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THE POTENTIOMETRIC TITRATION
OF P-AMINOPHENOL WITH
CERIC SULFATE

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~~CONFIDENTIAL~~



THE POTENTIOMETRIC TITRATION OF P-AMINOPHENOL
WITH CERIC SULFATE

by

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Introduction

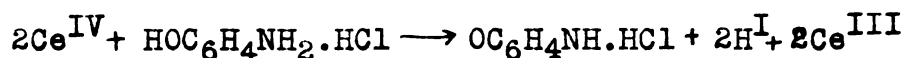
The use of ceric sulfate as a quantitative oxidizing agent was first suggested by Barbieri in 1905. The advantages due to its strong oxidizing action and its use in cerate oxidimetry were demonstrated by Willard (2) and Furman (3),(4),(5),(6) about 15 years ago. To cite all the work done with ceric sulfate to the present time would be beyond the scope of this paper. Young (8) and G. Frederick Smith (16) give excellent accounts of its numerous applications.

More particularly related to this paper are the applications of cerate oxidimetry to organic acids, such as maleic acid and tartaric acid, by Willard and Young (2b), to hydroquinone by Furman and Wallace (3a), and to various organic compounds by White (1). The last-named carried out in this laboratory preliminary studies on the possibilities of the potentiometric determination of p-aminophenol, mono-methyl-p-aminophenol sulfate, p-phenylene diamine, pyrogalllic acid, and glycine. His results tended to show that the reaction of ceric ammonium sulfate with all these substances was stoichiometric and quantitative, as determined potentiometrically and confirmed by the use of indicators.

Recent researches into the theory of the oxidizing action of the ceric ion by Smith and Getz (9),(10) show irregularities in its behavior not reported by Willard, Furman and others; but the main advantages of ceric sul-

fate as an oxidant remain firmly established: (a) its ease of preparation (as ceric ammonium sulfate solution), (b) its ease and accuracy of standardization, with several alternative methods available, (c) its rapid and positive action, (d) its great stability, (e) its adaptation to a number of indicators, and (f) its particular suitability to the potentiometric technique.

Due to the importance of p-aminophenol in the photochemical and biochemical fields, an extension of the study by White (1) of a method of determining it was deemed desirable. According to White, the potentiometric determination was accurate and clear-cut, the reaction being as follows:



Preliminary investigation showed, however, that without special conditions not specified by him the titration was not accurate; and the purpose of this study is to show how various conditions affect the titration and within what limits accurate results can be obtained.

Apparatus and Materials

The apparatus used was essentially that required for the most common potentiometric titrations. The indicator electrode was a bright platinum wire; the reference electrode was a saturated calomel half-cell. This latter was not changed during the experiment. However, a supply bulb and stopcock were arranged above the main cell so that the

immersed arm of the cell could be flushed out frequently with the saturated potassium chloride-calomel solution. Contact with the solution was made at this electrode in early trials by means of a tip of near capillary dimensions opening downward; later, a small ground-glass cap was fitted to the constricted tip of the arm, with no noticeable effect on the results.

The titration cell consisted of a 180-ml. tall form beaker fitted with a rubber stopper holding the two electrodes, burette tip, thermometer and stirrer. The latter was a glass rod, propeller-shaped at the end, and rotated by compressed air by means of the familiar "notched cork" mechanism. The potentiometer was a Leeds and Northrup Type K with reflection-beam galvanometer; it was unnecessarily sensitive and was read only to the nearest millivolt. Except for some of the preliminary trials, no part of this set-up was changed during the course of the experiment.

The ceric ammonium sulfate used was a high grade product provided for research work by O.T. Coffelt. It was made up according to Willard and Furman (13). The oxalate used in standardization was Bureau of Standards tested. The p-aminophenol hydrochloride was an Eastman commercial product. Silver nitrate, sulfuric acid, and incidental reagents were of C.P. grade or better. The ceric ammonium sulfate (hereafter referred to as ceric sulfate) was made up in several lots, only two of which were used in the titrations presented. Each was standardized carefully, how-

ever, both by a colorimetric method (13),(14),(19),(2c), and potentiometrically (11),(5a), with very close agreement on the basis of sodium oxalate. The normalities used for the main work were 0.0709N and 0.0826N.

