

T H E S I S

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A STUDY ON WHITE LEATHER TANNAGE

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A STUDY ON WHITE LEATHER TANNAGE

INTRODUCTION

Aluminium salts have been used for tanning skins and furs for at least two thousand years. Alum tanning was used by the Romans and at a earlier date by the Egyptians, but it is probable that the process originated in Arabia.

The methods employed were not true tanning processes and the leather so formed was not resistant to repeated wetting or washing. These older methods of "tawing" involved coating the flesh side of the skin with a thick paste of alum and salt and allowing the skins to lie so treated for some time. A method commonly used today is to drum the skins in a thin paste of potash alum, salt, flour and egg yolk, after which they are allowed to dry. Sometimes a mixture of egg yolk, oil and flour is rubbed in by hand. A more recent method is to pad on a basic solution of aluminium and salt, applying several coats after the previous one has dried.

The salt is present to prevent swelling of the pelt due to the acid formed by the hydrolysis of the aluminium salt, while the flour possibly acts as an extremely feeble base and takes up the excess acid slowly: the liquor is thus rendered basic very slowly during the course of tannage and danger of precipitation is avoided. Egg yolk serves to lubricate the fibre of the finished leather.

Fatliquoring of alum tanned skins by conventional methods is apt to be unsatisfactory because of the instability of the emulsion in the presence of

aluminium salts, but this difficulty is not encountered with egg yolk, or with certain cationic agents.

After fatliquoring, the skin must be dried and preferably "aged" for a week or two, then washed, recoiled and dried again. By this means a soft pliable leather is obtained after staking, whereas if fatliquoring were omitted the leather would be hard and horny. Alum leather, retanned with formaldehyde, easily takes up the fatliquor of the normal oil emulsion type.

Alum leather possesses certain special characteristics not shown by other tannages. The leather is pure white, has a characteristic soft handle and exhibits a remarkable degree of stretch, making it especially useful for glove-making, furs, etc. It is not, however, stable to washing and this constitutes a serious defect.

The amount of chrome necessary to produce good leather is between 4-5% on the weight of the finished leather, and the amount of aluminium to have the corresponding effect would be 5-6%, necessitating about 50% potash alum on the weight of the skins. The difficulty of obtaining absorption of such great quantities of alum by the skin fibres is no doubt one of the reasons why an unsatisfactory leather is produced by alum tanning.

When aluminium salts are dissolved in water hydrolysis takes place, giving a soluble basic salt and free acid. When a skin enters such a solution the free acid is absorbed and fixed by the skin collagen. This upsets the hydrolysis equilibrium and more salt is hydrolysed giving more basic salt and free acid. As the acid is absorbed swelling takes place, and the basic salt is also taken up and deposited upon the skin fibres where it has a tanning action.

Skin tanned with an aluminium salt alone would be thin and hard, but if salt is added it acts in the same way as in pickles, preventing swelling, and allowing the basic aluminium salt to penetrate. This salt also allows a more basic aluminium salt to be formed without precipitation occurring. Precipitation may be even more effectively prevented by the addition of "masking agents" (that is, certain organic acids or their salts) to the tanning solution; in this way higher basicities and pH values can be reached than are possible when these masking agents are not employed.

Salt alone will give something of the same effect and the "fullness" of alum leather produced by these methods is partly due to the presence of salt. If the leather is rinsed the salt is removed and the leather becomes hard and tinny.

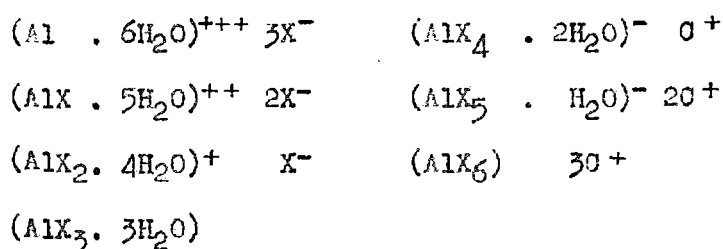
Until recently tanning with aluminium salts has been practised by essentially the same methods as for many centuries. With the introduction of masking agents, however, the process has been speeded up and the leather rendered more stable to washing. There is reason to believe that this is because the complex bound masking agent forms part of the linkage stabilising the bond, and the object of the present work was to investigate the influence of some of these masking agents in alum tanning.

From practical considerations attention has been directed mainly towards the effects of formate, acetate, lactate and tartrate anions.

THE CHEMISTRY OF ALUMINIUM TANNING SALTS WITH SPECIAL
REFERENCE TO COMPLEX FORMATION.

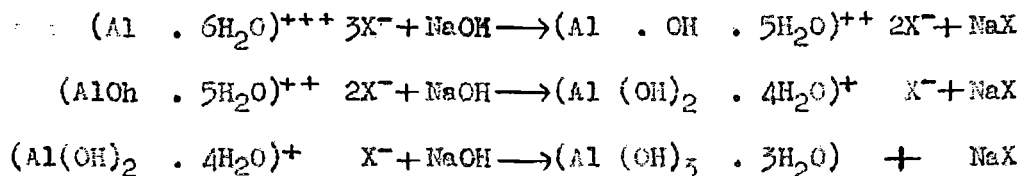
COMPLEX FORMATION.

Aluminium has a co-ordination number of six, so in theory, according to Sidgwick (1), the following types of compounds may be formed :



where X^- is a monovalent anion and O^+ a monovalent cation.

McLaughlin and Theis (2) have pointed out that on basifying the hexaquo salt $(\text{Al} \cdot 6\text{H}_2\text{O})^{+++} 3\text{X}^-$ we should obtain, theoretically, a series :



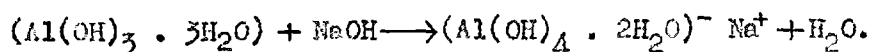
the final compound being the insoluble gelatinous substance, aluminium hydroxide and the intermediate products being the 33.33% and 66.67% basic salts. Each reaction may be regarded as governed by a constant, K , defined by the relationship:

$$K = \frac{(\text{Basic salt}) \text{H}^+}{\text{hexaquo salt}} = \text{hydrolysis constant}$$

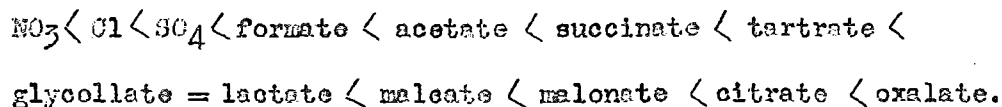
It appears that the constants for the three reactions are very nearly equal (3) so that on addition of sodium hydroxide the locally high pH in the vicinity of the drop causes the hexaquo salt to go immediately to the

hydroxide. This is completely different from the behaviour of the chromium ion, where the constants are unequal: the hydrolysis constant for the first stage is greater than for either of the others, and the first acid group must be largely neutralised to form the mono-hydroxo salt before the second or third groups are affected to any appreciable extent.

The series given above may be extended to include the soluble aluminate :



The addition of salts of the alkali metals to aluminium salt solutions causes a rise in pH which is dependent on the nature and amount of added anion. This effect was noted by Thomas and Whitehead (4) and Stiasny (5). Thomas and Whitehead have suggested that the rise in pH may be due in part at least to the replacement of hydroxyl ions in the complex by the anion of the added salt. Using pH as an indication, the penetrating power of different anions has been deduced, the average being :-

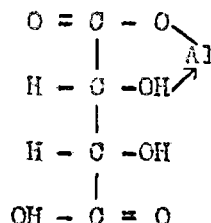
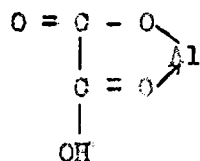


Kuntzel, Reiss and Konigfeld (6) have pointed out that in the case of salts of other than strong acids the rise in pH is due to the addition of a buffer salt of higher pH than the aluminium salt solution, and assert that it is unlikely that hydroxyl groups can be directly displaced from the complex, since there is considerable evidence to show that this group is strongly held by the complex. They consider that when an acid anion enters the

complex it displaces an aquo group or another acid group already present in the complex. This view is substantiated by the fact that the addition of a mixture of an acid and its salt, at a pH nearer that of the aluminium salt, causes an initial fall in pH which only begins to rise again when enough of the mixture has been added to allow the buffering effect of the latter to preponderate. This observation has been confirmed by Bowes and Morse (7). The fall in pH is correctly ascribed to the liberation of sulphuric acid from the complex, its place being taken by the weak acid originally present in the buffer mixture.

Bowes and Morse (7) have also found that the addition of sufficient alkali to a solution of a complex aluminium salt causes the hydroxide to be precipitated in many cases. The greater the tendency for the anion to enter into the complex, the higher the concentration of hydroxyl ion necessary to displace it. Thus the hydroxide is precipitated at a lower pH from chloride solution than from sulphate. An even greater hydroxyl ion concentration is required for precipitation in the presence of acetate, while in lactate, tartrate and citrate solutions precipitation may be completely prevented. This does not mean that the hydroxyl ion has been unable to displace the other anion in these cases but that the pH at which this occurs is sufficiently high to enable the aluminium ion to go to the aluminate form as soon as the complex is destroyed. The hydroxyl ion may thus be placed in the series somewhere in the region of the lactate ion.

With dibasic and hydroxy acids it is possible for the anion to form two links with the aluminium ion, the process being called chelation. Thus with oxalic and tartaric acids the following complexes are probably formed :



On stereochemical grounds Sidgwick (1) has shown that the stability of a five- or six-membered ring is greater than smaller or larger rings. On this basis the low complex forming tendency of the succinate ion compared with other dibasic acids may be explained. This may also explain why α hydroxy acids form highly stable complexes.

Bowes (8) suggests that the formation of complexes between aluminium ions and the free carboxyl groups of collagen may take place on tanning. It can be assumed that the effect of the different anions on tanning will be governed by the relative stability of the aluminium anion complex and that of the aluminium collagen complex. Therefore on general principles it would seem that in alum tanning it is desirable that the masking anion should form a complex with aluminium sufficiently stable to prevent precipitation of aluminium hydroxide when the pH is raised to the point where the protein carboxyl groups are fully ionised; but not so stable that these groups cannot enter the complex and displace it. It should thus be possible to place collagen in the series of anions given above.

By means of titration curves Thorstensen and Theis (9) have studied the effect of the addition of various proportions of different organic acids or their salts to solutions of aluminium sulphate. Those solutions that contained sodium formate or acetate showed little or no deviation from what would be expected from the corresponding blanks, indicating no complex

formation under these conditions. On the other hand, sodium glycollate caused a displacement of the titration curves from the aluminium sulphate curve such that considerably more alkali was required to bring the system to the desired pH, than if no complex formation had occurred.

Grall (10) showed that no complexes are formed when aluminium sulphate solutions are boiled or diluted, but sulphate complexes are formed when the aluminium sulphate solutions are rendered basic, or neutral salts added. Other complexes are formed when salts of organic acids are added.

From titration curves on solutions in which the ratio of oxalate to aluminium ions was varied, Lacroix (11) deduced that two stable oxalate complexes exist. $[Al(O_2O_4)_2]^-$ is stable when the oxalate/aluminium ratio is less than or equal to 2, and $[Al(O_2O_4)_3]^{3-}$ is stable when the oxalate/aluminium ratio is greater than 2 but less than or equal to 4. With higher proportions of oxalate other complexes can form, but these are unstable.

Kuntzel, Reiss and Konigfeld (6) compared the titration curves of chromium sulphate and aluminium sulphate and concluded that sulphate complexes of aluminium are not found under the conditions studied. Also the addition to solutions of aluminium salts, of salts whose anions have a strong tendency to co-ordinate with aluminium, modifies the complexes and stabilises them to ammonium hydroxide, in that immediate precipitation does not occur on adding this reagent. Various salts were used as masking agents by Kuntzel et al. (ibid) and shown to have different effects. Rochelle salt and sodium citrate completely mask the aluminium ion to ammonia.

Wilson, Peng and Li (12) made sodium dioxalate diaquo aluminate and used it to tan hide powder. They found that a concentration of 5 gm Al_2O_3 per litre at pH 5.0 gave the best results. Basic aluminium sulphate was used in another series of experiments in which the effect of masking agents, sodium tartrate, acetate and formate, was determined. It was found that a ratio of one mol tartrate to one of aluminium was sufficient to prevent precipitation. In the case of formate or acetate little difference was found in the precipitation figure.

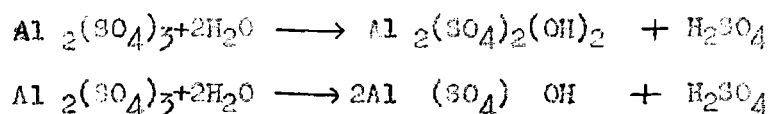
Bowes and Morse (7) however, have stated that in the presence of acetate very little precipitation occurs until pH 5.0 is reached, as against a value of about pH 4.0 for the control. Acetate thus appears to delay but does not prevent precipitation.

HYDROLYSIS AND OLATION.

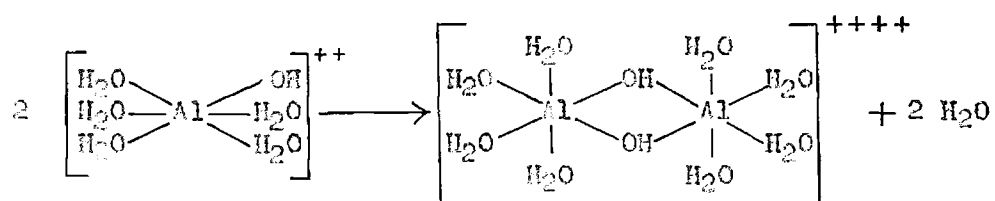
As previously mentioned aluminium has a co-ordination number of six, and according to the Werner-Pfeiffer hypothesis the first stage of hydrolysis of its salts may be represented by the following equation :



On the addition of alkali the hydrogen ions are removed and the equilibrium is displaced to the right. Polling (13) determined the hydrolysis of aluminium sulphate using both the hydrogen and quinhydrone electrode and showed that the hydrolysis could be represented by either of two equations :

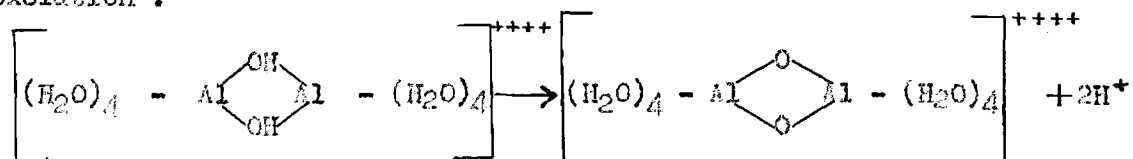


Bjerrum (14) has shown that when acid is added to a solution of an aluminium salt that has been made basic, only a part of the acid is neutralised immediately, the remaining portion reacting slowly and Thomas and Vertanian (15) have studied the effectiveness of various acids for this purpose. This phenomenon is probably due to the fact that some of the hydroxy groups are held firmly by the union of two or more complexes, the process being termed oxolation and represented by the following equation :



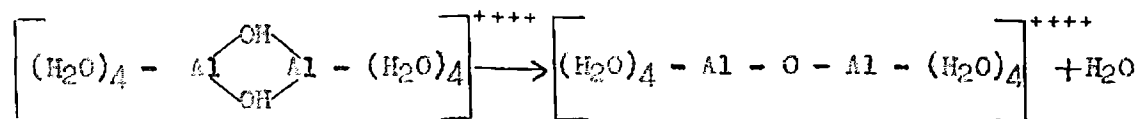
The reaction is taken to be analogous to that given for chromium by Sticsny and Balanyi (16).

Basic solutions are known to become more acid on standing or on boiling and cooling and Sticsny and Balanyi (16) suggest that this may be the result of "oxolation".



This may account for the decreased activity toward added acid since it is postulated that the breaking of the oxo bridge is more difficult than that of the hydroxo bridge.

Kuntzel, Reiss and Konigfeld (17) on the other hand hold that the change in reactivity is due to the formation of a single oxygen bridge because the change in pH is so slight. This may be represented as follows :



Shuttleworth (18) has suggested that in the case of chromium salts the first result of adding alkali is to cause aggregation through the linking

together of several molecules by single hydroxyl bridges, involving hydrogen bonds. At this stage the bonds are relatively unstable to acid but, on ageing, spatial rearrangements permit the formation of olated dimers involving the double hydroxyl bridge characteristic of olated complexes, and these are relatively stable towards acid. This hypothesis appears more reasonable than that involving "oxo" bridges for which there is no direct evidence from titration curves although Jander (19) has pointed out that certain facts support the oxygen bridge theory for iron and aluminium and the hydroxyl bridge for chromium.

It should be noted that the single oxygen bridge derived from the "diol" by the elimination of one molecule of water, as postulated by Kuntzel, Reiss and Konigfeld (17) does offer a reasonable explanation of the ageing phenomena and the stability to acid of the olated complexes, but the double oxygen bridge postulated by Stiasny and Balanyi may be rejected as untenable as evidence for this should be forthcoming from titration curves.

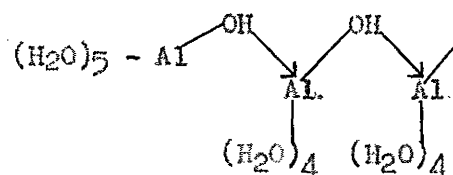
As the only difference between the double hydroxyl bridge and the single oxygen bridge structure is the single molecule of H_2O eliminated from each pair of metal atoms, it is evident that proof of either structure must depend on the isolation of either of these compounds in the pure state or on physical evidence which is not yet forthcoming.

Thomas and Tai (20), Thomas and Whitehead (21), and Wilson and Kuan (22) have also studied the hydrolysis of basic aluminium salts and have recorded that the changes they undergo are similar to those of chromium salts but aluminium salts reach equilibrium more quickly and the changes are less pronounced.

Perkin and Thomas (23) used a conductimetric method to measure the degree of olation. They found that the concentration of acid or metallic ion has little influence on the degree of olation. Freshly prepared solutions are appreciably olated ten minutes after preparation. The velocity of the reaction increases with basicity. Concentration has little effect on the velocity of olation. Increase of temperature from 16°C. to 25°C. causes an increase in the rate of olation, but above 25°C. the velocity appears to be unaffected. Stiasny and Konigfeld (24) studied chrome solutions and found they had much the same reactions.

AGGREGATION.

Instead of dlation leading to a group containing two atoms it is possible for the process to lead to large aggregates having a structure similar to the formula below as suggested by Bowes (8)



Both olation and aggregation are favoured by the same conditions, i.e., increase in pH, basicity, temperature and ageing but it does not follow that a high degree of olation is accompanied by a high degree of aggregation.

Jander and Jahr (25), using diffusion methods, found that at normal basicities the aggregate contains two atoms on the average while at high basicities the aggregates may contain as many as eight molecules.

It appears from these results that it is not necessary to have large

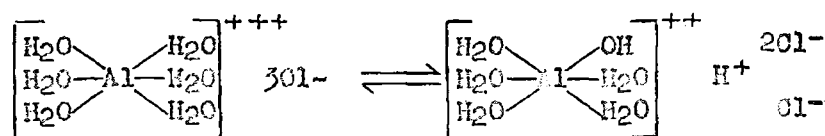
aggregates for tanning because at the basicities used in practice the aggregates do not appear to have more than two atoms.

ADDITION OF NEUTRAL SALTS.

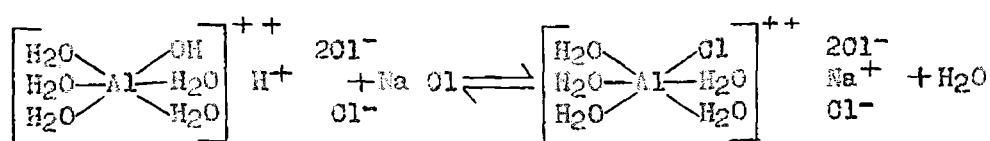
In alum salt systems it has been shown, McLaughlin and Theis (2), that the addition of neutral salt plays an important role in alum tannage, because the addition of neutral salt increases the adsorption of aluminium, rather than acid, by the pelt.

Thomas and Whitehead (4) studied the effect of the addition of neutral salts to aluminium salt solutions, the change in pH being taken as an indication of the extent of the reaction. It was found that the hydrogen ion activity was decreased by chloride and sulphate ions even when present in low concentrations, but the sulphate ion was more effective than the chloride ion. Thomas and Whitehead offered the following explanation of their results.

In the absence of added neutral salt hydrolysis may proceed thus :-



On the addition of sodium chloride, further amounts of chloride ions will tend to replace the hydroxo groups co-ordinated with the aluminium, and the displaced hydroxyl ions will react with free hydrogen ions in the solution to form water



It was suggested that the sulphate ion would also tend to replace the hydroxo groups of the complex, but another factor that may account for the greater decrease in hydrogen ion activity as compared with chloride, is that the sulphate ion is capable of uniting with the hydrogen ion to form the hydrosulphate ion HSO_4^- , thus tending to buffer the pH of the solution.

