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SYSTEMATIC STUDY ON THE PH RANGES AND BUFFERING CAPACITY OF MIXTURES OF TRISODIUM ORTHOPHOSPHATE OR TETRASODIUM PYROPHOSPHATE WITH POTASSIUM DIHYDROGEN ORTHOPHOSPHATE

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Abstract: *This study presents valuable systematic data on the pH ranges and potential buffering properties of two phosphate systems composed of alkaline components and anhydrous potassium dihydrogen orthophosphate (KH_2PO_4) as the acidic counterpart. The alkaline components investigated were trisodium orthophosphate dodecahydrate ($Na_3PO_4.12H_2O$) and tetrasodium pyrophosphate decahydrate ($Na_4P_2O_7.10H_2O$). The experimental work was carried out in two stages: (i) determination of pH ranges, and (ii) evaluation of buffering capacity. All measurements were performed in quintuplicate using a high-precision pH meter. The full set of results, including raw data, is provided in order to serve as a useful reference for future studies. Detailed descriptions of the procedures and calculations are also included to facilitate reproducibility and to guide further research in this field. Finally, the proposed phosphate mixtures are suggested as reliable pH buffers for technological and biotechnological applications, with particular relevance for metallic surface phosphating.*

Keywords: *$Na_3PO_4.12H_2O$, $Na_4P_2O_7.10H_2O$, KH_2PO_4, pH ranges, Buffering Capacity.*

INTRODUCTION

Painting and coating are common procedures in the production of metallic products, especially those intended for outdoor use. In this context, preliminary surface treatment is an indispensable step, regardless of the coating technology applied. Among the most widely used pretreatment methods is phosphating, which has long been established in industrial practice. Nevertheless, research continues to improve the conditions for its application. Numerous recent studies have focused on the phosphating of mild steel, exploring different bath compositions with practical potential for reliable coating formation (Liubenova et al., 2023; Rumyantseva et al., 2021; Ilieva et al., 2021; Fachikov et al., 2021).

More recently, phosphate sealing has emerged as an efficient approach for enhancing the protective properties of cerium oxide primer layers (Kozhukharov et al., 2024; Cherneva et al., 2025; Ma et al., 2025). In addition, reference tables of pH ranges for various phosphate buffer systems have been published, such as $Na_2HPO_4.2H_2O$-KH_2PO_4, and $Na_2B_4O_7.10H_2O$-HCl (Portolesi et al., 2022). Building on this, systematic datasets have also been developed for $Na_2B_4O_7.10H_2O$-H_3BO_3 and $Na_2HPO_4.2H_2O$-KH_2PO_4 (Georgieva et al., 2025-1), as well as for $Na_2B_4O_7.10H_2O$-KH_2PO_4 and $Na_2HPO_4.2H_2O$-H_3BO_3 (Georgieva et al., 2025-2).

Phosphate solutions also find use in other surface treatment technologies, for example plasma electrolytic oxidation (López et al., 2025).

In this sense, the present work focuses on the characterization of the pH ranges and buffering properties of two phosphate mixtures of KH_2PO_4 with $Na_3PO_4.12H_2O$ (assigned as M_1), or $Na_4P_2O_7.10H_2O$ (M_2). Moreover, the experimental procedures are presented in detail, and the raw data are included, with the aim of providing a valuable resource for future investigations.

EXPERIMENTAL

The experimental work was carried out in two main stages: (i) determination of the pH ranges, and (ii) evaluation of the potential buffering capacity of neutral phosphate solutions.

Stage 1. Determination of pH ranges

The first stage was conducted through fivefold repetitive pH measurements of solutions prepared in nine different proportions. Measurements were performed using a HI 255 combined meter (Hanna Instruments) equipped with a HI 1131 commercial universal glass electrode.

Before the experiments, stock solutions of the investigated compounds were prepared, their compositions are listed in Table 1.

Table 1. Initial solutions used for the pH range determinations of the studied phosphate mixtures

Component type	**Estimated solution content**	**Real content**	**Exact compound concentration (mol dm^{-3})**
First alkaline component	0.05 M solution of $Na_3PO_4.12H_2O$	19.3954 g of product (CAS-2570) with 98 %	52.066×10^{-3}
Second alkaline component	0.05 M solution of $Na_4P_2O_7.10H_2O$	22.6196 g of product (CAS 13472-36-1) with 99 %.	51.222×10^{-3}
Acidic component	0.05 M solution of KH_2PO_4	6.8387 g of product (CAS 7778-77-0) with 99.5 % purity grade.	50.402×10^{-3}

The pH range measurements were performed by mixing the alkaline and acidic stock solutions in defined proportions (described in the following section), followed by pH determination of the resulting mixtures. This procedure enabled monitoring of the pH variation upon gradual increase or decrease of the acidic component relative to the alkaline one.

