hydroxide using methyl orange as indicator.   The end reaction is best observed by using a porcelain casserole to contain the solution, adding the alkali in slight excess and titrating back with $\frac{N}{10}$ hydrochloric acid until the pink acid tint just reappears. From the number of cubic centimeters of alkali used the amount of bromine present as hydrobromic acid is calculated, and when expressed in per cent. gives the bromine substitution figure because for every atom of bromine which has replaced an atom of hydrogen, one molecule of hydrobromic acid has been formed. Twice the bromine substitution figure subtracted from the total absorption gives the bromine addition figure.

The following results were obtained:

Substance.	Total bromine absorption, eighteen hours.	Bromine. addition figure.	Bromine. substitution figure.
W. G. Rosin	212.7	0.0	106.35
E. Rosin	206.5	0.0	103.25
Second run Rosin Oil (a)	116.2	0.0	58.1
" " " " (b)	114.7	0.0	57.35
American Raw Linseed Oil	102.88	102.88	0.0
Same Oil Boiled	103.92	103.92	0.0
White Salad Cotton-seed Oil	65.54	64.26	0.64
Sperm Oil	56.60	54.52	1.04

A consideration of the above figures shows that the results are much more instructive than those obtained by the Hübl process which is the one in common use.   Rosin oil, rosin, and other resins may be detected and determined in mixture with fatty oils, or, if they are present in known quantity, the character of the fatty oil may be determined.   Investigations which are being made on a large number of oils and resins will probably furnish analytical data for the analysis of oils and varnishes.

ON THE DETERMINATION OF PHOSPHORIC ACID.[1]

BY H. PEMBERTON, JR.

LAST autumn I described a process for determining phosphoric acid by titration of the ammonium phosphomolybdate with standard alkali.   (This JOURNAL, **15,** 382.)   The ratio

[1] Read at the stated meeting of the Chemical Section of the Franklin Institute, held February 20, 1894.

between the P_2O_5 of the precipitate and the standard alkali was determined and found to be 23.2 molecules of Na_2O to one molecule of P_2O_5. Upon this ratio, as determined by direct analysis, the standard solution was prepared of such strength that one cubic centimeter should be equal to one milligram of P_2O_5 by diluting 326.5 cubic centimeters of normal alkali to one liter. The analyses upon which this ratio (23.2 molecules) was determined were carefully made. I was, therefore, at a loss to know the cause of the variation of this figure from the theoretical ratio of exactly twenty-three molecules of Na_2O. The difference is of more importance than might at first thought, be supposed, since the strength of the alkali solution is based upon the figure determined empirically, and not upon the theoretical one. If the 23.2 proportion is wrong and twenty-three correct, a standard solution based upon the former ratio would give too low results in the proportion of 23.2 : 23.0. Thus a phosphate rock containing eighty per cent. calcium phosphate would appear, by such an analysis, to contain only 79.31 per cent.

It was decided, therefore, to repeat this part of the work, and in this re-examination the conditions were the same as those previously existing, except in one particular: the amount of phosphoric acid operated upon was smaller than that previously used. By referring to the original paper, it will be found that about eighty cubic centimeters of alkali were used in each of the titrations in question. This represents a quantity of the yellow precipitate much larger than would ever be obtained in the analysis of even the richest phosphate rocks; and in operating upon so large a precipitate the liability of error from incomplete washing is great. Any free acid remaining in the precipitate would, of course, result in too high a reading of the burette, with a corresponding error in the standardizing of the solution.

The following are the results obtained in this re-examination:

Some di-sodium hydrogen phosphate, bought as chemically pure, was dissolved in hot distilled water, filtered, and crystallized; the crystals were washed, dissolved again in water, and recrystallized. Of the resulting crop of crystals, about forty-five grams were dissolved in one-half liter of water. The strength of this solution was then determined.

	Weight of Na$_2$HPO$_4$ solution. grams.	Grams.
I	20.0814 gave	0.7581 Na$_4$P$_2$O$_7$
II	17.9585 gave	0.6778 Na$_4$P$_2$O$_7$
III	36.9115 gave	1.1652 Mg$_2$P$_2$O$_7$

The magnesium-ammonium phosphate precipitate was filtered, dissolved in acid and reprecipitated by ammonia.

By a coincidence each of these three determinations gave precisely the same result ; *viz.*,

TABLE I.

	Grams P$_2$O$_5$ in 10 grams of solution.
I	= 0.2014
II	= 0.2014
III	= 0.2014

Therefore, ten grams of the sodium phosphate solution contained 0.2014 grams P$_2$O$_5$.

Weighed portions of this same solution were now precipitated by ammonium molybdate, thoroughly washed and titrated. The results are given in Table II.

TABLE II.

I.	II. Grams Na$_2$HPO$_4$ solution taken.	III. Equivalent to grams P$_2$O$_5$.	IV. cc. of KHO solution used.
A	2.0410	0.04110	41.05
B	2.3710	0.04775	47.70
C	2.2920	0.04616	46.20
D	2.4690	0.04972	49.60

Dividing the figures in Column III by those in Column IV, and multiplying the result by 100, we obtain the number of milligrams corresponding to 100 cubic centimeters of the potassium hydroxide solution, as follows:

TABLE III.