On the above postulate aluminium complexes differ from chrome complexes, since in the latter an anion entering the complex does so by displacing an aquo group in preference to an hydroxyl group. This distinction is important in that it implies that the analogy between aluminium and chromium complexes cannot be taken too far. However, as pointed out previously (see p.5) it is not likely that co-ordinated hydroxyl groups can be displaced directly by chloride and sulphate ions and the phenomenon noted by Thomas and Whitehead is possibly to be accounted for in terms of activity effects alone.

Chambard and Grall (26) have shown that whatever the basicity of the aluminium sulphate there is no formation of acid complexes in pure solutions, that is in the absence of neutral salts. In another paper they (27) have adduced evidence that the addition of potassium sulphate promotes the penetration of sulphate ions into the aluminium complex. The greater the concentration of sulphate the more acid complex is formed, and the amount of sulphate ions that enter the nucleus increases with basicity. Chloride ions do not have the same marked effect as sulphate ions.

Chambard and Grall (28) have also shown that the addition of alkali salts of organic acids has a similar, but much greater effect which varies with the particular anion, oxalates for example being much more effective

than formates.

As previously mentioned (see p.8) Kuntzel, Reiss and Konigfeld (6), have shown that in the presence of salts whose anions have a strong tendency to co-ordinate with aluminium, solutions of aluminium salts are stabilised to ammonium hydroxide, so that precipitation does not occur immediately on adding this reagent.

Cantarella (29) noted the masking effect of the addition of sodium formate, lactate, tartrate and citrate, when solutions of aluminium sulphate were titrated with sodium hydroxide to the precipitation point. His results are in line with other evidence and show that the stabilising effect increases in the order given above.

Griscuol and Cantarella (30) studied the reactions between aluminium sulphate and salts of different organic acids at various concentrations in order to obtain highly basic solutions with high tanning value. Tartrates and citrates form stable complexes not precipitated by soda or ammonia, while formates and lactates retard the reaction. Tartaric acid produced a highly basic aluminium salt containing six hydroxy groups.

FACTORS AFFECTING FIXATION AND TANNING ACTION OF ALUMINIUM SALTS.pH AND BASICITY.

Increase in the pH of a solution of a tanning salt may be expected to increase the basicity of the complex ion. Schachowskoy and Frolich (31), have shown that the fixation of aluminium by collagen increases with pH up to the point where the metal is precipitated as the hydroxide, and then decreases. Thus within these limits increase in pH is accompanied by an increase in tanning effect.

By studying gelatine films, (the decrease in solubility being an indication of tanning) Elod and Schachowskoy (32, 33) have shown that the tanning effect is at an optimum at a pH approaching the precipitation point of the hydroxide. On this criterion, Bowes (8) states that the tanning action is at an optimum when the salt is most basic.

Elod and Schachowskoy (33) and Bowes and Morse (34) have shown that the shrinkage temperature increases with increase in pH of the tanning solution. Other workers however, hold that the increase in shrinkage temperature is a function of the increased uptake of tanning agent caused by an increase in basicity and is not dependent on the pH of the solution alone. This has been stated by Bowes, Davies, Pressley and Robinson (35), to be the case for chrome and might be expected to hold for aluminium as well.

Nevertheless, since it is well established that the carboxyl ion (as distinct from the unionised carboxyl group) is involved in co-

ordination reactions with metal complexes, it is evident that the pH of the system at equilibrium will have a profound effect on the degree of combination, quite apart from the basicity of the complex itself. Thus it might be expected that increased combination would occur as the pH is raised towards the iso-electric point of the protein and beyond, if it were not for the fact that owing to the formation of insoluble basic compounds the effective concentration of the tanning agent is reduced at the same time. Partial stabilisation of the aluminium complex ion by means of masking agents should therefore facilitate the uptake of aluminium by collagen at pH values in the region of the iso-electric point.

A further indirect effect of pH is the swelling of the collagen fibres themselves due to electro-osmotic effects. Excessive osmotic swelling reduces the size of the pore spaces between adjacent fibres, fibrils and micelles and thus retards the diffusion of the tanning agent through the cross-section of the pelt; lyotropic agents on the other hand reduce the intermolecular cohesive forces of the polypeptide grid and may be expected to render the reactive groups more accessible to the tanning agent. At the iso-electric point therefore, where electro-osmotic effects are at a minimum, conditions should be most conducive to effective reaction while it should not be overlooked that many organic acids capable of masking are also lyotropic agents and may facilitate tannage for this reason.

INFLUENCE OF CONCENTRATION.

It has been shown by Elod and Schachowskoy (33), Bowes and Morse (34), Wilson and Yu (36) and Thomas and Kelly (37), that increase in concentration of aluminium ions in solution increases the amount fixed by collagen under any given set of conditions. Thomas and Kelly (37), found that

an optimum was reached when the concentration of Al_2O_3 was 2.5 gm/litre.

Dohogne and Rezabek (38), showed that higher basicities could be obtained if the solutions are more concentrated than those generally employed in actual practice. Stable solutions of 62% basicity can be formed. Kuntzel (39), found that on treating aluminium sulphate with sodium carbonate, basic aluminium sulphate is precipitated but re-dissolves if the concentration of the aluminium solution exceeds a certain limit; the higher the temperature the more easily does the precipitate dissolve. The maximum basicity of 62% can be obtained only by heating, as the critical concentration is not reached in the cold. On dilution precipitation occurs.

Pal and Das (40) have shown that absorption of aluminium from 50% basic aluminium chloride increases with concentration up to 7.5% Al_2O_3 . The tensile strength of the leather depends on the basicity and not on the percentage of adsorbed Al_2O_3 .

EFFECT OF SALTS ON UPTAKE OF ALUMINIUM BY PELT.

It is well known that the tanning action of aluminium and chromium salts varies with the amount and nature of the anions present. The effects caused by salts can be divided into three main groups.

According to Chambard and Grall (28), neutral salts, such as sodium chloride, effect aluminium complexes in that they increase the binding power of the complex salt, but decrease the total fixation of aluminium by the pelt. This may be due to the influence of the salt on aggregates but could also be due to the inhibition of swelling of the pelt which would otherwise be brought about by acid formed on hydrolysis. As

indicated in the previous section reduced plumping allows greater penetration and so a more even distribution of the aluminium through the leather.

Bowes and Morse (41) however, have confirmed that the addition of neutral salt decreases the fixation of aluminium so it is obvious that other factors must also be involved.

Apart from the general effect of the salts in reducing electro-osmosis there is the additional effect of the anion. Elod and Schachowskoy (33) showed that sulphate and formate gave a leather with a higher shrinkage temperature than other salts. Similar results were obtained by Bowes and Morse (41).

Chambard and Grall (28) have shown that the addition of salts that have a strong tendency to form complexes increased the thermal stability when they were present in low concentrations, but decreased it in high concentrations. The explanation is probably that when the salts are present in high concentration the complexes formed are so stable that the collagen is unable to combine with the metal. Generally, anions of organic acids show these properties to a greater or lesser degree. Thus Bowes and Morse (41) have shown that acetate increases the fixation of aluminium from aluminium sulphate solutions, but the addition of dicarboxylic and hydroxy acids or their salts decreased the fixation.

Wilson, Peng and Li (12) have shown that numerous salts of organic acids have a definite masking action. In some cases mixtures of masking agents give better results than single salts.

EFFECT OF MODIFICATION OF THE COLLAGEN.

By the action of nitrous acid it is possible to remove the amino

groups from collagen without affecting the other groups present. Bowes and Kenten (42) found that on deaminised collagen the amount of chromium fixed was reduced by half but the shrinkage temperature remained unaffected. As aluminium behaves similarly to chromium in many ways, similar results may be anticipated for this element. Wilson and Yu (36) and Bowes and Morse (7) have shown that inactivation of the amino groups definitely decreases the amount of aluminium fixed in accordance with this view.

The carboxyl groups of collagen may be "inactivated" by treatment with dimethyl sulphate, and after such treatment the amount of metal taken up is markedly reduced and the shrinkage temperature is greatly affected. Deamination together with methylation caused only a further small decrease in the amount of metal fixed (8).

Bowes (8) suggests that these results may be interpreted as indicating that the ionised carboxyl groups play an important part in the fixation of the metal, and the attainment of high thermal stability. Amino groups fix large quantities of the tanning agent, but since deamination of the methylated collagen causes only a small decrease in the fixation, Bowes reasons that the metal does not combine with amino groups independently of carboxyl groups and concludes that stable fixation requires co-ordination of both carboxyl and amino groups with the same complex.

These conclusions are open to criticism because, as has recently been shown by Shuttleworth (18), there is very little positive evidence that protein amino groups in the ionised form are capable of co-ordinating with chromium (or aluminium) under normal conditions in aqueous systems. The function of the amino groups in promoting fixation of chromium is an

indirect one in that these groups are able to absorb the excess acid generated when a relatively weak acidic group such as the carboxyl group displaces a more strongly acidic group, such as chloride or sulphate, from the complex.

THEORY OF MINERAL TANNING.

Many theories have been put forward to explain mineral tannage. 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 complex and 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.

ADSORPTION THEORIES.

The first theory was due to Knapp(43) in 1858 who stated that tanning involved the deposition of an insoluble basic salt on the fibres of the pelt. This explains the effect of pH and concentration, and the effect of different ions may be attributed to the way in which they affect precipitation.

In 1917 Nihoul (44) stated that alum tanning consists of the deposition of the hydrous oxide in and around the fibres. All the processes of tanning accelerate the deposition of this gelatinous substance, since flocculation of colloidal substances are accelerated by the application of heat and the addition of salts. The temperature of the tanning solution increases if drum tannage is used, due to the friction of the pelt in the drum. Much salt is used in alum tanning and this causes the deposition of the hydrogel in the hide as well as checking the swelling of the pelt.

Cameron and McLaughlin (45) have shown that in the case of basic

chromium sulphate tannages, tanning obeys all the requirements of a reversible adsorption process and that deposition of a basic salt takes place in and on the fibres. The mechanism envisaged is that in the first instance the sulphate hydrolyses to give free sulphuric acid and a basic complex. This acid is then taken up by the skin protein and the hydrolysis thus proceeds until the 66.67% basic complex is formed. Since this complex is insoluble it is precipitated on the fibres. When the acid combining capacity of the collagen is satisfied no further deposition occurs.

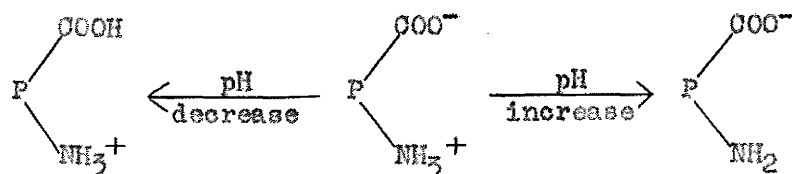
Wilson and Yu (36) have found that the fixation of aluminium from aluminium sulphate may be represented by exponential curves of the Freundlich adsorption isotherm type and concluded that adsorption processes were involved.

CHEMICAL THEORIES.

It seems unlikely that the mere deposition of small amounts of aluminium should have such a marked effect on the properties of collagen when the latter is converted to leather and it would appear that a chemical mechanism is necessary to account for these changes.

Bowes and Kenten (46) have considered the groups present in collagen which might participate in the reaction with metallic salts during tannage. The principal ones are carboxyl, amide, amino, guanidino, hydroxy and peptide. In the iso-electric region the carboxyl groups will carry a negative charge and the amino and guanidino groups a positive charge,

the net charge being zero. As the pH decreases an increasing number of carboxyl groups will combine with hydrogen ions and lose their negative charge, and as the pH increases the basic groups will lose hydrogen ions and hence their positive charge.



Thus the pH of the tanning solution determines the condition in which the different groups are present.

Thomas and Kelly (37) suggest that the tanning action of metals is due to simple salt formation between the cation and the carboxyl groups of the collagen. Thompson and Atkin (47) maintain that this is unlikely as under normal conditions of tanning both the collagen and the metal complex are positively charged.

Nihoul (48) discusses the principal combinations possible between compounds of aluminium and hide but all are dependent on the prior deposition and adsorption of the compounds and subsequent chemical combination.

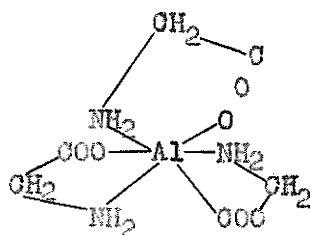
The hydrosol may react with carboxyl groups but this is not likely. Alumina however, reacts with various organic compounds to form insoluble lakes and this may occur in tanning.

Even when basic salts are used acid salts are present which are taken up by hide in such a way that the formation of basic salts would be accompanied by a fixation of alumina on the fibres. Here it is free

to react to give basic compounds of which the hide substance forms part.

The more generally held theories are those that involve the formation of co-ordinate complexes between the metallic complex and the protein. This can occur in many ways because complexes might be formed with the carboxyl, amino, guanidino, imino and hydroxy groups of the collagen.

Glycine is capable of forming a stable complex salt with aluminium as well as iron, cobalt and chromium. (Erneleus and Anderson (49)).



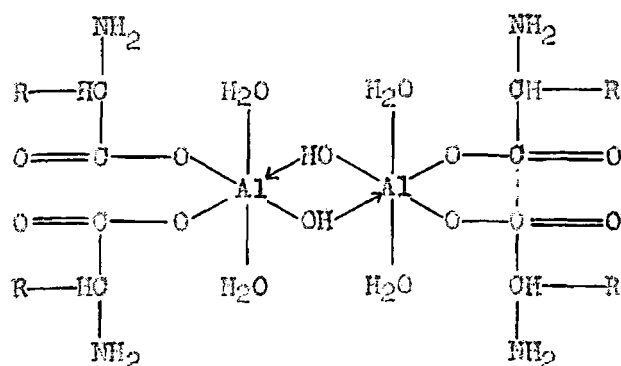
Non electrolyte complexes of this type, where the neutral and acidic groups are united in the same molecule, are known as inner complex salts and Kuntzel and Reiss (50) suggest that a similar mechanism is involved in tanning. The carboxyl group forms a co-ordinate link with the metal followed by another link with an amino group of an adjacent chain. For this to occur it is necessary to have two conditions satisfied, both of which are dependent on pH. The solution must be basic so that polynuclear complexes can be formed, otherwise they cannot bridge the space between polypeptide chains, and the carboxyl groups of the collagen must be ionised. Both of these conditions are favoured by high pH.

By X-Ray analysis Astbury (51) determined the distances between the principal recurring structures in the collagen molecule and found that

they are such that it would require only two atoms, linked by an oxygen bridge, to span the distance, and if several atoms are linked together several polypeptide chains may be joined to form a lattice.

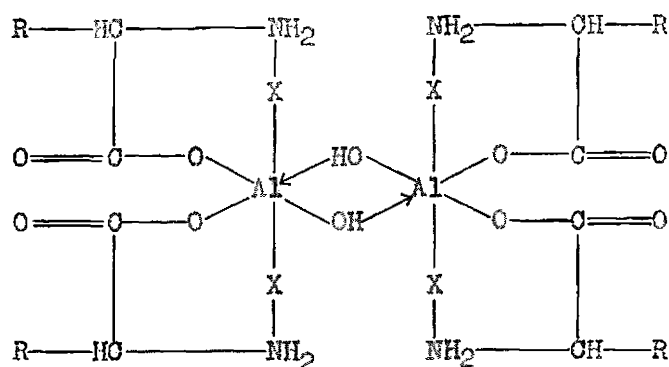
Stiasny (52) in 1927 suggested that the oxygen of the carboxyl groups and the nitrogen of the amino or peptide groups co-ordinate either directly with the central metallic atom or with a group in the complex. If co-ordination occurs with the central atom, then a group already in the complex must be displaced, and so a stable complex would be unable to react in this way and would have no tanning action. This would explain the effect of certain anions on inhibiting tanning.

Grall (53) states that in normal aluminium tanning solutions little complex formation occurs between the ions in solution. He suggests that in leather tanned under these conditions the metallic ions form the intermediate links because there are no anions in the complex to help in the linkage. As a result the bond is assumed to be of the form :



According to Grall this hypothesis is confirmed by the fact that the

addition of strong complex forming ions to tanning solutions improves the quality of the leather produced due to the formation of additional bonds resulting in a structure as follows :



where the amino groups form a bond with the complex bound anion represented by X in the above diagram.

Although the hypothesis that a complex bound ion may serve as a link between the free amino groups of lysine and the complex as a whole is worthy of consideration, the actual structures proposed by Grall and illustrated above are untenable because the amino groups and the associated carboxyl groups are involved in the peptide link of the protein and cannot react as ions in the manner shown. If the basic idea implied in Grall's hypotheses is applied to the free -COOH groups and -NH₂ groups present on the side chains in collagen it may still be criticised on the grounds that, as represented, the amino groups are shown in the uncharged state. If account is taken of the electrostatic charges on the ions, Grall's hypothesis (modified as suggested above) amounts simply to the suggestion that the effect of introducing additional negative ions into the complex renders the latter anionic,

and the co-ordinate link is thus reinforced by the electrostatic attraction between the anionic complex and the positively charged amino group.

Shuttleworth (18) has argued that the relatively high thermal stability of chrome tanned leather cannot reasonably be explained on the basis of residual valency forces involved in adsorption, nor in terms of electrovalent bonds alone, and considers that the penetration of carboxyl groups of collagen into the metal complex is the primary factor in chrome tannage. As indicated previously (Effect of Mod. of Collagen) there is considerable evidence in support of this view.

CONCLUSION.

It appears that a theory of mineral tanning which presumes the entry of the carboxyl group into the complex, followed, under certain conditions, by the formation of secondary links with the amino group, either directly, or through the presence of some other anion in the complex, would fit the present evidence available on the subject.

POTENTIOMETRIC TITRATION STUDIES.

INTRODUCTION.

Experiments on the influence of sodium formate, sodium acetate sodium lactate and sodium potassium tartrate (Rochelle salt) on the titration curve of sodium aluminate using nitric acid as titrant, are described in the present section. Sodium citrate was also employed because there is evidence (8,6,54,55) that strong complex formation occurs between the citrate ion and aluminium. The four first named salts were selected because they are all readily available commercially and can be obtained in a high state of purity.

In planning this work it was considered that sodium aluminate would be preferable to potash alum or other aluminium salt because competition from other anions in the solution would be eliminated and only the effect of the added anion need be considered. Moreover, by approaching the precipitation point from the alkaline side it would be ensured that the organic acid would be in the fully ionised form and thus have the same opportunity for complex formation in each case, the number of free ions not being dependent to the same degree upon the dissociation constant of the particular acid radical involved.

Since adequate supplies of pure sodium aluminate were not

available at the time it was necessary to adopt the following technique which, it was hoped, would at any rate reduce the concentration of sulphate ions to a relatively low level -

320 gms A.R. sodium hydroxide was dissolved in 500 mls distilled water in a 1½ litre flask. 606 gms A.R. aluminium sulphate was placed in 500 mls distilled water and heated to dissolve as much as possible. This solution was then added slowly to the sodium hydroxide solution, the reaction being sufficiently violent to cause the liquid to boil. The aluminium sulphate was added slowly with constant stirring until a slight but permanent precipitate, which was not dispersed on boiling, was formed. All of the aluminium sulphate was not added because a certain amount of free alkali is needed to keep the aluminium in solution. The solution was boiled for a further 15 minutes, allowed to cool to room temperature, and then placed in a stoppered flask in a refrigerator for three days. Most of the sodium sulphate formed during the reaction crystallised out under these conditions.

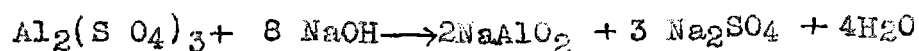
The clear supernatant liquor was filtered through a buchner funnel and the sodium sulphate crystals washed with a very little cold water. The filtrate was cooled for a further three days and again filtered as above. The resulting solution was then made up to 2 litres with distilled water. This stock

solution was aged for three weeks before the aluminium determination and titration curves were performed.

Various methods for the determination of aluminium were investigated and the method found to give the most consistent results was as follows -

Sufficient of the solution (containing 10-30 mgm of Al_2O_3) was evaporated to dryness in a nickel crucible and the ash fused with 0.5 gm NaOH at a dull red heat for about 15 minutes. After cooling the residue was leached out with boiling water and filtered through Whatman No.541 filter paper. Aluminium was then determined on the filtrate by means of the "oxine" method (8-hydroxy quinoline) following standard procedures (56,57,58). The solution was found to be 0.719 molar with respect to aluminium. The sulphate was also determined using the BaCl_2 method of Vogel (56) and was found to be 0.31 molar.

