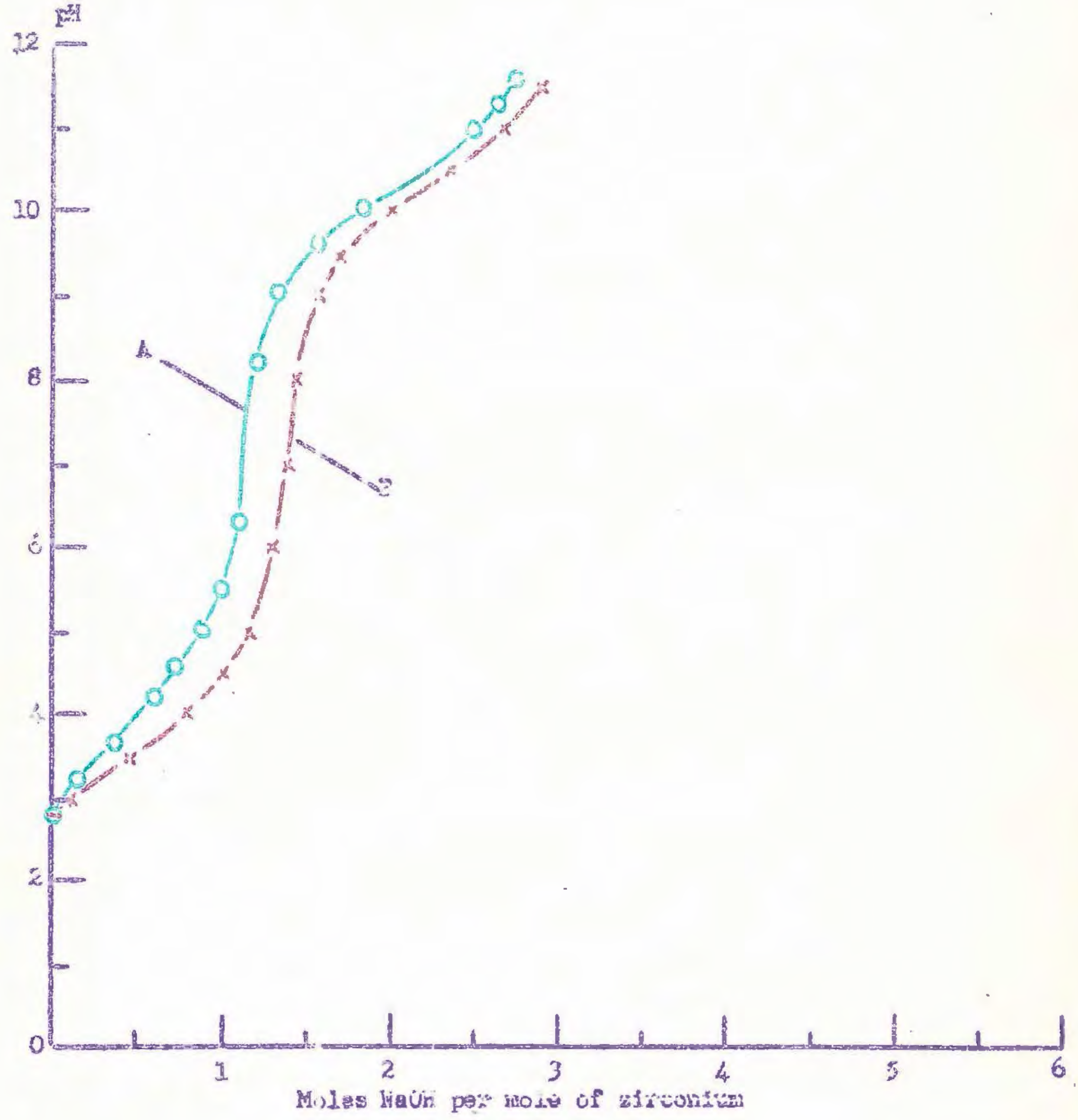


Fig. A31 Titration of zirconium oxychloride in the presence of 1 mole of β-amino-n-butyric acid, equilibrated to pH 2.8 before titration.

Curve A. Titration of mixture.
B. Blank.

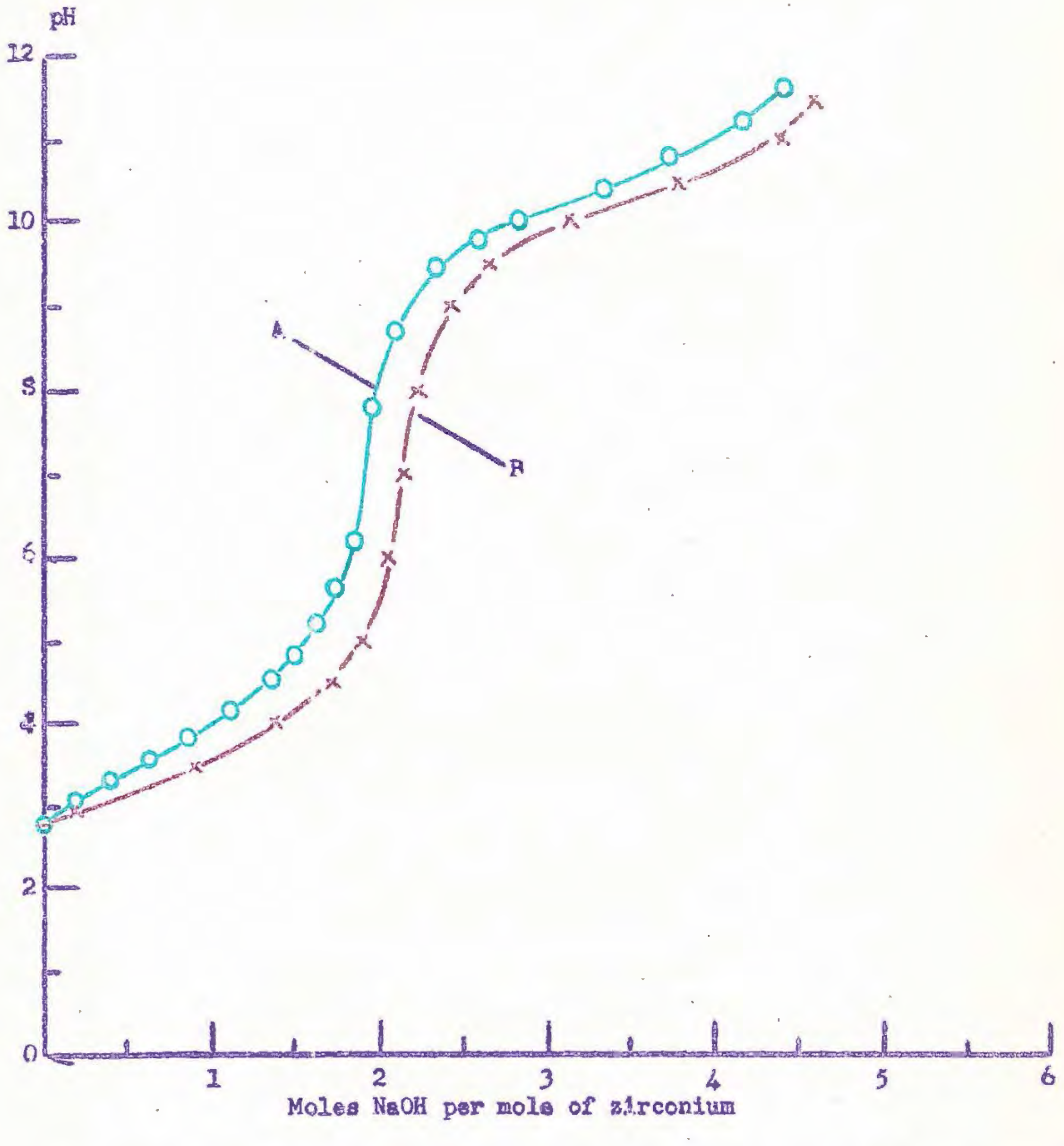


Fig. A32 Titration of zirconium oxychloride in the presence of 2 moles of β -amino-n-butyric acid, equilibrated to pH 2.8 before titration.

Curve A. Titration of mixture.
B. Blank.

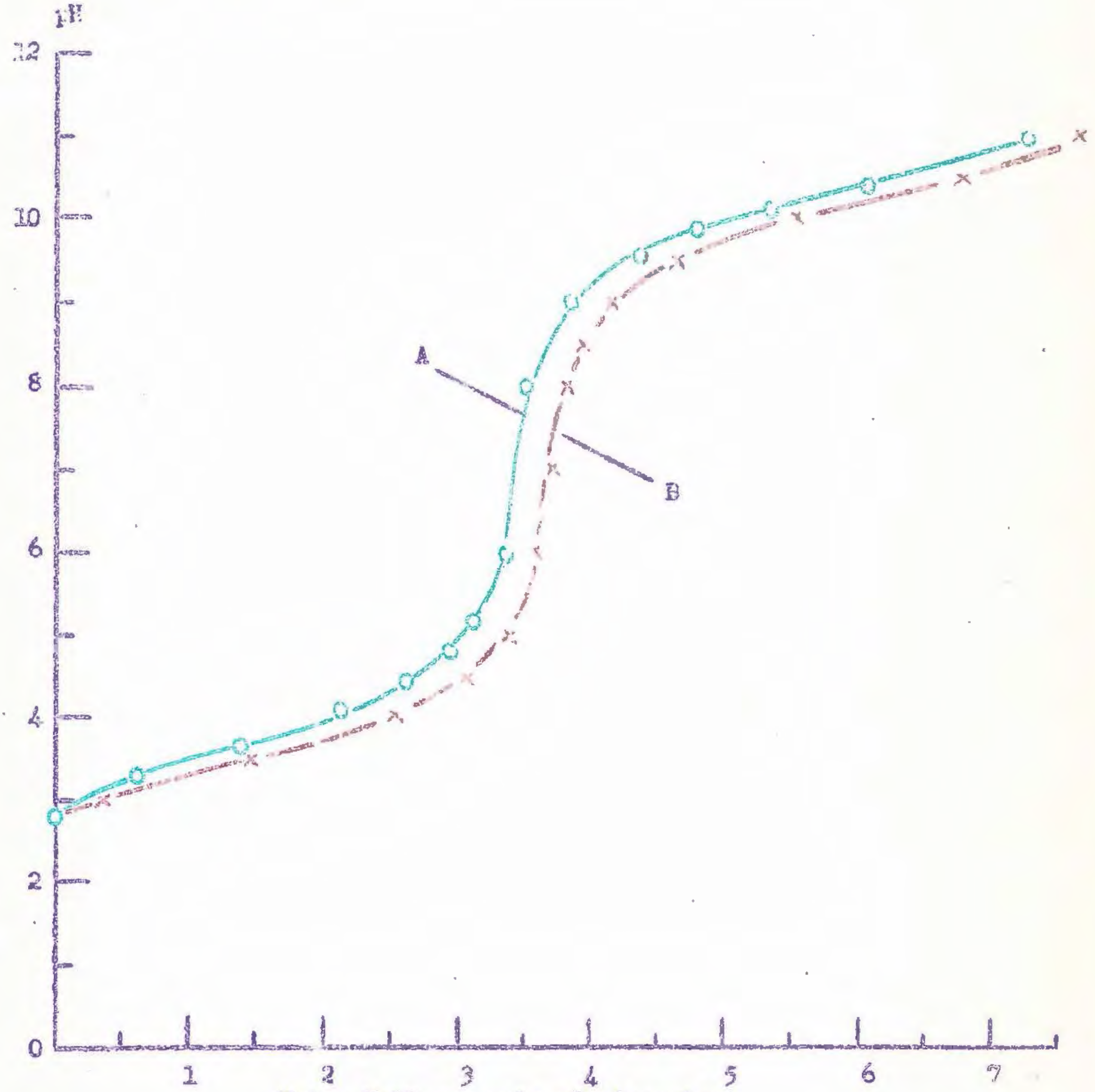


Fig. A33 Titration of zirconium oxychloride in the presence of 4 moles of β -amino-n-butyric acid, equilibrated to pH 2.8 before titration.

