Pergamon

0039-9140(95)01412-8

Talanta, Vol. 42, No. 3, pp. 365–373, 1995
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0039-9140/95 $9.50 + 0.00

A RAPID AND HIGHLY SELECTIVE METHOD FOR THE ESTIMATION OF PYRO-, TRI- AND ORTHOPHOSPHATES

D. R. KAMAT,[1] V. V. SAVANT[1] and D. N. SATHYANARAYANA[2]*

[1]Research and Development Laboratory, Ballarpur Industries Limited, Karwar 581 364, India
[2]Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India

(*Received* 5 *May* 1994. *Revised* 24 *August* 1994. *Accepted* 31 *August* 1994)

Summary—A rapid, highly selective and simple method has been developed for the quantitative determination of pyro-, tri- and orthophosphates. The method is based on the formation of a solid complex of bis(ethylenediamine)cobalt(III) species with pyrophosphate at pH 4.2–4.3, with triphosphate at pH 2.0–2.1 and with orthophosphate at pH 8.2–8.6. The proposed method for pyro- and triphosphates differs from the available method, which is based on the formation of an adduct with tris(ethylenediamine)cobalt(III) species. The complexes have the composition $[Co(en)_2HP_2O_7]4H_2O$ and $[Co(en)_2H_2P_3O_{10}]2H_2O$, respectively. The precipitation is instantaneous and quantitative under the recommended optimum conditions giving 99.5% gravimetric yield in both cases. There is no interferences from orthophosphate, trimetaphosphate and pyrophosphate species in the triphosphate estimation up to 5% of each component. The efficacy of the method has been established by determining pyrophosphate and triphosphate contents in various matrices. In the case of orthophosphate, the proposed method differs from the available methods such as ammonium phosphomolybdate, vanadophosphomolybdate and quinoline phosphomolybdate, which are based on the formation of a precipitate, followed by either titrimetry or gravimetry. The precipitation is instantaneous and the method is simple. Under the recommended pH and other reaction conditions, gravimetric yields of 99.6–100% are obtainable. The method is applicable to orthophosphoric acid and a variety of phosphate salts.

Of all the condensed phosphates, sodium triphosphate (STP) (also known commercially as sodium tripolyphosphate) and tetrasodium pyrophosphate are of industrial importance. Owing to its extensive use in the manufacture of detergents, anhydrous triphosphate is also of great commercial importance. Because of complexities in controlling the conditions for thermal condensation of orthophosphate to triphosphate, the commercially available anhydrous triphosphate is always contaminated with other phosphates, *viz.* orthophosphate, trimetaphosphate and pyrophosphate.[1]

Chromatographic[2] and infrared spectroscopic techniques[3–5] have been employed for the identification and for the estimation of phosphate compounds. A method based on tris(ethylenediamine)cobalt(III) species forming a solid adduct with pyrophosphate and triphosphate at pH about 6.5 and 3.5, respectively, is widely used for the quantitative estimation of these two compounds gravimetrically.[6] Hexamminecobalt(III) chloride has also been suggested as precipitant for use in the determination of pyrophosphate and triphosphate,[6] but this reagent suffers from nonselectivity when employed to estimate an admixture of pyrophosphate and triphosphate, and is hence not a very valuable reagent. In this paper, a rapid and simple method for the determination of pyrophosphate and triphosphate by forming a coordination complex with aqueous bis(ethylenediamine)cobalt(III) species at pH 4.2–4.3 and 2.0–2.1, respectively, is described. By physicochemical studies, it was found that the solid complexes formed correspond to $[Co(en)_2HP_2O_7]4H_2O$ and $[Co(en)_2H_2P_3O_{10}]2H_2O$, respectively.[7] Gravimetric yields of 99.5% were obtained in the case of pure pyro- and triphosphates.