The equation for the formation of sodium aluminate is as follows :



It was found from the subsequent titration curves that in the stock solution there is an excess of 0.5 equivs NaOH/mol Al over that required by the above equation.

GENERAL PROCEDURE FOR TITRATION STUDIES.

Solutions of the salts were made up such that the concentration of monovalent anion was 2 molar, the divalent anion

$1\frac{1}{3}$ molar and the trivalent anion $\frac{2}{3}$ molar. Thus the addition of equal volumes of the solution of the appropriate salt to a given quantity of solution of sodium aluminate resulted in the same final concentration of aluminium in each case. It will be noted that the ratio of each of the salts to Aluminium was six equivs/mol Al, except in the case of the divalent tartrate ion where the ratio used was 8 equivs/mol Al. For the concentrated series 108 mls of the masking salt solution was added to 50 mls of the 0.72 M. stock solution of sodium aluminate. As a result the initial concentration of the aluminium in the sodium aluminate organic salt solution was 0.22 molar. (At the end of the titration 0.12 molar). For the dilute series 22 mls of the organic salt solution was added to 10 mls of stock sodium aluminate solution previously diluted to 100 mls. Thus the concentration of aluminium in the solution at the commencement of the titration was 0.06 molar.

For each series (concentrated and dilute respectively) two identical solutions were prepared. One was boiled for 5 minutes keeping the volume constant and allowed to cool before titration. The remaining solution was titrated without prior boiling. In each case the addition of the masking agent was made the day before the titration was conducted. Thus, before titrating or boiling and titrating as the case may be, 16-20 hours had elapsed subsequent to the addition of the salt.

In view of the copious precipitate obtained with sodium format

and sodium acetate at six equivs/mol Aluminium it was considered that no useful degree of complex formation would have occurred under these conditions. Accordingly further titrations using lower relative proportions of these masking agents were not attempted. On the other hand the remaining three masking agents sodium lactate, and sodium citrate were studied at ratios of 3 equivs/mol Al and 2 equivs/mol Al and sodium potassium tartrate was studied at 4 equivs/mol Al and 2 equivs/mol Al in later experiments.

TITRATION TECHNIQUE.

The solutions prepared as above were each titrated with 1.5N nitric acid which was chosen for this purpose because of its very small complex forming tendency. The acid was added in small increments, the size of which depended on the change in pH. Generally the first few additions were of 10 mls each, the titre being reduced to 5 mls when the change in pH increased. In the dilute series the corresponding increments were 3 mls and 1 ml respectively.

A Marconi battery-powered pH meter (type Tf-511C) with glass electrode and dip calomel electrode (saturated type) was employed for the potentiometric determinations, the electrodes being standardised against potassium hydrogen benzoate buffer (59), pH 4.16 before and during each titration. After each addition of acid the solution was well stirred and 1 minute allowed to elapse before the pH was taken. The titration was conducted at

laboratory temperature (about 20°C).

For each ratio of masking agent two curves were obtained, one representing the titration of the unboiled solution and the other that of the boiled solution. These two curves were compared with a "blank" which was a composite graph derived from the separate titration curves of sodium aluminate and masking agent after adjusting each salt to the required concentration with distilled water. That is, 50 mls of the sodium aluminate stock solution was made up to 160 mls with distilled water and 108 mls of the masking agent was made up to the same volume with distilled water before titrating each solution separately with 1.5N nitric acid. The titres at similar pH values (0.5 pH unit intervals) were summed to form the blank. The graphs so derived thus represent the expected titration curves of sodium aluminate and masking agent in admixture on the assumption that no reaction occurs between them and that changes in activity liquid junction potentials, etc., are negligible.

For the blanks for the dilute series 10 mls of the sodium aluminate stock solution and the appropriate quantity of masking agent solution were each diluted to 120 mls and titrated separately, the titres being summed as described above. Titrations were conducted with 1.5N nitric acid in every case.

The three curves representing titrations of the boiled and unboiled solutions and the appropriate blank (unboiled) respectively are plotted for each masking agent at different ratios in graphs

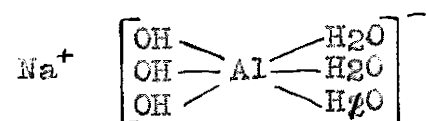
35.

1 to 20. These data are considered in detail in the following pages.

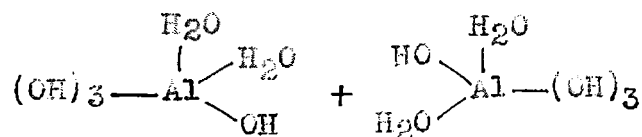
RESULTS.1. SODIUM FORMATE SERIES.

Consideration of graphs 1 and 2 shows that little or no deviation from the blank occurred for either the boiled or un-boiled solutions. Graphs obtained by Thorstensen and Theis (9) using smaller ratios of formate to aluminium also show no evidence of complex formation. On these grounds and the fact that a copious precipitate was formed during the titrations, no further data on this system are considered.

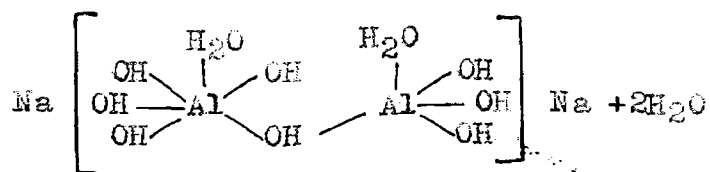
It will be seen from the graphs however, that the titration curve of the boiled solution is displaced toward the pH ordinate, an indication thatolation may have occurred on boiling. The formula for sodium aluminate in solution may be represented as follows, if it is assumed that the Al ion is fully hydrated :-



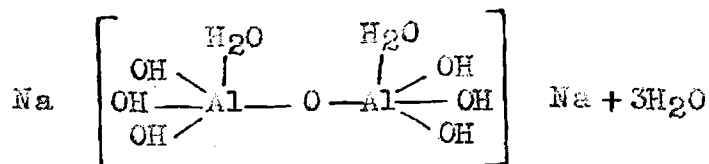
It is possible that on boiling the following reaction occurs :-



giving



or possibly



Since for every atom of Al involved in an isolated complex of this type there are now only 3-OH groups capable of reacting immediately with acid (as against four in the unolated complex) it is evident that less acid would be required in order to bring the pH of the solution to any specified pH value. While this accounts for the deviation of the boiled from the unboiled solution without invoking complex formation with the formate ion, it is considered that in any case the discrepancies are not large enough for accurate conclusions to be drawn. Although the titration curve of a boiled solution of sodium aluminate alone showed a relative shift of about the same order as that obtained above, it may be remarked that an opposite trend was apparent for the acetate series.

The displacement referred to above is more noticeable in the dilute series graph 2. At lower pH values the two graphs coincide suggesting that the isolated aluminium aggregates if present, might have been dispersed (de-isolated) during titration.

The high deviation between the blank curves and the experi-

mental curves above pH 10 could be accounted for by the sodium ion error of the glass electrode, for which no corrections have been made in the present work, and some caution is therefore required in interpreting these deviations. Below pH 10, although sodium ion errors may safely be taken to be negligible, there is a further difficulty that under the conditions of titration employed, any difference in rate of combination with acid after each incremental addition would be reflected in corresponding differences between the two titration curves. In view of these limitations it is obvious that attempts to explain the minor differences observed in terms of stoichiometric reactions of the components would be quite unjustified.

2. SODIUM ACETATE SERIES.

The appropriate curves are given together for comparison in graph 3 (concentrated series) and graph 4 (dilute series).

The initial pH values of the two curves in each series are lower than that of the corresponding blank but below pH 10 do not deviate much from the curve representing no reaction..

It may be noted that although the differences involved are small, the boiled samples require slightly more acid to bring the solution to pH 8 or thereabouts than are required for the blank or the unboiled solution. This trend is opposite to that which would occur if oxidation were involved and is opposite to that found with formate. However, in view of the fact that the

titrations were carried out on a heterogeneous (2 phase) system it is possible that the deviations may be ascribed simply to differences in rate of reaction with the titrant.

It is apparent that formate and acetate do not form complexes to any considerable extent, if at all, under the conditions studied and do not stabilise the system to precipitation. However, the buffering power of these salts in the region pH.4 to 5 may be of some value in controlling the tanning action of aluminium salts.

3. SODIUM LACTATE SERIES.

In this series two ratios of salt were used, namely 6 equivs/mol Al. and 3 equivs/mol Al. respectively. Lower ratios than 3 : 1 did not stabilise the solution to precipitation with acid, although at a ratio of 2 : 1 the concentrated series did not begin to precipitate until a relatively low pH was attained. Also a faint turbidity in the dilute solution containing 3 equivs/mol Al was observed during the titration of this solution. 4 equivs/mol Al. stabilised the solution completely even in the dilute series.

Graph 5 shows the curves for the concentrated series when 6 equivs/mol Al. were added. The curves roughly coincide in the upper pH range above 9.0 but below this they deviate quite appreciably. The experimental system is buffered to a greater extent in the region pH 6.0 to 9.0 (compared with the calculated blank) but

below pH 4.0 there is less buffering. It will be noted that the curves cross at about pH 9.0 and again at pH 4.2 and that the effect of boiling is negligible.

In the dilute series (graph 6) the system is more highly buffered. Below pH 4.0 the graph is steep, similar to the concentrated series.

It will be observed that the boiled and unboiled solutions give practically identical curves. The graphs for both the concentrated and dilute series are similar in form but apparently less complex formation occurs (or the complex is less stable) in the dilute system, there being relatively less deviation from the calculated blank, in this case.

In the series containing 3 equivs/mol Al. (graph 7) the pH at which masking is apparent, i.e. pH 8.5, is the same as that in the 6 equivs/mol Al. series, but the deviation from the curve of the blank is not as great. These curves show a greater buffering power between pH 5.0 and 8.5. Below pH 4.0 where the curve cross they are steeper. These curves are similar to those in graphs 5 and 6, but the deviations from the blanks are less so that it follows that at the lower ratio less complex formation must be occurring. This is brought out more strongly when we consider the dilute series (graph 8) where the same trends are observed and turbidity is apparent. Here too, the effect of boiling appears to be negligible as before.

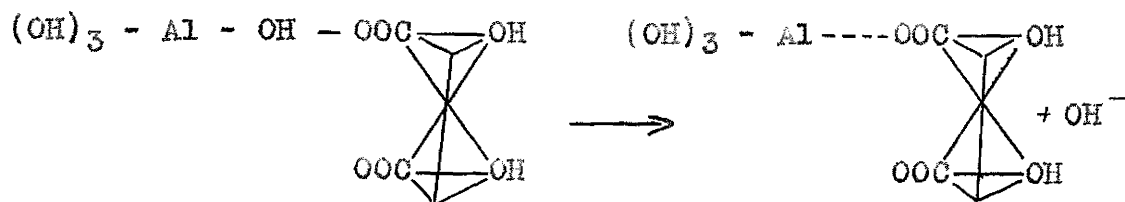
Solutions with a ratio of less than 3 equivs/mol Al. are not stable to precipitation but greater stability is obtained in the concentrated system.

4. SODIUM POTASSIUM TARTRATE SERIES.

Graph 9 shows the curves for the concentrated series when 8 equivs/mol Al. were used and graph 10 the curves for the corresponding dilute series. (Here 8 equivs/mol Al. were used in error, 6 equivs/mol Al. were used in all other series). Here too, as in the lactate series considerable deviation from the calculated blank does not occur until pH values of less than 8.0 are reached.

An interesting feature of graphs 9 and 10 is the divergence between the three curves of each set at high pH values. Owing to the errors of the glass electrode above pH 10.0 some caution must be observed in interpreting these graphs in the high pH region, but it is evident that the difference between the curve for the boiled and unboiled solutions could not be accounted for by such errors. Some reaction must therefore have occurred at pH 10.0 resulting in a higher concentration of OH ions in the solution than would be predicted from the sum of that due to the components (sodium aluminate and rochelle salt) considered separately. This effect is more marked in the case of the boiled solutions.

The explanation may be that the tartrate penetrates the complex displacing OH groups directly - thus :-



When 4 equivs/mol Al. are used, graph 11, a similar graph to the above is obtained, the deviation from the blank being only slightly greater than that for 8 equivs/mol Al. This indicated that the same degree of complex formation has occurred. Even on dilution (graph 12) the same degree of masking is observed and boiling has the same effect as in the concentrated system.

On reducing the ratio still further, i.e. to 2 equivs/mol Al. the degree of masking is very much the same (graph 13). Boiling has the same effect as above. In the corresponding dilute system (graph 14), however, the amount of complex formed is reduced or the complex is less stable because the deviation from the blank is not as great.

At lower ratios than 2 equivs tartrate/mol Al. the system is not stable, precipitation occurring. This indicated that 1 mol of tartrate combines with 1 mol Al. to form the complex and even in the presence of a large excess this ratio is still retained.

In the higher ratio levels, i.e. 8 equivs and 4 equivs/mol Al. respectively, precipitation of the acid sodium or potassium tartrate occurs showing that free tartrate must be present. This precipitate redissolves at low pH values when the dibasic acid

is formed. Confirmation was obtained from the following experiment :-

A solution containing 8 equivs tartrate/mol Al. was adjusted to pH 6.0, the precipitate filtered off and washed and then dissolved in acid. This solution did not contain aluminium. All the aluminium must therefore have formed a complex and become stable to precipitation.

From these results it is apparent that at least 1 mol tartrate combines with each mol aluminium under the conditions employed.

5. SODIUM CITRATE SERIES.

Citrate causes a large shift in the curve from the blank (graph 15) far greater in this case than the shift obtained with the tartrate series and the complex is apparently formed at pH values above 10.0. The curves obtained in the region pH 7.0 to 10.0 show a much sharper end-point compared with the blank. At pH values below 6.0 the curve flattens out but is still steeper than that of the blank. Thus throughout the whole titration range less buffering is obtained. Only at pH values below 3.0 does the curve become less steep than the blank and finally links up with it. The addition of sodium citrate does not raise the pH of the system appreciably although boiling raises it slightly. Below pH 10.0 the curve is shifted to the left which means that free acid has been liberated. This can be accounted for by olation but the

extent of olation, if any, must be small.

On dilution however, the shift of the curves from the blank (graph 16) is not as marked, so that the complex formation, although considerable is not stable. Here the effect of boiling is to raise the initial pH quite considerably, but in the pH range 5.0 to 9.0 it does not cause any appreciable difference. The other trends are similar.

When 3 equivs/mol Al. are used (graph 17) the amount of complex formation is not as great but the other trends are similar. Dilution (graph 18) in this case seems to favour complex formation as the deviation from the blank is greater than that obtained for the concentrated series.

Smaller ratios - 2 equivs/mol Al. - (graph 19) still stabilise the system to precipitation but the degree of complex formation is much reduced. The curve here is much steeper than the curves at greater ratios. Boiling reduces the pH at all values except below pH 4.0 where it increases it slightly. Dilution (graph 20) appears to reduce the complex forming capacity still further, the effect of boiling being the same as above.

The degree of complex formation is dependent not only on the ratio of citrate to aluminium but also on the concentration of the system. The temperature too, has an effect. This account for the inconsistency of the results obtained in the potentio-

metric method for aluminium estimation (55). This method can be used only if the approximate aluminium content is known so that the ratio of citrate to aluminium can be fairly accurately controlled.

DISCUSSION.

As has been noted in the previous section little or no complex formation occurs with either formate or acetate except possibly above pH 9.0 or so. These anions do not stabilise the aluminium solutions to precipitation - they may, however, be of value in controlling pH, as solutions of these salts buffer strongly in the region pH 4 to 5.

The other salts, lactate, tartrate and citrate all show tendencies to complex formation though the degree to which this occurs varies with the anion. The complexes formed by lactate at high pH must be very unstable because on the addition of acid the pH corresponds to the calculated blank. Below pH 9.0 however, the curves deviate quite considerably showing that more acid must be added to reach a certain pH value than is required by the blank. This means complex formation has occurred with loss of -COOH groups. In this system too, buffering is apparent. The same is true of tartrate but this salt is not as efficient a buffering agent. This is probably due to the fact that the excess tartrate is not available as a buffer as it is precipitated as the acid salt which is only sparingly soluble. Citrate on the other hand must form very stable complexes, the effect of which is apparent at even very high pH values. In other words, addition of strong acid liberates free -COOH groups which are immediately incorporated in the complex. This evidently does not occur with lactate or tar-

trate until lower pH values are reached.

The ratio of lactate and citrate to aluminium appears to have some influence on the degree of masking as greater complex formation is found to occur at the higher ratio levels. Tartrate on the other hand apparently has a fixed complex forming capacity between 1 and 4 mols/mol aluminium, since the same deviation from the blank was observed irrespective of which ratio of the masking agent to aluminium, was employed. However, at ratios of less than 1 mol tartrate/mol aluminium, deviations from the blank were reduced and less stabilisation occurred as evidenced by the formation of precipitates containing aluminium under these conditions. In view of these facts it may be suggested that 1 mol tartrate combines with 1 mol aluminium to form a complex containing equimolar proportions of aluminium and tartrate.

The effect of boiling apart from one or two exceptions always has the same effect, i.e. a shift to the acid side of the curve. Free acid must have been liberated which is an indication that oxidation might have occurred.

In the lactate and citrate series dilution appears to reduce the complex forming capacity of these ions but tartrate is unaffected. Thus it would appear that the tartrate complex is more stable than those formed by lactate. Citrate stabilises aluminium solutions with fewer equivalents than tartrate, but the complex does not contain a constant ratio of masking agent

to aluminium. Further quantities of tartrate cannot enter the complex even in the presence of large excess of the anion probably due to the effect of steric hindrance.

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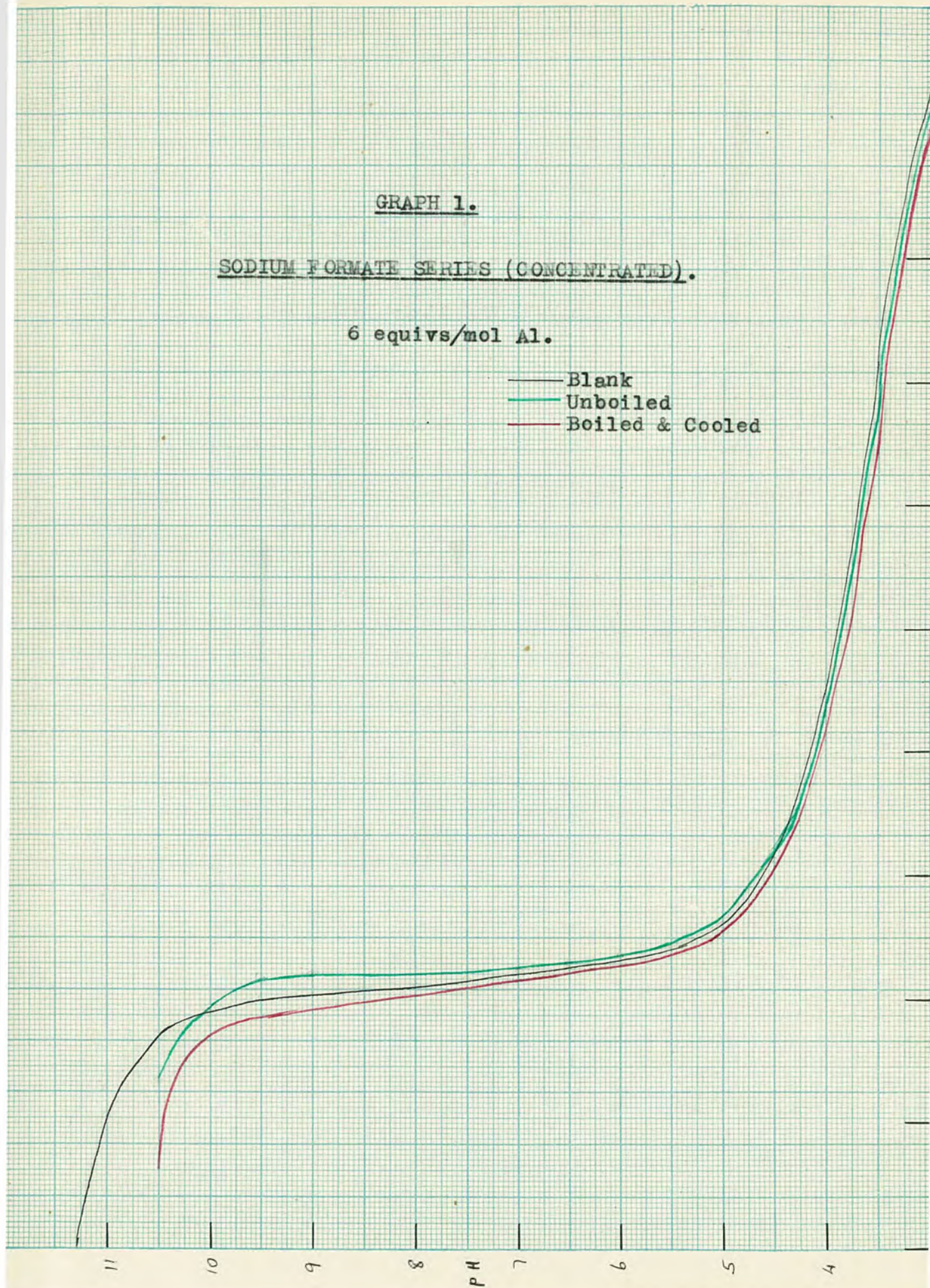
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-

GRAPH 1.