Curve A. Titration og mixture.
B. Blank.

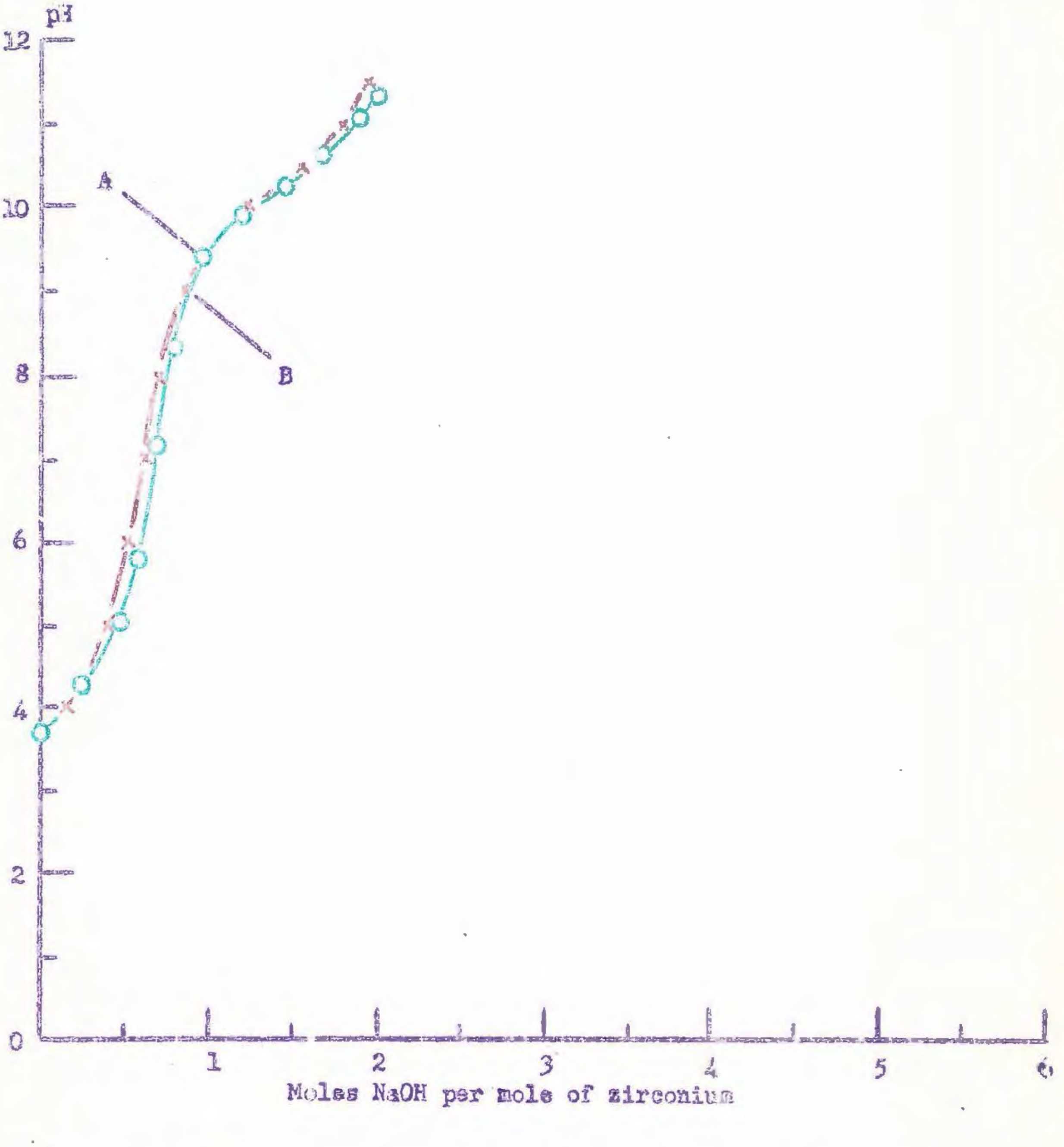


Fig. A34. Titration of zirconium oxychloride in the presence of 1 mole of β-amino-n-butyric acid, equilibrated to pH 3.7 before titration.

Curve A. Titration of mixture.
B. Blank.

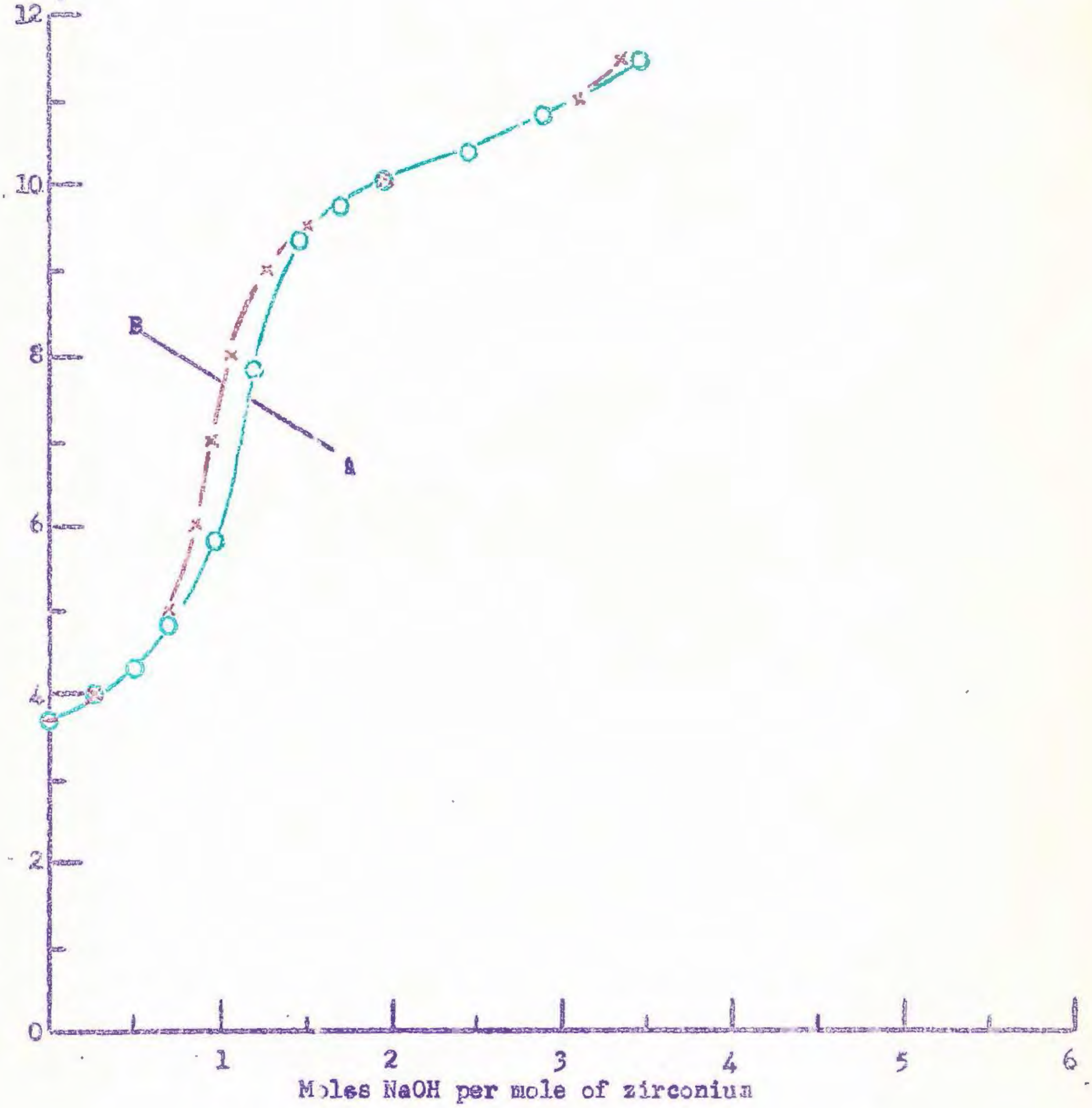


Fig. A35 Titration of zirconium oxychloride in the presence of 2 moles of β-amino-n-butyric acid, equilibrated to pH 3.7 before titration.

Curve A. Titration of mixture.
B. Blank.