Various analytical methods for the determination of orthophosphoric acid and phosphate salts have been reported.[8] They include direct titrimetric,[9–11] complexo titrimetric,[12] potentiometric,[13–16] complexo gravimetric,[11,17] colorimetric,[11,18–21] chromatographic[22–27] and atomic absorption spectroscopic techniques.[28] Orthophosphates are also known to form complexes

---

*Author to whom correspondence should be addressed.

with Co(III), Cr(III), *etc.*, containing other ligands such as ethylenediamine and ammonia. It was found that bis(ethylenediamine)cobalt(III) species also forms complex with orthophosphate anion under specific pH and other reaction conditions. Several phosphato complexes of cobalt(III) of the type $[Co(NH_3)_4PO_4]$, $[Co(NH_3)_5PO_4]$, $[Co(NH_3)_4H_2O \cdot HPO_4]^+$, $[Co(en)_2PO_4]$, $[Co(en)_2H_2O \cdot HPO_4]^+$, $[Co(en)_2OH \cdot HPO_4]$, $[Co(en)_2OH \cdot PO_4]^-$, $[Co(en)_2H_2O \cdot H_2PO_4]^{2+}$ and $[Co(en)_2H_2O \cdot H_3PO_4]^{3+}$ have been reported and characterized. Their hydrolytic properties have also been studied.[29] Although the synthesis of $[Co(en)_2PO_4]$ was reported starting from transdichloro bis(ethylenediamine)cobalt(III) perchlorate,[30] it has not been exploited for the quantitative estimation of orthophosphates.

The above method for the estimation of pyro- and triphosphates is extended for the quantitative estimation of orthophosphate based on the complex formation of orthophosphate anion with acidified solution of (carbonato)-bis(ethylenediamine)cobalt(III) chloride. The precipitation is quantitative between pH 8.2 and 8.6 under the recommended reaction conditions. The solid complex formed corresponds to $[Co(en)_2PO_4]$.[7] The method is also applicable to salts such as NaH_2PO_4, Na_2HPO_4, Na_3PO_4, $(NH_4)_2HPO_4$, KH_2PO_4 and other similar salts of orthophosphoric acid. Gravimetric yields of 99.6–100% are obtainable in the case of orthophosphoric acid and its salts. The method was employed for the phosphate estimation of commercial matrices such as tricalcium phosphate, dicalciumphosphate, *etc.* The *cis*- and *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride were also tried as alternative reagents for the quantitative determination of orthophosphate anion. The results were not encouraging.

EXPERIMENTAL

Reagents and instruments

(Carbonato)bis(ethylenediamine)cobalt(III) chloride was prepared by a known method.[31] It was recrystallized and air-dried. The purity of the compound was checked by chemical analysis. This complex (75 mg) was acidified with 1*M* hydrochloric acid (1 ml) to decompose the carbonate and obtain the aqueous bis(ethylenediamine)cobalt(III) species which was used as the reagent for the precipitation reaction. Tris(ethylenediamine)cobalt(III) chloride was prepared by a known method.[32] It was recrystallized and dried at 110°C before use. A 4% aqueous solution was used for all the experiments. One drop of toluene was added to inhibit mold growth. *cis*- and *trans*-Dichlorobis(ethylenediamine)cobalt(III) chloride were prepared by a known method.[27] These complexes are water soluble and 7% aqueous solutions were used as reagents. Sodium pyrophosphate, analytical reagent tetrasodium pyrophosphate, $Na_4P_2O_7 \cdot 10H_2O$ (Koch-Light, U.K.) was used as a standard pyrophosphate. Sodium triphosphate, from the commercially available anhydrous sodium triphosphate (Ballarpur Industries Ltd, Karwar, India), its hexahydrate was prepared.[34] Sodium trimetaphosphate was prepared by thermal dehydration of NaH_2PO_4 under controlled conditions. The condensation polymerization was carried out between 500 and 600°C for about 5 hr, followed by slow cooling.[35] From this product, the monohydrate was prepared by precipitating it from aqueous solution with ethanol at 40°C and then air-dried. Orthophosphoric acid, analytical reagent grade orthophosphoric acid (E. Merck) was used. Orthophosphates, analytical reagent grade $NaH_2PO_4 \cdot 2H_2O$, Na_2HPO_4, $Na_3PO_4 \cdot 12H_2O$, KH_2PO_4 and $(NH_4)_2HPO_4$ of BDH and Sarabhai chemicals were used. Sodium acid pyrophosphate ($Na_2H_2P_2O_7$) was prepared by a known method[36] by heating NaH_2PO_4 to 250°C for 5 hr. It was recrystallized from ethanol. Detergent powders, commercially available spray-dried premier detergent powders of Indian origin were employed.

