THE DETERMINATION OF SULFATES IN THE SPIN ACID BATH USED IN THE VISCOSE PROCESS FOR THE MANUFACTURE OF RAYON

A Thesis

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-H. L. G.

TABLE OF CONTENTS

Part Page

I

INTRODUCTION

A rapid accurate method for the determination of sulfates in the spin acid bath solution, used in the Viscose process of the manufacture of rayon has become particularly important in view of certain data which indicate the necessity of maintaining a definite sulfate content to act as a neutralizing bath. The action of the neutralizing bath is to harden each tiny stream of liquid viscose into a filament, which is drawn out of the solution and wound on the bobbins.

It is desired to have a relative simple and accurate method for the determination of sulfates in this solution, since the solution must be checked quite often to keep the sulfate content about constant. Because of this, it is necessary to use volumetric methods as much as possible. Gravimetric methods require greater time, together with the services of a laboratory balance, which is very delicate and subject to inaccuracies in the ordinary plant work. This method is the most accurate and is based on the precipitation of the sulfate ion by barium chloride, filtering, igniting and weighing in the form of barium sulfate.

The purpose of this investigation was to compare the accuracy of the recently published tetrahydroxyquinone method[6], the benzidine hydrochloride[10] and the turbidimetric method[2] with the gravimetric method[11] for the determination of sulfates in the spin acid bath in the Viscose process of the manufacture of rayon. The solutions on which this work was done, were spin bath solutions, made up by three frequently used formulas. In preparation for this investigation each method was studied by itself, and the technique of each step in the procedure was perfected.

II

HISTORICAL

A review of the chemical literature for the determination of sulfates shows that there are many methods, but most of these have the disadvantage of being time consuming or are too complicated for routine analysis. The methods which are suitable for a rapid determination of sulfates are considered in the present investigation. The suitable rapid methods may be classified according to the following classification: filtration methods, titration methods and turbidimetric methods.

The benzidine hydrochloride method[10] is the best known example of a filtration method. Benzidine ($C_{12}H_8(NH_2)_2$) is a weak organic base. In presence of strong mineral acids it forms stable salts, of which the sulfate is only slightly soluble in water. Aqueous solutions of the salts of this weak base undergo hydrolysis. An aqueous solution of benzidine hydrochloride behaves like a mixture of hydrochloric acid and benzidine, and the acid may be titrated with an alkali, using phenolphthalein as indicator. The insoluble benzidine sulfate formed in this method is filtered off, washed, suspended in water and the sulfuric acid is titrated with sodium hydroxide. There are several sources of error in the precipitation of sulfates by this method. The precipitate is slightly soluble and also absorbs some benzidine hydrochloride. These errors tend to counter balance each other, since they are in opposite directions. It has been found that this method gives excellent results in the analysis of all sulfates provided no substances are present which attack benzidine and provided the other salts and acids present are not too great.

Chromate salts[1] may be used in the determination of sulfates. The sulfate solution is treated with an excess of a hydrochloric acid solution of barium chromate in which barium sulfate is precipitated and chromic acid is set free. The solution is neutralized with ammonia or calcium carbonate and the excess of barium chromate is precipitated and can be filtered off with the barium sulfate. The free chromic acid is determined volumetrically by acidifying with hydrochloric acid, adding potassium iodide and titrating the liberated iodine with sodium thiosulfate solution. The barium chromate must be free from soluble chromate, soluble barium salts and soluble barium carbonate.

Carbonate salts[4], phosphate salts and oxalate salts may be used in a similar manner to the chromate salts, but the methods are complicated. These procedures are all long and require filtering, which gives evidence of the advantage of titration methods.

Titration methods are of two kinds: one in which outside indicators are used and the other in which internal indicators are used. The outstanding outside indicators[6] used to determine the end point are starch potassium iodide paper, congo red and ammonium dichromate, and benzidine paper. The method[3] in use at present at most rayon plants is the chromate method in which starch potassium iodide paper is used as outside indicator. In general the use of outside indicators is too slow and inaccurate for rapid routine analysis.

The most recent method, which promises to be accurate and rapid, was worked out in Germany. This method was furthered investigated by W.C.Schroeder[6] and is known as the tetrahydroxyquinone method for determination of sulfates. This method makes it possible to titrate the sulfate present in a sample directly with a standard barium chloride solution using tetrahydroxyquinone as indicator. The end point is indicated by the change in color from yellow to the appearance of a red barium salt of tetrahydroxyquinone. Tetrahydroxyquinone is not stable in water solutions, so it cannot be prepared and kept to be used later. It is ground up and mixed with a large amount of potassium chloride (ratio of 1-400) and a few tenths of a gram of the mixture is used as the indicator. In this form it is stable for over a year.