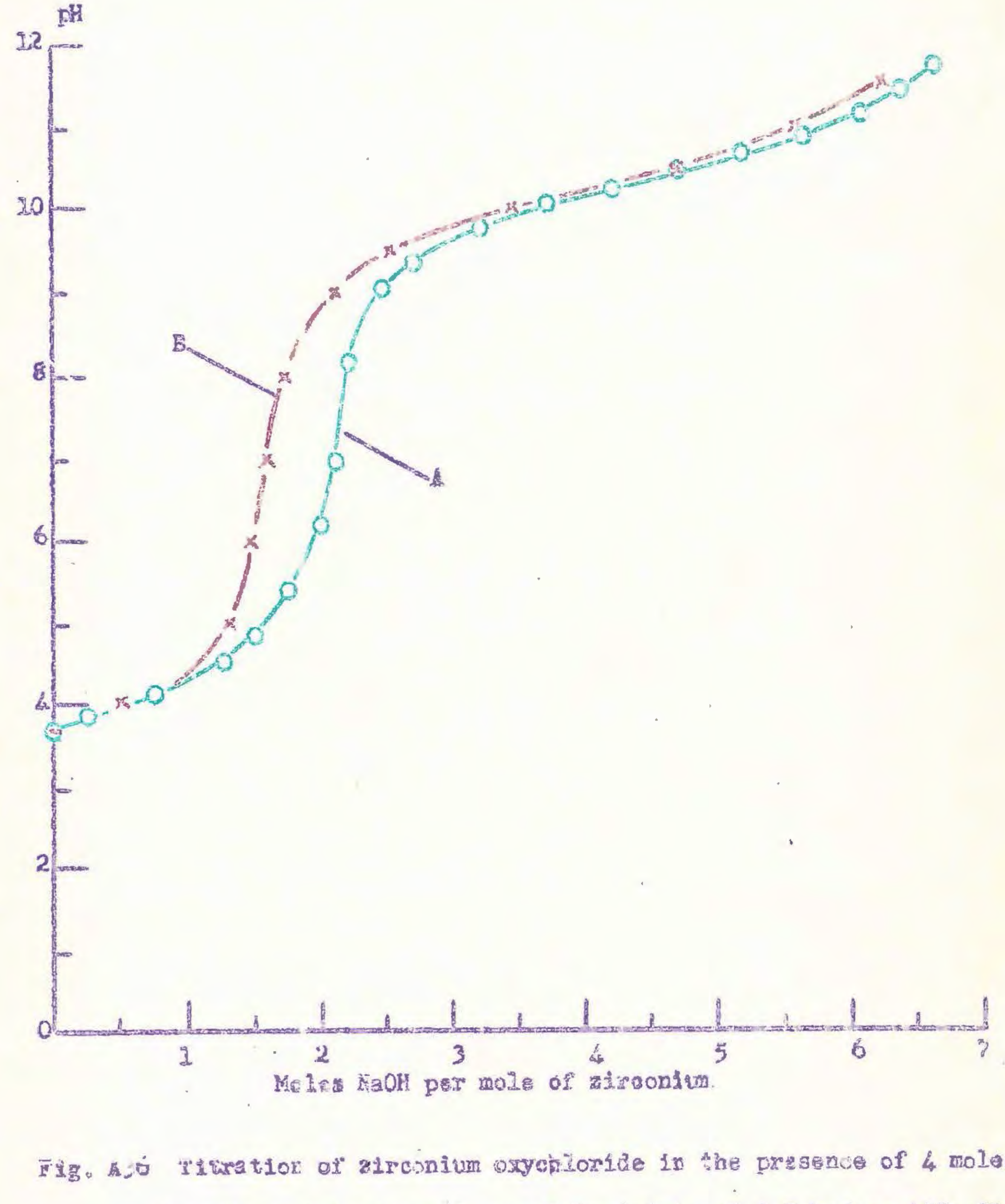


Fig. A.6 Titration of zirconium oxychloride in the presence of 4 moles of β-amino-n-butyric acid, equilibrated to pH 3.7 before titration.

Curve A. Titration of mixture.
B. Blank.

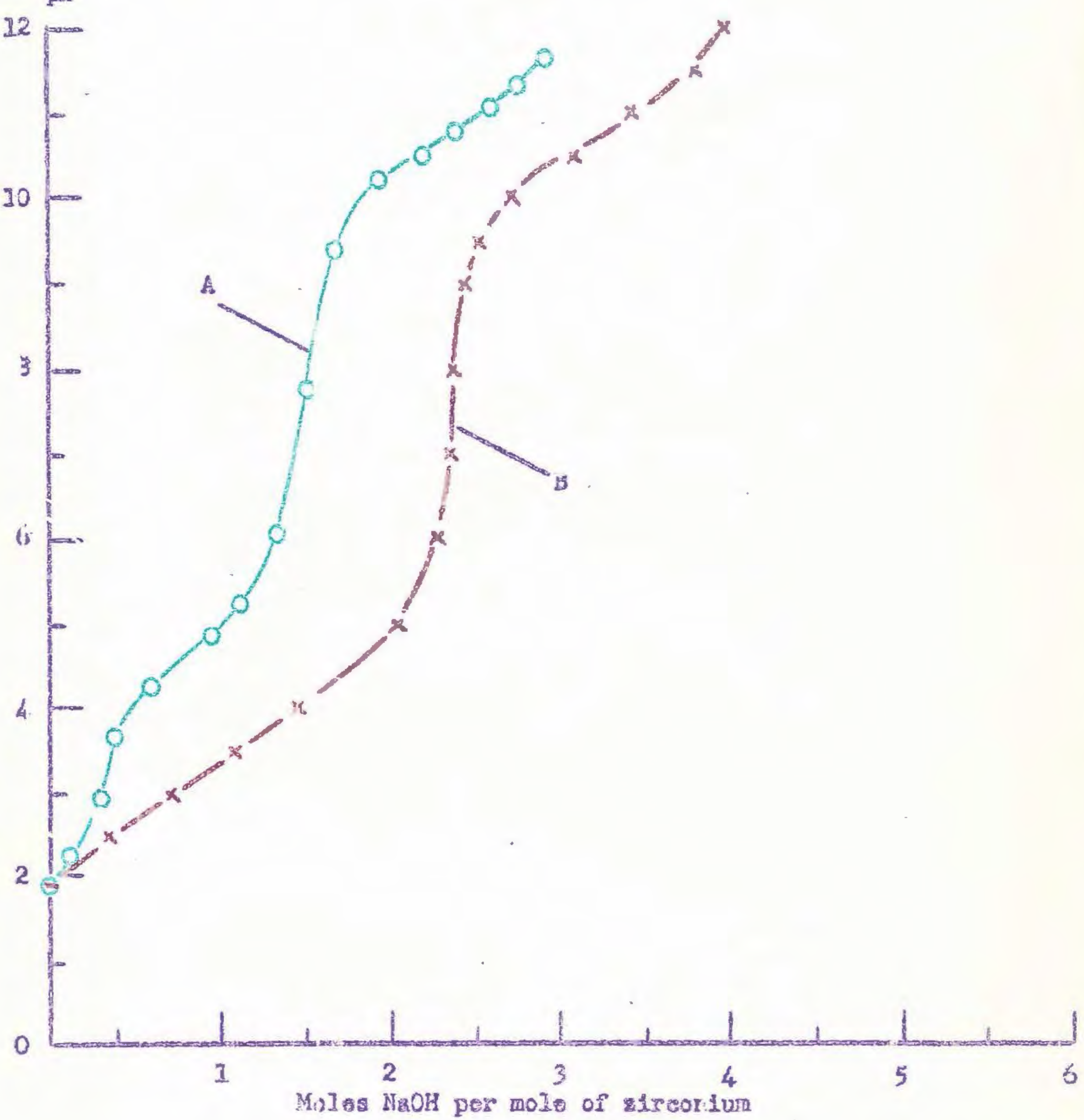


Fig. A37 Titration of zirconium oxychloride in the presence of 1 mole of γ-amino-n-butyric acid, equilibrated to pH 1.9 before titration.

Curve A. Titration of mixture.
B. Blank.

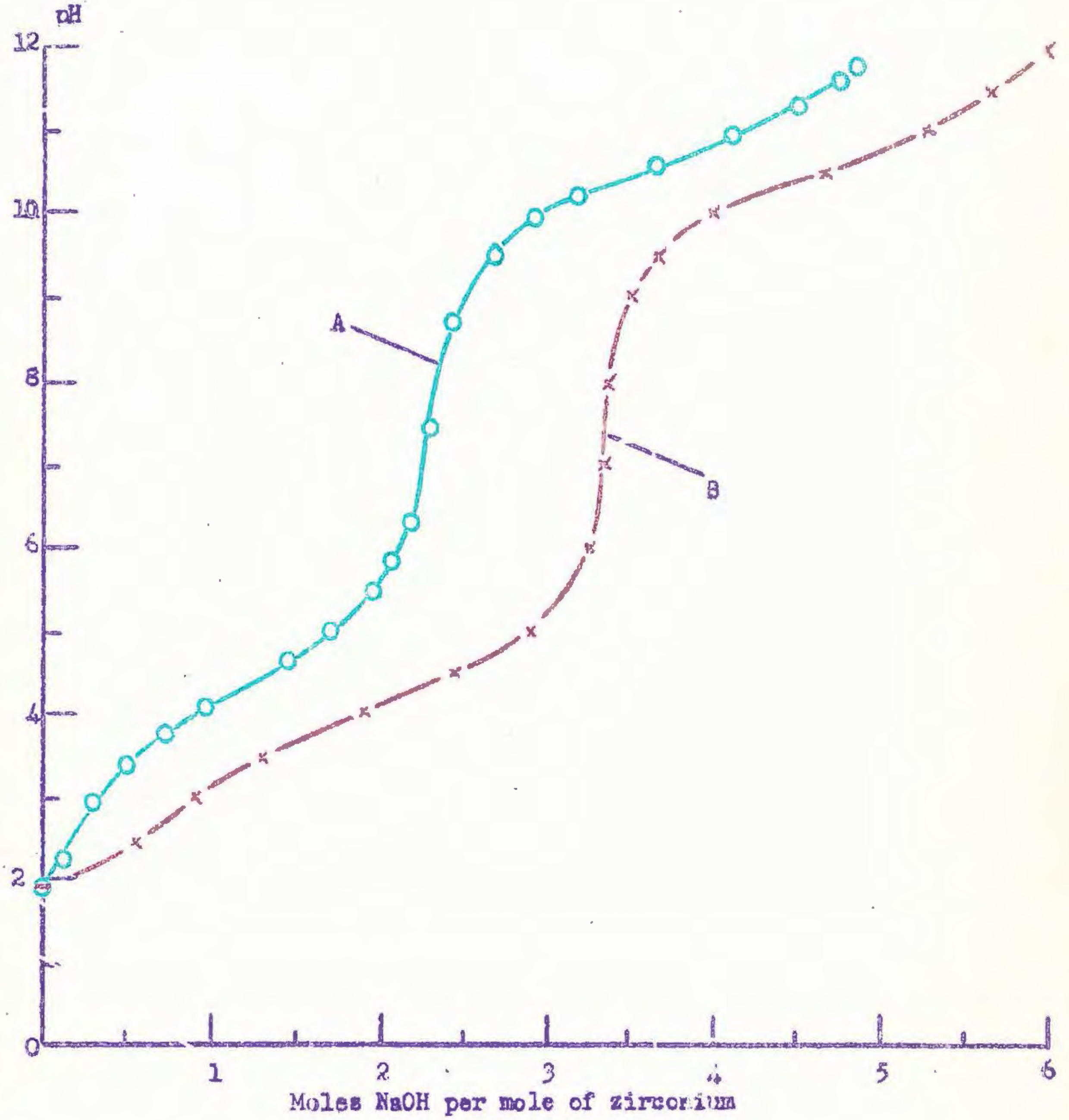


Fig. A38 Titration of zirconium oxychloride in the presence of 2 moles of γ-amino-n-butyric acid, equilibrated to pH 1.9 before titration.

Curve A. Titration of mixture.
B. Blank.

