

XI.—*Volumetric Estimation of Sodium.*

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Titration of Dihydroxytartaric Acid with Potassium Permanganate.

WHEN a few drops of potassium permanganate solution are run into a solution of dihydroxytartaric acid, mixed with excess of dilute sulphuric acid, at the ordinary temperature, there is at first no apparent change. After standing for a few minutes, however, the colour is discharged, and on continuing the addition of permanganate, the action, when once started, proceeds rapidly, the behaviour being in this respect analogous to that of hydrogen dioxide when similarly treated. The change becomes somewhat slower as it approaches completion, but the end point is well marked and definite.

The relation between dihydroxytartaric acid and permanganate will be seen from the following results. Using a solution of permanganate containing 3·200 grams KMnO_4 per litre,

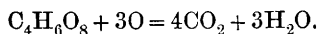
Gram acid taken.	c.c. KMnO_4 .	Gram KMnO_4 .	Atoms of oxygen required for 1 mol. acid.
0·3160	99·7	0·31904	2·90
0·2932	92·3	0·29536	2·90
0·1409	44·2	0·14144	2·89
0·2506	78·6	0·25152	2·89

and with a solution containing 6·3374 KMnO_4 per litre,

0·3145	49·9	0·31624	2·89.
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Taking the mean of these five observations, 1 gram $\text{KMnO}_4 = 0·99405$ gram $\text{C}_4\text{H}_6\text{O}_8$, or 182 grams $\text{C}_4\text{H}_6\text{O}_8 = 183·09$ grams KMnO_4 .

If the acid were entirely oxidised to carbon dioxide and water, 3 atoms of oxygen would be required for 1 molecule of acid



The difference observed may be due, in part, to the fact that an aqueous solution of the acid undergoes a slight decomposition, even at ordinary temperatures, into tartronic acid and carbon dioxide. In the experiments recorded in a former communication (Part I., Trans., Jan., 1898), it was observed that small quantities of carbon dioxide could be traced after the solution had been standing for about 10 or 12 minutes,

and this is about the usual duration of the experiment when titrating the acid with permanganate. It is true that tartronic acid also reduces permanganate, but the initial stage, at the ordinary temperature, is extremely slow. Thus 0.1625 gram of tartronic acid took about 50 minutes to bleach 1 c.c. of a solution of permanganate containing 0.0032 KMnO_4 per c.c.*

In any case, the relation between dihydroxytartaric acid and permanganate is a perfectly definite one, and it will be shown that the reaction affords a very convenient method for the estimation of the acid or its salts.

Volumetric Estimation of Sodium.

Bearing in mind the very sparingly soluble character of sodium dihydroxytartrate, and the definite relation between potassium permanganate and dihydroxytartaric acid, it appeared probable that a simple method might be devised for the quantitative estimation of sodium by a volumetric process.

In the first experiments, measured volumes of a standard solution of pure sodium chloride were mixed with excess of dihydroxytartaric acid dissolved in a small quantity (about 10 c.c.) of water; the mixture was made just ammoniacal and allowed to stand, with frequent stirring, for times varying from 10 to 75 minutes. The precipitated sodium salt was then collected, and after being drained with the aid of the pump was washed three times with small quantities of water, draining well each time; the precipitate was then dissolved off the filter with a considerable excess of dilute sulphuric acid, and the mixture titrated with permanganate.

In recording the results, it will be convenient to denote the quantities by the following symbols.

$a = \text{NaCl}$ taken (gram); $b = \text{KMnO}_4$, solution required (c.c.); $c = \text{Na}$ found (gram); $d = \text{Na}$ calculated (gram).

In the first trial experiment, the precipitation and washing were carried out at the *ordinary temperature*.

Strength of permanganate solution = 3.200 KMnO_4 per litre (sol. A).
Strength of sodium chloride solution = 49.629 NaCl per litre.

$a.$	$b.$	$c.$	$d.$
0.24814	114.2	0.0918	0.0975

* The difference is probably due also to traces of non-oxidisable impurity (water or acetic acid, for example) in the samples of dihydroxytartaric acid employed, since subsequent experiments show that when the potassium salt is used instead of the free acid, the oxygen value approaches more nearly to 3 atoms. The potassium salt crystallises extremely well, so that results obtained by its use are probably more trustworthy. It will be seen, however, that the numerical value of the oxygen ratio in no way affects the final results in the estimation of sodium.