R. Strebinger and L.Von Zombory[9] determined sulfates by titrating barium chloride with .25N sulfuric acid by using 5-8 drops of a freshly prepared .2% solution of sodium rhodizonate as indicator. The color changes at the end point from red to yellow in a neutral solution and from red to colorless in acids. Direct titration Of sulfate with barium chloride in presence of this indicator is not possible, but an excess of a known volume of barium chloride may be added and the excess titrated.

In general, there are three types of turbidimetric methods[2] in use for the determination of sulfates. The first compares the turbidity of the sulfate solution with the turbidity in a known solution. The second measures the time required for a solution to become turbid after the precipitating agent has been added. The third measures the depth of turbid liquid required to make a light disappear when observed through the suspension. Various methods of this type depend upon the disappearance of a light filament when observed through the solution in which sulfates have been precipitated by barium chloride. The disadvantages of this method are: the range of concentration is quite limited, the method is influenced by other salts, requires a calibration curve and special equipment and the accuracy is doubtful.

The Betz-Hellige method[8] for the determination of sulfates is recommended where it is desirable to determine sulfates in concentrations below 100 p.p.m. The turbidimeter used in this determination compares a beam of light with the Tyndall effect produced from a lateral illumination of the solution by the same light. This method does away with the use of standard suspensions and their tedious preparation, thus simplifying the work and increasing the speed.

III

THEORETICAL

Since the gravimetric method is very accurate and free from serious interference, it is considered as being correct in this investigation and the other methods under consideration are compared with it as to accuracy. It was decided to select the three most promising methods for the determination of sulfates in concentrated solutions for this comparison. The three methods selected are representative of each of the three types of sulfate methods. They are benzidine hydrochloride (filtration method), tetrahydroxyquinone (titration method), and turbidimetric method using the Parr Turbidimeter.

The method in use at the present time is the chromate method[5] with starch potassium iodide paper as outside indicator. In this method the sample is diluted, neutralized with dilute sodium hydroxide and heated to boiling. A small excess of standard barium chloride is added from a burette and the solution is heated to boiling. The excess of barium chloride is back titrated with standard potassium chromate using starch potassium iodide paper as outside indicator. The end point is determined by allowing a drop of the solution to fall on the test paper so that the barium chromate remains concentrated in one spot while the clear solution spreads around it. A drop of very dilute hydrochloric acid is then spotted on to the paper so that the acid runs into the clear rim of the first spot. A blue color develops when an excess of soluble chromate is present, due to liberation of iodine and the action of this on starch.

The reactions involved in this method are as follows:

$$H_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O$$

$$\begin{matrix} Na_2SO_4 \\ MgSO_4 \end{matrix} + 2BaCl_2 = 2BaSO_4 + \begin{matrix} 2NaCl \\ MgCl_2 \end{matrix}$$

$$BaCl_2 + K_2CrO_4 = BaCrO_4 + 2KCl$$

$$K_2CrO_4 + 8HCl + 4KI = CrCl_3 + 6KCl + 4H_2O + 2I_2$$

The last reaction takes place on the test paper. The use of outside indicators makes the method slow and inaccurate, especially in concentrated solutions. It is also necessary to prepare and keep on hand a fresh supply of standard potassium chromate solution and standard barium chloride. For these reasons the method was not included in this investigation.

In the gravimetric method[11], which is the standard method, the solution is heated to boiling and the sulfate is precipitated by adding a few c.c. of a 10% solution of barium chloride. The solution is filtered and the precipitate is washed free of chlorides. The precipitate is placed in a weighed porcelain crucible and heated to 800 degrees centigrade for one hour and then the crucible is cooled and weighed. The percent sulfate is calculated from the barium sulfate present. The reactions involved in this method are:

$$\begin{matrix} H_2SO_4 \\ MgSO_4 \end{matrix} + 2BaCl_2 = 2BaSO_4 + \begin{matrix} 2H\ Cl \\ MgCl_2 \end{matrix}$$

In the benzidine hydrochloride method the benzidine hydrochloride is prepared by triturating 6.7 grams of the base in a mortar with water. This is added to a liter flask containing 20 c.c. of concentrated hydrochloric acid and the solution is diluted to the mark. The solution may be filtered and kept for further use. Benzidine hydrochloride will undergo hydrolysis and is decomposed as follows:

$$C_{12}H_8(NH_2)_2 . 2HCl + 2H_2O = 2HCl + C_{12}H_8(NH_2)_2(HOH)_2$$

The benzidine hydroxide breaks down into benzidine and water as follows:

$$C_{12}H_8(NH_2)_2(HOH)_2 = C_{12}H_8(N\ H_2)_2 + 2H_2O$$

From these equations it is evident that benzidine hydrochloride behaves like a mixture of hydrochloric acid and benzidine and the acid may be titrated with sodium hydroxide.