SODIUM FORMATE SERIES (CONCENTRATED).

6 equivs/mol Al.

— Blank
— Unboiled
— Boiled & Cooled

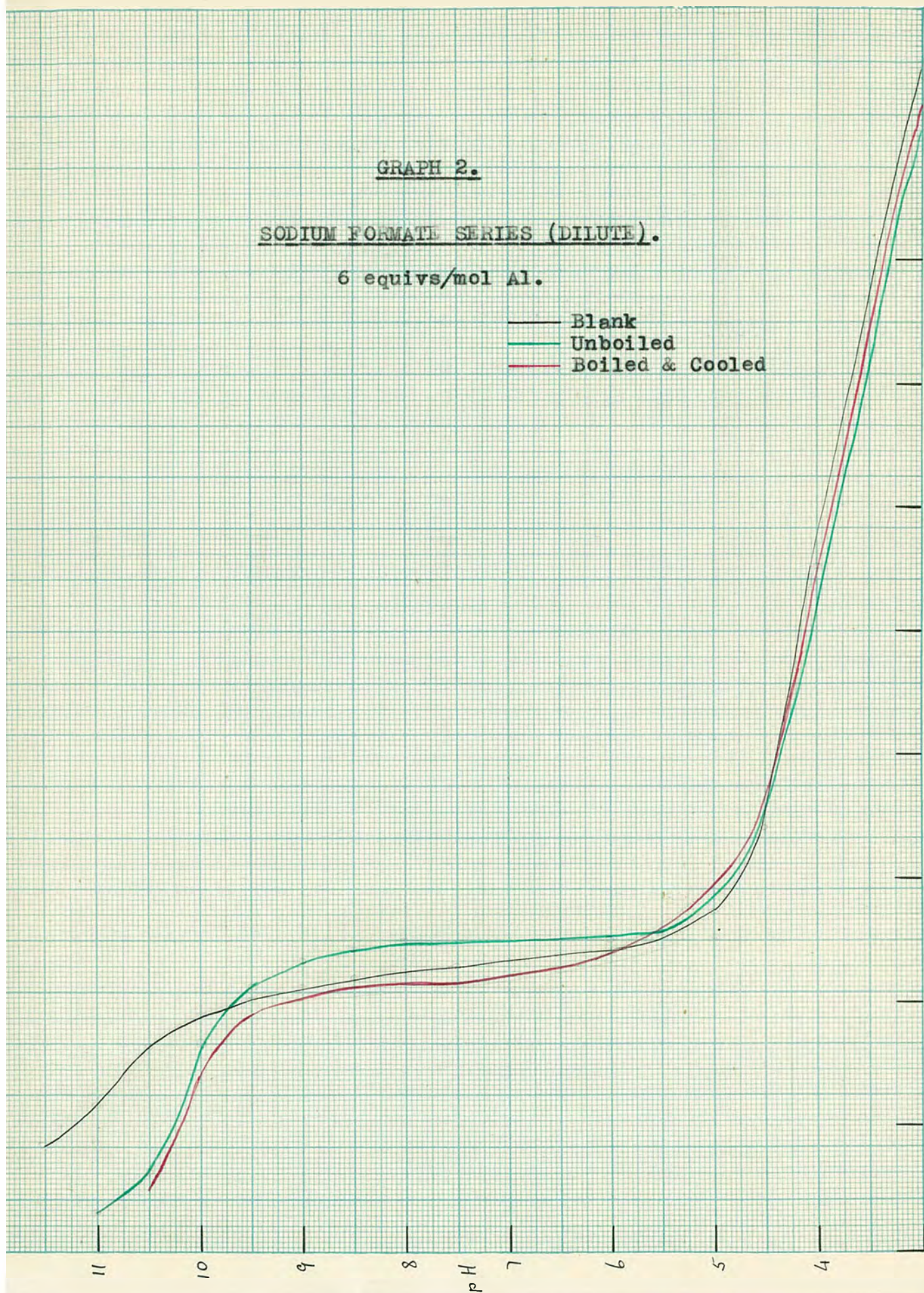


GRAPH 2.

SODIUM FORMATE SERIES (DILUTE).

6 equivs/mol Al.

Blank
Unboiled
Boiled & Cooled

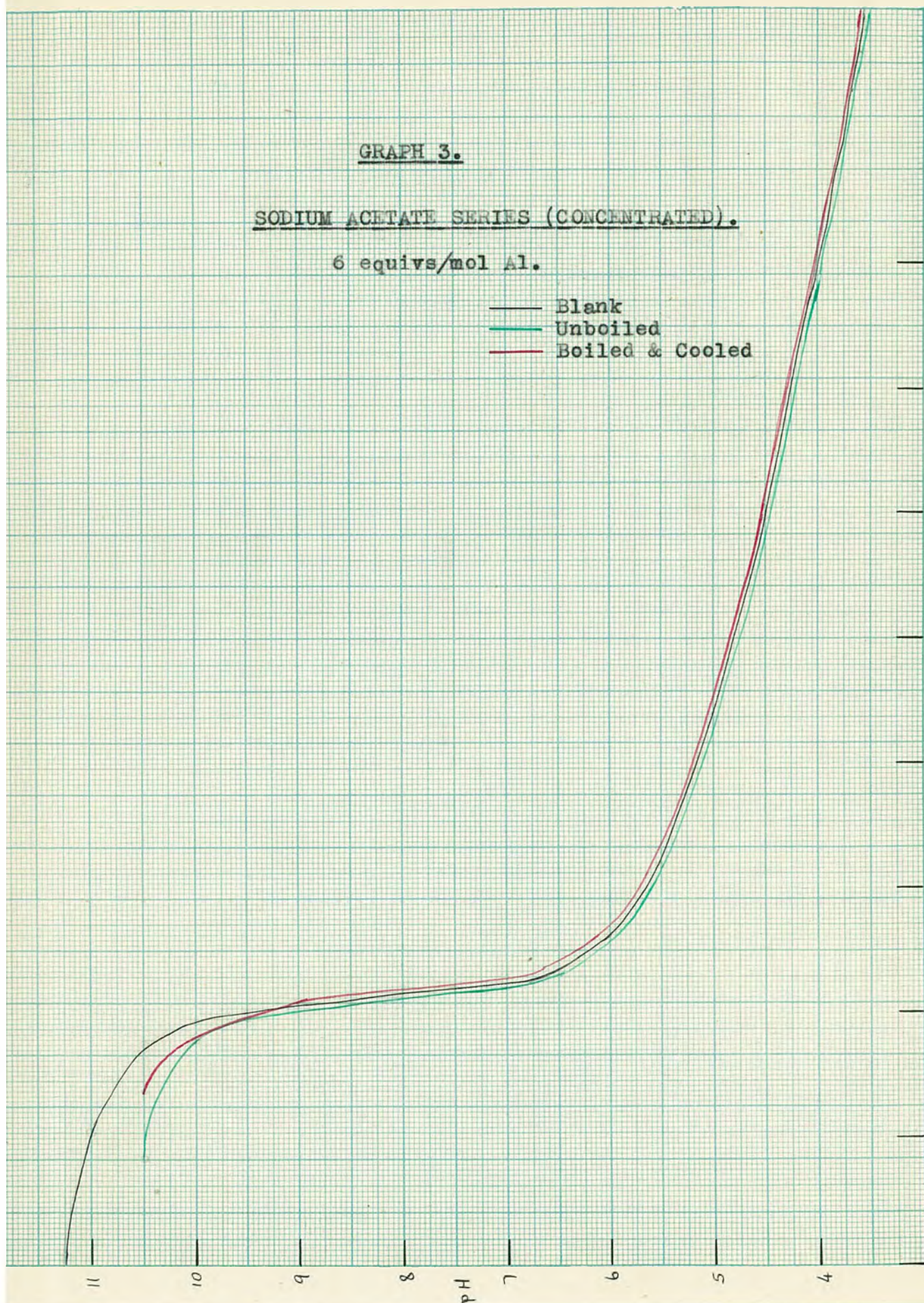


GRAPH 3.

SODIUM ACETATE SERIES (CONCENTRATED).

6 equivs/mol Al.

— Blank
— Unboiled
— Boiled & Cooled



GRAPH 4.

SODIUM ACETATE SERIES (DILUTE).

6 equivs/mol Al.

— Blank
— Unboiled
— Boiled & Cooled

Mols. HNO_3

11

10

9

8

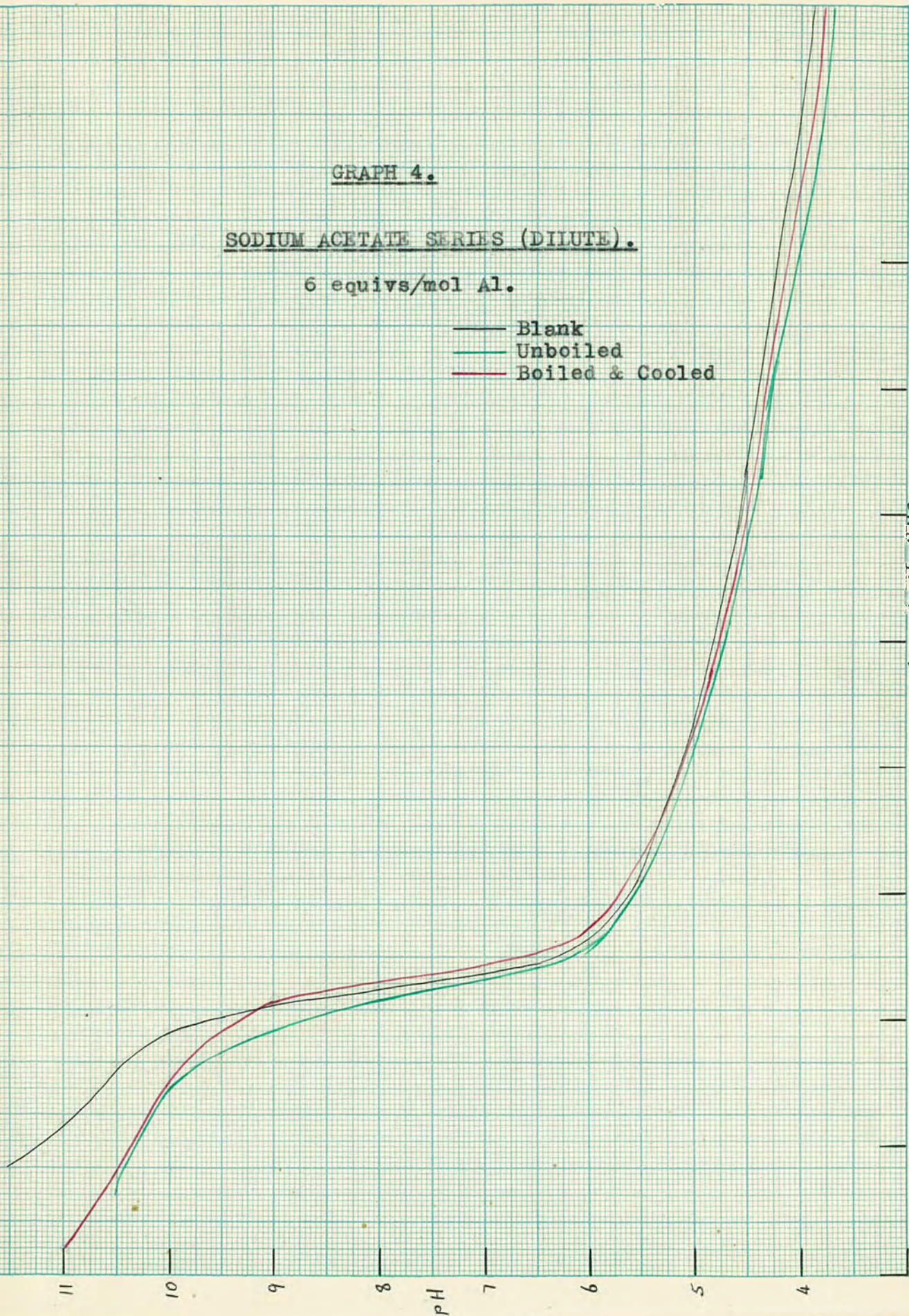
pH

7

6

5

4

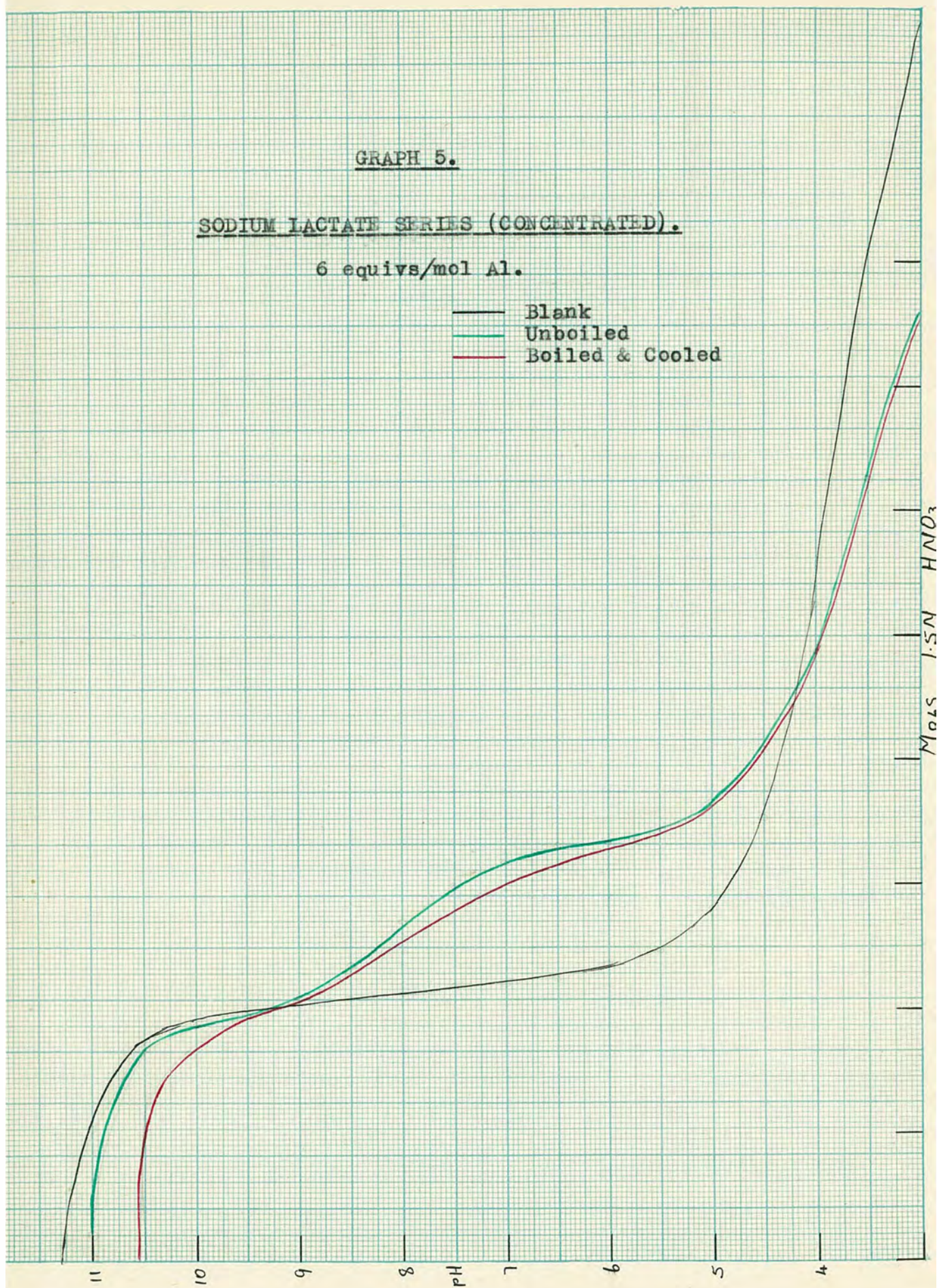


GRAPH 5.

SODIUM LACTATE SERIES (CONCENTRATED).

6 equivs/mol Al.

Blank
Unboiled
Boiled & Cooled

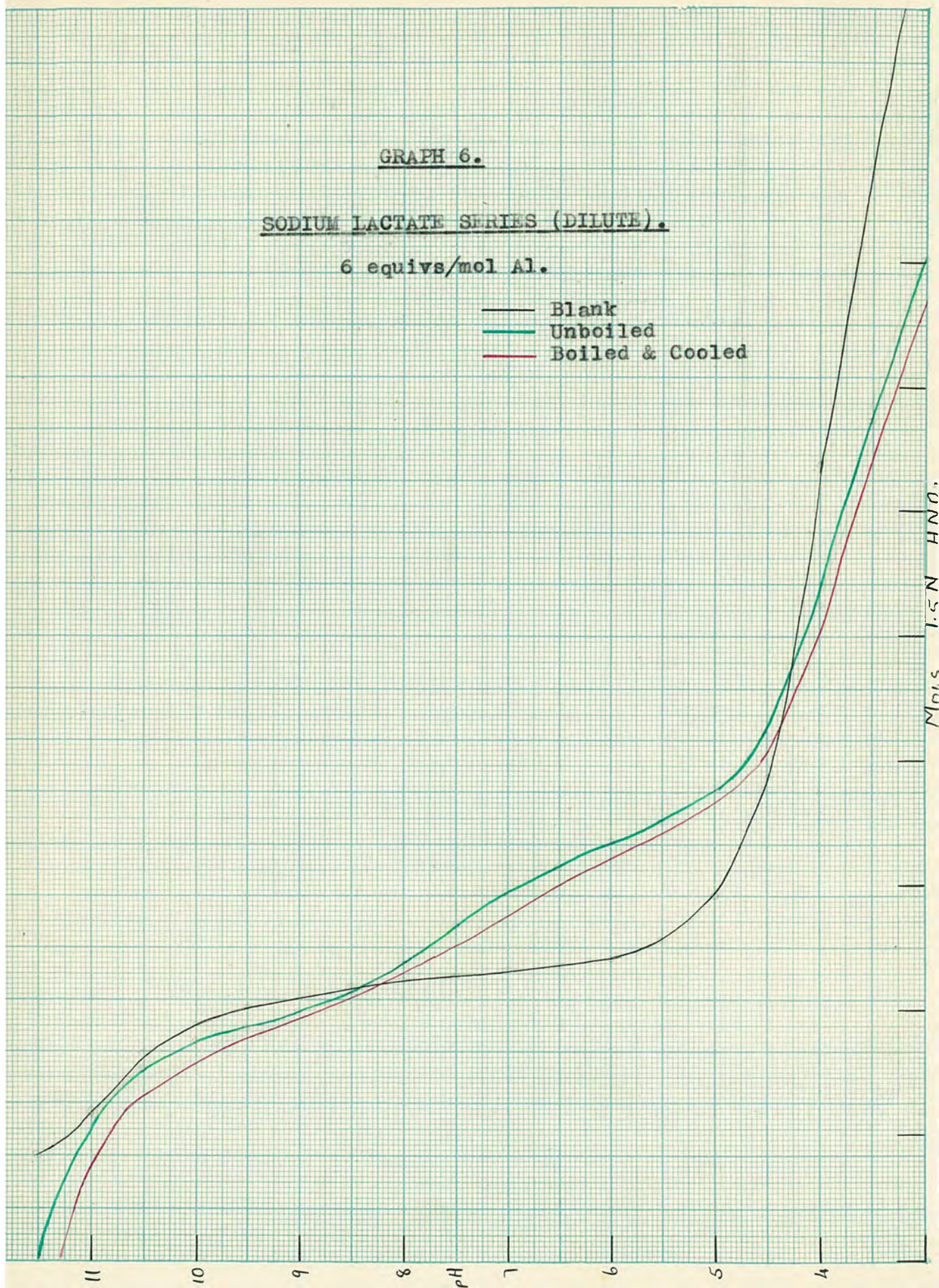


GRAPH 6.

SODIUM LACTATE SERIES (DILUTE).

6 equivs/mol Al.