Experimental Procedure

In the preliminary trials the following general procedure, which applies to all trials as far as manipulation is concerned, was followed:

A sample of p-aminophenol hydrochloride crystals was weighed out on a good analytical balance and dissolved in dilute sulfuric acid for immediate titration. The burette, previously calibrated, was thoroughly rinsed with the standard ceric sulfate solution and filled. After balancing the potentiometer and assembling the apparatus, the ceric sulfate was added by portions to the 50-ml. titrating portion of p-aminophenol hydrochloride in dilute sulfuric acid. Readings of voltage were taken after allowing time for equilibrium. The first portion of ceric sulfate solution added was usually somewhat over half the amount judged to be required, the next portion usually to within about 2 ml. of the anticipated end-point, and further portions were added dropwise. The last three or four portions before the end-point were single drops. Successively shorter times were allowed before readings as the quantities added grew smaller; at least two minutes were allowed on all readings. The immersed half-cell arm was flushed between trials, and the platinum wire cleaned in the Bunsen flame.

This routine was followed quite strictly, except for occasional variations to detect possible errors due to it. The speed of stirring was kept very nearly constant. The burette was read with the aid of a lens. All the recommended precautions for volumetric and electrical measurements were followed, except that, due to the closed titration cell, there was no rinsing of the burette tip and no "split drops".

The appearance of the titrated solution was almost invariably colorless at first, deep purple on addition of ceric sulfate, turning cherry red at a point three to six drops before the end-point, and rapidly turning to deep orange thereafter. The colors were much less intense in solutions containing less p-aminophenol. A titration curve, ml. added versus voltage, was plotted, usually simultaneously with each titration. This helped to prevent overstepping the end-point and to indicate the type of sample to run next.

Establishment of Optimum Conditions

Of about the first 50 titrations of p-aminophenol hydrochloride, only some five or six gave acceptably sharp voltage breaks, and in these the agreement of the actual and the calculated concentrations was not good. The weight used was 120 mg. in 50 ml. of solution for most of these trials. Temperature, acidity, dilution, and other factors were varied without positive effect, except that all the acceptable results were obtained with a solution of sulfuric acid of approximately 1:9 by volume (3.3N).

These trials indicated, however, that the following conditions, in addition to certain details of manipulation, affected the sharpness of the potential break and the accuracy of the end-point: (1) temperature, (2) light, (3) acidity of the titrating solution, (4) weight of sample, and (5) presence of the H Cl group in the p-aminophenol hydrochloride.

The last two factors seemed to be the most important. In an attempt to nullify the effect of the HCl group, silver nitrate was added just before the titration, the resulting solid silver chloride being allowed, at first, to remain in the solution. A great improvement in the sharpness of the potential break resulted, and it was soon observed that an even better curve could be obtained by adding silver nitrate 50-100% in excess of the calculated amount. This excess was used in all subsequent trials except where it was desired to check the effect of this particular factor.

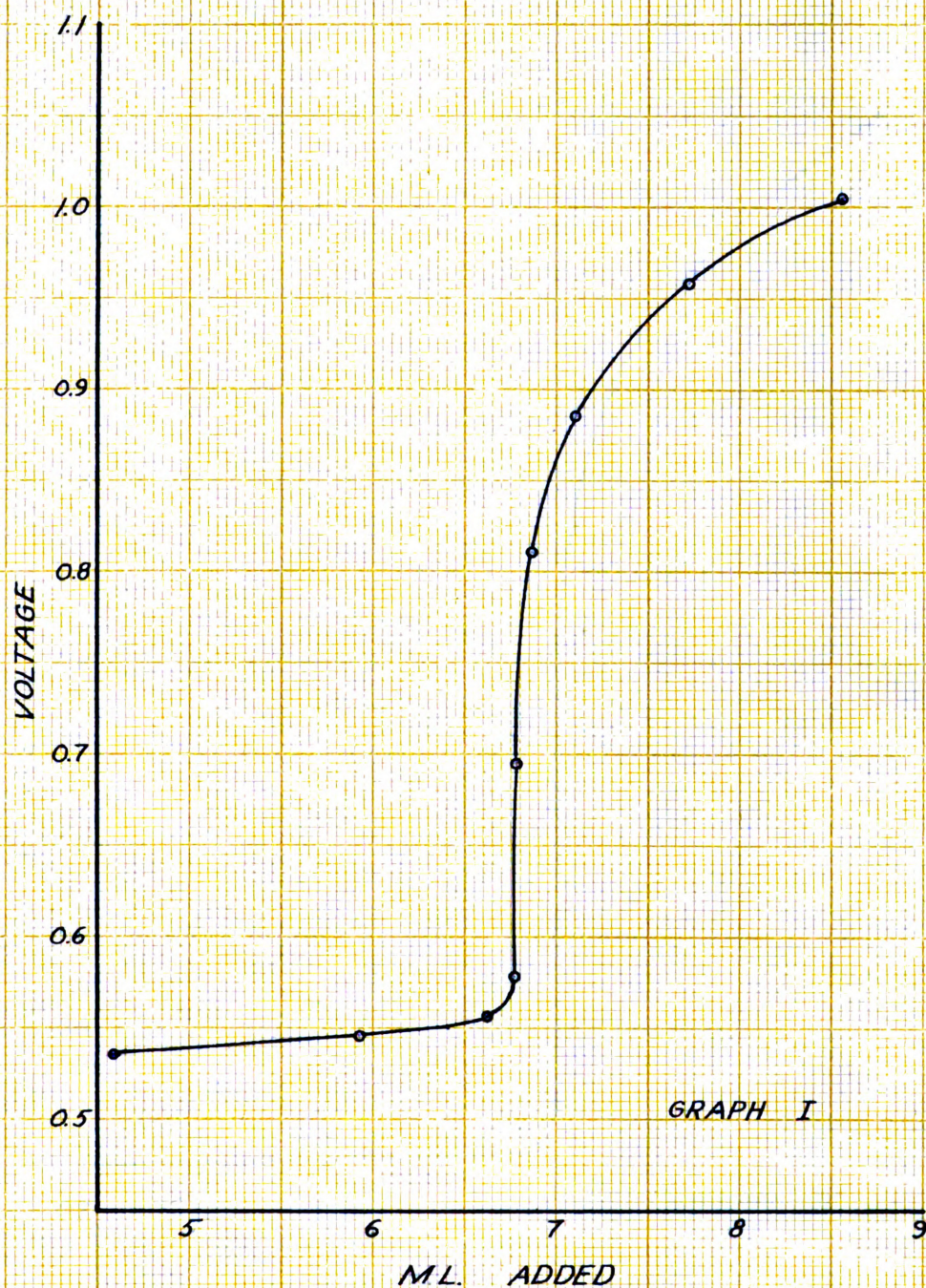
In general, the experimental procedure outlined above was changed only by the addition of the silver nitrate, and by the use of varying weights of p-aminophenol in the sample. It now became necessary to study the following conditions in addition to those listed above: (6) presence of excess silver nitrate, (7) presence of the solid silver chloride, and (8) time of standing of the p-aminophenol in solution, with and without silver nitrate treatment. Since the use of silver nitrate made possible consistently sharp breaks