In the sulfate determination the following reaction takes place:

$$C_{12}H_8(NH_2)_2.2HCl + Na_2SO_4 = 2\ NaCl + C_{12}H_8(NH_2)_2.H_2SO_4$$

The insoluble precipitate is filtered off, washed with a small quantity of cold water, suspended in water and the sulfuric acid produced is titrated with a .1 normal sodium hydroxide solution.

In the tetrahydroxyquinone method for the determination of sulfates the tetrahydroxyquinone is made by treating glyoxal sodium bisulfite, prepared by treatment of acetaldehyde with nitric acid and sodium bisulfite, with a solution of sodium carbonate. It is not stable and must be mixed with a large amount of potassium chloride in the ratio of about 1-400, and used as a powder when needed.

In this method the sulfate solution is neutralized just to the acid side of phenolphthalein with potassium hydroxide. An excess of acid will destroy the indicator and an excess of base will give an interfering pink color with phenolphthalein. The temperature of the sample must be kept below 30 degrees centigrade to cause the barium sulfate to precipitate out faster and to prevent the destruction of the indicator. Alcohol is added to the neutral solution to make the barium sulfate more insoluble, so as to speed up the precipitation. In concentrated sulfate solutions sodium chloride is added to make the end point more definite. The end point is determined by a color change from yellow to rose. This change is slow and gradual but is definite and accurate if performed by carefully following the procedure. The indicator forms a rose colored salt with barium chloride and this marks the end point.

The turbidimetric method was performed by use of a Parr[2] Turbidimeter in which the sulfate is precipitated with barium chloride crystals. The solution is placed in a tube and the disappearance of a light filament marks the end point. A scale on the apparatus enables the operator to read the depth of the solution that is required to make the light disappear. This reading may be converted to p.p.m. of sulfates by referring the reading to a standard curve for sulfates. The whole procedure is based on the fact that a concentrated solution will require a small depth to make the light obscure, while a dilute sulfate solution will require a greater depth. The reactions involved are:

$$2BaCl_2 + \begin{matrix} H_2SO_4 \\ MgSO_4 \end{matrix} = 2BaSO_4 + \begin{matrix} 2HCl \\ MgCl_2 \end{matrix}$$

IV

EXPERIMENTAL

The first spin acid bath solution prepared was made by the [12]Courtoulds and Napper formula, consisting of sulfuric acid 10%, sodium sulfate 12%, zinc sulfate 1%, glucose 10% and water 67%. The second acid solution consisted of sulfuric acid 12%, sodium sulfate 20%, magnesium sulfate 35% and water 33%. The third acid solution consisted of sodium sulfate 16%, sulfuric acid 10%, magnesium sulfate 32%, and water 42%. The fourth acid solution used was of the same solution as number three, but it had been used in precipitating about 800 yards of rayon in the rayon laboratory. This solution was used to see if the methods under investigation were affected by the impurities collected by the acid bath in the precipitation of the rayon.

Since the investigation was carried out with strong sulfate solutions, it was necessary to first dilute the solutions. Ten c.c. of the original solution were diluted to 1000 cc. and this was used in all of the determinations for that solution. The gravimetric method was used on each solution first and then the other methods were employed and the results compared.

In the gravimetric method 50 cc. of the dilute solution (10cc. diluted to 1000cc.) were diluted to 350cc. and neutralized with ammonium hydroxide with methyl orange as indicator. One cc. of hydrochloric acid was added and the solution was heated to boiling on a hot plate. Fifteen cc. of a 10% solution of barium chloride was added slowly with constant stirring. The solution was allowed to stand on the hot plate over-night and filtered while still hot. The precipitate was washed with hot water until free of chlorides. The filter paper was allowed to dry in the funnel for ten minutes and then placed in an ignited, cooled, and weighed porcelain crucible. The precipitate was dried and ignited in a muffle furnace at a temperature of 800 degrees centigrade for one hour. The crucible was cooled and weighed as barium sulfate. The percent of sulfate was calculated from the weight of barium sulfate present.