It has been previously shown (Part I.), in the experiments on titration by alkalis, that the salts of dihydroxytartaric acid undergo a considerable amount of decomposition in contact with water at the ordinary temperature, so that a low result was here to be expected.

In the following experiments, both the sodium salt and the dihydroxytartaric acid solutions were carefully *cooled by ice* before mixing, the mixture was allowed to stand in ice during precipitation, and the precipitate was washed with ice-cold water. The advantage of operating at 0° is not only that the decomposition of the salt is prevented (as previously shown), but that the solubility of the sodium salt at this temperature is exceedingly small. The solubility, as will be pointed out later on, is 0.039, at 0° , that is, 100 parts of water dissolve 0.039 part of the sodium salt, which is equivalent to 0.0064 part of sodium. The total volume of the filtrate and washings in each experiment usually amounts to about 25–40 c.c., so that, even in pure water, the amount of sodium dissolved would be almost negligible; but the solubility is of course still further diminished by the presence of excess of dihydroxytartrate, that is, in a solution containing a common ion.

	<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>
I.	0.24814	120.2	0.0966	0.0975
II.	0.24814	60.5	0.0963	0.0975
III took 65.5 c.c., and IV took 60.6 c.c. of permanganate.				

In II, III, and IV, a fresh solution of permanganate was now employed, containing 6.3375 KMnO_4 per litre (solution B). The times of precipitation, in minutes, were 15, 25, 75, and 45 respectively.

Although these results were constant and not much below the theoretical values, the process was hardly considered satisfactory, since, on further trial, it was found that excess of ammonia considerably vitiated the results, and exact neutralisation is not easy. Experiments were then made using pure *potassium carbonate* (prepared from potassium bitartrate) in calculated quantity for neutralisation in place of ammonia. The mixture was also made more concentrated, the acid being now dissolved in about 2 c.c. of water, instead of in 10 c.c. A fresh solution of sodium chloride was prepared containing 40 grams NaCl per litre, the permanganate used being the same as in the previous experiments (solution B). Five c.c. of NaCl solution were used, as before, for each experiment.

	<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>
V.	0.200	52.1	0.0815	0.0786

VI took 53 c.c., and VII 54 c.c. The times of precipitation were 30, 60, and 150 minutes respectively. Using twice the previous

proportion of dihydroxytartaric acid and potassium carbonate, the results were still higher, VII taking 57.3 c.c.

Substituting *ammonium carbonate* for potassium carbonate, similarly high results were obtained, VIII requiring 52.8 c.c.

The explanation of these high results when potassium or ammonium carbonates are used in concentrated solutions is found in the fact, subsequently discovered, that potassium and ammonium dihydroxytartrates, although fairly easily soluble at ordinary temperatures, dissolve with difficulty at 0° and thus tend to contaminate the precipitated sodium salt. This source of error would be avoided, and the process much simplified, by employing one of these salts for precipitation instead of using the free acid and subsequently neutralising.

The preparation and composition of the potassium and ammonium salts were therefore studied, with the results which will be given in a subsequent communication.

The potassium salt is easy to prepare, and appears to be quite permanent if kept in a closed vessel (it is also fairly permanent in the air, for some days, at any rate). It is likewise somewhat less soluble than the ammonium salt, so that its use does not involve any danger of contamination with ammonium, should salts of the latter be present. The potassium salt is, in fact, a most convenient reagent both for the qualitative and quantitative estimation of sodium.

Using the same sodium chloride and permanganate (B) solutions as before, and precipitating with excess (about 1½ equivalents) of the potassium salt, the following results were obtained.

<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>
0.200	49.4	0.0786	0.0786
0.200	48.4	0.0770	0.0786
0.200	48.8	0.0776	0.0786

Since measurement of the strong sodium chloride solution was probably hardly sufficiently accurate, in the next experiments weighed quantities of sodium chloride, each dissolved in 5 c.c. of water, were employed instead of measured volumes of standard solution.

<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>
0.0997	23.5	0.0374	0.0391
0.1915	47.6	0.0757	0.0752
0.4367	107.4	0.1710	0.1716

The process, therefore, when conducted in this manner, evidently gives satisfactory results.