The data were further analyzed using the volume ratios (VR_1 and VR_2) between the alkaline and acidic solutions, calculated according to Equation 1:

$$VR_1 = \frac{V_1}{V_1 + V_2} \qquad \text{or} \qquad VR_2 = \frac{V_2}{V_1 + V_2}\ , \tag{1}$$

where VR is the volume ratio of the used primary solutions; V_1 – volume of the alkaline solution (mL); V_2 – volume of the acidic solution (mL).

Stage 2. Determination of buffering capacity.

The buffering capacity of phosphate mixtures with nearly neutral pH was assessed by titration with standardized NaOH or HCl secondary solutions. Due to the well-known susceptibility of NaOH to absorb CO_2 from air, and the volatility of HCl, both solutions were standardized against a primary standard. Specifically, NaOH was standardized with oxalic acid, and the HCl solution was subsequently standardized against NaOH. This procedure ensured precise concentration determination of the secondary standard solutions, which were then used for titrations. All titrations were performed in fivefold repetition using the same pH meter described above. The resulting concentrations of the standardized titrants were 48.648×10^{-3} mol dm^{-3} of NaOH solution and 49.255×10^{-3} mol dm^{-3} of the HCl one.

The standardized NaOH and HCl solutions were subsequently used for the titration of mixtures of KH_2PO_4 with either $Na_3PO_4.12H_2O$ (M_1) or $Na_4P_2O_7.10H_2O$ (M_2) at nearly neutral pH. The required volume correlations between the alkaline and acidic components for obtaining neutral mixtures were derived from the pH range determinations described in the previous section. Afterwards, aliquots of 25 mL from these mixtures were subjected to titrations with either the standardized NaOH or HCl solutions.

The buffering capacity (BC) was calculated from the titration data according to Equation 2:

$$BC = \frac{MV_{ss}}{\Delta\left(pH\right)Vb_{uff}}.\frac{1}{n}, \qquad (2)$$

where BC is the buffering capacity (mol pH^{-1}), MV_{ss} is the amount (in moles) of the added standard solution of known alkaline or acidic compound. In the present case, the data for the standard solution molarity are shown in Table 1, whereas, their volumes, expended for the titrations are summarized in Tables 5 and 6. $\Delta(pH)$ is the pH change (dimensionless), in the present case, its value is assumed to be unit. V_{buff} is the volume of the buffer solution submitted to titration (25 mL). The coefficient ($1/n$) is attributed to the compound, whose solution is submitted to pH measurement. If it is alkaline, then n = number of OH^- anions from any compound molecule. If it is acidic, then n = number of H_3O^+ (i.e., H^+ cations) moieties from each molecule of the dissolved compound. In both cases of NaOH and HCl, its value is: $1/n = 1$.

RESULTS AND DISCUSSION

Determination of the pH ranges

The pH range determinations were carried out by fivefold pH measurements using the precision pH meter described in the experimental section. For each system (M_1 and M_2), nine mixtures were prepared by gradually altering the volume ratios between the alkaline and acidic components. The collected data are summarized in Table 2 for system M_1 and in Table 3 for system M_2.

Table 2. Volume ratios and resulting pH values for the M_1 system

Components (mL)		**Volume ratios**		**Raw data acquired from each measurement**					**Avg. Val.**	**St. Dev.**
Alkaline	**Acidic**									
$Na_3PO_4.12H_2O$	**KH_2PO_4**	**VR_1**	**VR_2**	**pH_1**	**pH_2**	**pH_3**	**pH_4**	**pH_5**		
50	**0**	**1.00**	**0.00**	12.008	12.007	12.001	11.998	11.995	12.002	0.006
40	**10**	**0.80**	**0.20**	10.535	10.531	10.510	10.497	10.487	10.512	0.021
30	**10**	**0.75**	**0.25**	8.840	8.827	8.820	8.819	8.824	8.826	0.008
30	**20**	**0.60**	**0.40**	7.675	7.672	7.670	7.673	7.674	7.673	0.002
20	**20**	**0.50**	**0.50**	7.352	7.343	7.343	7.338	7.337	7.343	0.006
20	**30**	**0.40**	**0.60**	7.069	7.068	7.068	7.063	7.061	7.066	0.004
10	**30**	**0.25**	**0.75**	6.720	6.718	6.719	6.712	6.711	6.716	0.004
10	**40**	**0.20**	**0.80**	6.585	6.574	6.570	6.566	6.564	6.572	0.008
0	**50**	**0.00**	**1.00**	4.583	4.573	4.572	4.566	4.562	4.571	0.008

