

TABLE III.—EFFECT OF OZONE AND LIGHT ON BLEACHING.

Time, minutes.	Reading.	Time, minutes.	Reading.
0	5	120	12
30	8	150	13
60	11	180	15
90	12

In Fig. 3 the above data are plotted together with those for the combined light and peroxide from the earlier table.

Summary.

It has been shown that the oxidizing power of hydrogen peroxide, as manifested in the bleaching of dyes, is increased by exposing the reaction mixture to light of short wave lengths.

This effect cannot be duplicated by substituting oxygen for hydrogen peroxide in the reaction mixture, indicating that the result is not due to formation of ozone.

EVANSTON, ILLINOIS.

[CONTRIBUTION FROM THE LABORATORY OF GRINNELL COLLEGE.]

FURTHER WORK ON POTASSIUM HYDROGEN PHTHALATE AS A STANDARD IN VOLUMETRIC ANALYSIS.

By W. S. HENDRIXSON.

Received January 28, 1920.

Several years ago the writer showed that potassium hydrogen phthalate and sodium hydrogen phthalate may be used with advantage as standard in volumetric analysis.¹ They can be prepared easily in a state of great purity, they have large molecular weights, 204.14 and 188.04, respectively, and only one hydrogen ion. The potassium salt has the great advantage of absence of water of crystallization. So little work has been done on these salts and so little is known of their properties that it seemed desirable to study further the potassium salt, which is to be preferred as a standard. The objects were: (1) to determine the practicability of the preparation and use of the salt as a standard, by others; (2) to determine the necessary degree of purification for ordinary purposes, and the yield on the basis of the phthalic anhydride used; (3) to determine the hygroscopic character of the salt and the means necessary to dry it.

The laboratory work on potassium hydrogen phthalate here described was done by Mr. Sereno Norton, then a senior in Grinnell College, now a chemist with the Hercules Powder Company.

The potassium hydrogen phthalate was prepared by the method described in the paper already cited. Several preparations were made and titrated. There is one chance of error in its preparation, which might easily be made by comparatively inexperienced hands, and which should

¹ THIS JOURNAL, 37, 2352 (1915).

be mentioned. Phthalic anhydride is very sparingly soluble even in hot water. If not enough potassium carbonate is used in the neutralization a portion of the anhydride will be left undissolved, and may easily be overlooked, since the sparingly soluble acid phthalate is likely to form a layer of crystals over the hot solution. Since the neutral potassium phthalate is extremely soluble even in cold water there is no danger of its contaminating the acid salt. Therefore, a slight excess of the carbonate should be used, and the hot solution should be filtered in the first instance.

A large volume of standard hydrochloric acid was made by the admirable and accurate method of Hulett and Bonner,¹ so as to contain 0.003647 g. of hydrogen chloride to one cc. This acid was titrated through the medium of sodium hydroxide against benzoic acid specially prepared for such purposes by the Bureau of Standards, which gave 0.003648 g. to one cc. This concentration was confirmed by means of silver. The solution of sodium hydroxide, free from carbonate, was prepared as described in the first paper, and was used as the intermediary between the acid phthalate and the hydrochloric acid. The indicator was phenolphthalein, and as pointed out in the former paper its error in marking the end-point was cancelled by the method of titration. The same weight burets and calibrated flasks described in the former paper were used in this work.

Titrations were made of samples of potassium hydrogen phthalate which had been 3, 4 and 5 times recrystallized from hot water. The objects were to determine the number of crystallizations necessary to secure a sufficiently pure product, and to determine the constancy of the acid salt as an individual compound. It is well known that some so-called acid salts do not show constancy in composition on being repeatedly crystallized. The results are given in the following table in which "three," "four" and "five" indicate the number of recrystallizations, and below each are the values given for the standard hydrochloric acid, assuming the formula value of the acid phthalate.

Evaluation of 0.1 N HCl with $\text{HKC}_8\text{H}_4\text{O}_4$ through Standard NaOH.

Numbers of titrations.	Three.	Four.	Five.
(1).....	0.0036489	0.0036470	0.0036519
(2).....	0.0036473	0.0036475	0.0036455
(3).....	0.0036484	0.0036449	0.0036448
(4).....	0.0036480	0.0036450	0.0036410
(5).....	0.0036471
(6).....	0.0036475
(7).....	0.0036478
(8).....	0.0036463
(9).....	0.0036463
(10).....	0.0036455
Averages:	0.003647	0.003646	0.003646

¹ THIS JOURNAL, 31, 390 (1909).

The results seem to show that there is nothing gained by more than 3 recrystallizations. Other results not here given seemed to show that for ordinary purposes even 2 recrystallizations, that is, 3 crystallizations in all would suffice. There seems to be no reason to doubt the constancy of the composition of the acid salt.