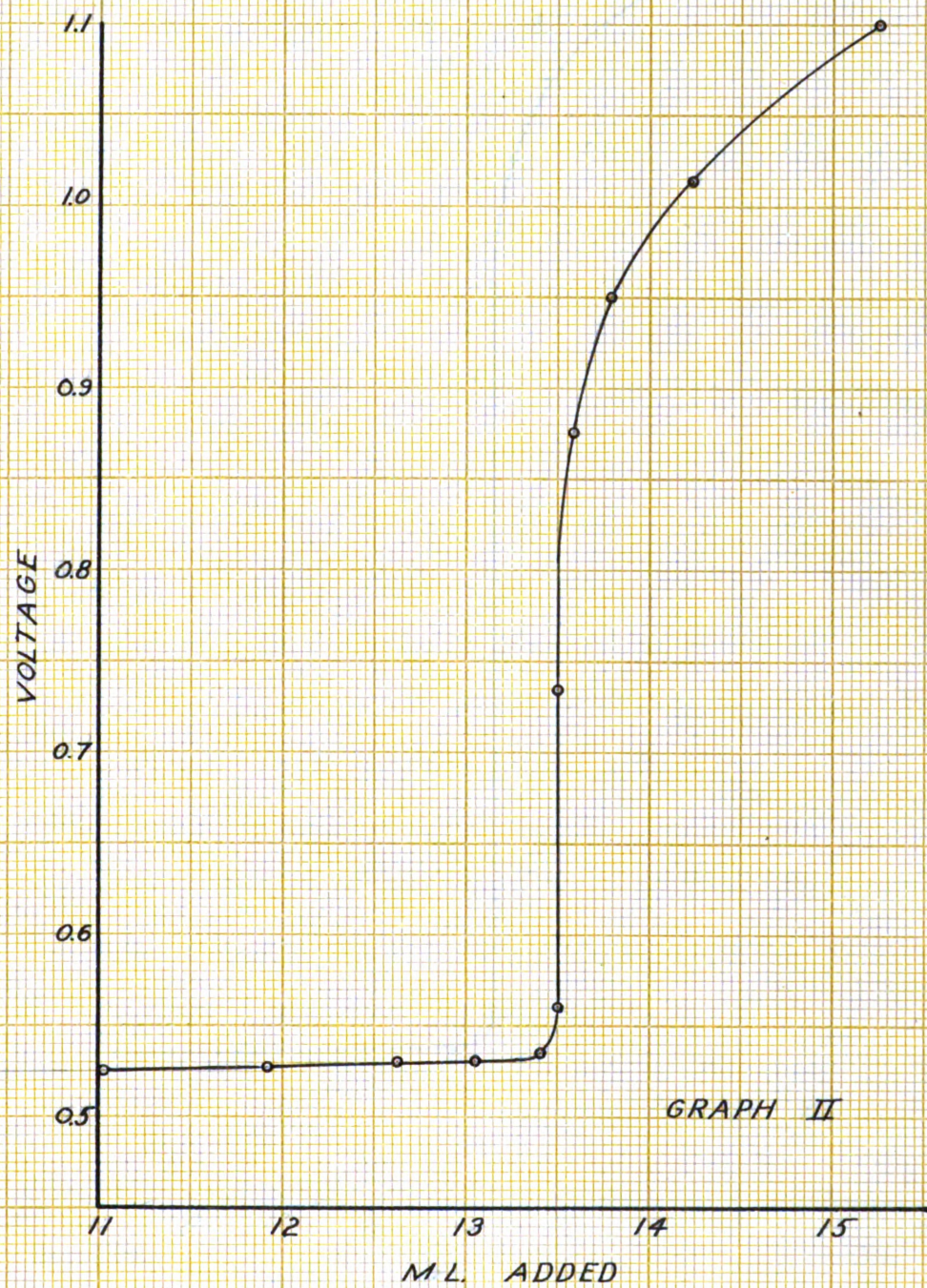
in potential, the primary concern thereafter was accuracy of the end-point. Further details of procedure will be presented as "Preferred Procedure" under "Discussion".