Model 3B Perkin Elmer double beam electronic spectrophotometer, model 2380 Perkin Elmer atomic absorption spectrophotometer and a model 361 microprocessor pHmeter (Systronics) were used.

Procedure

A known amount of pure tetrasodium pyrophosphate (about 150 mg) in a 100 ml beaker was taken. Distilled water (15 ml) followed by 15 ml of propanol was added, 2–3 ml of bis(ethylenediamine)cobalt(III) reagent was then added and precipitation occurred immediately. The pH of the solution was adjusted to between 4.2 and 4.3 using 1*M* sodium hydroxide and the contents of beaker were stirred for 10–15 min. The precipitate was filtered quantitatively through a G-3 sintered crucible. The filtrate was used for the complete transfer of the precipitate to the crucible. The precipitate was washed with 1:1 ethanol. It was dried at 110°C for 1 hr and weighed. The same procedure was used for the precipitation of triphosphate except that in this case, the pH was adjusted to between 2.0 and 2.1. In the case of orthophosphate, the reagent requirement was 8 ml and the pH was adjusted to between 8.2 and 8.6. The precipitate was washed with absolute ethanol instead of 1:1 ethanol. Since this complex is hygroscopic, immediately after drying the crucible is kept in a vacuum desiccator and weighed as soon as it attains ambient temperature.

Using the same procedure, *cis*- and *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride were used as precipitating agents for orthophosphates instead of the acidified solution of (carbonato)bis(ethylenediamine)-cobalt(III) chloride. The use of the aquo complex of *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride, obtained by the overnight aquation of the *trans*-dichloro bis(ethylenediamine)cobalt(III) chloride was also attempted.

RESULTS AND DISCUSSION

The electronic spectra of acidified solution of $[Co(en)_2CO_3]Cl$ and the filtrates of the precipitation experiments showed an absorption maximum at 494 nm. Stoichiometrically for each mole of pyro-, tri- and orthophosphates, one mole of bis(ethylenediamine)cobalt(III) species is required. It was also confirmed by the ratio of Co:P obtained by the analysis of the respective precipitates.

Effect of pH

In a series of beakers, the same amount of pure pyrophosphate (about 150 mg) was taken and the precipitations were carried out at different pH. Similarly, the effect of pH on the precipitation of triphosphate and orthophosphate were also studied. The plots of pH *vs*. mean yield values of pyro-, tri- and orthophosphates are shown in Figs 1–3, respectively. The results indicate that pH 4.2–4.3, 2.0–2.1 and 8.2–8.6 are optimum for the quantitative determination of pyro-, tri- and orthophosphates, respectively, and maximum yields of 99.5–100% are obtainable under these optimum conditions. The advantages of the present method are that it is simple, rapid and more accurate than the available method. The available method requires buffering and seeding for initiation of precipitation and takes 30 min for the precipitation to go to completion in the case of pyro- and triphosphates. However, the addition of a non-aqueous solvent, preferably propanol, is needed in the described method. A few precipitations were carried out by adding excess water during precipitation and without adding propanol before precipitation, to study the effect of dilution and absence of propanol on the quantitative estimations. Precipitations were also carried out using methanol and ethanol instead of propanol. Dilution with water and absence of propanol in the reaction mixture during the precipitation gave lower yields. Although methanol and ethanol could be used, propanol is preferred for the best results. The completeness of the precipitation was confirmed by the absence of phosphate in the mother liquor.