Working with no special precautions to secure a large yield our results show that about 50% of the theoretical yield of the acid salt may be obtained after 4 recrystallizations. Though expensive in war time, thanks to recent improvements in its preparation phthalic anhydride of great purity is again becoming abundant and cheap. Potassium carbonate of great purity is not difficult to obtain, and therefore, potassium hydrogen phthalate is one of the standards most easily and cheaply obtained.

We next directed our attention to the hygroscopic character of potassium hydrogen phthalate. It is very desirable that a substance used as a standard should have a low hygroscopicity. To test this character we carried out 2 sets of experiments. The first consisted in heating the air-dried salt in an electric oven at different temperatures, determining the losses in weight and the effect upon the titration value of the salt. The second consisted in exposing the substance thus dried in air of known moisture content, and determining the amount of moisture taken up from the air,

In carrying out the first set of experiments about 20 g. of the salt was heated in the electric oven in a platinum dish. At the end of each period the loss was determined and a portion of the substance was taken out without loss and titrated. The losses and titrations should thus form checks on each other. There were 11 such titrations, but since only 4 different temperatures were used, the results at the same temperature are combined in the following table:

Effect of Heat on Potassium Hydrogen Phthalate.				
Wt. of salt.	Time.	Temp.	Loss.	Value of HCl.
21.5940	4 hrs.	110	0.0006	0.0036471
20.4956	2 hrs.	120	0.0024	0.0036469
16.0100	8 hrs.	130	0.0034	0.0036490
11.6910	8 hrs.	150	0.0006	0.0036473

It is remarkable that the hygroscopic moisture which should have been eliminated at 110° is so small, one part in about 36,000. Doubtless a part of the loss at higher temperatures is to be ascribed to changing atmospheric conditions, possibly to undetected losses in taking out portions for analysis. Granting that all the apparent loss was due to water, its total, calculated on the basis of the original weight of salt taken, is 0.0088 g. or one part in about 2500, which is outside the limit of accuracy of titration in ordinary work.

The hygroscopic character was further studied by exposing the salt re-

maintaining, and dried as above, in an atmosphere of known moisture content. The platinum dish and salt were placed in a desiccator which contained sulfuric acid so diluted as to give to the air above it a humidity of 70%, which is not likely to be exceeded in the air of a laboratory. From time to time during 47 days the dish and contents were weighed. The gain or loss as compared with the previous weight never exceeded 0.002 g. and at the end of the period, summing up the gains and losses, there was found a loss of 0.0001 g.

These 2 sets of experiments seem to show that the hygroscopicity of potassium hydrogen phthalate is practically nothing, and in using it and weighing it attention need be directed only to the containing vessel. By use of an open platinum crucible in weighing it, it is believed that this source of error has been almost completely avoided.

In the preparation of potassium hydrogen phthalate it is desirable to know its solubility in hot and cold water, and this was determined at 25 and 35 degrees and at the boiling point of its saturated solution. At the lower temperatures the method used was one devised by the writer.¹ For the solubility at the boiling point the method of Pawlewski² was used.

Solubility of Potassium Hydrogen Phthalate in Water.

Temp.	Wt. solution.	Wt. acid phthalate.	% in sol.
At 25 degrees.....	21.025	2.1531	10.23
	21.028	2.1553	10.25
At 35 degrees.....	21.198	2.6859	12.67
At boiling point.....	9.18	3.3158	36.12

[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY, NEW YORK UNIVERSITY.]

THE EFFECT OF SOLVENT ON THE ULTRA VIOLET ABSORPTION SPECTRUM OF A PURE SUBSTANCE.

By F. O. RICE.

Received January 28, 1920.

In a previous paper³ some quantitative measurements were described showing the absorption of acetone and its homologues in the pure liquid condition. A large quartz spectograph fitted with a spectrophotometric arrangement was used and by this means the extinction coefficient, ϵ , is given by $\epsilon = 1/d (\log I_0/I)$, where I_0 is the intensity of the incident light, I the intensity of the emergent light, and d the thickness of the absorbing layer. ϵ may, therefore, be defined as the reciprocal of that thickness of medium which reduces the intensity of the light to $1/10$ of its original value. If c be the normality of the ketone (sp. gr. \times (1000/mol. wt.)) the molecular extinction is given by $M = \epsilon/c$.

¹ *Proc. Iowa Acad. Sci.*, **23**, 31 (1916).

² *Ber.*, **32**, 1040 (1899).

³ *Proc. Roy. Soc. (London)*, **91A**, 76 (1914).