Phosphorus (V) Oxide Accelerated Determination in Phosphates with Monovalent NH^{4+}, K^+, Na^+, H^+ Cations

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Abstract. *R*esults of accelerated gravimetric determination of phosphorus (V) P_2O_5 oxide content in monosubstituted potassium phosphate KH_2PO_4 without calcining the magnesium-ammonium phosphate precipitate at a high temperature of 950-1000 °C were presented. Application of this accelerated method for the determination of phosphorus pentoxide in phosphates simplifies the analysis method by eliminating the time-consuming and energy-intensive calcining operation.

Keywords: gravimetric method, phosphorus (V) oxide content, phosphates, precipitated form, calcination, drying, energy saving.

1. INTRODUCTION

Phosphorus element is an essential, non-replaceable substance in biological organisms and soils containing P pools required for plant growth, as raw materials containing phosphorus can provide a valuable base for mineral fertilizers new formulations [1, 2]. Mineral deposits considered as the major supply of phosphorus [3]. Phosphorus fertilizers are mineral substances, usually calcium or ammonium salts of phosphoric acid, provide agricultural crops with nutrient [4].

The anthropogenic phosphorus cycle resembles the natural as represented in Figure 1, except it uses only the higher concentration mineral phosphorus more intensively [5].
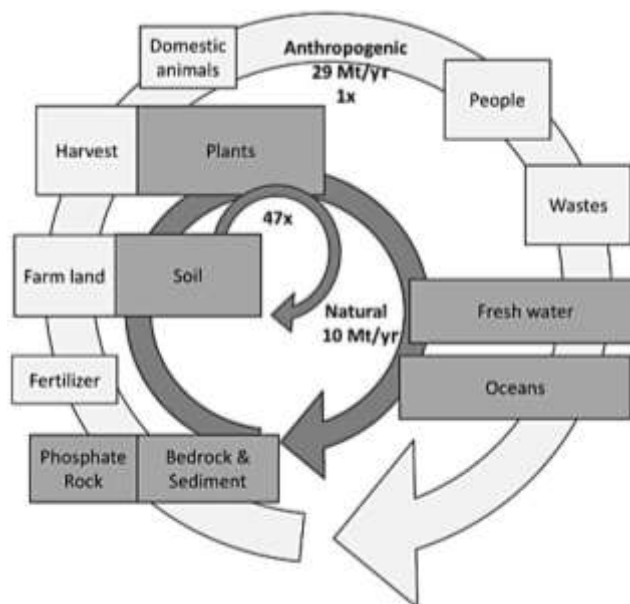

FIGURE I
THE NATURAL AND ANTHROPOGENIC AGRICULTURAL PHOSPHORUS CYCLES (REPRESENTED FROM REF. [5]).

Several methods are used to determine phosphate concentration (measured as PO_4 and expressed as % P_2O_5) in fertilizers [6].

2. RESEARCH METHODS AND MATERIALS

In this work, results of gravimetric determination of phosphorus (V) oxide P_2O_5 content in monosubstituted potassium phosphate were shown, where the famous method for determination of phosphoric acid in $Na_2HPO_4 \cdot 12H_2O$ was analyzed. Calculation formulas according to GOST 26261-84 were determined.

3. RESULTS AND DISCUSSIONS

Results of gravimetric determination of phosphorus (V) oxide content in monosubstituted potassium phosphate

The main tasks in the production of phosphorus-containing fertilizers are to increase the volume of production, expand the range, and reduce the cost of the produced phosphorus fertilizers. In this regard, the determination of the content of phosphorus (V) oxide P_2O_5 in phosphates by saving energy by reducing the stage of precipitation calcination is relevant.

There is a famous method for the determination of phosphoric acid in $Na_2HPO_4 \cdot 12H_2O$ [7], where $MgCl_2$ acts on a $Na_2HPO_4 \cdot 12H_2O$ solution in the presence of NH_4OH and NH_4Cl:

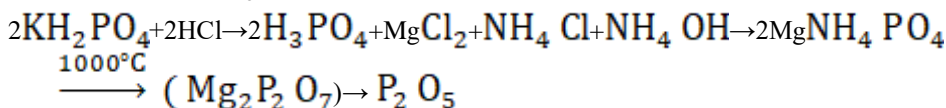$$Na_2HPO_4 + MgCl_2 + NH_4Cl + NH_4OH = \downarrow MgNH_4PO_4 + 2NaCl + H_2O$$
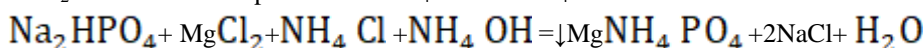
White crystals of precipitate dried at temperature 45-50 °C [2]. The $MgNH_4PO_4$ precipitate was filtered off, washed, ignited and heated. When calcined, $MgNH_4PO_4$ decomposes, releasing water and ammonia, forming magnesium pyrophosphate MgP_2O_7 [8]:

$$2\,MgNH_4PO_4 \xrightarrow{t=1000°C} Mg_2P_2O_7 + H_2O + \uparrow 2NH_3$$
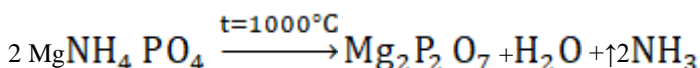
According to GOST 26261-84 [9], monosubstituted potassium phosphate K_2HPO_4, was taken as a method of preparing its standard solution with a mass concentration of phosphorus (V) oxide P_2O_5 of 0.1 mg/ml. For this purpose, KH_2PO_4 sample (pure for analysis) with a mass of 0.1917+0.0015g was weight up. By multiplying 0.1917g by ten (KH_2PO_4 x 10 = 1.917g) 1.917g KH_2PO_4 was weight up as a sample, which contains 1.0g P_2O_5).

According to analytical chemistry literature [10, 11] it is known that in the quantitative analysis of phosphates and determination of the Mg^{2+} percentage, a reagent $Na_2HPO_4 \cdot 12H_2O$ is always used. We decided to replace it with more reference and standard reactive KH_2PO_4 (pure for analysis grade). After examining the analysis flow charts of chemical transformations, we noticed that molecular weights of the reagents KH_2PO_4 and $\downarrow MgNH_4PO_4$ are almost the same. Following are the chemical reactions in the weight determination of P_2O_5 content from KH2PO4:

$$2KH_2PO_4 + 2HCl \rightarrow 2H_3PO_4 + MgCl_2 + NH_4Cl + NH_4OH \rightarrow 2MgNH_4PO_4$$
$$\xrightarrow{1000°C} (Mg_2P_2O_7) \rightarrow P_2O_5$$

142 conditional units mean that from two moles of H_3PO_4 one mole of P_2O_5 will form.

If compare molecular masses of Mr(KH_2PO_4)=136, Mr ($MgKH_2PO_4$)=160, Mr($MgNH_4PO_4$)=137, they are almost similar but only differs with a small unit. If we will compare analytical factors for these two substances: KH_2PO_4 and precipitate $\downarrow MgNH_4PO_4$

$$F_1 = \frac{P_2O_5}{2KH_2PO_4} = \frac{142}{272} = 0.522 \ (52\% \ P_2O_5) \ \text{with}$$

$$F_2 = \frac{P_2O_5}{2KH_2PO_4} = \frac{142}{274} = 0.518 \ (51.8\% \ P_2O_5),$$

there is a difference of 0.02 units. It can be neglected, since errors as ± 1% are allowed in weight analysis, within the limits of allowed errors.

If during the accelerated analysis, a sample KH_2PO_4 was taken in the amount of 1.92 g with a P_2O_5 content of 1.0 g [3], then with proper precipitation and drying of the precipitated form ↓ $MgNH_4PO_4$ at t = 45-50 °C to constant weight, a precipitate should fall out of the 1.92 g KH_2PO_4 sample 1, 92g Mg with a P_2O_5 content of 1.0g.

$$2KH_2PO_4 \xrightarrow{MgCL_2 + NH_4CL + NH_4OH} 2MgNH_4PO_4 \xrightarrow{t=1000°C} Mg_2P_2O_7 \rightarrow P_2O_5$$
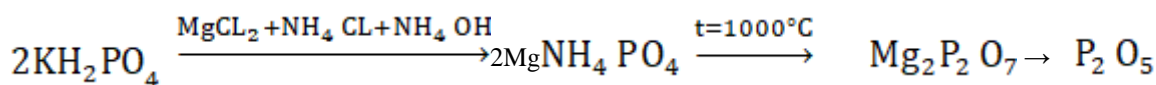
272 c.u./142 c.u.=1.915 g KH_2PO_4
196 c.u./142 c.u.=1.38 g H_3PO_4
274 c.u./142 c.u.=1.929 g $MgNH_4PO_4$
222 c.u./142 c.u.=1.56 g $Mg_2P_2O_7$
272 c.u./142 c.u.=1.0 g P_2O_5

It can be seen from the diagram that 1.38 g H_3PO_4 is formed from 1.915 g KH_2PO_4, from which 1.929 g of $MgNH_4PO_4$ is precipitated → 1.56 g $Mg_2P_2O_7$ and 1.0 g P_2O_5.

If we compare amount of 1.915g KH_2PO_4, which contains 52% P_2O_5 and the amount of 1.929g of $MgNH_4PO_4$ sludge containing 51.8% P_2O_5, then difference in percentage will be:

52.0%/51.8%=0.2%

In permissible values for this 1.915g ≈ 1.929g
KH_2PO_4 $MgNH_4PO_4$
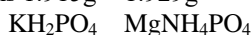
The accuracy of accelerated method for determination of phosphorus (V) oxide P_2O_5 in phosphates confirmed by experimental results shown in Table 1.

