THE STANDARDIZATION OF AMMONIUM VANADATE SOLUTIONS WITH SODIUM OXALATE

by

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The reaction between quinquevalent vanadium and oxalic acid has been the subject of a number of investigations, the results of which have been contradictory. In 1892, ROSENHEIM AND FRIEDHEIM[1] suggested the use of oxalic acid for estimating the concentration of vanadate solutions. More recently, SYROKOMSKII AND KLIMENKO[2] have reported that no reaction occurred, this finding being borne out by the work of RAO *et al.*[3] On the other hand, TSUBAKI[4], RAO AND SANKEGOWDA[5], and MORETTE AND GAUDEFROY[6] have indicated that oxalic acid is completely oxidized by means of acidic vanadate solutions. BOBTELSKY AND GLASNER[7] have studied the rate of reduction of vanadic acid with oxalic acid; however, the reaction conditions imposed for their study were such as to be of little interest from the standpoint of practical analytical chemistry.

The present investigation was undertaken in an effort to resolve in some measure the conflicting statements appearing in the literature, and to determine whether sodium oxalate would be a suitable primary standard for vanadate solutions. To date, the principal methods for the standardization of vanadates have involved the use of Mohr's salt or potassium dichromate. It would thus be of value to have available a supplementary substance for this function; the widespread availability of sodium oxalate would render it very useful for this purpose.

Under the reaction conditions employed, it has been found that oxalic acid is rapidly and quantitatively oxidized by acid solutions of ammonium *m*-vanadate. The reaction may be represented by the following equation:

$$2VO_3^- + H_2C_2O_4 + 6H^+ \rightarrow 2VO^{+2} + 2CO_2 + 4H_2O$$

The oxidation is carried out in the presence of an excess of vanadate in a strong (>50%) sulfuric acid medium. Upon diluting and cooling, the excess oxidant is titrated with a ferrous ammonium sulfate solution, using *N*-phenylanthranilic acid as indicator. The volume ratio of ferrous ammonium sulfate to vanadate is determined at the same time. Neither the excess of vanadate nor the sulfuric acid concentration is critical. Attempts to carry out the titration directly were not successful.

REAGENTS

Ammonium m-vanadate, approximately 0.3 normal. About 33 g of C.P. ammonium *m*-vanadate were dissolved in 900 ml of distilled water and 100 ml of concentrated sulfuric acid (d. 1.84). The solution was filtered through a sintered-glass crucible. Standardization was normally carried out against a ferrous ammonium sulfate solution of accurately known normality.

Ferrous ammonium sulfate, approximately 0.12 normal. About 120 grams of ferrous ammonium sulfate hexahydrate were dissolved in 2250 ml of distilled water and 250 ml of concentrated sulfuric acid. The titer of this solution was determined daily by titration with primary standard potassium dichromate.

Ferrous ammonium sulfate hexahydrate. Mohr's salt having a purity factor of 99.91% was used throughout this investigation where accurately weighed amounts of this substance were required.

N-phenylanthranilic acid, 0.066 molar. 0.213 g of Eastman Kodak N-phenylanthranilic acid was dissolved in 30 ml of 5% aqueous sodium carbonate; this was then diluted to 150 ml with distilled water. Three to five drops of the resulting solution were employed for each titration.

Sodium oxalate. National Bureau of Standards #40 Oxidimetric Standard sodium oxalate was used. Samples were either introduced with a calibrated volumetric pipet as 10 ml aliquots of prepared solutions or were weighed out directly; in the latter instance, they were dissolved in 10 ml of 10% sulfuric acid.

Potassium dichromate. Use was made of primary standard grade potassium dichromate in the form of a 0.1 normal solution.

PROCEDURE

A 10 ml aliquot of the vanadate reagent was transferred to a 250 ml Erlenmeyer flask containing the oxalate sample. Approximately 25 ml of concentrated sulfuric acid were then cautiously added. The flask was swirled to mix the contents; where a water-bath was not employed, the time required for the reaction was counted from this operation. Upon completion thereof the solution was diluted by the careful addition of 100 ml of distilled water; after thorough mixing by swirling, the flask was allowed to cool to room temperature, following which the excess vanadate was titrated with ferrous ammonium sulfate solution until the blue color of vanadyl sulfate was distinct. Then several drops of N-phenylanthranilic acid solution were added and the titration continued until the purple color of the indicator changed to bright green. While the indicator is stable toward a large excess of oxidant in the cold, it was found expedient to defer its addition until most of the excess vanadate was consumed, since little warning is given of the onset of color-change. Further, it was found advisable to proceed slowly toward the end of the titration in order to avoid over-running of the end-point. Where sodium oxalate was used for the determination of vanadate normality, it was necessary to obtain a volume ratio between the ferrous and the vanadate solutions. The procedure employed for this was the same as that described above, except that no oxalate was involved.