The permanganate solutions employed so far had been standardised by means of ammonium oxalate, and the results were calculated from the relations shown to exist between permanganate, dihydroxytartaric

acid and sodium. In preparing a fresh permanganate solution (solution C) for subsequent experiments, it appeared that the most direct way would be to standardise the solution by means of pure sodium chloride. The following were the observations.

S = strength of permanganate (C) in grams of Na *per litre*.

<i>a.</i>	<i>b.</i>	<i>S.</i>
0.2235	49.4	1.778
0.1865	40.4	1.814
0.3704	79.9	1.822
0.3032	66.2	1.800

Mean of the four experiments, $S = 1.805$.

This solution was now employed for the estimation of sodium in various common sodium salts.

Normal Sodium Sulphate.—This was a commercially pure specimen recrystallised and ignited. 0.3472 gram of substance, dissolved in about 5 c.c. of water and precipitated with excess (1 gram) of potassium dihydroxytartrate, required 62.75 c.c. of permanganate (C). Na Found = 32.62 per cent., Calculated 32.39 per cent.

Sodium Nitrate.—Commercially pure specimen recrystallised and dried at 100°. 0.3641 gram of substance in about 5 c.c. of water precipitated with 1.3 grams of potassium salt, required 55.2 c.c. of permanganate (C). Na Found = 27.36 per cent., Calculated 27.05 per cent.

Mixture of Sodium Chloride and Magnesium Sulphate.—Magnesium sulphate gives no precipitate with potassium dihydroxytartrate. 0.2307 gram NaCl mixed with 0.3 gram $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ dissolved in about 7 c.c. of water and precipitated with 0.8 gram of potassium salt, required 50.3 c.c. permanganate (C). Na Found = 39.35 per cent., Calculated 39.31 per cent.

The presence of magnesium, therefore, does not interfere with the accuracy of the sodium estimation.

Mixture of Sodium Chloride and Ammonium Chloride.—0.3225 gram NaCl mixed with 0.4 gram NH_4Cl dissolved in about 8 c.c. of water and precipitated with 1.1 grams of potassium salt, required 67.95 c.c. of permanganate (C). Na Found = 38.03 per cent., Calculated 39.31 per cent.

From this result, it would appear that the presence of excess of ammonium salt tends to give low results in the sodium value.

Rochelle Salt.—Commercially pure specimen: pressed. 1.2569 gram of substance precipitated with 1.2 grams of potassium salt, required 54.85 c.c. of permanganate (C). Na Found = 7.87 per cent., Calculated 8.15 per cent.

Sodium salts of weak acids whose solutions give an alkaline reaction

with litmus, such as phosphate and acetate, give somewhat low results when precipitated by means of the potassium salt. But with *free* dihydroxytartaric acid, such salts give normal, or nearly normal, results. This is probably due to the instability of sodium dihydroxytartrate in presence of alkalis, a fact which was indicated in the low results obtained in presence of free ammonia, and in the action previously mentioned of sodium hydroxide (Trans., 1898, 73, 74).

Free dihydroxytartaric acid gives a precipitate with all sodium salts which have been examined, with the exception of the borate (see below). Even salts of strong acids, such as sulphate, chloride, and nitrate, are, on standing, partially precipitated, and in the case of weaker acids, the precipitation appears to be complete, or nearly so. It is possible that the relative avidities of many acids might be compared in this manner.

Sodium Acetate.—A commercially pure specimen recrystallised and pressed.

I. 0.4014 gram substance dissolved in 5 c.c. water and precipitated with 1.05 grams of *potassium salt*, required 36.65 c.c. of permanganate (C). Na Found = 16.48 per cent.

II. 0.6458 gram substance dissolved in 5 c.c. of water and precipitated with 0.5 gram of *free dihydroxytartaric acid* required 60.9 c.c. of permanganate (C). Na Found = 16.98 per cent., Calculated 16.91 per cent.

Sodium Phosphate.—A commercially pure specimen recrystallised and pressed.

I. 0.8664 gram substance dissolved in 10 c.c. of water and precipitated with 1.2 grams of *potassium salt*, required 58.4 c.c. of permanganate (C). Na Found = 12.16 per cent.

II. 1.0814 gram substance dissolved in 10 c.c. of water and precipitated with 1 gram of *free dihydroxytartaric acid* required 73.8 c.c. of permanganate (C). Na Found = 12.31 per cent., Calculated 12.84 per cent.