TABLE I

RESULTS OF GRAVIMETRIC DETERMINATION OF PHOSPHORUS (V) OXIDE CONTENT IN MONOSUBSTITUTED POTASSIUM PHOSPHATE KH_2PO_4 WITHOUT CALCINING MAGNESIUM-AMMONIUM PHOSPHATE

No.	KH_2PO_4 Sample (clean for analysis), in grams	$MgNH_4PO_4$ dry weight, in grams	P_2O_5 calculated weight in grams	Notes
1	$\dfrac{0.48\ g}{25\ ml}$	0.47 g **f**	0.24 g	**f**=0.52 $MgNH_4PO_4$ analytical factor
2	$\dfrac{0.48\ g}{25\ ml}$	0.48 g **f**	0.25 g	**f**=0.52 $MgNH_4PO_4$ analytical factor
3	$\dfrac{0.48\ g}{25\ ml}$	0.5 g **f**	0.26 g	**f**=0.52 $MgNH_4PO_4$ analytical factor
4	$\dfrac{0.48\ g}{25\ ml}$	0.48 g **f**	0.25 g	**f**=0.52 $MgNH_4PO_4$ analytical factor
Σ	1.92 g KH_2PO_4 (pure for analysis)	1.93 g **f** $MgNH_4PO_4$	1.0 g P_2O_5	**f**=0.52 $MgNH_4PO_4$ analytical factor

As experimental results showing from Table 1, from 1.92 g of KH_2PO_4 taken for analysis, 1.93 g of $MgNH_4PO_4$ precipitated with the same content of phosphorus oxide (V) = 1.0 g or in the percentage of phosphorus pentoxide P_2O_5 52 %:
% P_2O_5 = "a" x **f** x 100% / G = 1.93 x 0.52 x 100% /1.92

here, "a" is weight of dry magnesium-ammonium phosphate precipitate; G is weight of KH_2PO_4 for analysis.; **f** 0.52 analytical factor ↓$2MgNH_4PO_4$ containing 52.2% P_2O_5.

In this regard, there is no necessity in calcining magnesium-ammonium phosphate at t = 950-1000 °C, i.e. sufficiently complete precipitation of magnesium-ammonium phosphate and drying it at t = 40-50 °C to constant weight.

Thus, in our proposed accelerated method for determining the content of phosphorus (V) oxide in phosphates, the calcination stage at t = 950-1000 °C is eliminated, it is enough to correctly precipitate and achieve the completeness of precipitation of magnesium-ammonium phosphate with further drying of resulting precipitate at a temperature not higher than 40-50 °C in order to prevent partial decomposition and weight loss of sediment due to the loss of ammonia.

Reduction in the stage of sludge calcination at 950-1000 °C gives a huge savings in electricity, time and labor costs.

Alternatively, it is possible to quickly determine the magnesium content (%) in its salts solutions, eliminating the stage of calcining the Mg precipitate. So, when analyzing crystalline magnesium Mg, a sample of 0.7-0.9 g is dissolved in 50-60 ml of water and the solution is acidified with 5 ml of 2N HCl, then add to it 15-20ml (7-10)% - solution and 10 ml 2 N solution. After that, solution was heated to 40-45 °C and magnesium is precipitated with 2.5% ammonia solution, proceeding as described in the determination of phosphoric acid.

The further analysis course is the same as in determination of phosphates by monovalent cations.

In course of calculation, following was proceed from the proportion:
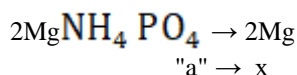
$2MgNH_4PO_4 \rightarrow 2Mg$
$"a" \rightarrow x$

Precipitated "a" is a sediment mass $\downarrow MgNH_4PO_4$, dried at t = 45-50 °C with mass 1.93 g

$$F = \frac{2Mg}{2MgNH_4PO_4}; \quad (F=\text{analytical factor for } 2Mg)$$

$$F = \frac{24 \cdot 2}{2 \cdot 137} = \frac{48}{274} = 0.175 \text{ is quantity of } Mg^{2+} =$$

"a" x **f** = (g)

% Mg="a"x 0.175 x 100% / G; where G is $MgCl_2 \cdot 6H_2O$

mass in g.
"a" is $MgNH_4PO_4$ in precipitate form.

CONCLUSIONS

Thus, by replacing the reagent $NaH_2PO_4 \cdot 12H_2O$ to reference and standard reagent KH_2PO_4 in the determination of Mg^{2+} amount in solutions it is possible to exclude the ignition stage of precipitate $MgNH_4PO_4$ by marking it as "a" for constant weight. Mg mass marked as "x"

$$Mg^{+2} = \text{"a"} \left(\frac{2Mg}{2MgNH_4PO_4} \right) = \left(\frac{48}{274} \right) = \text{"a"} = (\text{"a"} = 0.175) \text{ in (g)}.$$

Magnesium content Mg = a x 0.175x100% / G, here
G = (sample mass, in g) $MgCl_2 \cdot 6H_2O$ for analysis, and
"a" is precipitate form of Mg dried at t = 40-45 °C to constant weight.

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