— Blank
— Unboiled
— Boiled & Cooled

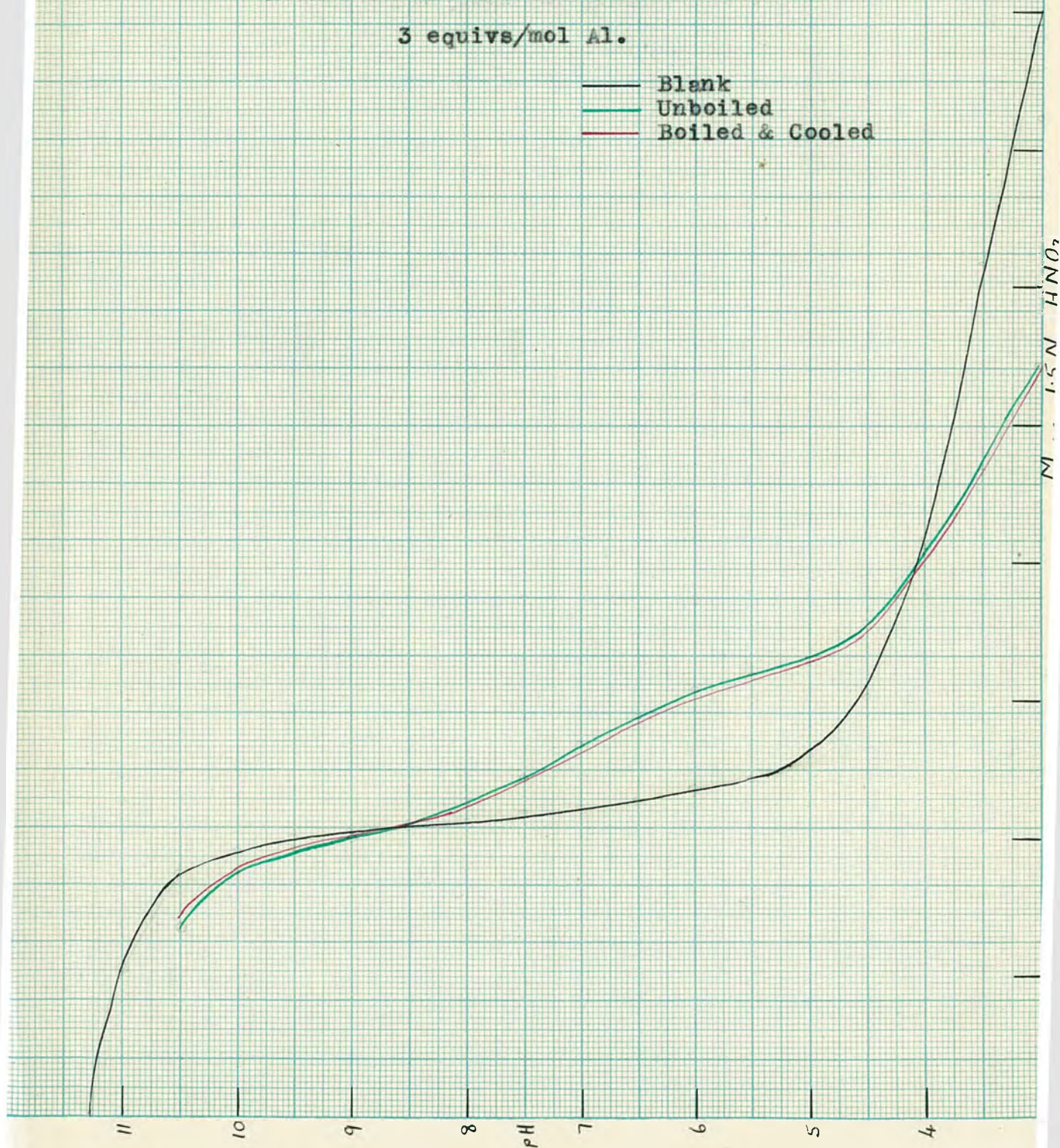


GRAPH 7.

SODIUM LACTATE SERIES (CONCENTRATED).

3 equivs/mol Al.

Blank
Unboiled
Boiled & Cooled

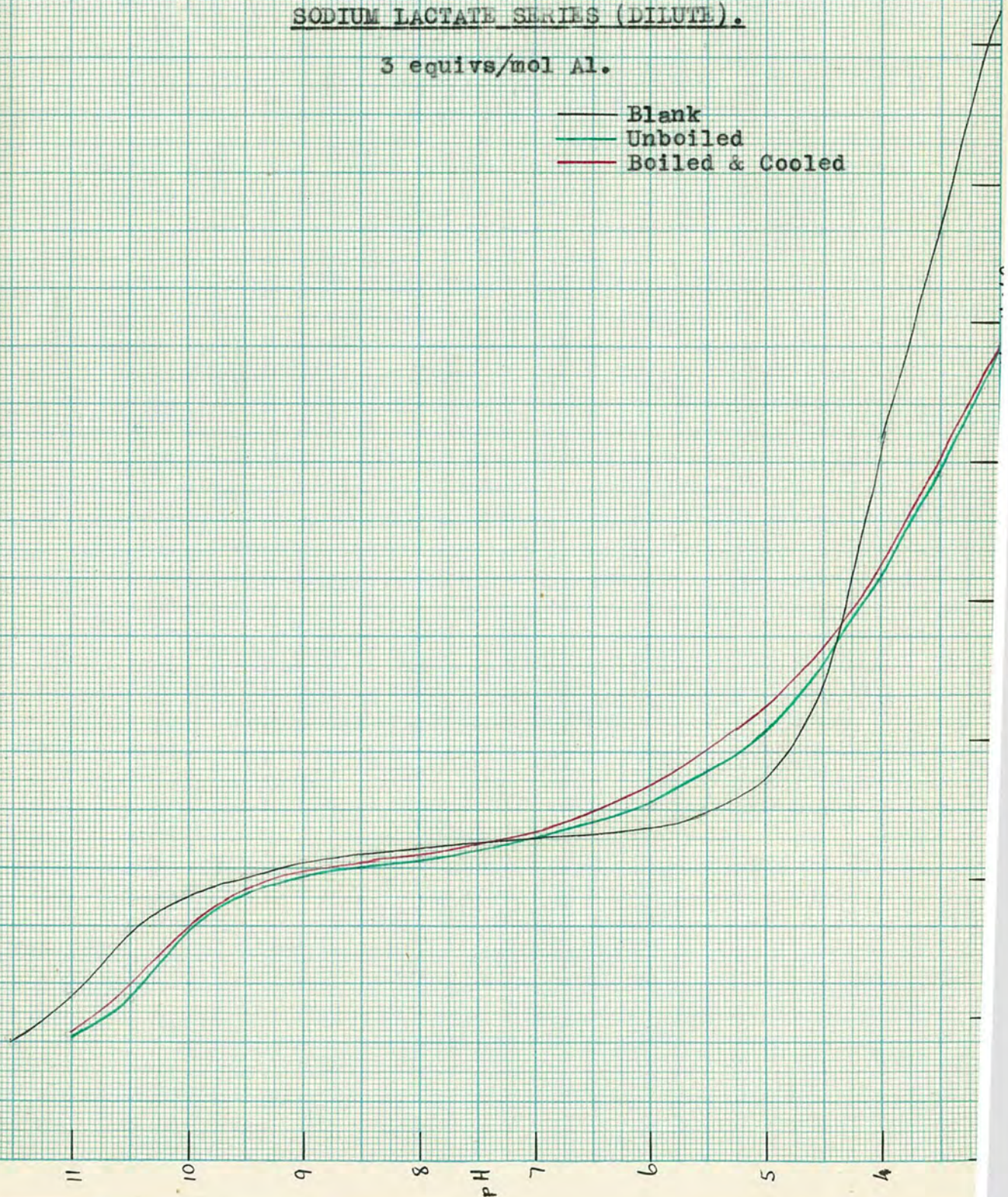


GRAPH 8.

SODIUM LACTATE SERIES (DILUTE).

3 equivs/mol Al.

— Blank
— Unboiled
— Boiled & Cooled

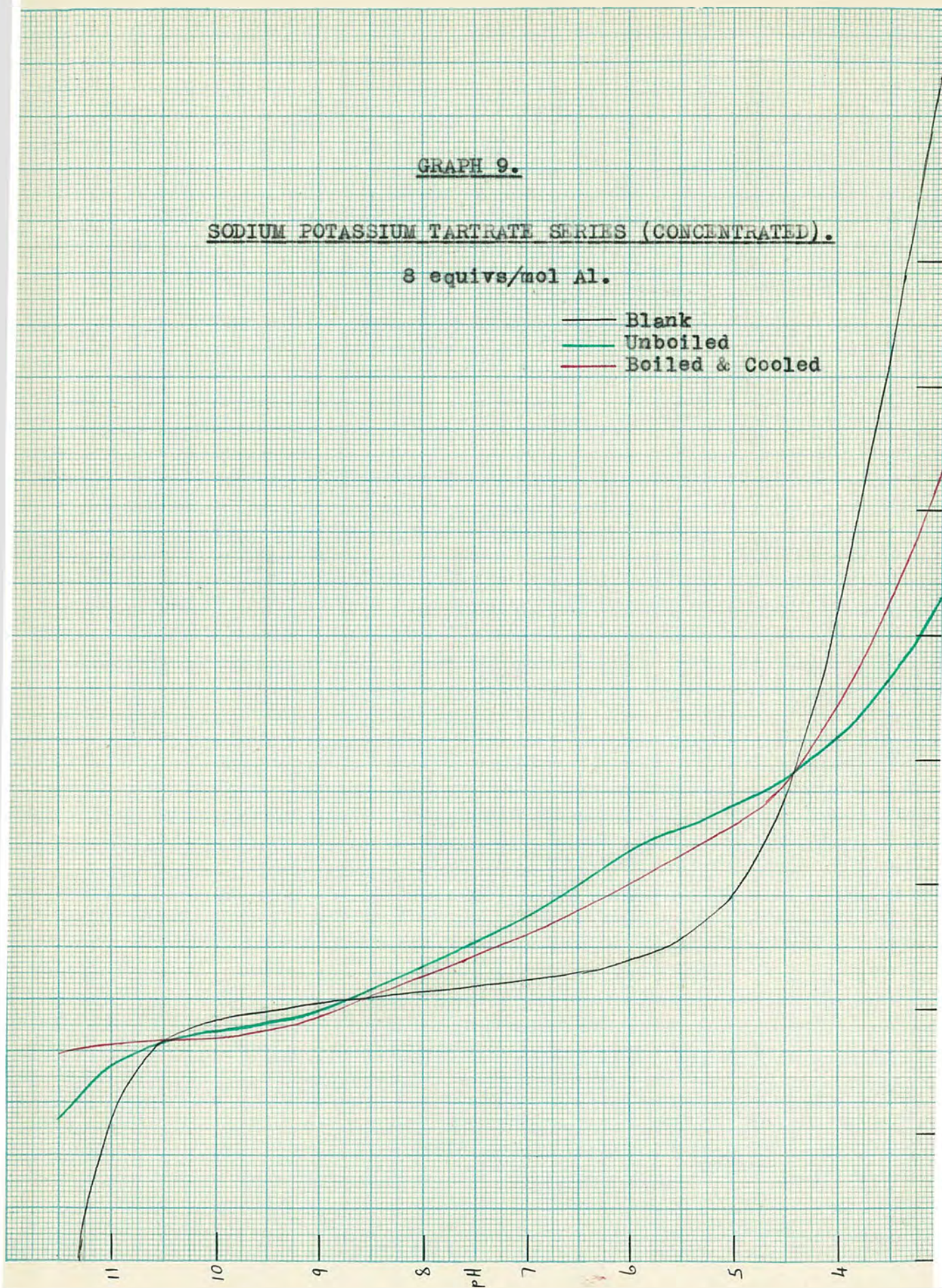


GRAPH 9.

SODIUM POTASSIUM TARTRATE SERIES (CONCENTRATED).

8 equivs/mol Al.

— Blank
— Unboiled
— Boiled & Cooled

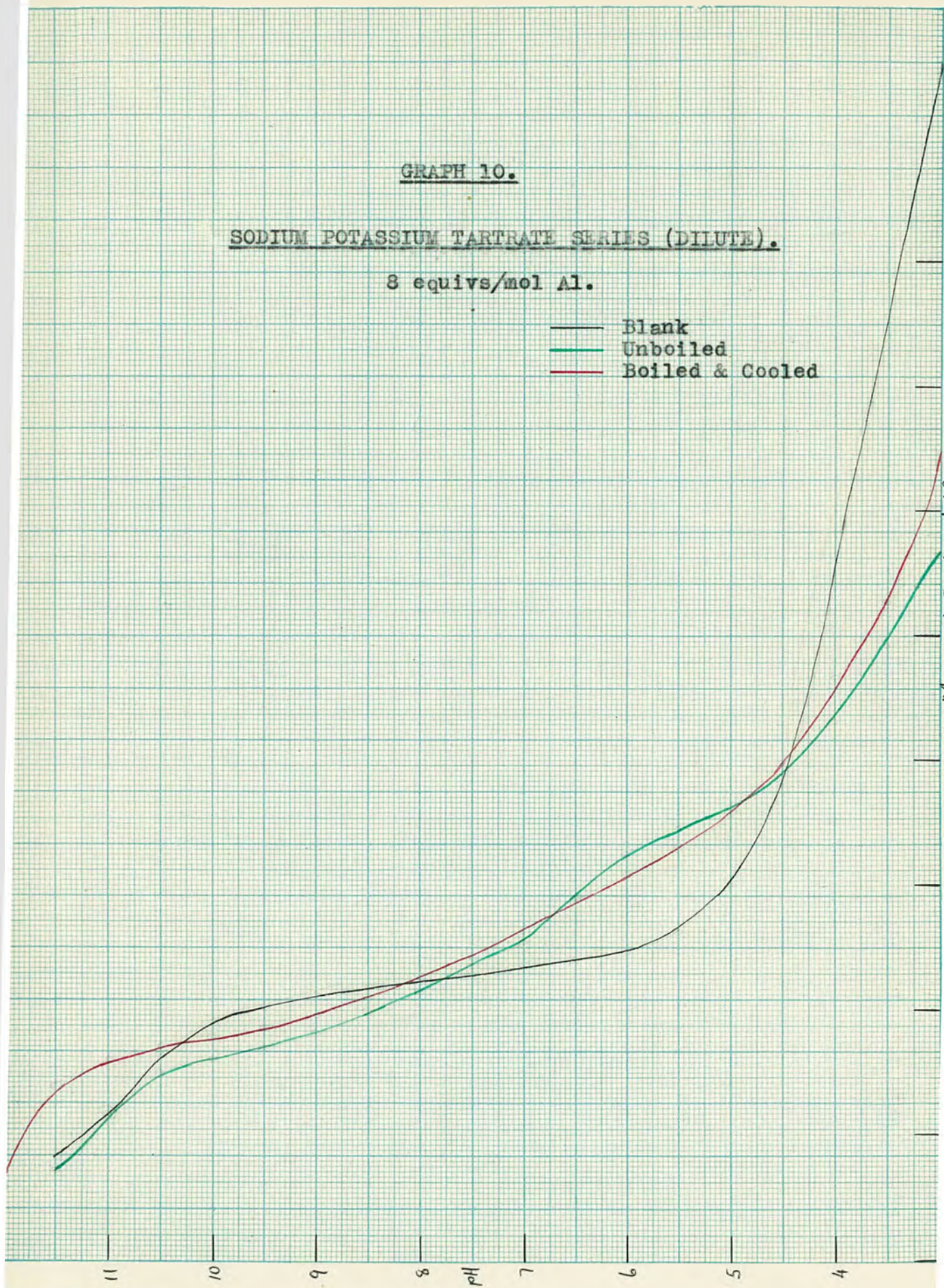


GRAPH 10.

SODIUM POTASSIUM TARTRATE SERIES (DILUTE).

3 equivs/mol Al.

Blank
Unboiled
Boiled & Cooled

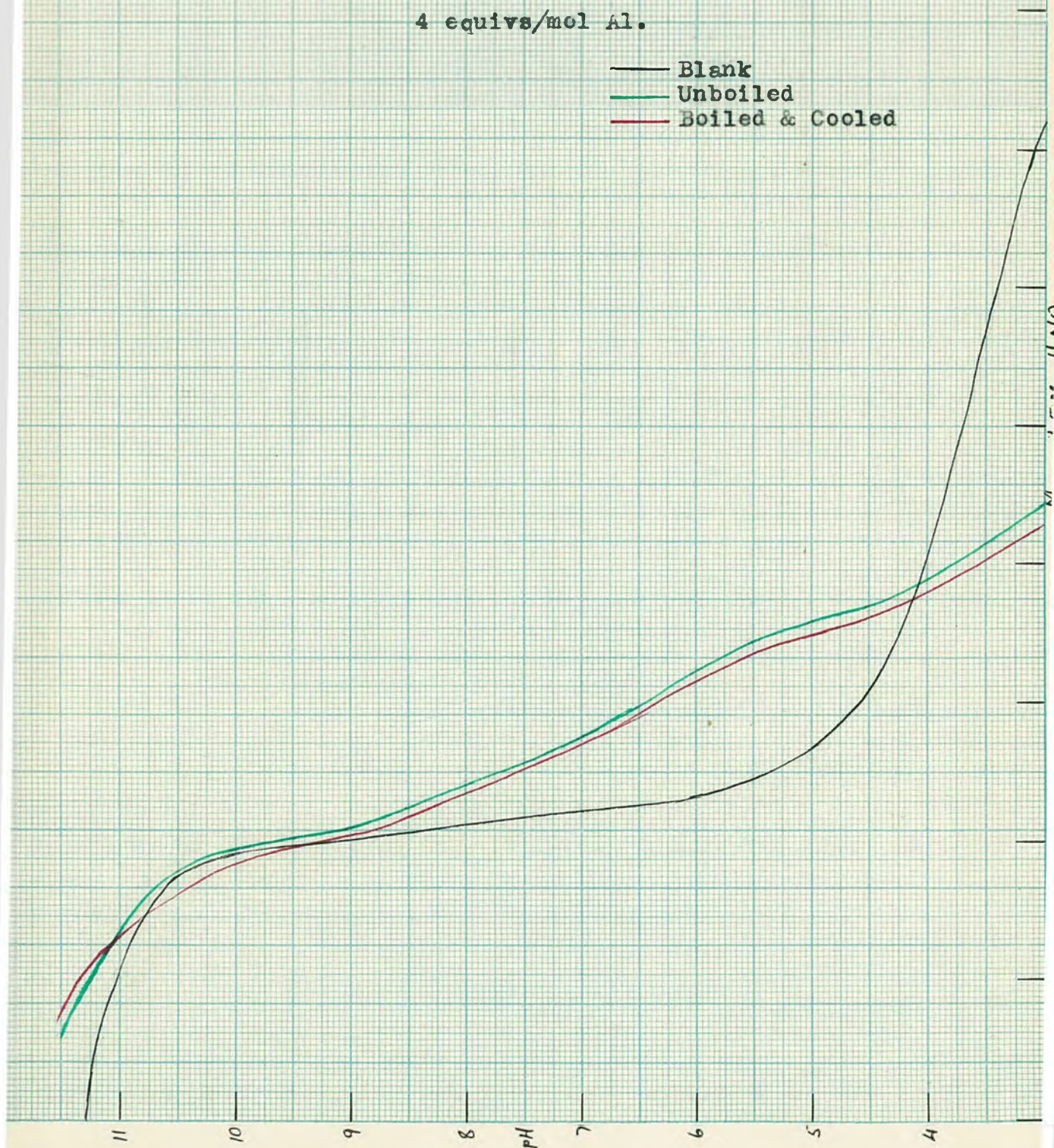


GRAPH 11.

SODIUM POTASSIUM TARTRATE SERIES (CONCENTRATED).

4 equivs/mol Al.