Sodium Carbonate.—This gives low results, even with the free acid. This is probably due to the difficulty of preventing loss by spirting without unnecessary dilution of the solution, by washing, and perhaps also to the difficulty of preventing a rise of temperature during neutralisation. With the potassium salt as precipitant, 38.68 per cent. Na was obtained, and with the free acid 42.85 per cent., theory requiring 43.43 per cent.

Carbonates should, therefore, be first acidified, say, by hydrochloric acid, with due precautions against loss by spirting, the solution evaporated to dryness, and the residue dissolved in a small quantity of water.

Borax.—This salt is altogether exceptional in its behaviour, since its solution gives *no precipitate whatever*, either with the potassium

salt or with the free acid. In this respect, it differs from all other sodium salts which have been examined. The reason for this difference is under investigation. Possibly, as with some other hydroxy-acids (for example, tartaric and salicylic), a compound is formed, which is soluble in water. Boric acid, if present, must therefore be removed by one of the usual methods, such as by methylic alcohol and hydrogen chloride, before sodium is estimated.

Directions for Working the Process.

In order to ensure accurate results, attention must be given to the following details.

Metals other than potassium, sodium, and magnesium must be absent. (Possibly some other metals may prove to be admissible, but only a few have been examined. Ammonium salts, if present in any quantity, appear to produce low results, so had better be removed.)

The metals should be present preferably as chlorides, sulphates, or nitrates. The solution to be examined must be concentrated and neutral.

Potassium dihydroxytartrate, $K_2(C_4H_4O_8) \cdot H_2O$, is dissolved in the least quantity (about 30 times its weight) of ice-cold water. The salt dissolves with some difficulty, and the solution, if not completely clear, is filtered before use.

Both solutions having stood in melting ice for a few minutes, the potassium salt is added in excess, the mixture kept in melting ice for half an hour, with occasional stirring, and the precipitated sodium salt, after being collected on a small filter, is drained with the assistance of the pump, and quickly washed three or four times with small quantities (about 4 or 5 c.c.) of ice-cold water, draining each time. The precipitate is then dissolved off the filter with a large excess of dilute sulphuric acid, and the solution titrated with potassium permanganate at the ordinary temperature of the laboratory.

The permanganate may be standardised by the usual methods (by oxalic acid or ammonium oxalate) and the result calculated from the relation which is shown to exist between permanganate and dihydroxy-tartaric acid; but the simplest and best method is to standardise the permanganate indirectly by means of pure *sodium chloride*, proceeding exactly as above directed.

If salts of weak acids, which give an alkaline reaction, such as acetates or phosphates, are to be examined, the free acid should be substituted for the potassium salt. Carbonates or hydroxides must first be neutralised, and boric acid, if present, must be removed by one of the usual methods, such as by methylic alcohol and hydrogen chloride. The results obtained appear to be as accurate as can be expected from

any volumetric process of the kind. The method could, of course, be varied in several ways. For instance, a measured excess of potassium dihydroxytartrate might be employed and the excess estimated after precipitation. Or the sodium salt could be determined gravimetrically by converting it into sulphate, chloride, &c., or it could be heated with water and the carbon dioxide estimated.

This volumetric process is probably much more economical than the estimation of potassium by platinum chloride; it is certainly very much more rapid, and probably quite as accurate, so that in the case of a mixture consisting entirely of potassium and sodium salts, where it is desired to estimate one of the metals only, it would be more advantageous to determine the sodium than the potassium.*

Qualitative Detection of Sodium.

In a former communication (Trans., 1895, 67, 48), the use of free dihydroxytartaric acid was proposed as a reagent for the detection of sodium, the solution to be examined being mixed with a solution of the acid, neutralised with ammonia, and the mixture stirred, preferably on a watch-glass. The *potassium salt*, however, affords a far more convenient reagent, since the necessity for neutralisation is dispensed with, and the introduction of ammonia is avoided; it was shown above that the presence of ammonia and of ammonium salts tended to give low results in the sodium value, so that for qualitative detection of small quantities its presence is objectionable. By using ice-cold solutions of the potassium salt and of the substance to be examined, and keeping the mixture for some time at 0°, it is fairly easy to detect one part of sodium in over 2000 parts of water.