Experimental Results

The results of study of the above factors are presented in Tables I to VII-B. A total of 169 recorded titrations was made, exclusive of standardizations and rough trials. The only Table which is intended to give any comprehensive survey of the whole work is Table VII-B, which consists of averages grouped to show the effect of the most important factor of all those mentioned, namely weight of sample used. Tables I to VI inclusive are selected data grouped to show the trend with regard to the respective controlled condition. Table VII-A is somewhat more comprehensive. A statement is made concerning each Table, and indication is given as to the other supporting evidence.

Three graphs of the titration curves are presented. Graph I shows the very best curve obtained without the use of silver nitrate; Graph III represents a trial identical in every respect except that silver nitrate was used, and the curve is one of the best obtained. Graph II represents a trial in which silver nitrate was used, but the weight of sample (concentration of p-aminophenol) was greater than in Graph III, and a less satisfactory curve resulted. Curves referred to as "fair" in the tables were roughly similar to Graphs I and II; the "good" curves approach Graph III in form.





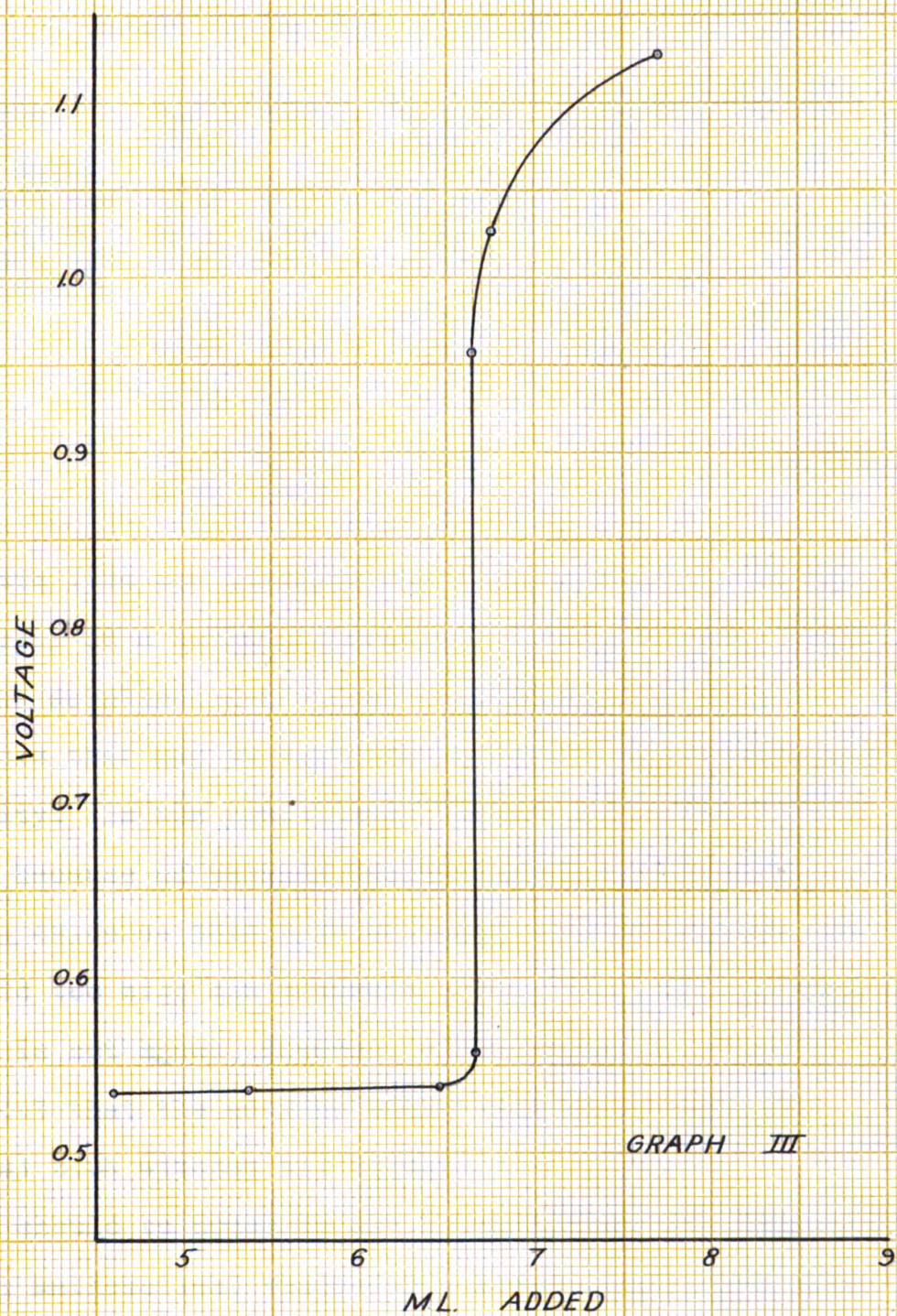


Table I. Effect of Acidity.

Conditions: 24-26°C.	H ₂ SO ₄ used	Curve	Wt.p-am. used	Wt.p-am. found	% found
Excess AgNO ₃					
No effect due	N/10	poor	120.0 mg.	-----	-----
to standing.	N/10	fair	20.0	20.41 mg.	102.15%
No effect due	N/10	fair	20.0	19.65	98.25%
to filtering.					
	3.3N	good	120.0	122.42	102.00%
	3.3N	good	40.0	39.97	99.93%
	6.0N	fair	40.0	40.63	101.57%
	8.0N	good	20.0	20.13	100.65%
	8.2N	poor	120.0	-----	-----

Table I is not presented as conclusive proof of the superiority of a certain strength of sulfuric acid in the titrating solution, but rather as a brief indication of the errors that may be expected outside of certain limits of acidity. In the preliminary trials, not cited individually because of varying conditions, there was overwhelming evidence that N/10 sulfuric acid is too low and 8.0N acid too high for accurate work. The exact optimum acidity is not known, however, as it seemed evident throughout that the acidity could vary about 20% from the usual 3.3N without ill effect.