Table 3. Volume ratios and resulting pH values for the M_2 system

Components (mL)		**Volume ratios**		**Raw data acquired from each measurement**					**Avg. Val.**	**St. Dev.**
Alkaline	**Acidic**									
$Na_4P_2O_7.10H_2O$	**KH_2PO_4**	**VR_1**	**VR_2**	**pH_1**	**pH_2**	**pH_3**	**pH_4**	**pH_5**		
50	**0**	**1.00**	**0.00**	10.794	10.797	10.795	10.792	10.788	10.793	0.003
40	**10**	**0.80**	**0.20**	9.315	9.311	9.313	9.320	9.322	9.316	0.005
30	**10**	**0.75**	**0.25**	9.135	9.141	9.144	9.149	9.157	9.145	0.008
30	**20**	**0.60**	**0.40**	8.555	8.546	8.567	8.569	8.575	8.562	0.012
20	**20**	**0.50**	**0.50**	8.003	8.008	8.014	8.017	8.020	8.012	0.007
20	**30**	**0.40**	**0.60**	7.438	7.438	7.445	7.446	7.449	7.443	0.005
10	**30**	**0.25**	**0.75**	6.830	6.821	6.814	6.807	6.809	6.816	0.009
10	**40**	**0.20**	**0.80**	6.657	6.653	6.648	6.647	6.651	6.651	0.004
0	**50**	**0.00**	**1.00**	4.583	4.573	4.572	4.566	4.562	4.571	0.008

The data in Tables 2 and 3 were visualized in order to define accurately the most suitable volume ratio (VR) ranges for achieving neutral pH. The respective *pH = f(VR)* plots are shown in Figure 1.