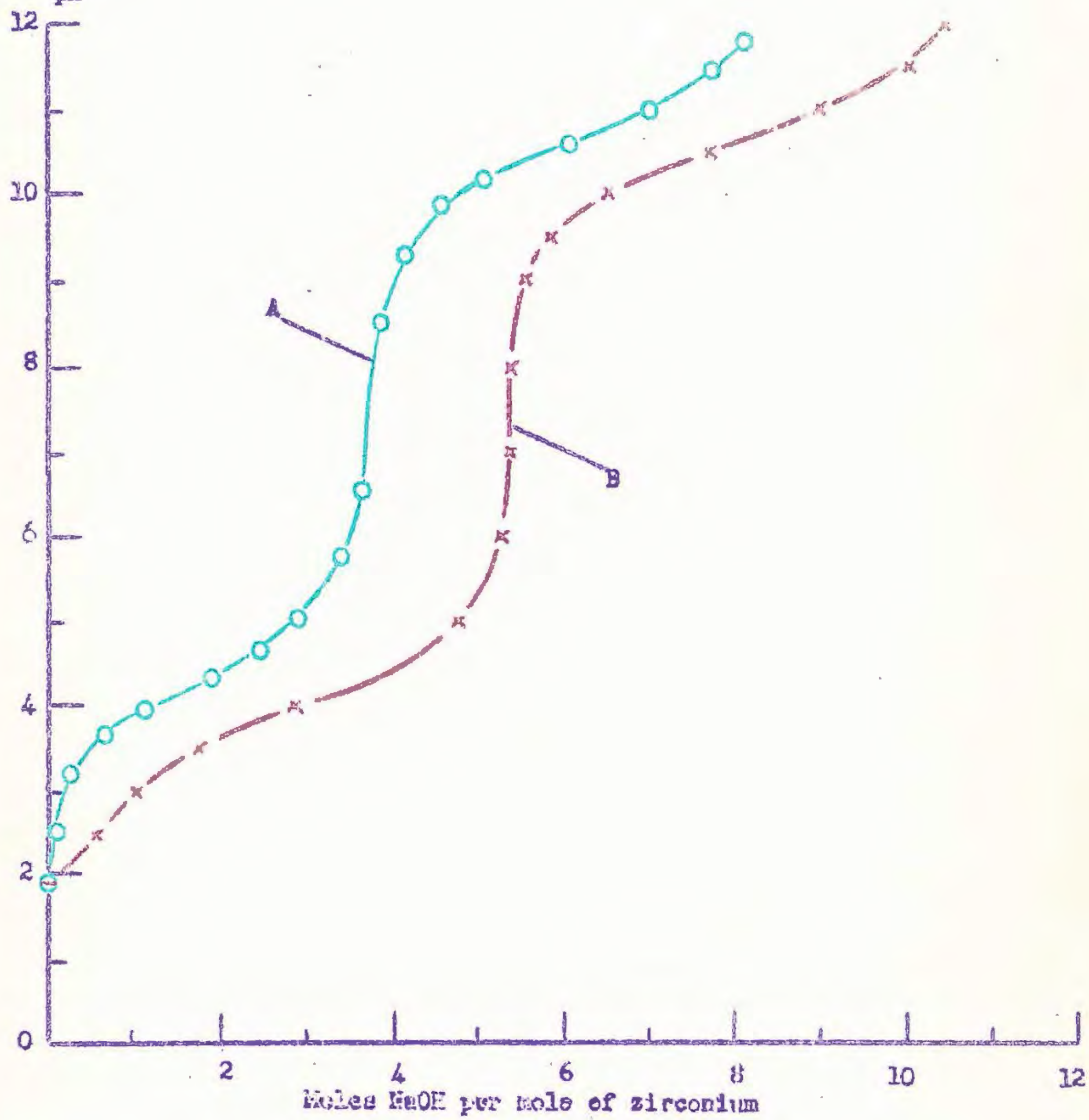


Fig. A39 Titration of zirconium oxychloride in the presence of 4 moles of γ-amino-n-butyric acid, equilibrated to pH 1.9 before titration.

Curve A. Titration of mixture.
B. Blank.

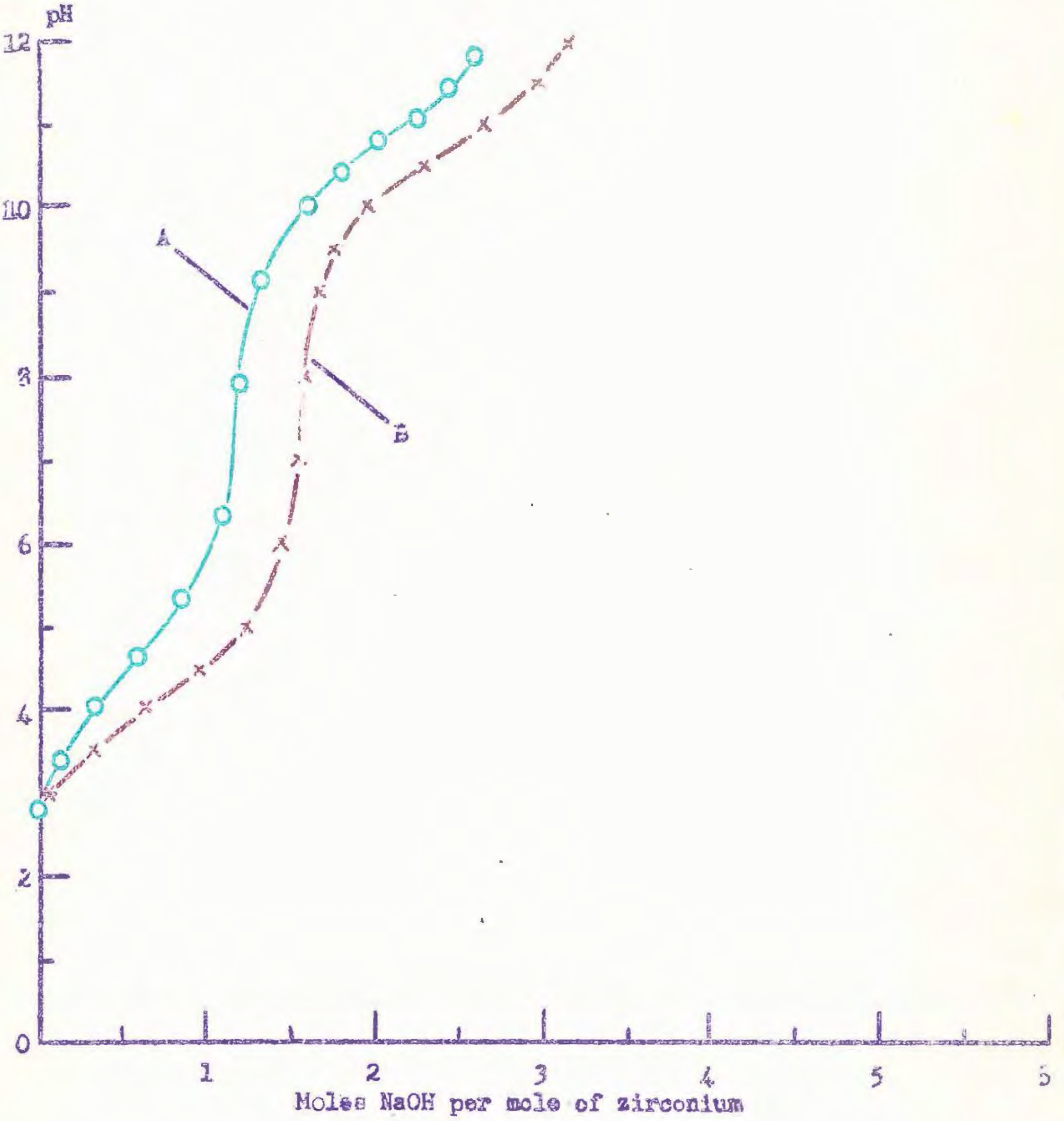


Fig. A40 Titration of zirconium oxychloride in the presence of 1 mole of γ-amino-n-butyric acid, equilibrated to pH 2.5 before titration.

Curve A. Titration of mixture.
B. Blank

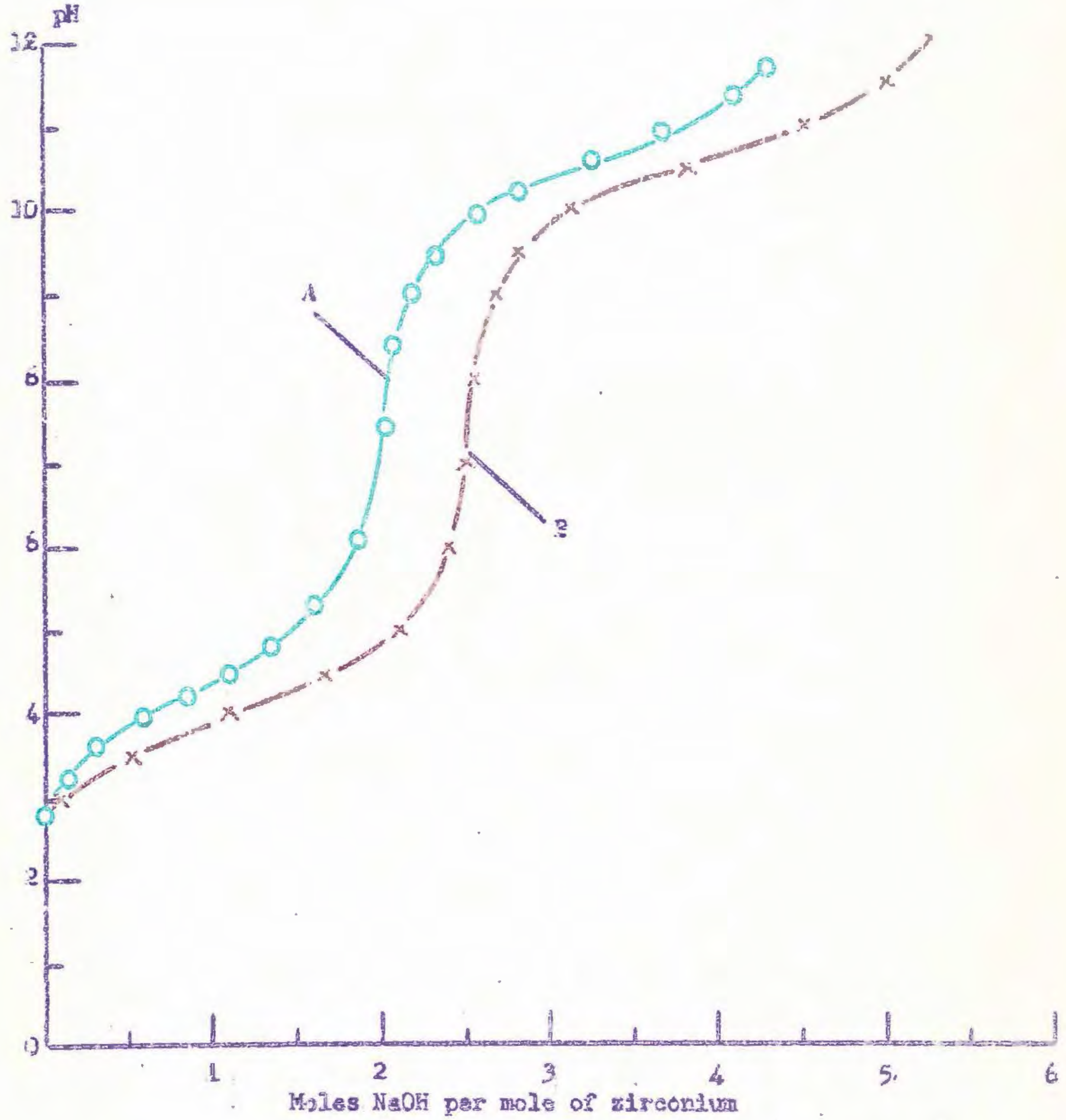


Fig. A41 Titration of zirconium oxychloride in the presence of 2 moles of γ-amino-n-butyric acid, equilibrated to pH 2.8 before titration.