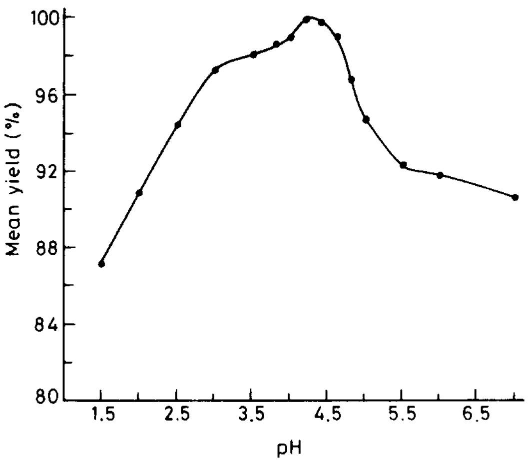

Fig. 1. Effect of pH on the estimation of pyrophosphate.

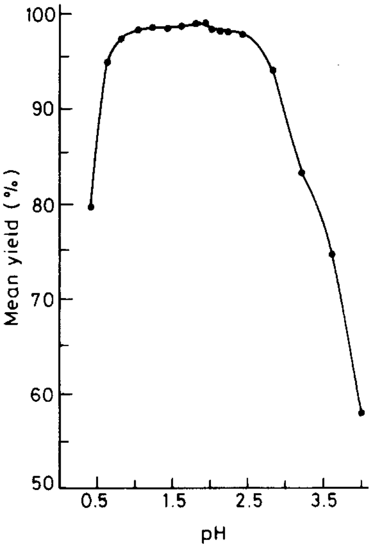

Fig. 2. Effect of pH on the estimation of triphosphate.

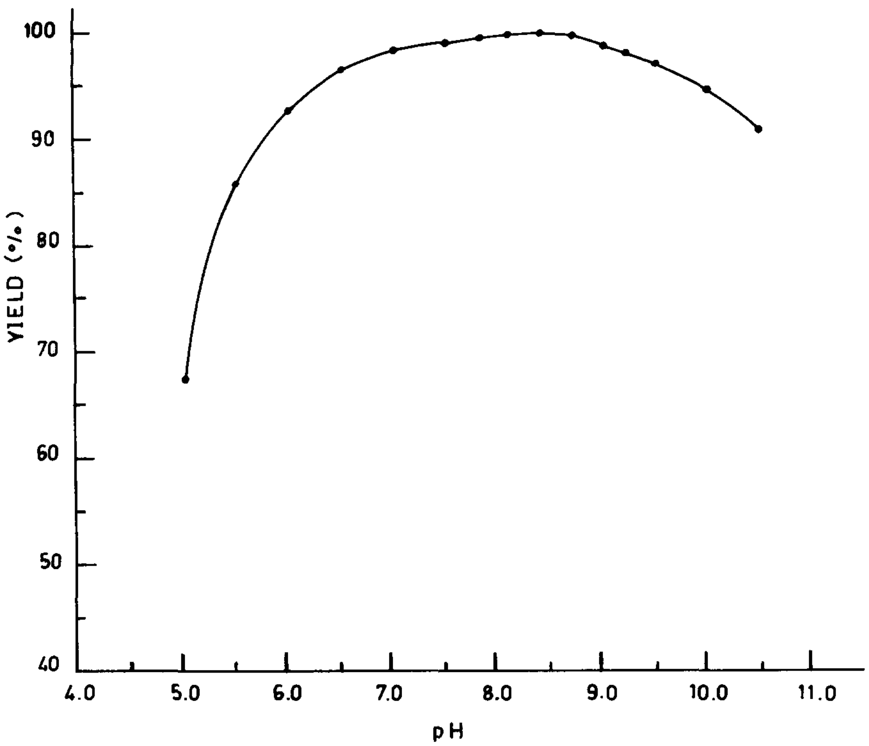

Fig. 3. Effect of pH on the estimation of orthophosphate.