It should be noted in all these tables that from a purely mathematical viewpoint a large sample will give a "% found" value closer to 100% than a small sample of the same error in terms of weight of p-aminophenol. That is, if the sample is small, a relatively large variation in "% found" may yet represent a very small deviation from the theoretical equivalence-point.

Table II. Effect of Silver Nitrate.

Conditions:	AgNO ₃ used	Curve	Wt.p-am. used	Wt.p-am. found	% found
Acid 5.3N 24-26° C.					
AgCl filt- ered out.	no	fair	20.0 mg.	20.9 mg.	104.55%
	no	fair	20.0	20.5	102.75%
No effect due to standing.	no	fair	80.0	81.3	101.60%
	excess	good	20.0	20.01	100.05%
	excess	good	20.0	19.95	99.75%
	excess	good	80.0	81.13	101.41%

Table II shows the particular effectiveness of the silver nitrate (excess) treatment of samples low in p-aminophenol. It also indicates that its effect is not sufficient to produce quantitative results with higher weight samples. Many other results confirmed these conclusions, but could not be included here because of variation of other conditions.

Table III. Effect of Temperature.

Conditions:	Temp.(C)	Curve	Wt.p-am. used	Wt.p-am. found	% found
3.3N Acid					
Excess AgNO ₃	24-26°	poor	120.0 mg.	-----	-----
AgCl present	24-26	good	40.0	39.97mg.	99.93%
No effect due to standing.	24-26	good	20.0	19.95	99.75%
	36-38	poor	120.0	-----	-----
	36-38	fair	40.0	41.47	103.87%
	36-38	fair	20.0	20.49	102.45%
	48-50	poor	120.0	-----	-----
	48-50	fair	40.0	50.00	125.00%
	48-50	fair	20.0	21.00	105.20%

Table III shows that at room temperature (24-26° C.) the titration is satisfactory, at 36-38° C. it is unsatisfactory, and even more so at 48-50° C. The adverse effect of heat is greater at higher concentration of p-aminophenol. Some twelve other trials under varying conditions support these conclusions.

