Alkalimetric Determination of Phosphoric Acid and Phosphates

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Various methods have been worked out for determination of phosphoric acid and phosphates on the basis of the following principle: With a suitable indicator present, the sample is neutralized to the first equivalence-point of the phosphoric acid ($\text{pH} = \text{ca. } 4.5$ corresponding to H_2PO_4^-). Then a suitable excess of a salt is added, the cation of which — by the methods hitherto worked out at a somewhat higher pH — reacts with the phosphate and quantitatively forms a precipitate of the tertiary phosphate (or a *welldefined* basic phosphate).

The precipitation may be:

The liberated — or gradually liberated — hydrogen ions are titrated with a strong base.

A calcium salt (or a barium salt) can be used as mentioned by Kolthoff and Stenger¹, who also give the most important literary references. Titration is carried out by addition of a calcium salt until $\text{pH} = \text{ca. } 9$ (phenolphthalein).

Also a silver salt can be used. This method has been thoroughly investigated by Brunisholz², who, too, refers to earlier literature. A further specified excess of silver nitrate is used and titration is carried out until $\text{pH} = \text{ca. } 6$ (chlorophenol red).

In the present paper a method is proposed, according to which precipitation of phosphate is carried out by means of cerous nitrate:

As was shown by the experiments, the precipitation of cerous phosphate at the first equivalence-point of the phosphoric acid was so complete that the

liberated hydrogen ions could be titrated to the pH of the first equivalence-point. This procedure offers the following advantages:

1) The experimental and theoretical advantage that the same indicator can be used when fixing the pH as well as when carrying out the titration itself.

2) The theoretical advantage that the possibility of the presence of acids consuming the base between the pH of the first equivalence-point and the end-point of the titration is eliminated. (The actual metal ions added (cerous ions) precipitate only when $\text{pH} > 7$).

On the other hand, like the above-mentioned methods, the present method will be inhibited or rendered impracticable by the presence of acids consuming the base in the proximity to the first equivalence-point and thus preventing an accurate fixation of pH being made. Furthermore, the method will be inhibited by the presence of substances which — like dihydrogen phosphate ions — react with cerous ions under liberation of hydrogen ions.

As to the choice of indicator when the sample is to be neutralized to the first equivalence-point, we have followed Pierre *et al.*² These authors recommend a mixed indicator consisting of 0.02 % methyl orange and 0.1 % bromocresol green. They state that the pH-range of methyl orange is 3.1 — 4.4 and that of bromocresol green 4.0 — 5.6, while the mixed indicator in question at $\text{pH} = 4.3$ has a characteristic change of colour from greenish yellow to light green. However, it is not clear at which ion strength these values off pH are valid.

During our titrations a white porcelain plate was used as underlay, and in the experiments a daylight bulb was used when necessary as source of illumination. In preparing the mixed indicator the method of Pierre *et al.* was followed:

"The most satisfactory method of bringing both indicators into solution is to weigh 0.1 gram of bromocresol green and 0.02 gram of methyl orange into an agate mortar, and to grind these with a pestle as small amounts of sodium hydroxide solution are added, using a total of 2 cc 0.25 *N* sodium hydroxide or its equivalent. The solution is transferred to a beaker and then to a 100-cc volumetric flask and made up to volume with water.

Ten drops of the indicator mixture are used per 150 cc of the solution titrated. While small variations from this amount give equally satisfactory results, it seems best to keep the ratio of indicator to solution to near one drop to 15 cc of solution titrated."

For the alkalimetric titration 0.1 *N* sodium hydroxide (made of 50 % sodium hydroxide diluted with boiled and cooled water) was used. This sodium hydroxide was standardized against hydrazine sulfate. For the fixation of the first equivalence-point 0.1 *N* hydrochloric acid was used. The cerous salt solution was prepared from the purest $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$.

Table 1. The solution of phosphate used contains 1.140 % PO_4 (gravimetrically determined). After fixation at $\text{pH} = \text{ca. } 4.3$ a cerous salt is added, and the hydrogen ions liberated are titrated alkalimetrically to the same pH .

Series of expts.	Number of determinations	% PO_4 found	Greatest deviation from mean value (absolute)	Deviation from gravimetric determination (relative)	Remarks
I	6	1.152	0.003	+ 1.1 %	No addition of NaCl.
II	7	1.151	0.002	+ 1.0	As I, but heating and cooling down before titration.
III	6	1.147	0.002	+ 0.6	Addition of 1 g NaCl
IV	5	1.141	0.001	+ 0.1	» » 2 » »
V	5	1.139	0.002	— 0.1	» » 3 » »
VI	5	1.138	0.002	— 0.2	» » 4 » »
VII	3	1.136	0.001	— 0.4	» » 5 » »
VIII	9	1.140	0.001	0	» » 2.5 » » + CaCl_2 equivalent to the amount of phosphate.
IX	9	1.140	0.002	0	As VIII, but twice as much CaCl_2 .

As sample was used a *ca.* 0.125 *M* solution of Na_2HPO_4 *p.a.* The phosphate content of the solution was determined gravimetrically as magnesium pyrophosphate; result: 1.140 % PO_4 . In the following experiments 10.182 ml of this solution of Na_2HPO_4 were used.

METHOD

The indicator (and in some of the experiments also sodium chloride) is added to the sample. Fixation at the first equivalence-point is carried out by means of 0.1 *N* hydrochloric acid. A small excess of the cerous nitrate solution is added, and titration is made with a standard 0.1 *N* sodium hydroxide until the indicator assumes the same colour as at the first equivalence-point. Total volume: 75–100 ml.