— Blank
— Unboiled
— Boiled & Cooled

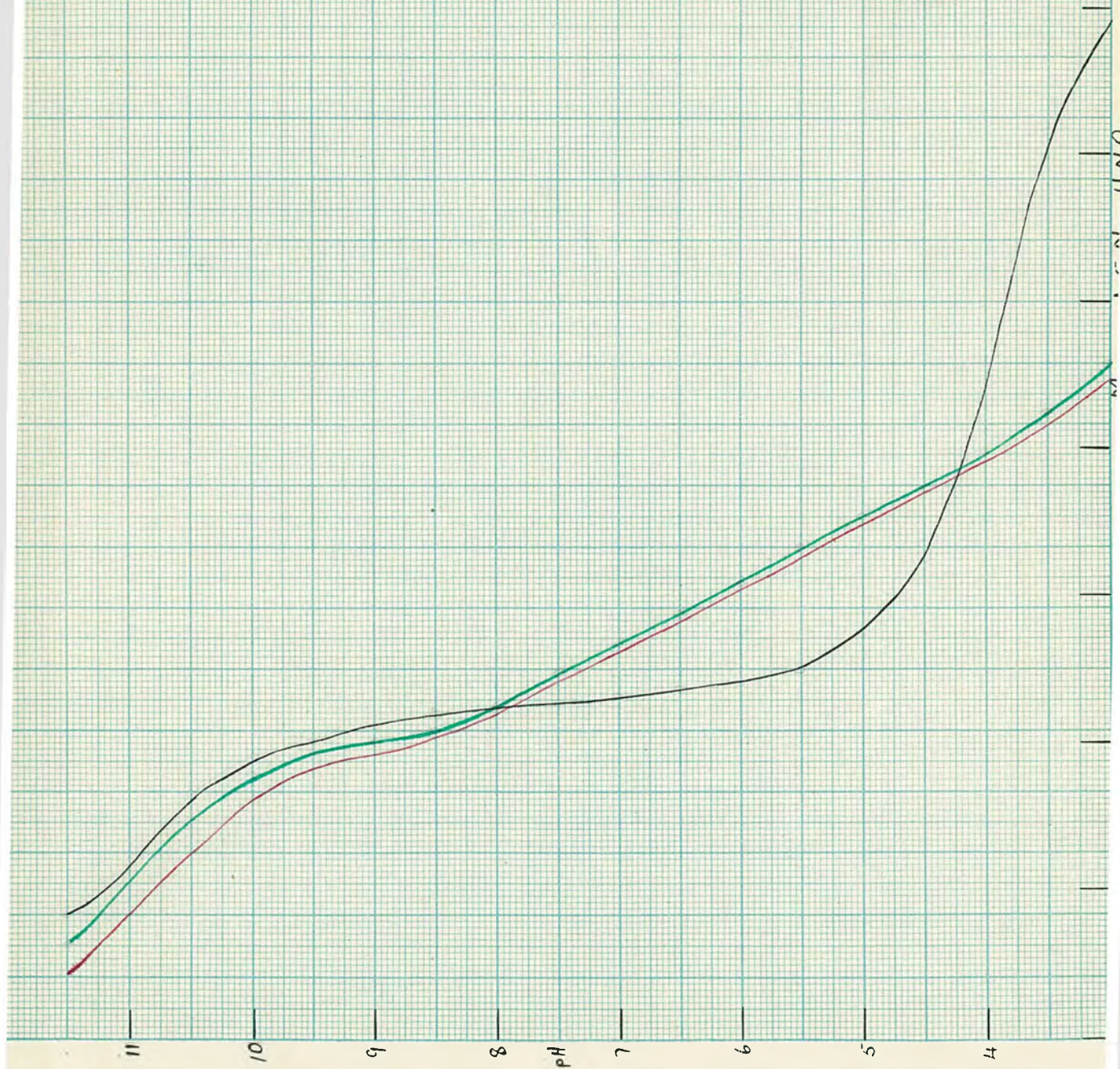


GRAPH 12.

SODIUM POTASSIUM TARTRATE SERIES (DILUTE).

4 equivs/mol Al.

Blank
Unboiled
Boiled & Cooled

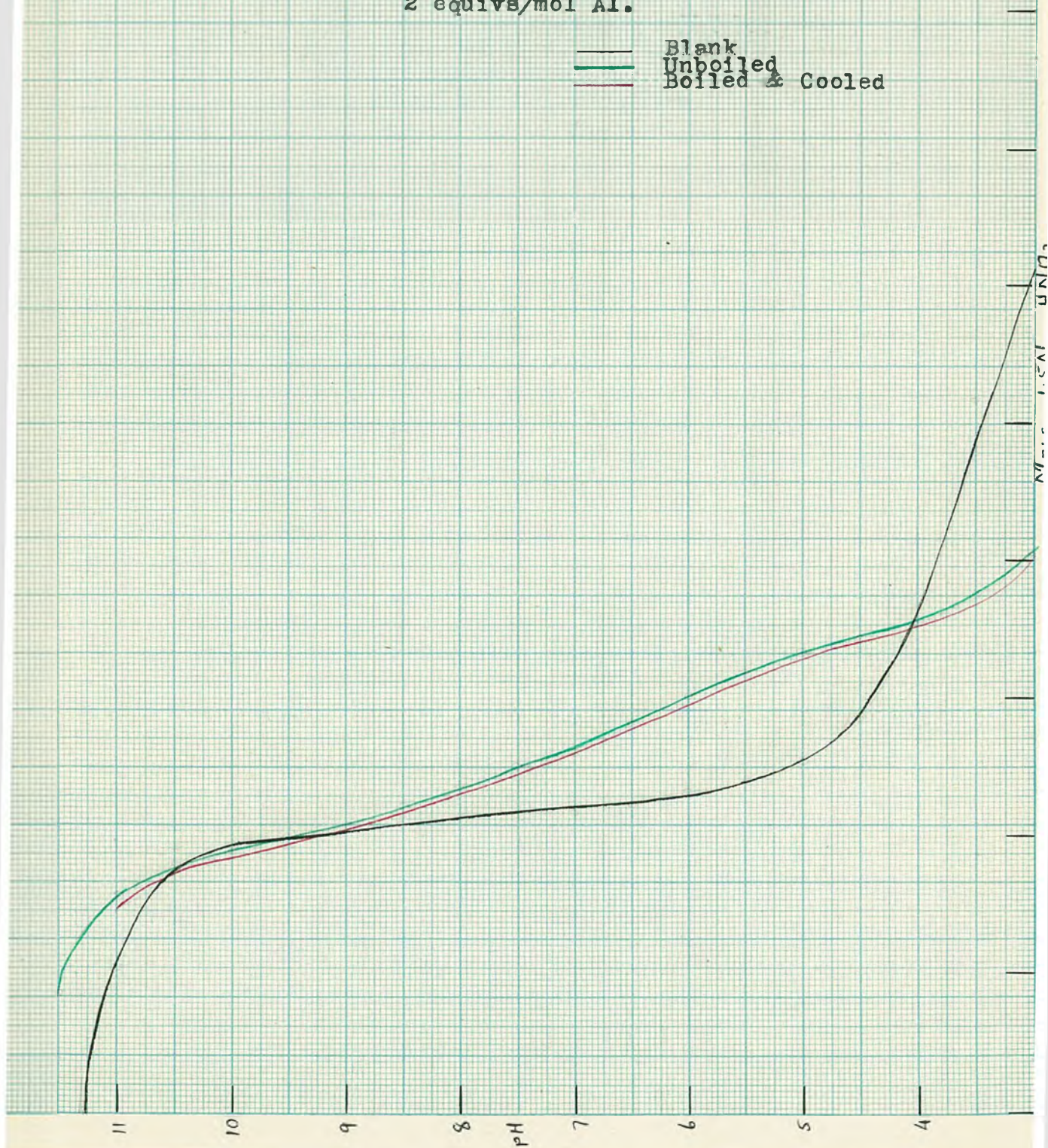


GRAPH 13.

SODIUM POTASSIUM TARTRATE SERIES (CONCENTRATED).

2 equivs/mol Al.

— Blank
— Unboiled
— Boiled & Cooled

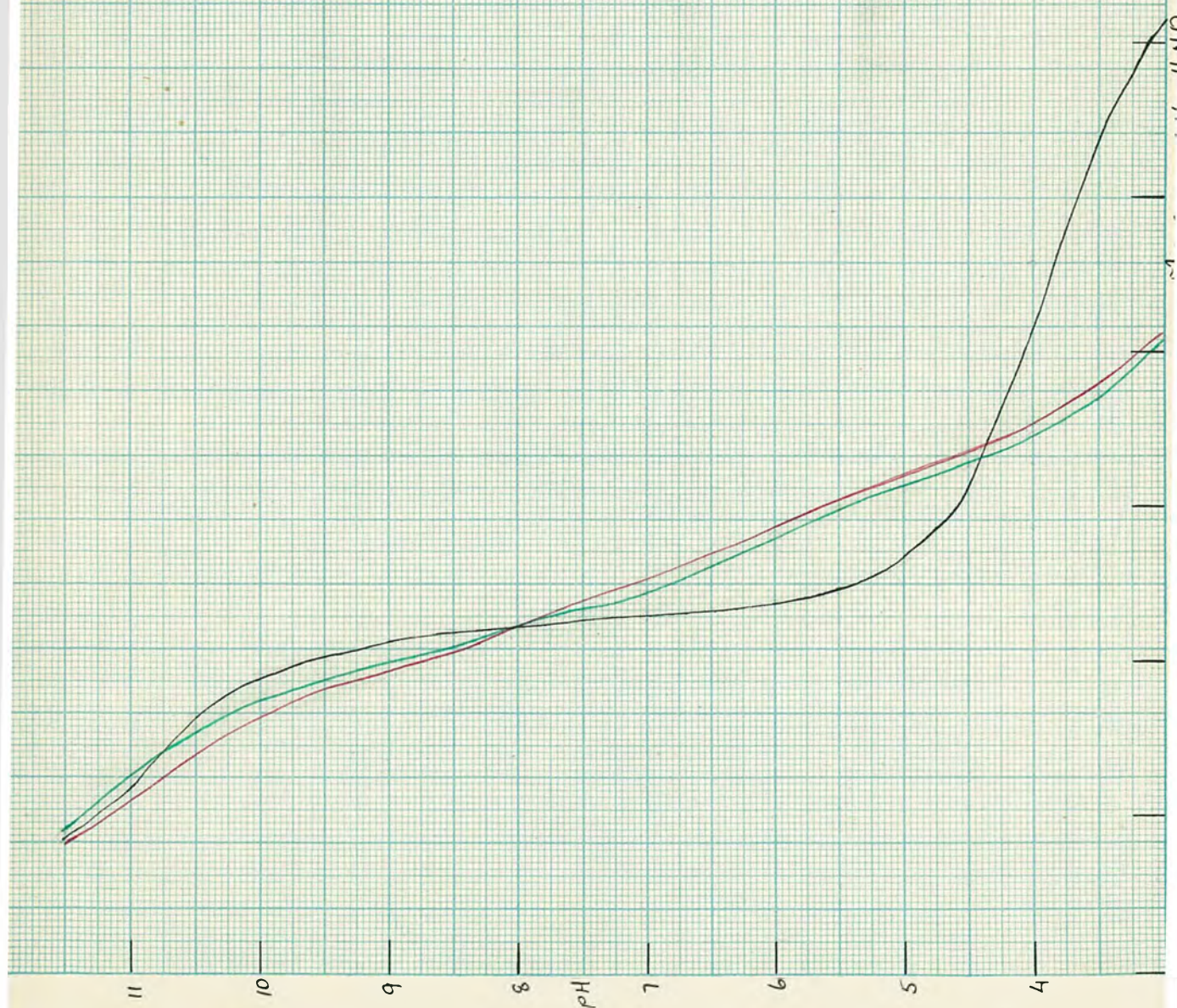


GRAPH 14.

SODIUM POTASSIUM TARTRATE SERIES (DILUTE).

2 equivs/mol Al.

— Blank
— Unboiled
— Boiled & Cooled

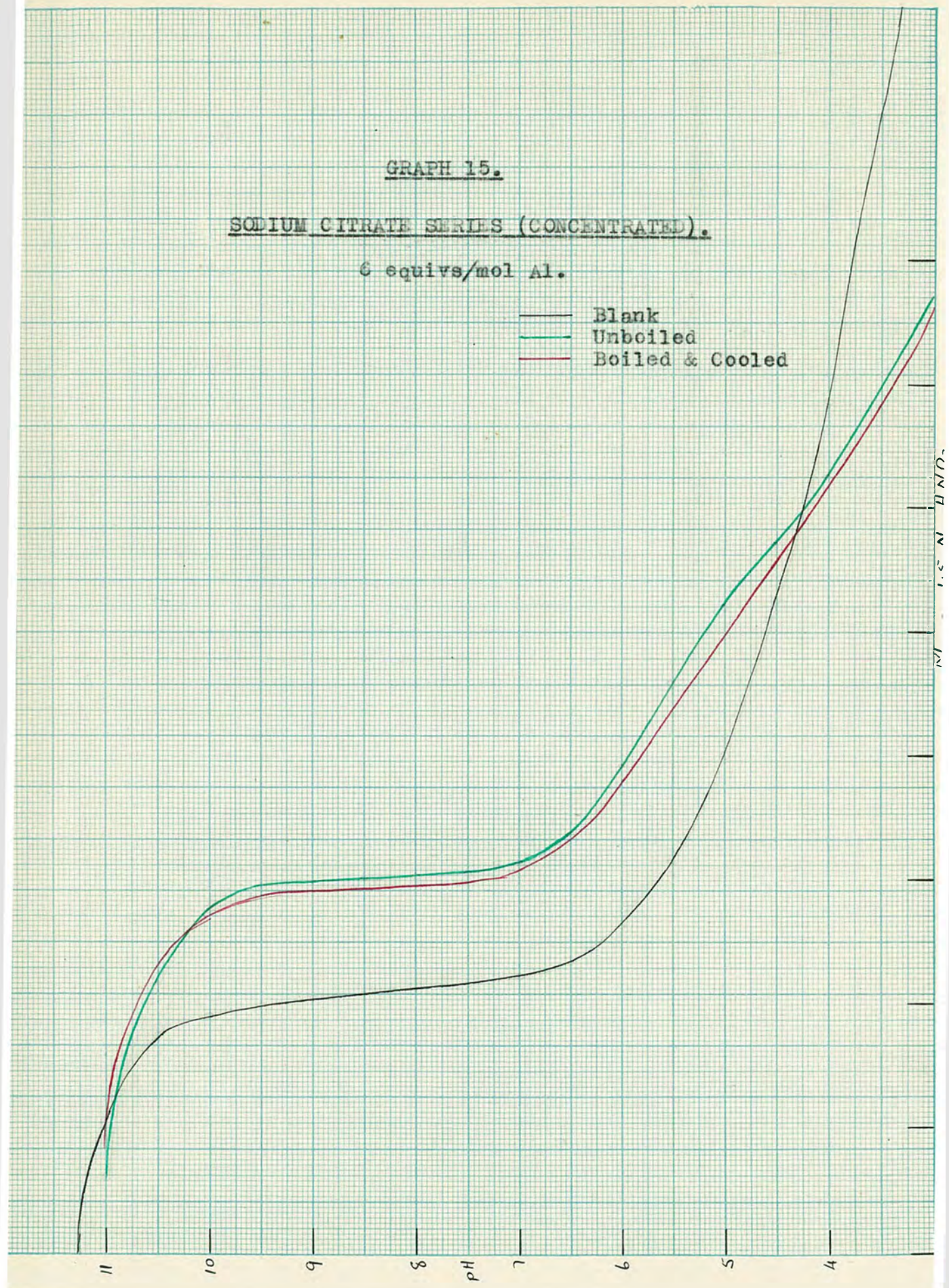


GRAPH 15.

SODIUM CITRATE SERIES (CONCENTRATED).

6 equivs/mol Al.

- Blank
- Unboiled
- Boiled & Cooled

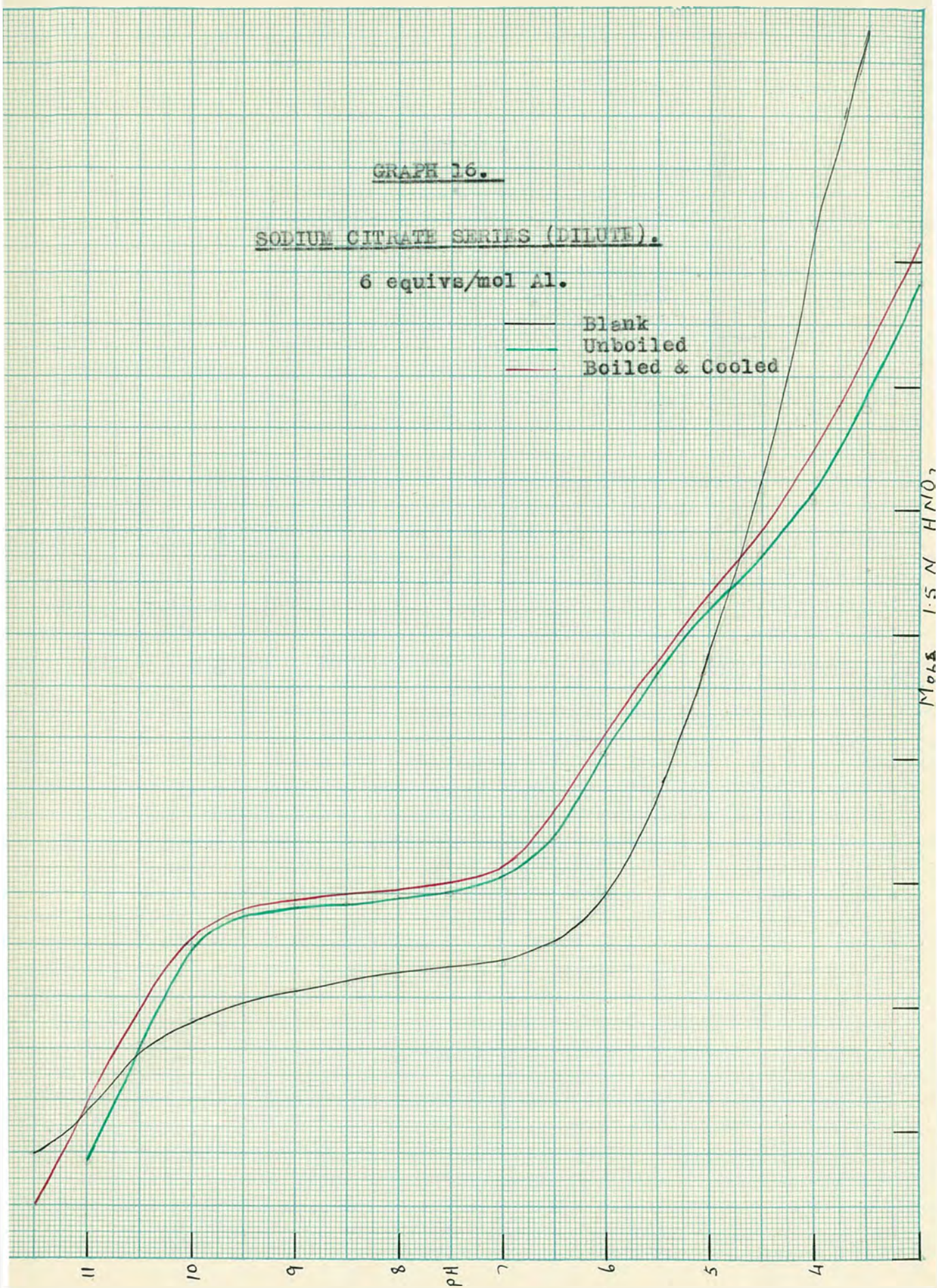


GRAPH 16.

SODIUM CITRATE SERIES (DILUTE).

6 equivs/mol Al.