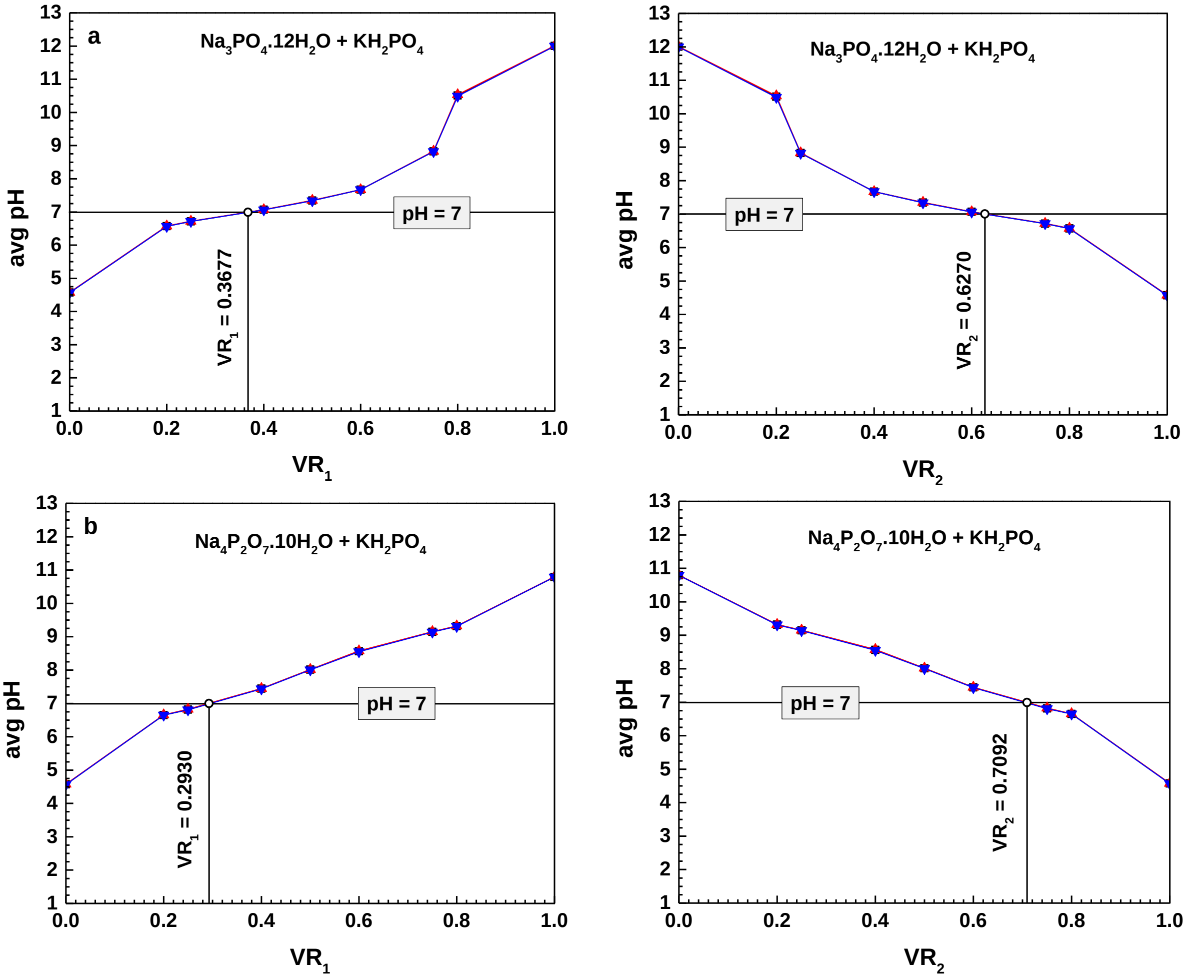

Fig. 1. Correlations between the volume ratios of the obtained mixtures and the resulting pH values: a) system M_1, b) system M_2

Figure 1a shows that neutral M_1 solutions can be obtained within relatively broad VR intervals. For VR_1, the neutral zone lies between points P_1 and P_3, corresponding to VR_1 = 0.31–0.45. In practice, this means that mixing 31–45 mL of $Na_3PO_4.12H_2O$ solution with KH_2PO_4 up to 100 mL yields a neutral pH. In turn, regarding VR_2 neutral conditions were observed between P_4 and P_6, where the acidic component volume ranged between 52 mL and 71 mL, complemented by alkaline solution up to 100 mL. In both VR_1 and VR_2 cases, preparation of neutral M_1 solutions required a slight predominance of the acidic component.

Additionally, further pH decreases were observed in the VR ranges 0.75–0.80 (VR_1) and 0.20–0.25 (VR_2). These secondary effects, though noteworthy, lie outside the main scope of this study and will not be discussed in detail here.

Figure 1b presents the results for M_2, where neutral pH was reached within narrower intervals compared to M_1. For VR_1, neutrality was observed between P_7 and P_9 (VR_1 = 0.26–0.33), corresponding to approximately 30 mL $Na_4P_2O_7.10H_2O$ mixed with 70 mL KH_2PO_4 (P_8). For VR_2, neutrality was achieved between P_{10} and P_{12} (KH_2PO_4 volumes of 63–75 mL), complemented with alkaline solution ($Na_4P_2O_7.10H_2O$) up to 100 mL. The most balanced neutral point was found at P_{11}, corresponding to 70 mL of 0.05 M KH_2PO_4 and 30 ml of 0.05 M $Na_4P_2O_7.10H_2O$.

It should be emphasized that, in practice, the pH of phosphate mixtures should be fine-tuned on the following day. This is due to unavoidable small deviations in the initial solution concentrations, as well as external factors such as the pH of distilled water (which may vary depending on the technical state of the distiller) and ambient temperature.

Definition of the potential buffering capacity of neutral phosphate solutions

It was performed by fivefold titration of probes (25 mL) of relatively neutral mixtures, by the secondary standard solutions, described in the experimental part. The respective data, acquired from these titrations are provided in Tables 5 and 6.

The buffering capacity was evaluated by fivefold titration of 25 mL probes of relatively neutral mixtures using the secondary standard solutions described in the experimental section. The corresponding experimental data are presented in Tables 5 and 6.