In the benzidine hydrochloride method 5cc. of the original solution were diluted with water to 250 cc. of solution and 35 cc. of the benzidine hydrochloride solution were added with constant stirring. After ten minutes the precipitate was filtered off through a Witt perforated porcelain filter plate. The precipitate was washed with several portions of water. The precipitate and filter paper were transferred to a beaker with 100 cc. of water and heated to 50 degrees centigrade. A few drops of phenolphthalein were added and the solution was titrated with .1 normal sodium hydroxide. When the end point was nearly reached the solution was boiled and the titration completed. The color change is from colorless to pink.

In the tetrahydroxyquinone method for the determination of sulfates 25 cc. of the diluted solution was carefully neutralized to the acid side of phenolphthalein with potassium hydroxide. Twenty-five cc. of ethyl alcohol were added and the temperature was kept below 30 degrees centigrade. About two grams of sodium chloride were added to make the end point more definite. About .4 gram (1-2 dippers) of the tetrahydroxyquinone indicator were added, which gave the solution a yellow color. It was titrated with a standard dilute solution of barium chloride, to a rose color. The solution required much shaking and a low temperature. The number of cc. of barium chloride required for the titration and the normality of the barium chloride multiplied by the milli-equivalent of sulfate gives the weight of sulfate in the sample taken. This may be converted into p.p.m. by marking off six places to the right.

In the turbidimetric method 5 cc. of the dilute sulfate solution were taken and 25 cc. of the Reagent A[2] were added. (Reagent A is prepared by dissolving 240 grams of sodium chloride in water, adding 20 cc. Of concentrated hydrochloric acid and diluting to one liter. It is used to regulate the acidity of the solution and supply an excess of sodium ions.) The solution was diluted to 200 cc. and one dipper of barium chloride crystals added. The solution was shaken for one minute and then placed in the tube of the turbidimeter. The depth of the turbid liquid required to make a light filament disappear was regulated by means of a hand screw and the reading was recorded. The p.p.m. of sulfate were determined by referring to the standard sulfate chart on page 18, prepared from standard solution of sodium sulfate.

The following tables give a comparison of the results obtained from the various methods and the percent of error in each case.

Results of solution # I

Gravimetric	Tetrahydroxy-quinone	Benzidine HCl	Turbid-imetric	Percentage Error		
P.P.M.-SO_4	P.P.M. -SO_4	P.P.M.-SO_4	P.P.M.-SO_4	THQ	B.-HCl	Turbid.
195,472	194,400	194,939	194,000	- .6	- .3	- .8
195,225	194, 880	196,850	204, 000	- .35	+ .7	+4.35
195, 801	195,840	196,577	204,000	+ .2	+ .5	+4.35
195,636	194,880	197,123	200,000	- .35	+ .8	+2.3
195,636	195,360	196,031	192,000	- .1	+ .25	-1.8
195,307	196,806	193,851	200,000	+ .6	- .85	+2.3
195,390	197,760	195,490	188,000	+1.15	------	-2.8
195,801	196,320	194,124	197,000	+ .4	- .7	+ .7
195,390	193,440	196,309	200,000	-1.1	+ .4	+2.3
195,554	194,880	197,401	197,000	- .35	+ .95	+ .7