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Effect of heating period

Using the foregoing procedure, weighed samples of sodium oxalate were oxidized with ammonium *m*-vanadate at the temperature of a boiling water-bath for periods of 1-60 minutes. As shown in Table I, the reaction was complete in every instance. The heating requirements necessary for a quantitative reaction were then further examined; aliquot portions of an oxalate solution were employed in this case. Since the addition of sulfuric acid to the vanadate-oxalate mixture resulted in the evolution of a considerable amount of heat, the possibility of dispensing with the water-bath was investigated. Following addition of the sulfuric

TABLE I

OXIDATION OF SODIUM OXALATE AS A FUNCTION OF THE HEATING PERIOD

Quantity NH_4VO_3 taken, milliequivalents	Quantity $Na_2C_2O_4$ taken, millimols	Heating time, minutes	$\frac{\text{Eq. vanadate consumed}}{\text{Mol sodium oxalate}}$	
3.018	0.8626	60	2.010	Heated on water-bath, 100°C
3.018	0.8708	30	2.007	,, ,, ,, ,, ,,
3.018	0.9029	16	1.995	,, ,, ,, ,, ,,
3.018	1.057	5	2.006	,, ,, ,, ,, ,,
3.018	1.020	5	1.997	,, ,, ,, ,, ,,
3.018	1.020	4	1.995	,, ,, ,, ,, ,,
3.018	1.020	3	1.997	,, ,, ,, ,, ,,
3.018	1.020	2	2.000	,, ,, ,, ,, ,,
3.018	1.020	1	1.997	,, ,, ,, ,, ,,
3.018	1.020	0	1.991	Immediately diluted.
3.018	1.020	0	1.997	1 Minute elapsed before dil.
3.018	1.020	0	1.995	2 ,, ,, ,, ,,
3.018	1.020	0	1.997	3 ,, ,, ,, ,,
3.018	1.020	0	2.004	4 ,, ,, ,, ,,

acid, the samples were allowed to stand for varying periods of time prior to the addition of water. Again referring to Table I, it was found that allowing a few minutes to elapse between the addition of sulfuric acid and the dilution with water was sufficient to assure a complete oxidation of the oxalic acid. In subsequent work, the time for reaction varied from 3-10 minutes with no apparent effect upon the results.

Influence of sulfuric acid

In order to investigate the dependence of the reaction upon the acid concentration, samples of sodium oxalate were oxidized with ammonium *m*-vanadate in sulfuric acid media ranging from 50-60%. At least three minutes were allowed to elapse between the addition of the acid and dilution with water. It was found (Table II) that within this range, the sulfuric acid concentration is not critical with respect to the reaction; however, the indicator was observed to change color in a rather sluggish fashion during back-titration of samples representing the two lower acid concentrations.

TABLE II

OXIDATION OF SODIUM OXALATE AS A FUNCTION OF THE SULFURIC ACID CONCENTRATION

Quantity NH_4VO_3 taken, milliequivalents	Sulfuric acid ml	Sulfuric acid %, by vol	Quantity sodium oxalate taken, millimols	Quantity sodium oxalate found, millimols
3.018	18	50	1.020	1.020
3.018	20	52	1.020	1.018
3.018	22	55	1.020	1.018
3.018	24	57	1.020	1.020
3.018	26	59	1.020	1.020
3.018	28	60	1.020	1.018

Use of sodium oxalate as a primary standard for vanadate solutions

The suitability of sodium oxalate as a primary standard for vanadate solutions was investigated by concurrently standardizing a solution of the latter against (a) Mohr's salt of known purity, (b) primary standard potassium dichromate indirectly through the agency of a standardized ferrous ammonium sulfate solution, and (c) sodium oxalate of primary standard purity. Sodium oxalate was found to be a perfectly satisfactory material against which to determine the titer of vanadate solutions. The results of these determinations are summarized in Table III.