Table 5. Results of the potential buffering capacity of neutral $Na_3PO_4.12H_2O$ / KH_2PO_4

Number	Expended NaOH (mL)	pH before titration	pH after titration	Expended HCl (mL)	pH before titration	pH after titration
I	**8.80**	**7.076**	**8.067**	**15.55**	**6.994**	**5.999**
II	**8.75**	**7.074**	**8.066**	**15.50**	**6.995**	**6.002**
III	**8.70**	**7.082**	**8.064**	**15.55**	**6.994**	**6.007**
IV	**8.70**	**7.064**	**8.047**	**15.15**	**7.012**	**6.056**
V	**8.75**	**7.068**	**8.067**	**15.00**	**7.047**	**6.035**
Avg. val.	**8.74 ± 0.04**	**7.074 ± 0.007**	**8.062 ± 0.009**	**15.35 ± 0.26**	**7.008 ± 0.023**	**6.020 ± 0.025**

Table 6. Results of the potential buffering capacity of neutral $Na_4P_4O_7.10H_2O$ / KH_2PO_4

Number	Expended NaOH (mL)	pH before titration	pH after titration	Expended HCl (mL)	pH before titration	pH after titration
I	**8.35**	**7.003**	**8.004**	**13.55**	**7.042**	**6.061**
II	**8.25**	**7.084**	**8.070**	**13.55**	**7.015**	**6.023**
III	**8.30**	**7.071**	**8.065**	**13.40**	**7.056**	**6.057**
IV	**8.25**	**7.069**	**8.070**	**13.80**	**7.006**	**6.009**
V	**8.30**	**7.065**	**8.074**	**13.60**	**7.010**	**6.028**
Avg. val.	**8.29 ± 0.04**	**7.058 ± 0.032**	**8.057 ± 0.03**	**13.58 ± 0.14**	**7.026 ± 0.022**	**6.036 ± 0.023**

The data in both tables show that the volumes of diluted NaOH necessary for titration of 25 mL probes converge to 8.7 mL for M_1 and 8.3 mL for M_2. In contrast, the volumes of the respective HCl standard solutions required to change the pH of the examined potential buffer solutions by one unit are nearly twice as high as those of NaOH. Specifically, 15.35 mL and 13.58 mL of the HCl standard solution were expended for titration of 25 mL probes of M_1 and M_2, respectively.

Based on these measurements, the buffering capacities were calculated using Equation 2. The calculations for the M_1 system, composed of $Na_3PO_4.12H_2O$ and KH_2PO_4, are shown below (Eqs. 3 and 4):

$$BC_{M_1}^{NaOH} = \frac{48.648\times10^{-3}\times8.74}{\left(|7.074-8.062|\right)\times25} = 17.21\times10^{-3}\,mol\;pH^{-1} \tag{3}$$

$$BC_{M_1}^{HCl} = \frac{49.255\times10^{-3}\times15.35}{\left(|7.008-6.020|\right)\times25} = 30.61\times10^{-3}\,mol\;pH^{-1} \tag{4}$$

In turn, the respective calculations for the M_2 system, composed of $Na_4P_2O_7.10H_2O$ and KH_2PO_4 are given below (Eqs. 5 and 6):

$$BC_{M_2}^{NaOH} = \frac{48.648\times10^{-3}\times8.29}{(|7.058-8.057|)\times25} = 16.15\times10^{-3}\,mol\;pH^{-1} \qquad (5)$$

$$BC_{M_2}^{HCl} = \frac{49.255\times10^{-3}\times13.58}{(|7.026-6.036|)\times25} = 27.03\times10^{-3}\,mol\;pH^{-1} \qquad (6)$$

The results reveal that the buffering capacity values are quite similar for both systems. Besides, it appears that the system M_1 ($Na_3PO_4.12H_2O$ + KH_2PO_4) shows slightly higher stability in alkaline media, whereas the system M_2 ($Na_4P_2O_7.10H_2O$ + KH_2PO_4) exhibits better stability in acidic media. However, these differences are minor, and the buffering capacities of both systems may be considered essentially equivalent.

Finally, comparison with results obtained from titrations of a commercial buffer (Georgieva, M. et al., 2025, both parts) indicates that these systems can be reliably used as buffers for various technological and biotechnological processes, as well as phosphorus sources for metal phosphating solutions.

CONCLUSIONS

This paper presents valuable data on the pH ranges and buffering properties of two phosphate systems: M_1 ($Na_3PO_4.12H_2O$ and KH_2PO_4) and M_2 ($Na4P_2O_7.10H_2O$ and KH_2PO_4). The experimental procedures, including direct measurements and raw data, are described in sufficient detail to enable replication and application in further research. The results identify the possible pH ranges and suitable volume proportions of the acidic and alkaline components required for preparing neutral M_1 and M_2 mixtures.

The key conclusion is that both systems, based on $Na_3PO_4.12H_2O$ or $Na_4P_2O_7.10H_2O$ mixed with KH_2PO_4 can be used as reliable pH buffers in technological and biotechnological processes, with particular relevance for the phosphating of metallic surfaces.

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