RESULTS

The results are shown in Table 1. In No. I series of experiments the addition of cerous nitrate caused immediate precipitation of cerous phosphate. In series No. II heating until boiling was carried out after the precipitation of

cerous phosphate, by which procedure the precipitate disappeared and re-appeared only when, during the titration, about 0.5 ml 0.1 *N* sodium hydroxide was still left to be added. Such a variation in procedure may be used to denote that the end-point of the titration is being approached, otherwise it does not seem to be of any advantage.

In Nos. I and II series of experiments the fixation is evidently made at a pH-value in the solution which is below the first equivalence-point. The first equivalence-point here is roughly estimated to be at pH = 4.5 (*cf.* below), while titration is carried out until pH = *ca.* 4.3. Accordingly, more hydrogen ions are bound in the phosphate than corresponding to the first equivalence-point, and the addition of cerous ions consequently liberates too many hydrogen ions, which makes the results too high.

In the following series of experiments the ionic strength in the solution is increased by addition of sodium chloride, and so the pH for the equivalence-point is decreased. On the basis of series Nos. III–VII it is seen that in connection with the concentrations used here an addition of *ca.* 2.5 g sodium chloride will bring about such an ionic strength that the first equivalence-point will become identical with the pH-value at which the mixed indicator has its characteristic change of colour.

In series Nos. VIII and IX this ionic strength has been roughly adhered to, and the experiments show that addition of reasonable amounts of a calcium salt does not handicap the method. If calcium ions are present, however, titration must be carried out at a somewhat slower rate in order to leave time for a possible precipitate of calcium phosphate to be converted into cerous phosphate.

In some experiments in a later series the precipitated cerous phosphate was filtered off, and then washed, dried and weighed. Calculated under the assumption that the precipitate is pure CePO_4 , this precipitate should weigh 0.2905 g; three experiments gave the following results: 0.2910 g; 0.2915 g; 0.2925 g. Consequently, the cerous phosphate precipitation should be practicable also as a gravimetric method.

Theory: An addition of 2.5 sodium chloride evidently gives a suitable ionic strength, which is in agreement with what is to be expected theoretically. Bjerrum and Unmack ⁴ state the following expressions for the first two dissociation constants in solutions of sodium chloride (at 18° C):

$$pk_{\text{H}_3\text{PO}_4} = 2.178 - 0.35 \sqrt[3]{c} + 0.18 c$$

and

$$pk_{\text{H}_2\text{PO}_4^-} = 7.277 - 1.13 \sqrt[3]{c} + 0.185 c$$

where c is the concentration of sodium ions and where the formulae are valid for $0.1 > c > 0.003$. Bjerrum and Unmack also state:

$$pk_{H_3PO_4} = 2.120 \quad \text{and} \quad pk_{H_2PO_4^-} = 7.227$$

when the ionic strength is nil.

In the titrations carried out, where the volume during the fixation at the first equivalence-point before the titrations was *ca.* 75 ml, c is approximately equal to 0.03 without addition of sodium chloride. From the above formulae we get:

$$pk_{H_3PO_4} = 2.074 \quad \text{and} \quad pk_{H_2PO_4^-} = 6.932$$

Further, the approximate value of c is 0.6 after addition of 2.5 g sodium chloride. Certainly this value is far above the exact validity range of the above-mentioned formulae, but if these are still used, we get:

$$pk_{H_3PO_4} = 1.991 \quad \text{and} \quad pk_{H_2PO_4^-} = 6.435$$

If the first equivalence-point is calculated by means of the approximated formula:

$$pH = \frac{1}{2} (pk_{H_3PO_4} + pk_{H_2PO_4^-})$$

we get:

$$pH = 4.50 \quad \text{for} \quad c = 0.03$$

and

$$pH = 4.21 \quad \text{for} \quad c = 0.6$$

Also the interval of transition of the indicator is somewhat altered, and even if no exact statement can be made with regard to the mixed indicator, reference can be made to papers dealing with methyl orange by Güntelberg and Schiödt⁵ and with bromocresol green by Chase and Kilpatrick⁶. In these papers the classical dissociation constants for the two indicators have been determined in solutions of potassium chloride, and conditions here cannot be essentially different from conditions in solutions of sodium chloride. The experimental results from the two papers cited have been used in Table 2.

Table 2. The classical dissociation constant indicated by pk for methyl orange (according to Güntelberg and Schiödt⁵) and for bromocresol green (according to Chase and Kilpatrick⁶) in dependence with the concentration of the electrolyte (mainly KCl).

Electrolyte moles per liter	Methyl orange pk (18°)	Bromocresol green pk (25°)
0.0	3.49	
0.1	3.37	4.51
0.2	3.36	
0.5	3.43	4.39
1.0	3.58	4.44
2.0	3.85	4.53

The values of pK for both indicators, initially decreasing and later on increasing, explain, when compared with the decreasing (finally only slightly decreasing) values of pH for the first equivalence-point, the results of Nos. III–VII series of experiments.

SUMMARY

An alkalimetric method for determination of phosphoric acid and phosphates has been worked out. Principle: The solution is neutralized to the first equivalence-point of phosphoric acid ($H_2PO_4^-$). By addition of cerous ions cerous phosphate is precipitated and two hydrogen ions per group of phosphate are liberated. This amount of acid is titrated with a strong base to the same pH as before.

REFERENCES

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