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TABLE III

STANDARDIZATION OF A VANADATE SOLUTION

Against sodium oxalate			Against potassium dichromate*		Against Mohr's salt		
Quantity taken, grams	*N*	deviation	*N*	deviation	Quantity taken, grams	*N*	Deviation
0.1001	0.3185	0.0006	0.3174	0.0002	0.9946	0.3170	0.0005
.1148	.3188	0.0009	.3172	.0004	1.0399	.3173	.0002
.1277	.3181	.0002	.3171	.0005	1.0611	.3177	.0002
.1338	.3178	.0001	.3174	.0002	1.0626	.3176	.0001
.1354	.3186	.0007	.3179	.0003	1.1257	.3173	.0002
.1367	.3178	.0001	.3173	.0003	1.1280	.3174	.0001
.1428	.3182	0003	.3176	.0000			
.1431	.3172	.0007	.3173	.0003			
.1433	.3187	.0008	.3183	.0007			
.1450	3184	.0005	.3181	.0005			
.1470	.3172	.0007	.3178	.0002			
.1472	.3181	.0002	.3180	.0004			
.1476	.3176	.0003	.3175	.0001			
.1503	.3172	.0007	.3175	.0001			
.1513	.3170	.0009	.3175	.0001			
.1517	.3185	.0006	.3177	.0001			
.1613	.3186	.0007	.3177	.0001			
.1629	.3168	.0011	.3177	.0001			
.1634	.3176	.0003					
.1660	.3176	.0003					
.1739	.3183	.0004					
.1768	.3180	.0001					
.1796	.3176	.0003					
.1802	.3179	.0000					
.1803	.3179	.0000					
.1822	.3180	.0001					
.2016	.3180	.0001					
Averages	0.3179	0.0004	0.3176	0.0003		0.3175	0.0002

* Since the titer of the ferrous ammonium sulfate solution used for these titrations was obtained by reference to primary standard potassium dichromate, the normality of the vanadate solution is thus indirectly referred to this latter substance.

DISCUSSION

Inspection of the data contained in Table III shows that a satisfactory agreement exists among the several methods of standardization. In effect, these titrations were carried out against the three primary standard substances, sodium oxalate, potassium dichromate, and Mohr's salt. The average normality values fall within a range only slightly greater than one part per thousand. The standard deviation of 0.0005 in the case of the oxalate titrations is somewhat greater but still compares favorably with 0.0003 when a standardized ferrous ammonium sulfate solution was employed, and 0.0003 for the few standardizations carried out against weighed samples of Mohr's salt. It is worthy of note that samples of the reducing agents used as primary standards in this work were titrated with a solution of ceric sulfate according to customary procedures and were found to give concordant results. Likewise, the standard Mohr's salt was titrated with the dichromate solution; satisfactory checks were again obtained. Thus it was found that excellent internal consistency existed between the various standard substances; that they continued to show this in the case of the vanadate standardizations is indicative of the validity of the method in question.

It is of interest to note that no correlation exists between the weight of oxalate taken and the value for vanadate normality obtained.

Several attempts were made to titrate sodium oxalate directly with a solution of ammonium *m*-vanadate; none was successful. The reaction was found to proceed too slowly at room temperature to be of analytical importance, while at elevated temperatures, the indicator was rapidly attacked by any quinquevalent vanadium which was momentarily present. In one instance, an acidified sample of sodium oxalate was titrated at about 100°; addition of the first drop of vanadate reagent caused formation of the oxidized form of the indicator, the color of which persisted after further heating. In another experiment the titration was carried to within one milliliter of the theoretical end-point prior to the addition of indicator. Upon adding a drop of the latter, the oxidized form immediately appeared, which again was not discharged by further heating. Osmium tetroxide failed to exhibit any catalytic effect upon the reaction.

A potentiometric titration at 95° was carried out, making use of a Beckman Model G pH meter equipped with a platinum and a calomel electrode. Even at this temperature, the reaction proceeded quite slowly, as evidenced by the prolonged drift of the meter readings after each addition of reagent; this effect became more pronounced as the end-point was approached. The end-point break in the curve was found to be about 3.5% premature. While it is possible that some improvement over this figure might have been attained by suitable adjustment of experimental conditions, no attempt was made to do so in view of the very long period of time required to carry out the titration.

SUMMARY

The results of a study of the reaction between ammonium *m*-vanadate and sodium oxalate in strong sulfuric acid solution are given. It has been found that the latter is a suitable and convenient primary standard for solutions of quinquevalent vanadium.

RÉSUMÉ

Une étude a été effectuée sur la réaction métavanadate d'ammonium et oxalate de sodium, en solution sulfurique concentrée et les résultats sont donnés. L'oxalate de sodium peut être utilisé comme étalon pour titrer le vanadium (V).

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ZUSAMMENFASSUNG

Die Reaktion von Ammoniummetavanadat mit Natriumoxalat in konzentrierter Schwefelsäurelösung wurde untersucht und die Resultate werden gegeben. Das Natriumoxalat kann als Vergleich verwendet werden bei der Titration von Vanadium (V).

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