Results of solution # II

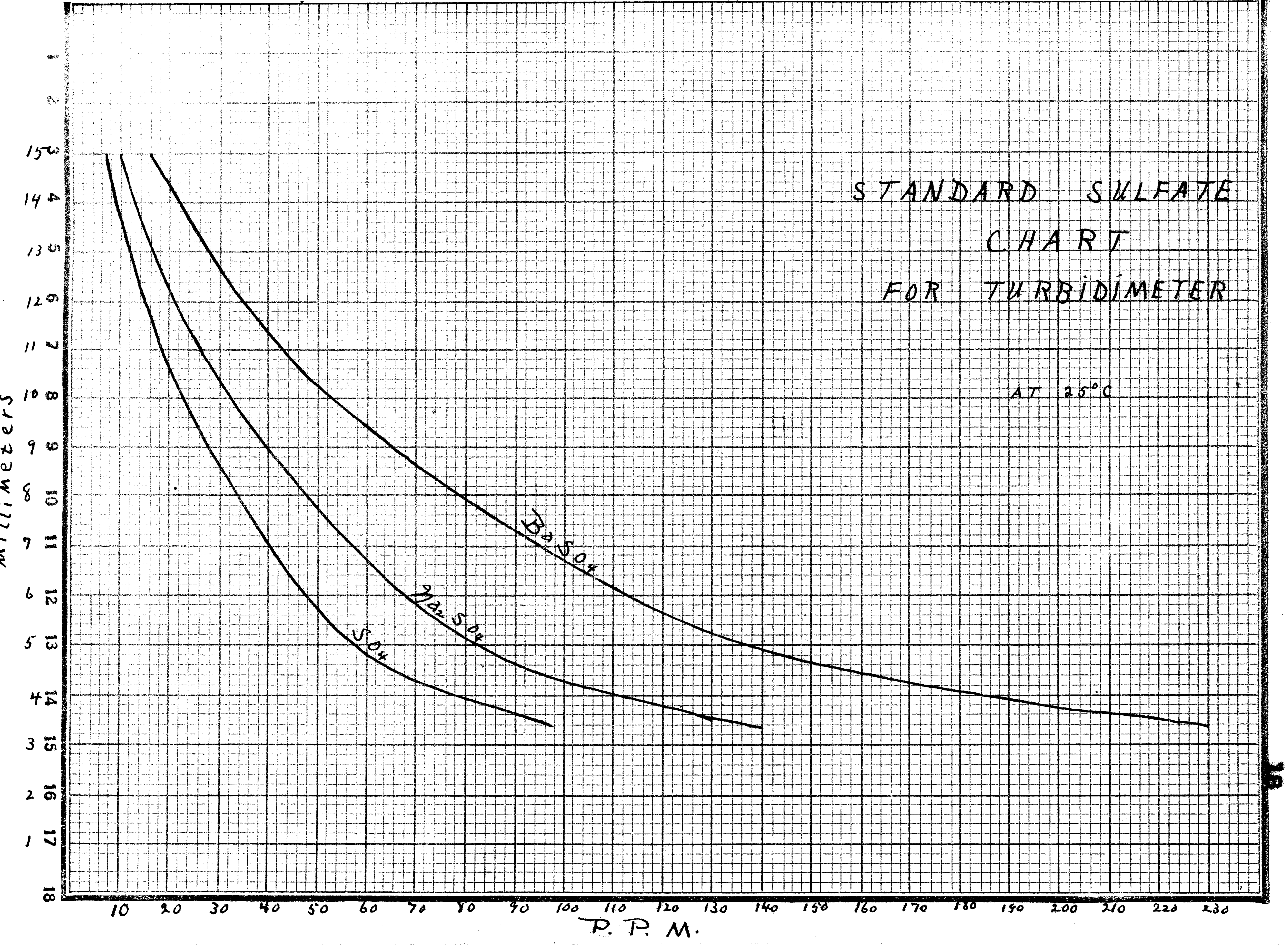
Gravimetric	Tetrahydroxy-quinone	Benzidine HCl	Turbid-imetric	Percentage Error		
P.P.M.-SO_4	P.P.M. -SO_4	P.P.M.-SO_4	P.P.M.-SO_4	THQ	B.-HCl	Turbid.
432,794	441,600	430,592	424,000	+2.06	- .5	-2.00
433,028	438,400	431,616	440,000	+1.4	- .25	+1.7
433,001	444,800	432,128	432,000	+2.8	- .1	- .2
432,619	438,400	428,989	440,000	+1.4	-1.1	+1.7
432,454	435,200	431,616	424,000	+ .45	- .25	-2.00
432,373	436,800	436,156	448,000	+ .95	+ .85	+3.7
432,260	440,000	433,710	428,000	+1.7	+ .25	-1.1
433,028	441,600	431,104	448,000	+2.06	- .35	+3.7
432,794	438,400	428,989	428,000	+1.4	-1.1	-1.1
432,619	436,800	432,630	424,000	+ .95	-----	-2.00

Results of solution #III

Gravimetric	Tetrahydroxy-quinone	Benzidine HCl	Turbid-imetric	Percentage Error		
P.P.M.-SO_4	P.P.M.- SO_4	P.P.M.-SO_4	P.P.M.SO_4	TH Q	B.HCl	Turbid.
480,130	480,000	478,645	500,000	-------	- .3	+4.2
480,541	483,200	478,133	490,000	+ .65	- .4	+2.1
480,295	481,600	476,086	480,000	+ .3	- .8	----
479,555	476,800	473,014	472,000	- .65	-1.45	-1.7
479,884	480,000	478,645	467,000	-----	- .3	-2.7
479,555	481,600	481,717	485,000	+ .3	+ .4	+1.05
480,295	484,800	479,669	463,000	+1.00	- .1	-3.6
480,706	473,420	483,765	472,000	-1.35	+ .8	-1.7
479,966	481,600	479,157	476,000	+ .3	- .2	- .85
479,226	478,400	475,574	485,000	- .3	- .9	+1.05