	Mgms. P$_2$O$_5$.
A	= 100.12
B	= 100.11
C	= 99.91
D	= 100.24
Average	= 100.09

Therefore, 100 cubic centimeters of the potassium hydroxide

solution neutralize an amount of the yellow precipitate corresponding to 100.09 milligrams of P_2O_5.

The standard acid was now titrated against the standard alkali, using phenolphthalein as the indicator, whereby the two solutions were found to be of exactly equal strength.

The standard acid was then titrated against pure sodium carbonate, using phenolphthalein at boiling heat:

	Grams Na_2CO_3 used.	cc. of acid used.	100 cc. acid equal to mgms. Na_2CO_3.
I......................	0.9099	52.95	1719
II......................	0.9168	53.35	1719

Therefore, 100 cubic centimeters of acid are equivalent to 1719 milligrams sodium carbonate, and since the alkali solution is of the same strength as the acid, 100 cubic centimeters of it also are equivalent to 1719 milligrams sodium carbonate.

As we have already seen, by Table III, that 100 cubic centimeters of the alkali are required to neutralize 100.09 milligrams of P_2O_5 (in the form of ammonium phosphomolybdate), it follows that 1719 milligrams sodium carbonate are required for 100.09 milligrams P_2O_5.

Dividing each by its molecular weight we have

$$\text{for } P_2O_5 \ \tfrac{100.09}{142.06} = \ 0.7045$$
$$\text{for } Na_2CO_3 \ \tfrac{1719.0}{106.1} = 16.20$$

Therefore,

$$P_2O_5 : Na_2CO_3 = 0.7045 : 16.20 = 1 : 22.99$$

In other words, 23 molecules of sodium carbonate (or of Na_2O) are required to neutralize the yellow precipitate containing one molecule of P_2O_5, and the former figure (that given in my paper of last autumn) 23.2 molecules, is incorrect.

Referring to Table II of the present paper, it may be stated that in analysis A the yellow precipitate was washed on an ordinary filter without using suction, the precipitate being washed on the filter, transferred to the beaker and then again filtered and washed. In analysis B, of the same table, the precipitate was washed on the ordinary filter, with the aid of the suction pump. In analyses C and D, the precipitates were washed with suction on a porcelain funnel with a fixed perforated plate in it.

This form of funnel is known as the Hirsch funnel.[1]

As in all cases the results were nearly identical; it is evident that the different methods of washing the precipitate had no influence upon the result. Exactly twenty-three molecules of Na_2O are required for one molecule of P_2O_6. The standard acid is prepared by diluting 323.7 cubic centimeters of normal sulphuric acid to one liter, and not 326.5 cubic centimeters as previously stated. The alkali solution, after removing carbon dioxide by barium hydroxide, is brought to the same strength as the acid, volume for volume.

One cubic centimeter of either solution is then equal to one milligram of P_2O_5.

PHILADELPHIA, PA., February 20, 1894.

NOTE ON PEMBERTON'S METHOD OF PHOSPHORIC ACID DETERMINATION AS COMPARED WITH THE OFFICIAL METHODS.[2]

BY WM. C. DAY AND A. P. BRYANT.

HAVING occasion to make a series of determinations of phosphoric acid in Florida phosphate rock, we have used the method recently described by Mr. H. Pemberton, Jr., and incidentally have made a number of comparisons between it and the official method. The following are the results:

GRAVIMETRIC DETERMINATIONS.

No. 1.   From 0.7867 gram $Na_2HPO_4 + 12H_2O$, obtained 0.2426 gram $Mg_2P_2O_7$

No. 1.   From 1.1100 grams $Na_2HPO_4 + 12H_2O$, obtained 0.3433 gram $Mg_2P_2O_7$

No. 2.   From 1.0000 gram Florida rock, obtained 0.5828 gram $Mg_2P_2O_7$

No. 3.   From 0.3807 gram Florida rock, obtained 0.0262 gram $Mg_2P_2O_7$

No. 3.   From 0.4831 gram Florida rock, obtained 0.0333 gram $Mg_2P_2O_7$

No. 4.   From 1.0036 grams Florida rock, obtained 0.0227 gram $Mg_2P_2O_7$

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[1] To be had from Bullock and Crenshaw, Philadelphia. A disk of filter paper of the diameter of an American silver quarter dollar (fifteen-sixteenths inch) is used, when employing the smallest size funnel. I can highly recommend this funnel in all cases in which the precipitate is to be titrated. The precipitate presents a perfectly flat surface, is easily and quickly washed, and is readily transferred with the aid of the wash bottle to the beaker. The funnel can be employed only when using the suction pump, but it has the advantage of not requiring a platinum cone, and the size of the filter is reduced to a minimum.

[2] Read at the stated meeting of the Chemical Section, of the Franklin Institute held February 20, 1894.