Determination of excess reagent

Since the reagent, bis(ethylenediamine)-cobalt(III) is coloured, pyrophosphate and triphosphate were precipitated using a known amount of the reagent and then the excess reagent was measured spectrophotometrically. A calibration curve was made by diluting a known amount of the acidified solution of $[Co(en)_2CO_3]Cl$ and measuring the absorbance. Similarly, the filtrates of pyrophosphate and triphosphate precipitations were collected and diluted to a known volume with water. Absorbances of all these solutions were measured at 494 nm using cells of 1 cm path length. From the calibration curve, the quantity of excess reagent in the filtrate and hence the net amount of the reagent consumed for complexation was determined. From the reagent consumption, condensed phosphate present in a given aliquot was calculated.

The results of the spectrophotometric determination of excess reagent are presented in Table 1. Although the quantity of pyro- and triphosphates could be calculated by determining spectroscopically the quantity of the reagent consumed, the accuracy of the results obtained would depend upon the quantitative collection of filtrate. However, the yield was calculated based on the quantity of precipitate in all further experiments.

Effect of ortho-, trimeta- and pyrophosphates in triphosphate estimation

Phosphate solutions of known concentrations were prepared and a known amount of it was added to a known quantity of triphosphate (for fractional volumes, microburette was used) so that the total phosphate in the aliquot was 150 mg. A series of precipitation experiments were carried out using the proposed procedure on binary and quaternary mixtures containing varying amounts of ortho-, trimeta-, pyro- and triphosphates to determine the interference of these components and their effect on the estimation of triphosphate. Similarly, the effect of varying amounts of sodium sulphate in triphosphate estimation was investigated.

The results of interference of ortho-, trimeta- and pyrophosphates in the binary mixtures of each with triphosphate are shown in Tables 2–4. The results indicate that there is no interference up to 10% of orthophosphate in the mixture. However, as noted above, orthophosphate also forms a complex with the new reagent, the precipitation starts at pH 6.5, and it is quantitative between pH 8.2 and 8.6.

Table 1. Determination of tri- and pyrophosphates by excess reagent method

Sample number	STP/pyrophosphate taken (*mg*)	Reagent added (*mg*)	Reagent in filtrate from absorbance (*mg*)	Reagent consumed for complexation (*mg*)	STP/pyrophosphate found (*mg*)	Deviation (%)
1	150.00 (STP)	120.00	9.00	110.00	149.00	−0.66
2	120.00 (STP)	120.00	27.00	93.00	124.00	+3.30
3	90.90 (pyro)	150.00	57.00	93.00	90.10	−0.88
4	87.20 (pyro)	150.00	58.00	92.00	89.10	+2.10

Table 2. Effect of orthophosphate in the estimation of triphosphate

			In the mixture		Found*		
Sample number	Triphosphate taken (*mg*)	Orthophosphate added (*mg*)	Triphosphate (%)	Orthophosphate (%)	I (%)	II (%)	Mean (%)
1	150.00	Nil	100.0	Nil	99.4	99.8	99.6
2	148.50	1.50	99.0	1.0	99.4	99.6	99.5
3	147.00	3.00	98.0	2.0	99.3	99.7	99.5
4	144.00	6.00	96.0	4.0	99.4	99.9	99.6
5	141.00	9.00	94.0	6.0	99.7	99.5	99.6
6	135.00	15.00	90.0	10.0	99.8	100.0	99.9

*Calculated as $[Co(en)_2H_2P_3O_{10}]2H_2O$.

Trimetaphosphate also does not interfere in the precipitation of triphosphate. It is interesting to note that trimetaphosphate does not precipitate as a complex with an acidified solution of bis(ethylenediamine)cobalt(III) species at all pHs. The yields of triphosphate are quantitative, if pyrophosphate present in the mixture is less than 5%. When the pyrophosphate present in the mixture is higher than 5%, owing to the co-precipitation of pyrophosphate complex, the yields were unrealistic, over 100%. This is contrary to the observations made in the literature method, wherein the precipitation is said to be incomplete at increased levels of pyrophosphate.[6]

The results of the studies on the interference of sodium sulphate in triphosphate estimation are presented in Table 5. It was found that sodium sulphate does not interfere up to 10% in the binary mixture with triphosphate.