Curve A. Titration of mixture.
B. Blank.

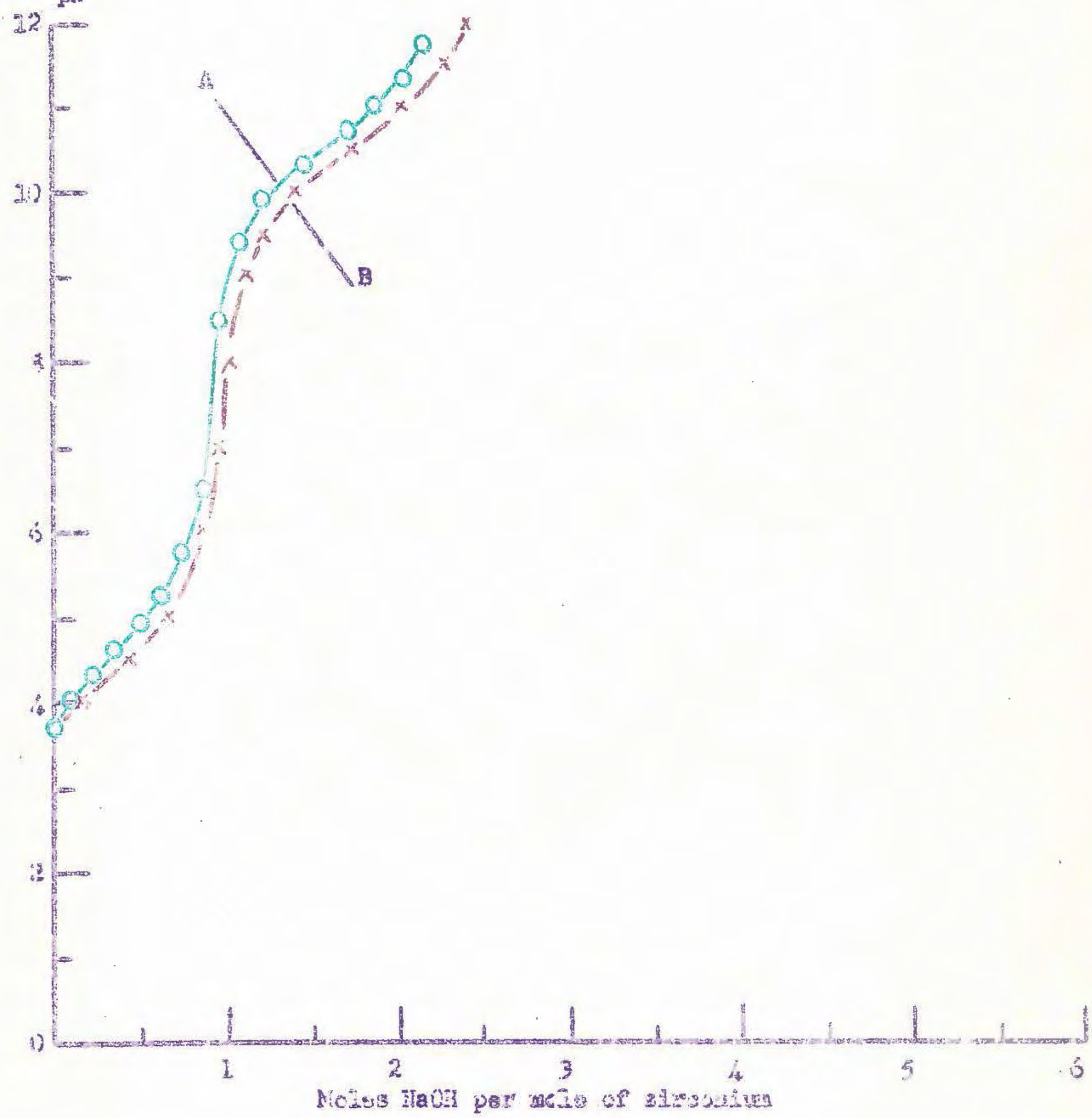


Fig. A.12 Titration of zirconium oxychloride in the presence of 1 mole of γ-amino-n-butyric acid, equilibrated to pH 3.7 before titration.

Curves A. Titration of mixture.
B. Blank

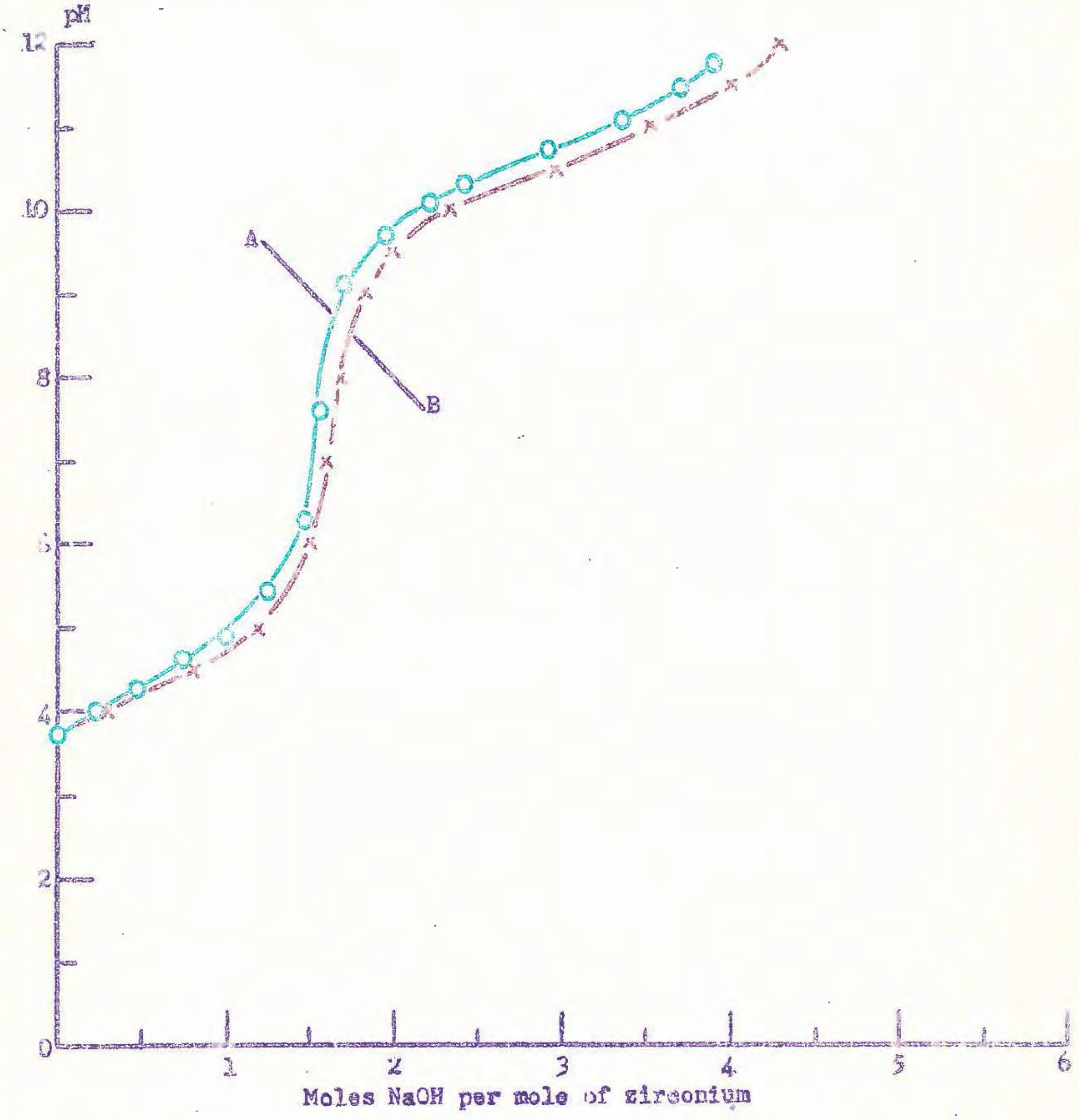


Fig. A44 Titration of zirconium oxychloride in the presence of 2 moles of γ-amino-n-butyric acid, equilibrated to pH 3.7 before titration.

Curve A. Titration of mixture.
B. Blank.