Table IV. Effect of Light.

Conditions:	Light	Curve	Wt.p-am. used	Wt.p-am. found	% found
24-26° C.	present				
3.3N Acid					
Excess AgNO ₃	yes	good	120.0 mg.	122.96mg.	102.46%
AgCl present	yes	good	40.0	40.09	100.23%
No effect due to standing.	no	good	120.0	123.20	102.66%
	no	good	40.0	40.27	100.67%

Table IV shows that the influence of light upon the reaction in the titrating cell is not important. At any rate, it does not increase the error appreciably and may even exert a helpful effect. The light was excluded by wrapping the titrating cell in heavy brown paper and reducing the time of preparing and inserting the solution to a minimum. Some seven other trials support the above conclusion.

Table V. Effect of Filtering out Silver Chloride.

Conditions:	Filtered	Curve	Wt.p-am. used	Wt.p-am. found	% found
3.3N Acid					
24-26° C.	yes	fair	120.0 mg.	122.66 mg.	102.20%
Excess AgNO ₃	yes	good	40.0	40.03	100.07%
No effect due to standing.	yes	good	40.0	39.97	99.93%
	yes	good	20.0	20.19	100.95%
	no	fair	120.0	122.96	102.46%
	no	good	40.0	40.21	100.52%
	no	good	20.0	19.95	99.75%

Table V shows that the effect of filtering out the solid silver chloride is not appreciable. The question of filtering is closely related to that of time of standing (Table VI) and weight of sample (Table VII), and the tabulations cited show that the above conclusion is correct. Of all the 169 trials mentioned, about 40-50% were with filtered solution and a like number with unfiltered solution, and no striking differences were noted.

Table VI. Effect of Standing.

Conditions:	Time of standing	Curve	Wt.p-am. used	Wt.p-am. found	% found
3.3N Acid 24-26° C.					
Excess AgNO ₃	none	good	80.0 mg.	80.35 mg.	100.44%
Filtered	none	good	40.0	39.97	99.93%
	none	good	20.0	20.19	100.95%
	1 day	good	80.0	81.13	101.41%
	9 days	good	40.0	40.15	100.37%
	7 days	good	20.0	20.13	100.65%
	5 days	good	20.0	19.96	99.95%

Table VI shows only a few of the cases in which the time of standing allowed after the solution is prepared before titrating might have been expected to affect the results markedly. The conclusion from this, and from some twenty other trials in which time of standing (and other conditions) were varied, is that prolonged standing has a definitely adverse effect on samples high in p-amino-phenol.

It became clear toward the end of the investigation that the samples containing only 20 mg. (0.4 g./liter) did not furnish valid criteria for comparing effects of specific factors. Only carefully selected ones of these have been used in the above tabulations, i.e. only those which were considered actually to have been affected by the particular factor involved. At best, these samples are noteworthy mainly because of their indifference to the particular factor. This applies to all tabulations, and is probably due to the fact that error in these small samples is mainly error of manipulation.

Table VII-A. Effect of Weight of Sample (Concentration).

Gen'l. Conditions: 24-26° C., 3.3N Acid, Light, No standing.

Special Conditions:	Curve	Wt.p-am. used	Wt.p-am. found	% found
I.				
AgCl filt. out.	poor	160.0 mg.	163.47 mg.	102.17%
	poor	120.0	122.66	102.21%
	fair	80.0	80.83	101.03%
	good	40.0	40.03	100.07%
	good	40.0	39.97	99.93%
	good	20.0	19.95	99.75%
	good	20.0	20.13	100.65%
Not filt. out	poor	160.0	-----	-----
	poor	120.0	122.54	102.11%
	good	80.0	81.43	101.78%
	good	40.0	40.21	100.53%
	good	20.0	19.95	99.75%
II.				
No AgNO ₃ used	good	80.0	81.31.	101.63%
	good	40.0	40.57	101.42%
	good	20.0	20.55	102.75%

Table VII-B. Averages of Trials Affected by Weight.