Blank
Unboiled
Boiled & Cooled

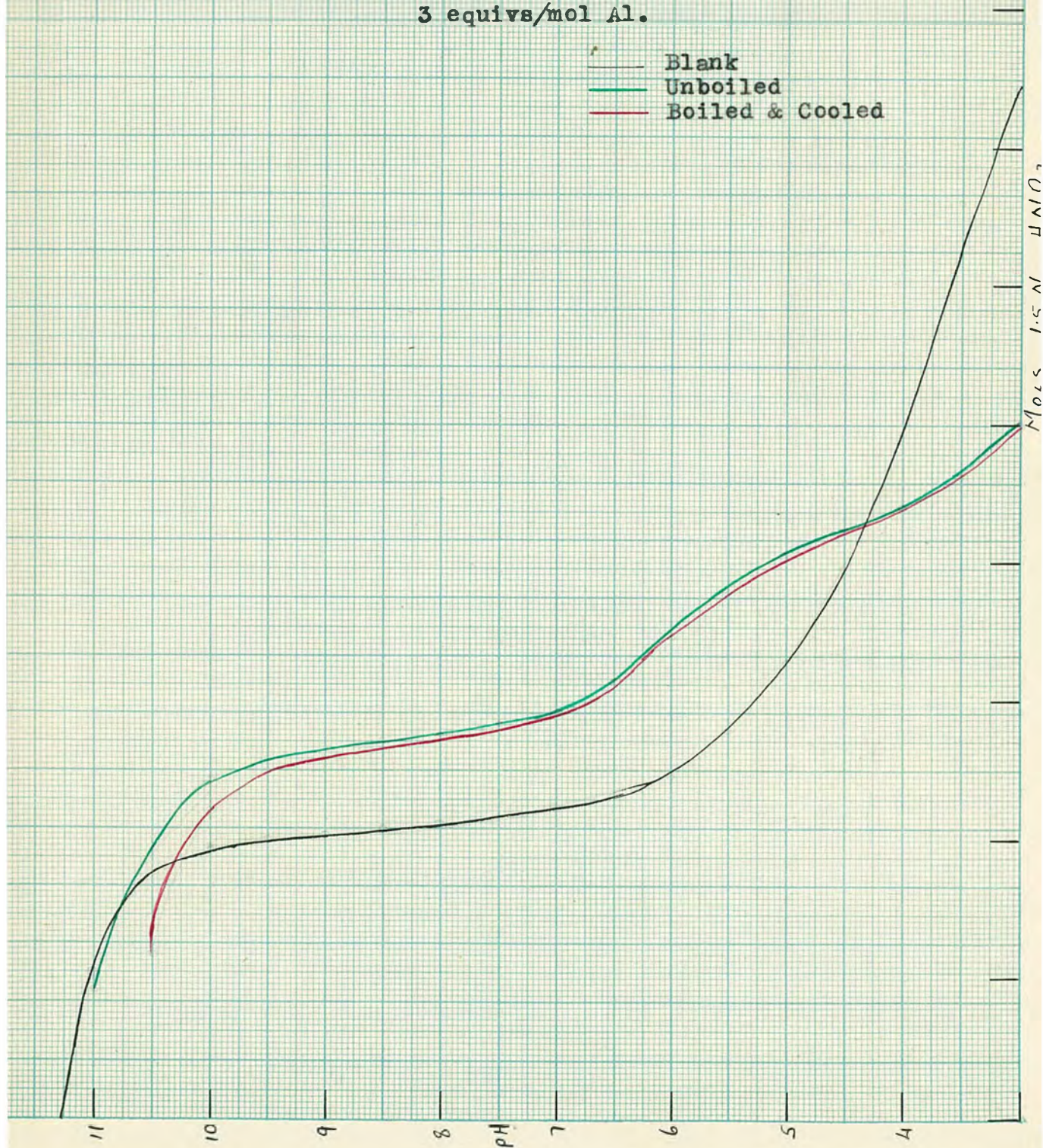


GRAPH 17.

SODIUM CITRATE SERIES (CONCENTRATED).

3 equivs/mol Al.

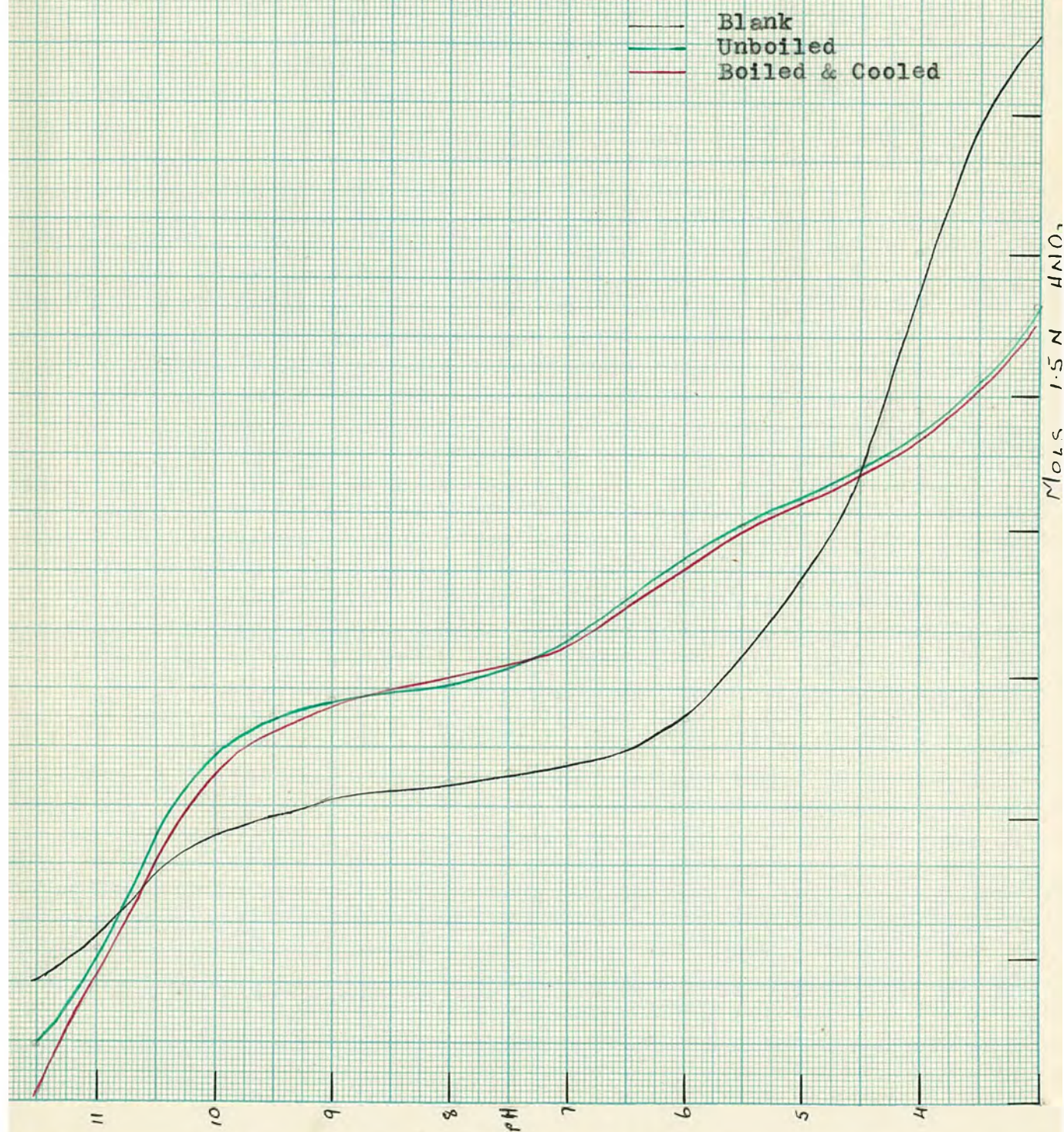
Blank
Unboiled
Boiled & Cooled



GRAPH 18.

SODIUM CITRATE SERIES (DILUTE).

3 equivs/mol Al.

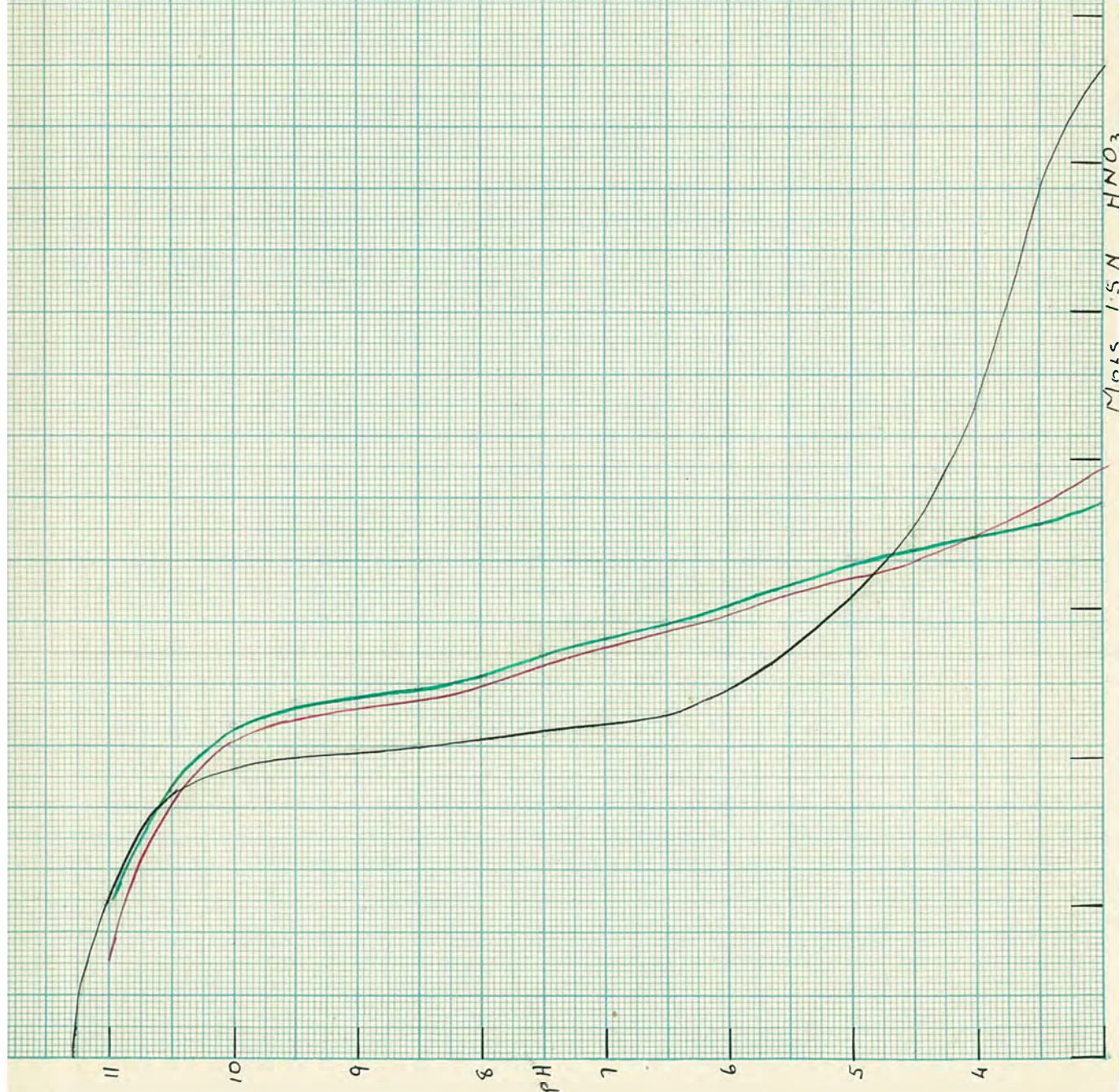


GRAPH 19.

SODIUM CITRATE SERIES (CONCENTRATED).

2 equivs/mol Al.

— Blank
— Unboiled
— Boiled & Cooled



GRAPH 20.

SODIUM CITRATE SERIES (DILUTE).

2 equivs/mol Al.

Blank
Unboiled
Boiled & Cooled

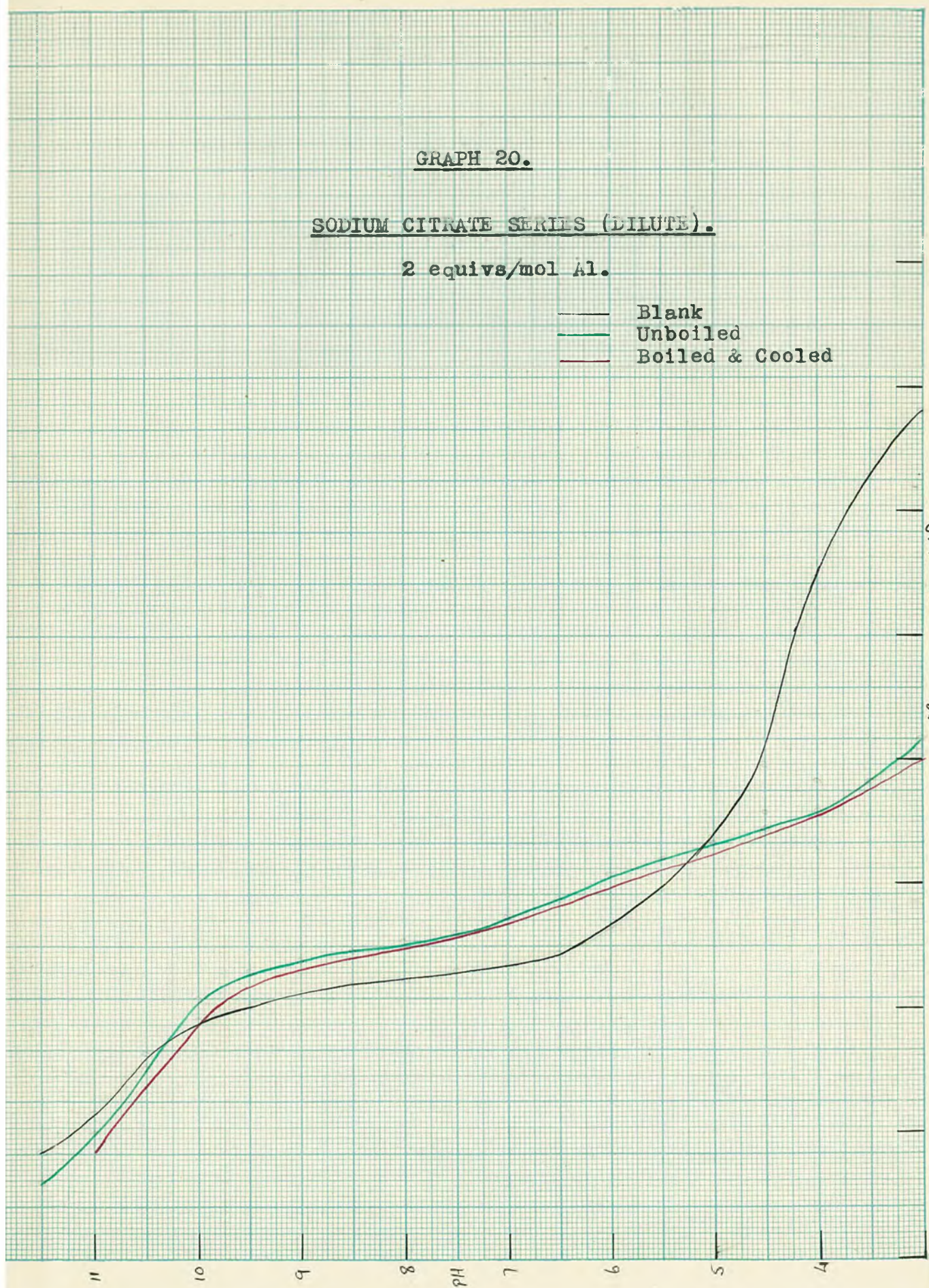


TABLE 1

for Graph 1

pH	NaAlO ₂	Na For- mate.	Blank Total	Unboiled	Boiled	Difference	
				Na AlO ₂ Na Form- ate.	NaAlO ₂ Na For- mate.	Unboiled	Boil
12			-	-	-		
11.5							
11	25		25				
10.5	42		42	32	17	-25	-25
10	46		46	46	42	-2.5	-4
9.5	48		48	52	45	5	-3
9	49		49	53	47	4	-2
8.5	50		50	53	47	3	-3
8	51		51	53	47	2	-4
7.5	51.5	0.5	52	53	48	1	-4
7	52	1	53	53	49	0	-4
6.5	53	1	54	55	51	1	-3
6	54.5	2	56.5	56.5	54	0	-2.
5.5	55.5	2.5	58	59	58	1	0
5	56.5	6	62.5	64	64	2	2
4.5	59	16.5	75.5	77	72.5	1.5	-3
4	70	36.5	106.5	103	92.5	-3.5	-14
3.5	98	72.5	170.5	162	162	-8.5	-8.
3	107	117	224				

TABLE 2.

for Graph 2

pH	NaAlO ₂	Na For- mate	Blank Total	Unboiled	Boiled	Difference	
				Na Al O ₂ Na Form- ate.	Na Al O ₂ Na For mate.	Unboiled	Boiled
12			-	-	-		
11.5	4.0		4.0				
11	5.6		5.6	1.5		-4.1	
10.5	7.9		7.9	3.0	2.3	-4.9	-5.6
10	9.1		9.1	8.0	7.0	-1.1	-2.1
9.5	9.7		9.7	10.2	9.2	0.5	-0.5
9	10.2		10.2	11.2	9.8	1.0	-0.4
8.5	10.5		10.5	11.7	10.0	1.2	-0.5
8	10.7		10.7	12.0	10.1	1.3	-0.6
7.5	10.9	.1	11.0	12.0	10.3	1.0	-0.7
7	11.0	.2	11.2	12.0	10.7	0.8	-0.5
6.5	11.1	.3	11.4	12.0	11.2	0.6	-0.2
6	11.2	.3	11.5	12.0	12.0	0.5	0.5
5.5	11.4	.5	11.9	12.1	12.5	0.2	0.6
5	11.8	1.3	13.1	13.5	14.0	0.4	0.9
4.5	13.0	3.4	16.4	16.7	16.8	0.3	0.4
4	18.5	8.0	26.5	22.0	22.5	-4.5	-4.0
3.5	20.7	16.2	36.9	31.0	31.5	-5.9	-5.4
3	21.6	24.2	45.8	44.0	46.2		

TABLE 3.

for Graph 3.

pH	Na Al O ₂			Na Ace- tate.	Blank Total.	Unboiled	Boiled	Difference	
						Na Al O ₂ Na Acet- ate.	Na Al O ₂ Na Acet- ate.		
12					-	-	-		
11.5									
11	25				25				
10.5	42				42	20	33	-22	-9
10	46				46	43	42.5	-3	-3.5
9.5	48				48	47.5	47	-0.5	-1
9	49				49	48.5	50	-0.5	1
8.5	50				50	49	51.5	-1	1.5
8	51		0.5		51.5	49.5	53	-2	1.5
7.5	51.5		1		52.5	50	54	-2.5	1.5
7	52		1		53	50.5	55	-2.5	2
6.5	53		3		56	53.5	58	-2.5	2
6	54.5		8.5		63	62	66	-1	3
5.5	55.5		21		76.5	79	80	2.5	3.5
5	56.5		49		105.5	104	104.5	-1.5	-1
4.5	59		84		143	143	146	0	3
4	70		120		190	184	187	-6	-3
3.5	98		147.5		245.5				
3	107								

TABLE 4.

for Graph 4.

pH	Na Al O ₂	Na Ace- tate.	Blank Total	Unboiled	Boiled	Difference	
				Na Al O ₂ Na Acet- ate.	Na Al O ₂ Na Acet- ate.	Unboiled	Boiled
12			-	-	-		
11.5	4.0		4.0				
11	5.6		5.6		1.0		4.6
10.5	7.9		7.9	3.0	3.8	-4.9	-4.1
10	9.1		9.1	7.1	7.7	-2.0	-1.4
9.5	9.7		9.7	8.3	9.3	-1.4	-0.4
9	10.2		10.2	9.4	10.3	-0.8	0.1
8.5	10.5		10.5	9.8	10.7	-0.7	0.2
8	10.7	0.1	10.8	10.3	10.9	-0.5	0.1
7.5	10.9	0.2	11.1	10.7	11.1	-0.4	0
7	11.0	0.4	11.4	11.1	11.4	-0.3	0
6.5	11.1	0.6	11.7	11.7	12.0	0	0.3
6	11.2	1.4	12.6	12.5	13.0	-0.1	0.4
5.5	11.4	3.6	15.0	15.0	15.8	0	0.8
5	11.8	9.1	20.9	20.5	21.3	-0.4	0.4
4.5	13.0	17.6	30.6	28.3	30.5	-2.3	-0.1
4	18.5	25.1	43.6	39.7	42.0	-3.9	-1.6
3.5	20.7	30.3	51.0	47.5	49.8	-3.5	-1.8
3	21.6	34.0	55.6				

TABLE 5.

for Graph 5.

pH	Na Al O ₂	Na Lac- tate.	Blank Total.	Unboiled	Boiled	Difference.	
				Na Al O ₂ Na Lac- tate.	Na Al O ₂ Na Lac- tate.		
12			-	-	-		
11.5							
11	25		25	5		-20.0	
10.5	42		42	40.5		-1.5	
10	46		46	45	42	-1.0	-4.
9.5	48		48	47	46	-1.0	-2.
9	49		49	50	48	1.0	-1.
8.5	50		50	56.5	52.5	6.5	2.
8	51		51	65	61	14.0	10.
7.5	51.5	1	52.5	72	68.5	19.5	16.
7	52	1	53	76.5	74.5	23.5	21.
6.5	53	1	54	79	78	25.0	24.
6	54.5	2	56.5	80.5	80.5	24.0	24.
5.5	55.5	4	59.5	83.5	83	24.0	23.
5	56.5	11	67.5	88	87	20.5	19.
4.5	59	26	85	98	96	13.0	11.
4	70	56	126	117.5	114.5	-8.5	-11.
3.5	98	96	194	150	144.5	-44.0	-49.
3	107	130	237	182	178	-55.0	-59.