The results of the determination of triphosphate in the quaternary mixtures containing ortho-, trimeta- and pyrophosphates are presented in Table 6. The results indicate that there is no interference from these up to 5% each of the components in the triphosphate estimation. This study of the multicomponent system was carried out keeping in view the composition of the commercially available sodium triphosphate.

Accuracy

The reproducibility of the results by the described method was determined by carrying out five replicate determinations of five different commercial triphosphate samples and a standard sample. Five replicate determinations of triphosphate in all the six samples were also made using the known method.[6] Based on the results, mean and standard deviations have been calculated (Table 7). From the results, it is observed that standard deviations of the present method are lower than those of the available method, showing that more accurate and precise results are obtainable from the present method.

Table 3. Effect of trimetaphosphate in the estimation of triphosphate

			In the mixture		Found*		
Sample number	Triphosphate taken (*mg*)	Trimetaphosphate added (*mg*)	Triphosphate (%)	Trimetaphosphate (%)	I (%)	II (%)	Mean (%)
1	150.00	Nil	100.0	Nil	99.7	99.3	99.5
2	149.25	0.75	99.5	0.5	99.6	99.4	99.5
3	148.50	1.50	99.0	1.0	99.4	99.4	99.4
4	147.00	3.00	98.0	2.0	99.4	99.6	99.5
5	145.50	4.50	97.0	3.0	99.5	99.5	99.5
6	142.50	7.50	95.0	5.0	99.6	99.2	99.4

*Calculated as $[Co(en)_2H_2P_3O_{10}]2H_2O$.

Table 4. Effect of pyrophosphate in the estimation of triphosphate

Sample number	Triphosphate taken (*mg*)	Pyrophosphate added (*mg*)	In the mixture: Triphosphate (%)	In the mixture: Pyrophosphate (%)	Found*: I (%)	Found*: II (%)	Mean (%)
1	150.00	Nil	100.0	Nil	99.4	99.6	99.5
2	147.50	2.50	98.4	1.6	99.6	99.6	99.6
3	145.00	5.00	96.6	3.4	99.6	99.8	99.7
4	142.50	7.50	95.0	5.0	99.9	100.1	100.0
5	140.00	10.00	93.3	6.7	102.0	102.3	102.1
6	135.00	15.00	90.0	10.0	103.0	103.9	103.4
7	120.00	30.00	80.0	20.0	107.4	107.6	107.5
8	105.00	45.00	70.0	30.0	110.4	109.5	110.0

*Calculated as [Co(en)$_2$H$_2$P$_3$O$_{10}$]2H$_2$O.

Table 5. Effect of sodium sulphate in the estimation of triphosphate

Sample number	Triphosphate taken (*mg*)	Sodium sulphate added (*mg*)	In the mixture: Triphosphate (%)	In the mixture: Sodium sulphate (%)	Found*: I (%)	Found*: II (%)	Mean (%)
1	150.00	Nil	100.0	Nil	99.6	99.8	99.7
2	150.00	3.10	98.0	2.0	99.5	99.9	99.7
3	150.00	7.90	95.0	5.0	99.8	100.0	99.9
4	150.00	16.60	90.0	10.0	99.7	99.9	99.8

*Calculated as [Co(en)$_2$H$_2$P$_3$O$_{10}$]2H$_2$O.

In the case of orthophosphates, the reproducibility of the results by the described method was determined by carrying out six replicate determinations on six samples of analytical reagent grade orthophosphate salts. The mean and standard deviations have been calculated and the results are given in Table 8. It shows that the standard deviations of the present method are low, demonstrating the precision and accuracy of the results obtainable by the described method.