Conditions:	No. of trials	Curves	Wt.p-am. used	Wt.p-am. found	% found
Excess AgNO ₃					
24-26° C.					
3.3N Acid	2	poor	160.0 mg.	-----	-----
Light	11	fair	120.0	122.54 mg.	102.11%
No effect due to standing.	9	good	80.0	80.79	101.00%
	9	good	40.0	39.99	99.99%
No effect due to filtering.	9	good	20.0	20.07	100.35%

Table VII-A shows that the effect of weight of sample (concentration of p-aminophenol) is, as has been indicated in other tables, very great. The tabulation is divided into two parts, with silver nitrate (I) and without silver nitrate (II), to show how the effect of

weight of sample exceeds that of most other factors. Part I shows that, regardless of such other factors as are cited, the accuracy is greater when the weight of the sample is decreased, at least down to 40 mg. Part II is not as definite in its implications, in fact the examples cited are rather extreme cases. Due to the absence of silver nitrate, the 80 mg. trial might have been expected to give a much poorer result; whereas the two smaller samples gave less accurate results here than in other situations even less favorable. Additional proof of the bad effect of high p-aminophenol concentration is found in the fact that a large number of 120.0 mg. trials resulted in extreme inaccuracy or in curves impossible to interpret quantitatively.

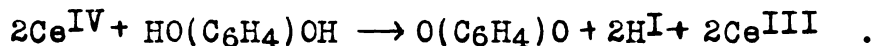
Table VII-B is the only table of averages presented. Representing forty trials, it indicates clearly that the tendency of accuracy to decrease with increase of p-aminophenol concentration is general. It is upon this tabulation that the main conclusions of the "Discussion" and "Summary" are based. As in other tabulations, however, many trials were necessarily omitted because of variation of minor factors. Briefly, the table shows that a 40.mg. sample is optimum, 80 mg. acceptable under the best conditions, and 20 mg. allowable if one wishes to undertake the difficulties of handling such a small amount. This means that the optimum concentration of p-aminophenol is 0.8 g. per liter.

Discussion

A. Significance of the Results.

The preceding tabulations with their accompanying statements are largely self-explanatory, but some of the tendencies noted should be emphasized.

First, the large number of unsuccessful trials (not directly cited) shows that the titration can only be performed under carefully controlled conditions. However, there is ample proof that the reaction can be made to proceed stoichiometrically and that considerable accuracy is attainable. The main purpose of this study is thereby achieved. No attempt was made to trace the theoretical details of the reaction, which is evidently quite complex. Parenthetically, it is suggested that the equation given by White (1) is substantially correct (see Introduction, p. 2), no evidence to the contrary having been observed either in the experimental work or the search of the literature. This equation is at least compatible with that given by Furman and Wallace (3a) for the analogous case of the oxidation of hydroquinone by ceric sulfate:



Second, the marked effect of the concentration of p-aminophenol (weight of sample) is apparent. Next in importance, disregarding those which are easily controlled, such as temperature, is the silver nitrate treatment, the use of which is helpful in all cases and essential in some. It is clear that the concentration of p-aminophenol is a factor of primary importance under

all conditions. For accurate results, 0.8 g. to 1.0 g. per liter is the optimum concentration. There seems to be no lower limit of concentration if one wishes to entail the manipulative difficulties which accuracy demands in such titrations. It is possible to obtain good results at twice the concentration just specified, but at about that point accuracy becomes difficult.

The broad view of the whole study indicates to the investigator, with a certainty that is difficult to impart by means of tables, the truth of the generalization: given the optimum concentration, it is fairly easy to adjust all other conditions to obtain accurate results; but, given all other conditions optimum, there is little chance of successful titration unless the concentration be held within the above suggested limits.

Third, the opening up of new problems should be noted. It is clear that this study does not solve the problem of how p-aminophenol may be titrated under all conditions, but merely shows that it is possible within certain limits. Presumably it should be possible to devise a rapid method of estimating the concentration of a p-aminophenol solution and to dilute it to the optimum concentration if necessary. Further, time did not permit the study of the effect of interfering substances. In the electrolytic preparation of p-aminophenol, for instance, there would be reducing substances present at all stages which would interfere. A means of masking their effects without the necessity of removing them analytically would be essential to the

efficient use of the ceric sulfate titration technique. Another possibly fruitful study would be that of the application of other electrode systems.

B. Preferred Procedure for the Titration of P-aminophenol.

1. Set up the apparatus as described under "Apparatus", p. 2*
2. Prepare the p-aminophenol solution in one of two ways, according to convenience:
 - a. Add 40-50 mg of dry crystals (hydrochloride) to 50 ml. of 3.5N sulfuric acid, and add approximately 70 mg. of silver nitrate (50-100% excess).**
 - b. Make up a solution of dry crystals (hydrochloride) of 0.8 to 1.0 g./liter.*** Add silver nitrate equivalent to about 1.8 g. per gram of solute, filter in a Buechner funnel, and pipette a 50 ml. portion for each trial.
3. Titrate in a 180 ml. beaker.**** Look for the approach of the end-point as indicated by a color change from light purple to reddish. Do not add more than one drop at a time after this until the sharpest potential break has been passed. Minimum time between voltage readings, two minutes.