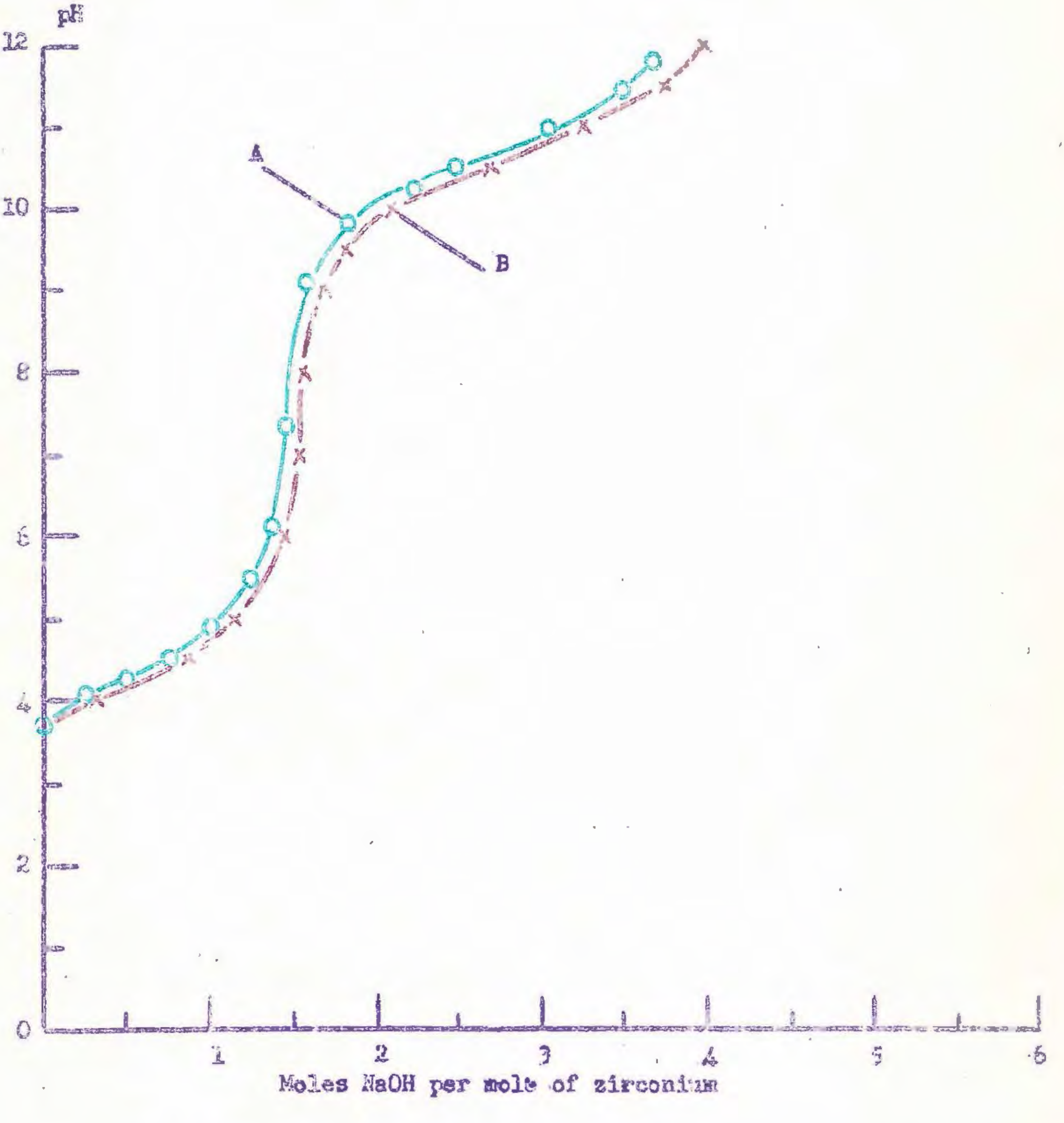


Fig. A45 Titration of zirconium oxychloride in the presence of 4 moles of γ-amino-n-butyric acid, equilibrated to pH 3.7 before titration.

Curve A. Titration of mixture.
B. Blank.

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ZIRCONIUM TANNAGE — A REVIEW OF THE LITERATURE RELATING TO ZIRCONIUM TANNAGE.

By **D. A. Williams-Wynn.**

Summary.

The literature relating to zirconium tannage is reviewed, particular attention being paid to published work dealing with the practical aspects of this tannage.

Introduction.

The tanning action of zirconium salts was first reported by Garelli[1] but not until 1931 was a satisfactory method of tannage evolved in America, the process being patented in 1933[2]. During this work the superiority of the sulphate as the tanning agent, compared with chloride or nitrate, was observed. Shortly afterwards two patents were taken out for tannage with soluble zirconium salts with the addition of carboxylic or sulphonic acids or salts[3], or tannage with zirconium oxychloride in the presence of sodium or ammonium sulphates[4]. I. G. Farbenindustrie also patented the use of water soluble compounds of silicic acid added during or after zirconium tannage, the amounts added being insufficient to effect tanning on their own account[5].

The literature relating to more recent work, both in America[6–14] and in France[15–25], has been reviewed by Ranganathan and Reed[26] with particular reference to the theory and mechanism of zirconium tannage. Other work by Schachowskoy and Frohlich[27] showed that although the consumption of tanning material was very high, in certain cases leather tanned with zirconium offers advantages, viz. firmer, plumper leather. In addition, three papers from Japan[28–30] described tanning trials using laboratory-prepared zirconium compounds, and confirm earlier reports of the superiority of sulphate complexes.

PICKLING.

Very little literature is available on this aspect of zirconium tannage. Somerville *et al.*[7–12, 14] recommended a pickle pH of between 1·5 and 2·5 for general work but no details of type or amount of acid or salt are given. Paquet[19] suggested an all sulphate pickle using sodium and magnesium salts with about 2·5% of sulphuric acid to bring the equilibrium pH to 1·8 to 2·0, since chlorides favour the formation of colloidal basic zirconium salts, but later Paquet and Martin[23] found that a sulphuric acid/sodium chloride pickle was satisfactory, the critical factor being an equilibrium pickle. No increase in the amount of acid compensates for a short time in pickle.

Work by Mitton and Wyatt[31], Kendall, Mitton and Williams-Wynn[32], and Kendall and Williams-Wynn[33] has shown that better penetration and more satisfactory tannage is obtained in the presence of chlorides. Pickle conditions using as little as 0·75% of sulphuric acid[31] and a final equilibrium pH of 3·0 instead of 2·0 or below[33] were also shown to have little effect on the rate of penetration of the zirconium tanning salt.

Factors Affecting Fixation and Tanning Action of Zirconium Salts.

(1) pH AND BASICITY.

Tanning with zirconium occurs under much the same conditions as with chrome, the tanning material being added to pickled stock in a salt solution. The notable difference between the two mineral tanning materials is the fixation of zirconium by collagen under strongly acid conditions where chrome is not fixed[12]. Leather with the highest shrinkage temperature is produced from zirconium solutions of zero basicity—for chrome tannage about 30% basic liquors are optimum—but these have an extremely low pH and as shrinkage temperatures are not significantly reduced until basicities of more than 50% are reached, it is convenient to work with a salt of basicity 45–50%.

Chambard and Lasserre[18] found that despite variations in the basicity of the zirconium tanning solutions, the zirconium complex fixed by the skin is always 35% basic. This fixed salt of course is altered in subsequent basifying and neutralising processes, and according to Somerville[12] has a value of about 75% for a final pH of 4·5 to 5·0. Lasserre[21] states that the overall basicity of the zirconium tan liquors is important, the amount of zirconium fixed increases slowly with basicity to 30% then falls rapidly.

Paquet[19], and Turley and Somerville[8] found the optimum pH for zirconium tannage to be between 1·6 and 2·4 whilst Schachowskoy and Frohlich[27] set rather wider limits of pH 1·0 to 3·0. Under varying pH conditions different types of zirconium tannage are said to occur[19]: a salt tannage which occurs at pH values below 1·0 giving shrinkage temperatures of 88 to 90°C; a tannage obtained with zirconium complexes in the pH range 1·6 to 2·4 producing shrinkage temperatures of 94 to 98°C; a colloidal tannage with hydrated zirconia in the pH range 5·5 to 6·0 giving a shrinkage temperature of 82 to 83°C. In practice a combination of effects is obtained. The first two types correspond to the first type suggested by Schachowskoy and Frohlich[27].

The effect of pH on the uptake of mineral tanning materials is dependent on the extent to which various groups on the collagen are charged or uncharged and if a chemical mechanism involving these groups is involved in zirconium tannage, pH might affect their reaction with zirconium. This is unlikely, in the light of work by Lasserre[18, 20–22] and Ranganathan and Reed[26] showing that zirconium fixation does not involve carboxyl or amino groups.

A pH effect indirectly affecting the uptake of zirconium from acid solutions is the swelling of the collagen fibres themselves. Excessive osmotic swelling, although making available more reactive groups for combination with zirconium, reduces the size of the pore spaces between adjacent fibres and thus retards the diffusion of the tanning agent through the cross-section of the pelt. Strongly swollen pelt fixes more zirconium than less swollen pelt[21, 22]; but penetration is improved in the presence of neutral salt which represses swelling.

(2) INFLUENCE OF CONCENTRATION.

Portes[25] has found that diffusion of zirconium sulphates into gelatin at pH 4·0 increased with increase in concentration of zirconium salt. Kendall and Williams-Wynn[33] have confirmed the effect of the increase in concentration and further found that the equilibrium pH of the pickle to values up to 3·0 has little effect on the penetration of the tan into the hide provided a minimum, viz. 5% ZrO_2 is added.

Lasserre[21] maintains that amounts of zirconium tanning salt up to 5% ZrO_2 on raw skin are completely taken up. With increasing concentration the amount of zirconium taken up increases but the excess of zirconium in the spent liquor also increases. When 5% ZrO_2 on skin weight is offered, exhaustion is 100%, but with 10% ZrO_2 offered, the exhaustion is only 90%.

(3) EFFECT OF SALTS ON THE UPTAKE OF ZIRCONIUM BY PELT.

The effect of salts can conveniently be divided into two groups, (1) the neutral salt effect, and (2) the anion effect.

The addition of neutral salts to solutions of zirconium salts reduces the uptake of zirconium by pelt[21, 32]. This is probably due to the inhibition of swelling of the pelt which would otherwise occur at the pH at which tannage is effected. The presence of these salts would, therefore, improve the penetration of zirconium into hide, although according to Paquet[19] chlorides favour the formation of colloidal basic zirconium sulphates so sodium chloride should be avoided in the pickle and be replaced by sulphates of sodium, magnesium or aluminium. Mitton and Wyatt[31], however, found that penetration is much better with sodium chloride than with sodium or magnesium sulphates. The improved penetration with chloride was confirmed by Kendall, Mitton and Williams-Wynn[32], and Kendall and Williams-Wynn[33] who found that the optimum was in the region of 8% of added salt, resulting in a more even distribution of the zirconium through the leather.

Apart from the general effect of the salts in reducing electro-osmosis there is the additional effect of the anion. The type of anion in the zirconium tanning liquor has an effect on the tanning action and the quality of the leather produced. Somerville[2] has shown that leather produced from chloride and nitrate solutions is inferior to that obtained from sulphates and this is confirmed by the Japanese work[28–30], and the claim that zirconium oxychloride gives an improved tannage in the presence of sulphates[4].

Addition of salts of organic acids are claimed to improve penetration. Portes[25] has found that diffusion of zirconium sulphates into gelatin gels at pH 4·0 was faster and more homogeneous in the presence of lactic acid, and occurs in the presence of lactic and acetic acids at pH values above the normal precipitation point of the sulphate. These factors would therefore be expected to improve the penetration of zirconium into hide. Contrary to these results, Kendall, Mitton and Williams-Wynn[32], and Mitton and Wyatt[31] found that masking with lactate was quite ineffective in promoting the penetration of zirconium, although the methods of estimating penetration were really for penetration and tanning action. In the two results reported, lactate masked zirconium salts may have penetrated but not fixed and so no hydrothermal stability or leathering was imparted to the centre layer of the pelt. Mitton and Wyatt also found that there is an optimum amount of formate and acetate—about 0·3 mol/mol ZrO_2—to use as masking agent, but the effect is so small as to be of negligible importance. Paquet and Martin[23] recommended the addition of 10% sodium formate to the tanning salt for optimum results.

Portes[24], Ranganathan and Reed[34], and the writer[35] found during potentiometric titration studies that the addition of salts of organic acids raised the pH at which precipitation commenced. This indicates that the complex is more stable, the masking agent being less readily displaced than sulphate groups by hydroxyl ions. Masking with strongly complexing materials —hydroxy or dicarboxylic acids—is likely to be unsatisfactory due to the extreme stability of the complex and the resulting inability of collagen to displace the radicals from the complex. This has been shown to be the case with oxalate[24, 31] and may also occur with lactate.