TABLE 6.

for Graph 6.

pH	Na Al O ₂	Na Lac- tate.	Blank Total.	Unboiled Boiled		Difference	
				Na Al O ₂ Na Lac- tate.	Na Al O ₂ Na Lac- tate.	Unboiled	Boil
12			-	-	-		
11.5	4.0		4.0	0.1		-3.9	
11	5.6		5.6	5.6	3.1	0	-2.5
10.5	7.9		7.9	7.3	6.1	-0.6	-1.2
10	9.1		9.1	8.4	7.6	-0.7	-1.5
9.5	9.7		9.7	8.9	8.5	-0.8	-1.2
9	10.2		10.2	9.5	9.0	-0.7	-1.2
8.5	10.5		10.5	10.2	9.7	-0.3	-0.8
8	10.7		10.7	11.3	10.5	0.6	-0.2
7.5	10.9		10.9	12.8	11.7	1.9	0.8
7	11.0	0.1	11.1	14.1	13.1	3.0	2.0
6.5	11.1	0.2	11.3	15.1	14.3	3.3	3.0
6	11.2	0.4	11.6	16.1	15.1	4.5	3.5
5.5	11.4	0.9	12.3	16.8	16.0	4.5	3.5
5	11.8	2.2	14.0	18.2	17.2	4.2	3.2
4.5	13.0	5.6	18.6	21.0	19.4	2.4	0.8
4	18.5	12.1	30.6	25.2	23.6	-5.4	-7.0
3.5	20.7	21.2	41.9	32.3	30.8	-9.6	-11.5
3	21.6	27.8	49.4	38.5	36.8	-10.9	-12.0

TABLE 7.

for Graph 7.

pH	Na Al O ₂			Blank Total.	Unboiled			Boiled			Difference:	
	Na	Al	O ₂		Na	Al	O ₂	Na	Al	O ₂	Unboiled	Boi
12					-			-				
11.5												
11		25			25							
10.5		42			42		32		34		-10	-8
10		46			46		42		42		-4	-4
9.5		48			48		46.5		46		-1.5	-2
9		49			49		48.5		48		-0.5	-1
8.5		50			50		50.5		50.5		0.5	0.
8		51			51		54.5		55		3.5	4
7.5		51.5		0.5	52		58.5		59.5		6.5	7.
7		52		1	53		64.5		64.5		11.5	11.
6.5		53		1.5	54.5		69.5		68.5		15	14
6		54.5		2	56.5		74		72.5		17.5	16
5.5		55.5		3	58.5		76.5		76		18	17.
5		56.5		6	62.5		79.5		80.5		17	18
4.5		59		14	73		85.5		86.5		12.5	13.
4		70		29.5	99.5		98		97		-1.5	-2.
3.5		98		50	148		112		113		-36	-35
3		107		66.5	173.5		130		130		-43.5	-43.

TABLE 8.

for Graph 8.

pH	Na Al O ₂	Na Lac- tate.	Blank Total.	Unboiled	Boiled	Difference	
				Na Al O ₂ Na Lac- tate.	Na Al O ₂ Na Lac- tate.	Unboiled	Boiled
12			-	-	-		
11.5	4.0		4.0				
11	5.6		5.6	4.1	4.2	-1.5	-1.4
10.5	7.9		7.9	5.5	5.9	-2.4	-2.0
10	9.1		9.1	7.8	7.9	-1.2	-1.2
9.5	9.7		9.7	9.2	9.3	-0.5	-0.4
9	10.2		10.2	9.7	9.7	-0.5	-0.5
8.5	10.5		10.5	10.0	10.0	-0.5	-0.5
8	10.7		10.7	10.3	10.2	-0.4	-0.5
7.5	10.9		10.9	10.7	10.6	-0.2	-0.2
7	11.0	0.1	11.1	11.1	11.1	0	0
6.5	11.1	0.1	11.2	11.6	11.9	0.4	0.7
6	11.2	0.2	11.4	12.2	12.8	0.8	1.4
5.5	11.4	0.6	12.0	13.3	14.0	1.3	2.0
5	11.8	1.2	13.0	14.6	15.6	1.6	2.0
4.5	13.0	3.1	16.1	18.7	17.6	0.6	1.1
4	18.5	6.3	24.8	20.0	20.1	-4.8	-4.1
3.5	20.7	11.1	31.8	23.6	23.6	-8.2	-8.1
3	21.6	14.1	35.7	28.0	28.4	-7.7	-7.1

TABLE 9.

for Graph 9.

pH	Na Al O ₂	Na K Tartrate	Blank Total.	Unboiled	Boiled	Difference.	
				Na Al O ₂ Na K Tartrate	Na Al O ₂ Na K Tartrate	Unboiled	Boiled
12			-	-	-		
11.5				27.5	40.5		
11	25		25	38.5	43.5	13.5	18.5
10.5	42		42	42	44.5	0	2.5
10	46		46	44	44.5	-2	-1.5
9.5	48		48	46.5	45.5	-1.5	-2.5
9	49		49	48.5	47	-0.5	-2
8.5	50		50	52	50	2	0
8	51		51	56	52.5	5	1.5
7.5	51.5		51.5	60.5	56.5	9	5.5
7	52	1	53	66.0	61	13	8
6.5	53	2	55	72.5	67	17.5	12
6	54.5	3	57.5	79.5	72.5	22	15
5.5	55.5	6	61.5	83.5	77.5	22	15.5
5	56.5	13	69.5	86.5	83	17	13.5
4.5	59	29	88	91	91	3	3
4	70	53	123	100	105.5	-23	-17.5
3.5	98	78	176	111.5	126	-65.5	-50
3	107	104	211	127	151.5	-84	59.5

TABLE 10.

for Graph 10.

pH	Na Al O ₂	Na K Tartrate	Blank Total.	Unboiled	Boiled	Difference.	
				Na Al O ₂ Na K Tartrate	NaAl O ₂ Na K Tartrate	Unboiled	Boiled
12			-	-	2.8		
11.5	4.0		4.0	3.4	6.6	-0.6	2.6
11	5.6		5.6	5.6	7.7	0	2.1
10.5	7.9		7.9	7.1	8.2	-0.8	0.3
10	9.1		9.1	7.7	8.6	-1.4	-0.5
9.5	9.7		9.7	8.1	8.9	-1.6	-0.8
9	10.2		10.2	8.7	9.4	-1.5	-0.8
8.5	10.5		10.5	9.5	10.1	-1.0	-0.4
8	10.7		10.7	10.3	10.8	-0.4	0.1
7.5	10.9		10.9	11.3	11.6	0.4	0.7
7	11.0	0.2	11.2	12.2	12.6	1.0	1.4
6.5	11.1	0.4	11.5	13.9	13.9	2.4	2.4
6	11.2	0.6	11.8	15.6	14.8	3.8	3.0
5.5	11.4	1.2	12.6	16.6	15.8	4.0	3.2
5	11.8	2.6	14.4	17.4	17.1	3.0	2.5
4.5	13.0	5.3	18.3	18.5	19.0	0.2	0.7
4	18.5	10.6	29.1	20.7	22.4	8.4	6.7
3.5	20.7	15.6	36.3	23.6	27.3	12.7	-9.0
3	21.6	20.8	42.2	27.1	33.0	15.1	-9.3

TABLE 11.

for Graph 11.

pH	NaAlO ₂	NaK Tartrate.	Blank Total.	Unboiled	Boiled	Difference.	
				Na AlO ₂ NaK Tartrate.	NaAl O ₂ Na K Tartrate	Unboiled	Boiled
12			-	-	-		
11.5				14	17		
11	25		25	32.5	32.5	7.5	7.5
10.5	42		42	41.5	39	-0.5	-3
10	46		46	46.5	43	0.5	-3
9.5	48		48	49	45	1	-3
9	49		49	50.5	48	1.5	-1
8.5	50		50	54	51.5	4	1.5
8	51		51	58	55.5	7	4.5
7.5	51.5		51.5	61.5	58.5	10	7
7	52	0.5	52.5	66	62.5	13.5	10
6.5	53	1	54	71	68.5	17	14.5
6	54.5	1.5	56	77.5	75	21.5	19
5.5	55.5	3	58.5	82.5	80	24	21.5
5	56.5	6	62.5	85.5	83	23	20.5
4.5	59	14	73	88.5	86	15.5	13
4	70	26	96	93	90	-3	-6
3.5	98	39	137	99	96	-38	-41
3	107	52	159	106	103	-53	-56

TABLE 12.

for Graph 12.

pH	Na Al O ₂	Na K Tartrate	Blank Total.	Unboiled		Boiled		Unboiled	Boiled
				Na K Tartrate	Na Al O ₂	Na K Tartrate	Na Al O ₂		
12			-	-	-	-	-		
11.5	4.0		4.0	3.0	2.1	-1.0	-1.9		
11	5.6		5.6	5.2	4.1	-0.4	-1.5		
10.5	7.9		7.9	7.2	6.1	-0.7	-1.8		
10	9.1		9.1	8.5	7.7	-0.6	-1.4		
9.5	9.7		9.7	9.3	8.5	-0.4	-1.2		
9	10.2		10.2	9.6	8.9	-0.6	-1.3		
8.5	10.5		10.5	10.0	9.6	-0.5	-0.9		
8	10.7		10.7	10.8	10.4	0.1	-0.3		
7.5	10.9		10.9	11.9	11.5	1.0	0.6		
7	11.0	0.1	11.1	12.8	12.4	1.7	1.4		
6.5	11.1	0.2	11.3	13.8	13.4	2.5	2.1		
6	11.2	0.3	11.5	14.8	14.6	3.3	3.1		
5.5	11.4	0.6	12.0	16.0	16.0	4.0	4.0		
5	11.8	1.3	13.1	17.0	16.9	3.9	3.8		
4.5	13.0	2.6	15.6	17.9	17.7	2.3	2.1		
4	18.5	5.3	23.8	19.1	18.9	-4.7	-4.9		
3.5	20.7	7.8	28.5	20.4	20.4	-8.1	-8.1		
3	21.6	10.4	32.0	22.0	22.1	-10.0	-9.9		

TABLE 13.

for Graph 13.

pH	NaAlO ₂	NaKTartrate.	Blank Total.	Unboiled	Boiled	Difference.	
				NaAlO ₂ NaKTartrate	NaAlO ₂ NaKTartrate	Unboiled	Boiled
12			-	-	-		
11.5				20.5			
11	25		25	38	34	13	9
10.5	42		42	43	40	1	-2
10	46		46	46.5	45	-0.5	-1
9.5	48		48	48	47.5	0	-0.5
9	49		49	50	49	1	0
8.5	50		50	53	51	3	1
8	51		51	56.5	55.5	5.5	4.5
7.5	51.5		51.5	60	59	8.5	7.5
7	52		52	62.5	62	10.5	10
6.5	53	0.5	53.5	67.5	66.5	14	13
6	54.5	1	55.5	72.5	71.5	17	16
5.5	55.5	2	57.5	77	76	19.5	18.5
5	56.5	4.5	61	80	78.5	19	17.5
4.5	59	9.5	68.5	82.5	81.5	14	13
4	70	17.5	87.5	85	84	-2.5	-3.5
3.5	98	26	124	90	89	-34	-35
3	107	35	142	97	96	-45	-46

TABLE 14.

for Graph 14.

pH	Na Al O ₂	Na K Tartrate	Blank Total.	Unboiled Na Al O ₂ Na K Tar- trate.	Boiled Na Al O ₂ Na K Tar- trate.	Difference.	
						Unboiled	Boiled
12			-	-	-		
11.5	4.0		4.0	4.3	2.8	0.3	-1.2
11	5.6		5.6	6.0	5.1	0.4	-0.5
10.5	7.9		7.9	7.5	6.6	-0.4	-1.3
10	9.1		9.1	8.5	7.9	-0.6	-1.2
9.5	9.7		9.7	9.0	8.7	-0.7	-1.0
9	10.2		10.2	9.6	9.2	-0.6	-1.0
8.5	10.5		10.5	10.2	9.9	-0.3	-0.6
8	10.7		10.7	10.6	10.5	-0.1	-0.2
7.5	10.9		10.9	11.1	10.9	0.2	0
7	11.0		11.0	11.7	11.5	0.7	0.5
6.5	11.1	0.1	11.2	12.5	12.4	1.3	1.2
6	11.2	0.2	11.4	13.5	13.7	2.1	2.3
5.5	11.4	0.4	11.8	14.4	14.6	2.6	2.8
5	11.8	0.9	12.7	15.0	15.3	2.3	2.6
4.5	13.0	1.7	14.7	15.6	16.0	0.9	1.3
4	18.5	3.5	22.0	16.7	16.9	-5.3	-5.5
3.5	20.7	5.2	25.9	17.8	18.0	-8.1	-7.9
3	21.6	6.9	28.5	19.6	19.6	-8.9	-8.9

TABLE 15.

for Graph 15.

pH	NaAlO ₂	Na Cit- rate.	Blank Total.	Unboiled	Boiled	Difference.	
				Na Al O ₂ Na Cit- rate.	Na Al O ₂ Na Cit- rate.	Unboiled	Boil
12			-	-	-		
11.5							
11	25		25	14.5	21.5	-10.5	-3.
10.5	42		42	52.5	57	10.5	15
10	46		46	67.5	64	21.5	18
9.5	48		48	71	66	23	18
9	49		49	72	68	23	19
8.5	50		50	72.5	68	22.5	18
8	51		51	73	69	22	18
7.5	51.5	0.5	52	73.5	69.5	21.5	17.
7	52	1.5	53.5	75.5	71.5	22.5	18
6.5	53	3	56	81	76.5	25	20.
6	54.5	8.5	63	94	88	31	25
5.5	55.5	20	75.5	110	102.5	34.5	27
5	56.5	40	96.5	125	112	28.5	15.
4.5	59	67.5	126.5	137	130.5	10.5	4
4	70	94.5	164.5	150	145	-14.5	-19.
3.5	98	121.5	219.5	163	161	-56.5	-58.
3	107	147.5	254.5	185	180	-69.5	-74.

TABLE 16.

for Graph 16.

pH	Na Al O ₂	Na Cit- rate.	Blank Total.	Unboiled	Boiled	Difference.	
				Na Al O ₂ Na Cit- rate.	NaAlO ₂ Na Cit- rate.	Unboiled	Boil
12			-	-	-		
11.5	4.0		4.0		2.0		-2.
11	5.6		5.6	3.6	6.6	-2.0	1.
10.5	7.9		7.9	8.2	11.1	0.3	3.
10	9.1		9.1	11.9	12.9	2.8	3.
9.5	9.7		9.7	13.1	13.6	3.4	3.
9	10.2		10.2	13.5	13.8	3.3	3.
8.5	10.5		10.5	13.6	13.8	3.1	3.
8	10.7		10.7	13.8	13.9	3.1	3.
7.5	10.9	0.2	11.1	14.0	14.1	2.9	3.
7	11.0	0.3	11.3	14.6	14.6	3.3	3.
6.5	11.1	1.0	12.1	16.2	16.3	4.1	4.
6	11.2	2.8	14.0	19.4	19.2	5.4	5.
5.5	11.4	6.3	17.7	22.4	22.5	5.7	4.
5	11.8	11.3	23.1	25.2	25.2	2.1	2.
4.5	13.0	16.4	29.4	27.1	27.8	-2.3	-1.
4	18.5	21.4	39.9	29.4	30.6	-10.5	-9.
3.5	20.7	26.5	47.2	32.7	34.0	-14.5	-13
3	21.6	32.0	53.6	37.6	40.0	-16.0	-13

TABLE 17.

for Graph 17.

pH	NaAlO ₂	Na Cit- rate.	Blank Total.	Unboiled		Boiled		Difference.	
				Na AlO ₂ Na Cit- rate.	Na AlO ₂ Na Cit- rate.	Na AlO ₂ Na Cit- rate.	Na AlO ₂ Na Cit- rate.	Unboiled	Boiled
12			-	-	-	-	-		
11.5									
11	25		25	22				-3	
10.5	42		42	46.5	28			4.5	-14
10	46		46	58.5	53			12.5	7
9.5	48		48	62	60.5			14	12.5
9	49		49	64	63			15	14
8.5	50		50	65	64.5			15	14.5
8	51		51	66	65			15	14
7.5	51.5	0.5	52	68	66.5			16	14.5
7	52	1.5	53.5	70.5	70			17	16.5
6.5	53	2.5	55.5	75.5	75			20	19.5
6	54.5	4.5	59	83	81.5			24	22.5
5.5	55.5	11.5	67	91	89.5			24	22.5
5	56.5	23	79	97.5	96			18.5	17.5
4.5	59	36	95	102	100			7	5
4	70	48.5	118.5	105.5	103.5			-13	-15
3.5	98	60.5	158.5	111	109			-47.5	-49.5
3	107	71.5	178.5	120	118			-58.5	-60.5

TABLE 18.

for Graph 18.

pH	Na Al O ₂	Na Cit- rate.	Blank Total.	Unboiled Na Al O ₂ Na Cit- rate.	Boiled NaAlO ₂ Na Cit rate.	Difference.	
						Unboiled	Boiled
12			-	-	-		
11.5	4.0		4.0	1.9	0.3	-2.1	-3.7
11	5.6		5.6	5.1	4.0	-0.5	-1.6
10.5	7.9		7.9	9.1	7.3	1.2	-0.6
10	9.1		9.1	11.8	11.1	2.7	2.0
9.5	9.7		9.7	13.0	12.5	3.3	2.8
9	10.2		10.2	13.6	13.3	3.4	3.1
8.5	10.5		10.5	13.9	13.9	3.4	3.4
8	10.7	0.1	10.8	14.1	14.3	3.3	3.8
7.5	10.9	0.2	11.1	14.7	15.0	3.6	3.9
7	11.0	0.4	11.4	15.7	15.8	4.3	4.4
6.5	11.1	0.8	11.9	17.0	16.8	5.1	4.9
6	11.2	1.3	13.0	18.4	18.3	5.4	5.1
5.5	11.4	3.6	15.0	19.6	19.5	4.6	4.1
5	11.8	5.8	17.6	20.4	20.4	2.8	2.8
4.5	13.0	3.1	21.1	21.5	21.2	0.4	0.3
4	13.5	10.4	23.9	22.6	22.3	-6.3	-6.6
3.5	20.7	12.5	33.2	24.4	23.8	-8.3	-9.4
3	21.6	14.6	36.2	27.0	26.0	-9.2	-10.1

TABLE 19.

for Graph 19.

pH	Na Al O ₂	Na Cit- rate.	Blank Total.	Unboiled	Boiled	Difference	
				Na Al O ₂ Na Cit- rate.	Na Al O ₂ Na Cit- rate.	Unboiled	Boil
12			-	-	-		
11.5							
11	25		25	24.5	15.5	-0.5	-9.
10.5	42		42	43	35.5	1	-6.
10	46		46	53.5	51	7.5	5
9.5	48		48	57	55	9	7
9	49		49	58.5	57	9.5	8
8.5	50		50	59.5	58.5	9.5	8.
8	51		51	61	59.5	10	8.
7.5	51.5	0.5	52	65	61	13	9
7	52	1	53	67.5	64	14.5	11
6.5	53	2	55	70	67	15	12
6	54.5	4.5	59	73	71	14	12
5.5	55.5	9.5	65	76.5	75.5	11.5	10.
5	56.5	17.5	74	80	79	6	5
4.5	59	26	85	82	81.5	-3	-3.
4	70	35	105	84	85	-21	-20
3.5	98	43	141	86	89	-55	-52
3	107	53	160	89	95	-71	-65

TABLE 20.

for Graph 20.

pH	NaAlO ₂	Na Cit- rate.	Blank Total.	Unboiled	Boiled	Difference:	
				Na Al O ₂ Na Cit- rate.	NaAlO ₂ Na Cit- rate.	Unboiled	Boiled
12			-	-	-		
11.5	4.0		4.0	2.9		-1.1	
11	5.6		5.6	4.8	3.9	-0.8	-1.8
10.5	7.9		7.9	7.3	5.6	-0.6	-2.3
10	9.1		9.1	10.0	8.5	0.9	-0.6
9.5	9.7		9.7	11.0	10.2	1.3	0.5
9	10.2		10.2	11.4	11.0	1.2	0.8
8.5	10.5		10.5	11.8	11.4	1.3	0.9
8	10.7		10.7	12.1	11.9	1.4	1.2
7.5	10.9	0.1	11.0	12.5	12.2	1.5	1.2
7	11.0	0.2	11.2	13.1	12.6	1.9	1.4
6.5	11.1	0.6	11.7	13.8	13.2	2.1	1.5
6	11.2	1.5	12.7	14.7	14.3	2.0	1.6
5.5	11.4	2.8	14.2	15.4	15.1	1.2	0.9
5	11.8	4.4	16.2	16.0	15.8	-0.2	-0.4
4.5	13.0	6.0	19.0	16.5	16.2	-2.5	-2.8
4	18.5	7.7	26.2	17.2	17.0	-9.0	-9.2
3.5	20.7	9.4	30.1	18.3	18.0	-11.8	-12.1
3	21.6	11.0	32.6	20.0	19.5	-12.6	-13.1

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