Notes:

- *Observe all ordinary precautions of manipulation and:
 - a. Clean the platinum wire with a flame periodically; if solid silver chloride is present, clean it at the end of each trial.
 - b. Ceric solution should not be allowed to stand in an open vessel for more than a few minutes.
- ** This may be prepared in solution, diluting in such a way that it may be conveniently added by pipette.

*** This method is recommended if it is desired to study the effect of standing in solution, also as a more rapid method of conducting a large number of trials. It is probably somewhat more accurate than separate weighing of each sample. The prepared solution, after filtering, may stand several days, preferably in the dark. Concentrated "stock" solution of as high as 2.5 g./liter has been used successfully, a small portion being diluted to 50 ml. with dilute sulfuric acid before titrating.

- ****a. See Apparatus, p. 2, and Procedure, p. 4.
b. The initial reading before adding any ceric sulfate should be preceded by 2 to 4 minutes of stirring.
c. For the larger portions of ceric sulfate added at first and at the last, allow about one minute per ml. before reading, up to a maximum of about ten minutes.

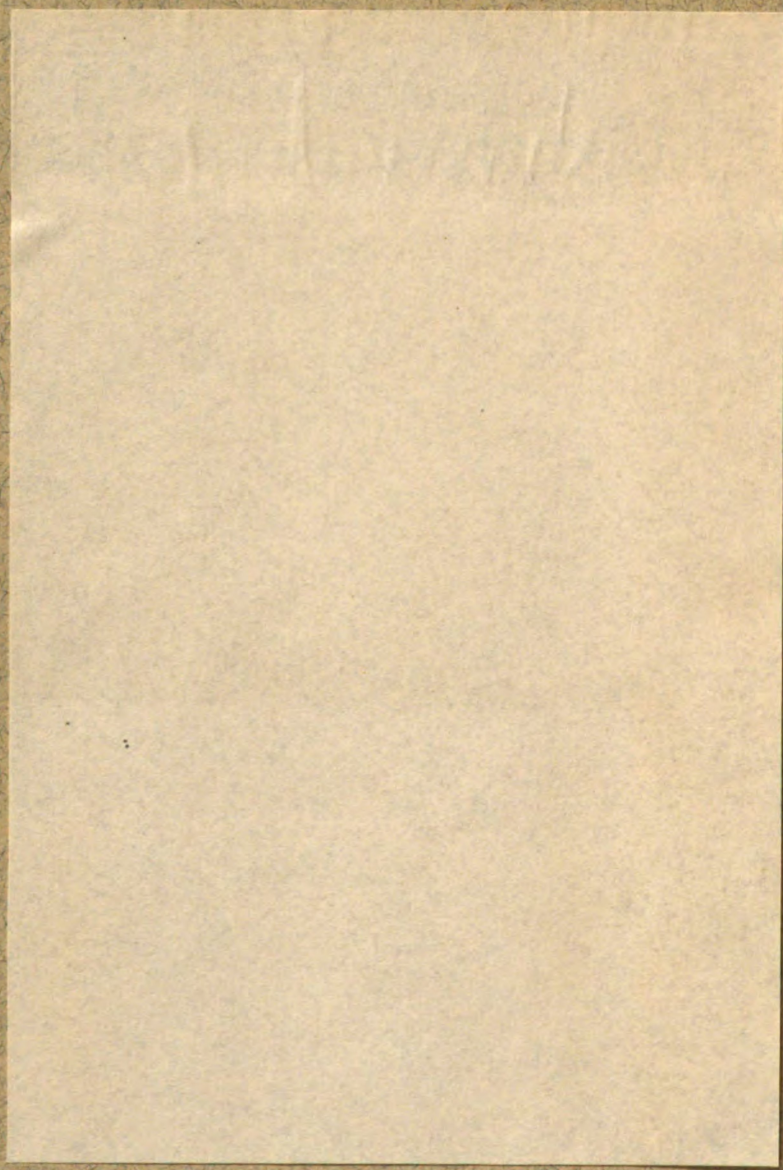
Summary

The definite findings of this study are:

1. P-aminophenol can be accurately titrated potentiometrically with ceric sulfate, within the limits of concentration of about 0.8 to 1.0 g./liter, in a solution about 3-4N in sulfuric acid.
2. Lower concentrations can be titrated quite accurately, but the upper limit is about 2 g./liter.
3. The titration curve is made more nearly ideal by the addition of a 50-100% excess of silver nitrate.
4. The only condition other than concentration which is imperative is that of temperature: 26° C. is allowable, 35° C. is too high.
5. Time of standing of the solution is a minor factor; the effect of light and the presence of solid silver chloride are probably immaterial for work done within the concentration limits suggested.

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The potentiometric titration of
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