The charge of the zirconium complex has been studied by a number of workers using ion exchange resins and electrophoresis techniques, but ion exchange resins are of doubtful accuracy because of the tendency of the zirconium compounds to hydrolise. Lasserre[21] noted that there was a different reaction between zirconium sulphate solutions prepared at the boil and solutions prepared at room temperature, when these were passed through cation exchange resins. In the solutions prepared at room temperature the zirconium was mainly cationic but this was not the case in the solutions prepared at the boil. Ranganathan and Reed[36] using resin columns, determined the relative proportions of cationic, anionic and non-ionic zirconium sulphate solutions masked with varying amounts of citrate. Their results show that increasing the amount of complexing material increases the amount of anionic zirconium present. This is confirmed by the results of their electrophoresis experiments, but Portes[24], working over a range of pH, found that basic zirconium sulphate is predominantly anionic below pH 3·0 and cationic above, but zirconium oxychloride is cationic over the whole pH range 2·0 to 7·0. In the presence of organic acids the complexes become more electro-negative, confirming the observations of Ranganathan and Reed, and in the case of one acetate compound reported by Blumenthal[37], formula $H_2\,ZrO_2(C_2H_3O_2)_2$, was unaffected on passing through a cation exchanger.

(4) EFFECT OF THE MODIFICATION OF THE COLLAGEN.

Chambard and Lasserre[18, 20–22], and Ranganathan and Reed[26] have investigated the effect of inactivating the reactive groups of collagen on its ability to fix zirconium. The conclusion reached in each case was that neither deamination nor inactivation of the carboxyl groups affected the uptake of zirconium. This is quite different from the effect on chromium fixation, where co-ordination with carboxyl groups is the principal reaction[38].

Basifying and Neutralising.

The precipitation point of normal zirconium tanning solutions is in the pH range of 2·5 to 3·0. As the tannage is completed at pH values appreciably higher than this, very little zirconium can be left in solution and any that is not taken up from solution must be deposited in the leather. This may account for the firm plump leather obtained with zirconium tannage.

Addition of alkali must be made to neutralise some of the acid present, although Lasserre[22] maintains that sufficient washing will remove all the sulphate groups from zirconium tanned leather. After basifying to pH 3·7, some of the sulphate must be left in thick pelt even after extensive washing and the pH is constant at 5·4, because after retannage with vegetable tannins the pH of the leather dropped and the leather became tender on storage[31]. Other leathers, thoroughly neutralised with further amounts of alkali after basifying to pH 3·7, did not show this defect.

Paquet and Martin[23] advocate the use of a buffer salt to obtain the slow rise in pH desired in basifying and also that neutralisation should commence immediately after basifying for optimum leather properties. This latter point was confirmed by Kendall, Mitton and Williams-Wynn[32]. When leathers are neutralised to a pH value between 4·6 and 5·4 the normal splitting or shaving can be done.

Basification of zirconium solutions can be effected with either hydroxide or carbonate, but the resulting basic material differs depending on the alkali used. With —OH ions, hydrous zirconia is formed — $Zr\,O_2xH_2O$ but with carbonate basic zirconyl hydroxide is obtained — $Zr_2O_3\,(OH)_2$[37]. Work in these laboratories has shown that precipitation of insoluble zirconium compounds from M/10 zirconium oxychloride solution occurs at pH 2·25 and 3·40, and from M/10 zirconium sulphate solutions at pH 2·40 and 3·50 for additions of N/5 hydroxide and carbonate respectively.

Dyeing.

Somerville and Turley[10] have found that there is no special difficulty in dyeing zirconium leathers although the dye formula has to be considerably modified. Acid and direct dyes are quite satisfactory and the white base is particularly suitable for pastel shades or bright colours[14]. The author has found that zirconium leather has much less affinity than has chrome leather for anionic dyes, penetration being to a greater depth, but basic dyes are taken up readily by zirconium leather. Pankhurst, Lanham and Villiers[39] have shown that washfastness of dyed zirconium leathers is inferior to that of chrome leather except in the case of a basic dye. Only in the production of clearer shades was zirconium leather superior to chrome leather.

Fatliquoring.

Turley and Somerville[6] have found that a sulphated oil fatliquor of good penetrating quality and stability to moderate amounts of free acid is the most satisfactory. It has also been observed[33] that the addition of a non-ionic surface active agent to ordinary sulphated oils gave excellent results, whereas fatliquors based on only sulphated oils were not sufficiently stable resulting in the deposition of gummy material, especially on the flesh. Paquet and Martin[23] suggest a non-ionic oil emulsion which is completely absorbed after 30 to 40 min. drumming and then is broken by the addition of formic acid. Temperature does not seem to be critical but most formulae recommend between 40° and 50°C.

Analytical.

Zirconium in solution can easily be detected using sodium alizarin sulphonate[22]. A red or orange colour in acid solution which is sensitive to 10^{-4} gm. Zr per litre, confirms the presence of zirconium. The method is specific for zirconium which can be detected in the presence of aluminium and titanium[40].

Quantitative determination is usually done gravimetrically. Somerville and Wendkos[41, 42] recommend p-hydroxyphenylarsonic acid as precipitant but the method usually employed is the phosphate precipitation method[43] which is recommended by Grach[44]. Recently a colorimetric method using sodium alizarin sulphonate was developed in these laboratories[45]. The determination of other mineral constituents likely to be present in zirconium leathers is given by Somerville and Wendkos, and by Grach.

Basicity is normally determined by titration of the zirconium solution at the boil with standard sodium hydroxide solution[41, 42, 44], but Kuntzel and Rosenbusch[46] maintain that this method gives inaccurate results due to the precipitation of basic zirconium sulphates. They recommend a method in which the hydroxy groups, forced out by fluoride, are determined.

Discussion.

Many recipes for the production of satisfactory zirconium tanned leather are available from the literature. Optimum conditions seem to be: equilibrium pickle but not necessarily at low pH, a minimum of 4 to 5% ZrO_2 offered, addition of 7 to 8% of neutral salt to the tan liquor, and sufficient mechanical action to assist penetration. Factors about which there is a difference of opinion are: the type of neutral salt anion in the pickle and tanning liquor, the use of masking salts in tanning and basifying, and the type of fatliquor to be used.

Zirconium tannage has aroused a considerable amount of interest, and despite the introduction of new synthetic tannins for the production of white leather, the unique properties imparted to leather by zirconium, viz. greater plumpness and fuller flanks and in the case of sole leather, improved wear, should maintain the leather chemists' interest in this material.

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ZIRCONIUM TANNAGE I.—A COLORIMETRIC METHOD FOR THE DETERMINATION OF ZIRCONIUM IN LEATHER.

By D. A. Williams-Wynn.

Summary.

This paper gives details of a colorimetric method for the determination of zirconium in leather which is suitable for either routine analysis or research and development work. Zirconium and sodium alizarin sulphonate give, in strongly acid solution, a red colour which is almost specific for zirconium. The colour formed in this way is very intense and tartrate has been found to reduce the colour intensity and to stabilise the system against precipitation.

Summary of the proposed method

Digest approx. 0·3 gm. of leather (10% ZrO_2) with 10–15 ml. perchloric/sulphuric acid mixture (2+1) and 15 ml. conc. nitric acid. Cool, dilute with 50 ml. N hydrochloric acid, boil 5 min and make to 500 ml. A 10 ml. aliquot is run into a 100 ml. volumetric flask containing 25 ml. N hydrochloric acid, and 20 ml. of 0·1% alizarin-S and 0·5% sodium tartrate solution added. Heat in boiling water for 5 min, cool, make to 100 ml. and measure absorption density at 520 mμ. Titanium, aluminium, iron and trivalent chromium have been shown not to interfere. Hexavalent chromium must be reduced before taking aliquots for colour development.

Introduction.

Methods[1,2] so far proposed for the determination of zirconium in leather are tedious. For that reason a rapid, accurate method would be of value, particularly in experimental work. Widespread acceptance of the wet oxidation[3] method for chromium led to an investigation of its use for dissolving other mineral tanning materials in these laboratories. The method was found to be very satisfactory, obviating the need for ashing and fusing the leather in order to get zirconium into solution.

Once the zirconium is in solution several analytical procedures are available:

a. gravimetric: involving precipitation, filtration and ignition.
b. volumetric: involving titration using E.D.T.A.
c. colorimetric: involving colour formation under standard conditions.

Gravimetric methods although remarkably accurate are, by their nature, involved and time-consuming and many of the methods are affected by other cations in solution. The phosphate precipitation method[4] is the one generally accepted and was therefore used as the standard in this work.

Volumetric methods are rapid and usually accurate but the conditions for the method of Fritz and Johnson[5] were found to be difficult to maintain.

Colorimetric methods are beginning to find wider acceptance in the leather industry, e.g. Roux[6] and in the search for a suitable method for zirconium, that of Mayer and Bradshaw[7] was selected for investigation, although the method due to Thamer and Voight[8] also looks promising.

Investigation of the use of Alizarin-S for the Colorimetric Determination of Zirconium in Leather.

Mayer and Bradshaw[7] measure the optical density of the coloured complex formed between zirconium and alizarin-S. However their method, which is proposed for the metallurgical industry, suffers from various defects which prevent its direct application to leather analysis. Due to the intense colour produced, the readings must be taken on the least sensitive part of the scale or on solutions of very high dilution if the wavelength of absorption maximum, viz. 520 mμ, is used. Mayer and Bradshaw overcame this difficulty by working at a wavelength of 560 mμ but this means that other materials, e.g. trivalent chromium salts which absorb strongly at this wavelength, would interfere.

Use could be made of the differential method[9] in which the absorption density of the intensely coloured solution is measured against a standard grey solution[10] of known absorption density in place of the reagent blank usually employed. This reduces the relative absorption density so that it can be read on the more accurate part of the scale.

The above two methods overcome the effect of the intense colour, but sulphate also interferes in the development of the colour and as sulphate is inevitably present (sulphuric acid is an essential constituent of the mixture for the wet oxidation process) a modification must be found which reduces the colour and eliminates sulphate interference. The intensity of the colour formed by alizarin-S with zirconium can be reduced by adding hydroxy acids and in this paper use was made of this effect by adding tartaric acid which also has the advantage of stabilising zirconium solutions[5,11].

Preliminary Experiment to study the effect of Variables on Colour Development and Stability.

The method of Mayer and Bradshaw requires the aliquot of zirconium solution to be added to a 100 ml. volumetric flask containing 2·5 ml. conc. hydrochloric acid, followed by the addition of alizarin solution. The flask is then immersed in boiling water for 2·5 to 3·5 min. To check on the above technique when tartrate is present, a ¼ replicate of 2^8 factorial was carried out in which the following factors were varied.

AB Amount of hydrochloric acid added to 100 ml. volumetric flask.

(1)	10 ml. N HCl
a	20 ,, ,, ,,
b	30 ,, ,, ,,
ab	40 ,, ,, ,,

CD Interfering anions added to 100 ml. volumetric flask.
- (1) None
- c 0·3 gm. Na_2SO_4
- d 0·15 gm. $NaClO_4$
- cd 0·3 gm. $NaSO_4$ and 0·15 gm. $NaClO_4$

EF Amount of sodium tartrate added to 100 ml. volumetric flask.
- (1) None
- e 1 ml. 10% soln.
- f 2 ml. „ „
- ef 4 ml. „ „

GH Conditions for reaction after addition of reagents.
- (1) prepared at room temp.
- g „ in boiling water for 2 min.
- h „ „ „ „ „ 5 min.
- gh „ „ „ „ „ 10 min.