Results of solution # IV

Gravimetric	Tetrahydroxy-quinone	Benzidine HCl	Turbid-imetric	Percentage Error		
P.P.M.-SO_4	P.P.M.- SO_4	P.P.M.-SO_4	P.P.M.SO_4	THQ	B .HCl	Turbid.
397,026	401,600	399,282	408,000	+1.15	+ .6	+2.75
397,191	393,440	398,274	400,600	- .9	+ .35	+ .75
397,108	400,000	400,306	404,000	+ .75	+ .75	+1.75
396,615	396,800	396,210	400,000	- .05	- .2	+ .75
396,697	401,600	399,774	392,000	+1.15	+.7	-1.25
397,355	398,400	399,282	388,000	+ .35	+ .6	-2.3
397,026	403,200	397,234	400,000	+1.55	+ .05	+ .75
397,191	400,000	395,187	392,000	+ .75	- .45	-1.25
396,944	396,800	394,163	388,000	- .05	- .7	-2.3
396,862	401,600	392,627	404,000	+1.15	-1.1	+1.75


STANDARD SULFATE
CHART
FOR TURBIDIMETER
AT 25°C
$BaSO_4$
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15 14 13 12 11 10 9 8 7 6 5 4 3 2 1
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230
P. P. M.

It will be noticed from the above comparisons that fairly good agreement was obtained with the gravimetric tetrahydroxyquinone and the benzidine hydrochloride methods. The percentage error in the tetrahydroxyquinone method was not more than 2.3%, while that of the benzidine hydrochloride was not more than 2.4%. The percentage error in the turbidimetric method was much greater, being 7.15% in concentrated solutions. It appears evident that the turbidimetric method is not applicable in the concentrated solutions, if an accurate check is necessary.

It was found from the above comparison, that the impurities collected by the acid bath in precipitating the rayon,do not appreciably affect the methods of sulfate determination. Even the presence of zinc and magnesium ions in these solutions can be tolerated up to the concentrations commonly found in the acid bath.

The pH was kept around 8.3 in the tetrahydroxyquinone method,since an excess of acid destroys the indicator and an excess of base gives an interfering pink color with phenolphthalein.The temperature was kept below 30 degrees Centigrade, since a higher temperature destroys the indicator. It was found best to add one extra dipper of indicator just before the end point was expected.This indicator is unstable and easily destroyed and thus a dipper at this point will assure a sufficient supply. Sodium chloride will cause a rapid color change and increase the precision in concentrated sulfate solutions.

V

CONCLUSION

A comparison of the gravimetric, tetrahydroxyquinone and benzidine hydrochloride methods for the determination of sulfates in the acid bath solution in the Viscose process of the manufacture of rayon shows acceptable results in all concentrations. The turbidimetric method shows a greater error in these concentrated solutions.

The tetrahydroxyquinone method is accurate to within 2.3%. The method is not materially affected by the ions commonly found in the acid baths for the Viscose process of the manufacture of rayon. This method is not only accurate but is quite short and involves no special equipment. It is a titration method with an inside indicator. The only standard solutions necessary for the method is barium chloride and this is stable. Once the technique is mastered and the precautions noted, the method may be applied with ample accuracy for the acid bath.

The benzidine hydrochloride method, while not quite as simple, may be applied to the determination of the sulfates of the acid bath with a fair degree of precision. The method is more involved and requires filtering, which is time consuming and requires special equipment.

The turbidimetric method is not precise for such a concentrated solution and thus must be eliminated. It is accurate and very rapid for very dilute solutions of sulfates.

*note

After completing this investigation, a letter was received from the Betz Laboratories of Philadelphia, announcing an improved tetrahydroxyquinone indicator. This improved indicator is used in exactly the same manner as the original material, but gives a very sharp and improved end point in the titration of sulfates. This improvement was made by changing the dispersion medium to a special organic compound instead of potassium chloride as was originally used.

They sent a five gram sample to be tried in our sulfate determinations. This new indicator was tried on the above sulfate solutions, and although no comparison as to accuracy was attempted, it showed a sharper end point. The change in color is from a yellow-orange to a deep red and is permanent. This new indicator should shorten the time of titration and make the end point more definate.

VI

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