Procedure.

It will be noted that the method is suitable for final concentrations of 1 mgm Zr per 100 ml. and therefore a standard solution of zirconium oxychloride was made up containing 0·75 mgm Zr per 10 ml. aliquot. 10 ml. aliquots were run into each of the 100 ml. volumetric flasks containing the requisite amounts of hydrochloric acid and interfering anions where necessary. The colour was developed by adding 10 ml. 0·15% alizarin-S solution and then the tartrate where applicable. The flasks containing the solutions that had to be heated, were immersed in boiling water for the required length of time, cooled and all made up to volume. The absorption density at 520 mμ was read immediately and after 24 hr standing at room temperature.

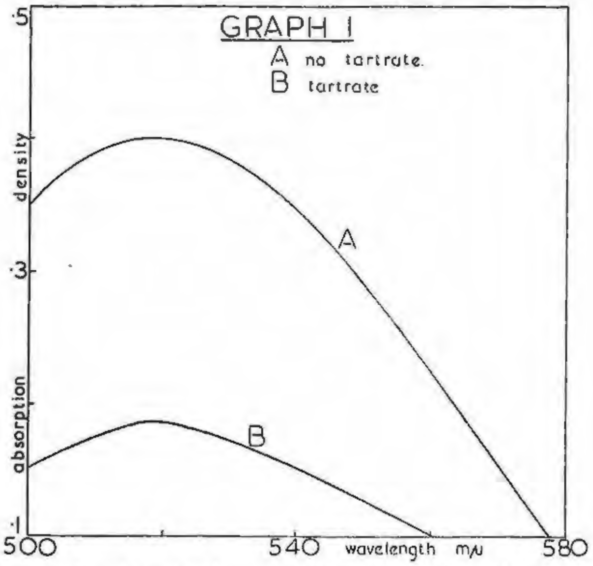
Summarised Results of Preliminary Experiment.

The addition of tartrate caused a most significant reduction in colour intensity and eliminated precipitation which was apparent in most of those solutions which contained no tartrate. The smallest amount of tartrate was obviously sufficient to do this.

TABLE I.

Tartrate added	Absorption density Initial	Aged
None	411	417
1 ml. 10%	189	193
2 ml. 10%	137	139
4 ml. 10%	101	103

Ageing had little effect, although the solutions without tartrate were affected more than the other. Treatment with tartrate did not alter the wavelength of maximum absorption, see Graph I.



The amount of acid added was unimportant but the lower amounts of acid gave solutions which were not optically clear, especially after standing, although the change in absorption density was unaffected.

TABLE II.

HCl added	Absorption density Initial	 Aged
10 ml. N	208	211
20 ml. N	211	214
30 ml. N	209	213
40 ml. N	211	215

As expected, sulphate interfered but where tartrate was present the interference was reduced. Perchlorate was completely without effect. The interaction between tartrate and the interfering anion is given in the Table III below.

TABLE III.

Tartrate added	Interfering anion None	 SO_4	 ClO_4	 ClO_4 $+SO_4$	Mean
None	446	380	442	378	411
1 ml. 10% ...	202	178	200	177	189
2 ml. 10% ...	146	129	144	129	137
4 ml. 10% ...	107	96	106	95	101
Mean	225	196	223	195	210

Heating the solutions did not affect the absorption density but not all the solutions prepared cold, or heated for only 2 min., were optically clear.

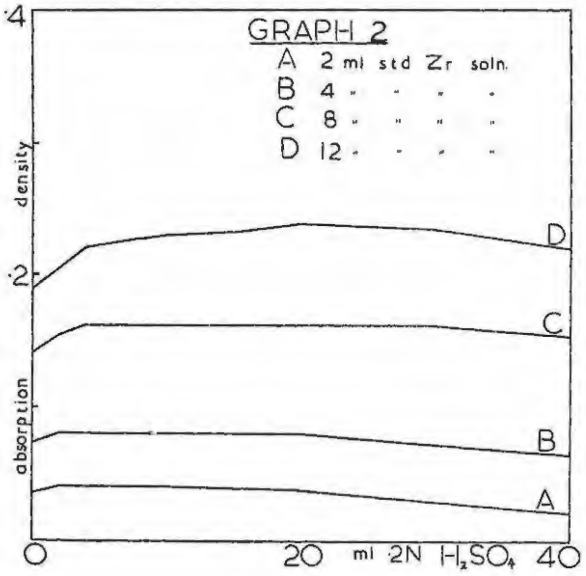
The Effect of Small Variations in the Amount of added Tartrate.

From the previous experiment it is seen that large variations in the amount of tartrate added gave big differences in the absorption density. It was decided therefore, to test the effect of small variations, of the order of ± 10%, of tartrate. This was done in order to determine what care is needed in the preparation of the tartrate solution and whether measuring cylinder accuracy is sufficient when adding the reagent.

The colour was developed in 100 ml. volumetric flasks containing 25 ml. N hydrochloric acid, 10 ml. standard zirconium solution with 10 or 15 ml. 0·15% alizarin-S solution, the variable amounts of tartrate being added before heating for 5 min. in boiling water. No significant difference was found in the absorption density as determined by an analysis of variance, see Table IV.

TABLE IV.

Alizarin-S added 0·15%	Tartrate added 1% soln. 9 ml.	10 ml.	11 ml.	Mean
10 ml.	203	201	200	201
15 ml.	201	200	200	200
Mean	202	201	200	201



EFFECT OF SULPHATE CONCENTRATION.

Chloride and perchlorate are without effect but sulphate has been shown to interfere. In order to determine the effect of the sulphate in detail, four series containing 2, 4, 8 and 12 ml. aliquots of the standard zirconium solution were prepared, and to each of these varying amounts of sulphate were added. The result was that with increasing sulphate content the absorption density increased until the solution was N/50 with respect to sulphate. With further addition of sulphate the absorption density was constant until the sulphate concentration reached N/10, then decreased slowly with further increase in concentration of sulphate, see Graph 2. It will be seen that curve D is erratic, confirming earlier observations that the method is applicable to a maximum of 0·1 mg. ZrO_2 in the reaction flask.

Recommended Method.

From the above it is seen that fairly wide conditions exist for the reproducible development of a colour. The following reagents are necessary.

REAGENTS.

Perchloric/sulphuric acid digestion mixture[3] :— mix 200 ml. 70% $HClO_4$ and 77 ml. conc. H_2SO_4.

Approx. N Hydrochloric acid :— Dilute 90 ml. conc. HCl to 1 litre.

Sodium alizarin sulphonate/sodium tartrate reagent :— Dissolve 1 gm. alizarin-S and 5 gm. sodium tartrate in about 500 ml. of hot water, acidify with a few drops of conc. HCl, filter through Whatman No. 42 filter paper and dilute to 1 litre.

PROCEDURE.

Weigh out approx. 0·3 gm. of the leather, of about 10% ZrO_2 content, into a 100 ml. Kjeldahl digestion flask, add 10 to 15 ml. perchloric/sulphuric acid digestion mixture and 15 ml. conc. nitric acid. Heat gently to digest organic matter then heat strongly to fumes of SO_3. Cool, dilute with about 50 ml. N hydrochloric acid and boil for 5 min. Transfer to a 500 ml. volumetric flask and make up to the mark with distilled water.

Run a 10 ml. aliquot into a 100 ml. volumetric flask containing 25 ml. N hydrochloric acid. Add 20 ml. of the sodium alizarin sulphonate/sodium tartrate reagent and heat in boiling water for 5 min., allow to cool and make up to 100 ml. with water. Measure the absorption density in a 1 cm. cell at 520 mμ using a solution of 25 ml. N hydrochloric acid and 20 ml. alizarin-S/tartrate reagent made to 100 ml. as blank. **Note.** Where sulphate is present potassium must be avoided because sparingly soluble double sulphates are formed with zirconium[12]. This means that Rochelle salt must not be used for the preparation of the alizarin-S/tartrate reagent.

PREPARATION OF STANDARD GRAPH.

Dissolve 8 gm. zirconium oxychloride octahydrate in water and make to 250 ml. Standardise the solution gravimetrically with phosphate[4]. 1 ml. of this solution should contain about 10 mg. of zirconium. Dilute this solution 100 times and use aliquots of up to 10 ml. in 100 ml. volumetric flasks containing 25 ml. N hydrochloric acid and 5 ml. N/2 sulphuric acid. Develop the colour as recommended and measure the absorption density at 520 mμ in a 1 cm. cell.

Comparison of Results by Gravimetric and Spectrophotometric Methods.

Eighteen experimentally prepared leathers were analysed by the above methods. In order to avoid sampling errors, aliquots for the two determinations were taken from the same diluted digestion solution. The results quoted below are calculated back to the original amount of ZrO_2 taken.

A t test gave a value of $t=0\cdot109$, $\emptyset=17$, which indicates a completely insignificant difference between the two methods.

Interference from Other Cations.

Mayer and Bradshaw[7] have shown that a number of cations do not interfere but in leather chromium, iron, aluminium and titanium may be present. To test the effect of these cations, the equivalent of 5% of Fe_2O_3, Cr_2O_3, Al_2O_3 and 10% TiO_2 on leather weight, the maximum normally found in leather, was added. The effect of these additions is shown in Table VI.

TABLE V.

Comparison between Spectrophotometric and Gravimetric Methods.

	Spectrophotometric method x1 mgm. ZrO_2	Gravimetric method x2 mgm. ZrO_2	Difference (x1 − x2) mgm. ZrO_2
1.	26·1	25·8	+0·3
2.	42·6	42·4	+0·2
3.	30·1	30·1	0
4.	45·8	46·0	−0·2
5.	35·6	35·6	0
6.	32·4	32·2	+0·2
7.	51·9	51·8	+0·1
8.	40·7	41·0	−0·3
9.	27·6	27·4	+0·2
10.	41·3	41·2	+0·1
11.	44·1	44·3	−0·2
12.	41·9	42·1	−0·2
13.	35·6	35·5	+0·1
14.	35·2	35·3	−0·1
15.	41·9	41·7	+0·2
16.	42·4	42·4	0
17.	26·7	26·5	+0·2
18.	33·8	34·3	−0·5
Total	675·7	675·6	+0·1
Mean	37·54	37·53	+0·0556

TABLE VI.

ml. standard Zirconium soln.	Absorption Densities Zr only	Zr+Ti	Zr+Al	Zr+Fe	$Zr+Cr^{VI}$	$Zr+Cr^{III}$
2	41	40	41	41	117	42
4	81	80	82	82	158	84
8	163	161	163	163	239	166

Titanium, aluminium and iron do not interfere but hexavalent chromium seriously increases the absorption density. This interference can be overcome by reducing the chromium with sodium sulphite, boiling and making to volume before taking aliquots for colour development. It is seen that trivalent chromium gives a small but negligible increase in absorption density.

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