Since the total PO_4^{3-} content present in the aliquot is complexed, it is difficult to distinguish between various types of orthophosphates present in the admixture. However, in the case of a single component pure orthophosphate system, such as NaH_2PO_4, Na_2HPO_4, *etc*., it can be distinguished by the weight of the complex, since different orthophosphates contain different weight percentage of PO_4^{3-}.

In the case of *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride and also its aquo form as complexing agent, the yields were about 98% for PO_4^{3-} ion. The adjustment of pH was rather difficult owing to the gradual decrease of the pH of the solution with time. The precipitates obtained in these cases were amorphous in nature and the filtration was extremely slow. The same situation was observed in the case of *cis*-dichlorobis(ethylenediamine)cobalt(III) chloride. Hence, these reagents are not suitable for the quantitative estimation of orthophosphates.

Table 6. Effect of ortho-, trimeta- and pyrophosphates in the estimation of triphosphate

Sample number	Triphosphate taken (*mg*)	Orthophosphate added (*mg*)	Trimetaphosphate added (*mg*)	Pyrophosphate added (*mg*)	In the mixture: Tri (%)	In the mixture: Ortho (%)	In the mixture: Trimeta (%)	In the mixture: Pyro (%)	Found* mean (%)
1	150.00	Nil	Nil	Nil	100.0	Nil	Nil	Nil	99.6
2	147.70	0.75	0.75	0.75	98.5	0.5	0.5	0.5	99.5
3	145.50	1.50	1.50	1.50	97.0	1.0	1.0	1.0	99.9
4	141.00	3.00	3.00	3.00	94.0	2.0	2.0	2.0	99.7
5	136.50	4.50	4.50	4.50	91.0	3.0	3.0	3.0	99.8
6	127.50	7.50	7.50	7.50	85.0	5.0	5.0	5.0	99.8
7	123.00	9.00	9.00	9.00	82.0	6.0	6.0	6.0	100.1

*Calculated as [Co(en)$_2$H$_2$P$_3$O$_{10}$]2H$_2$O.

Table 7. Comparison of the present method with the available method for the determination of triphosphate

Manufacturer's code number	Triphosphate content by Reported method I (%)	II (%)	III (%)	IV (%)	V (%)	Mean (%)	This method I (%)	II (%)	III (%)	IV (%)	V (%)	Mean (%)	Reported method[6] Mean (dev.%)	Standard (dev.%)	This method Mean (dev.%)	Standard (dev.%)
I	86.5	86.2	89.1	86.9	87.5	87.2	87.4	88.0	87.7	87.4	88.0	87.7	0.84	1.10	0.24	0.30
II	92.3	93.2	93.9	93.5	92.7	93.1	94.9	94.3	95.2	94.3	95.3	94.8	0.50	0.63	0.40	0.48
III	88.9	91.2	92.9	90.0	92.0	91.0	93.2	92.7	92.9	92.5	93.3	92.9	1.24	1.58	0.26	0.33
IV	87.7	89.9	89.9	88.6	89.6	89.1	90.0	89.4	90.0	89.5	90.1	89.8	0.80	0.96	0.28	0.32
V	92.0	93.6	94.5	93.2	93.6	93.4	95.8	95.0	94.0	95.8	94.8	95.3	0.62	0.91	0.42	0.48
VI*	76.6	76.0	76.9	76.2	76.8	76.5	77.2	76.9	77.0	76.9	76.7	76.9	0.30	0.39	0.12	0.19

*Standard triphosphate namely $Na_5P_3O_{10}6H_2O$ (77.3% $Na_5P_3O_{10}$).

Application of the method for pyro-, tri- and orthophosphates in commercial matrices

Estimation of triphosphate in commercial samples. The present method was employed for the estimation of triphosphate samples obtained from four different manufacturers spread over four different countries. The estimations were carried out in replicate using both the present and the reported methods. The results are given in Table 7. There are some differences in the results for the triphosphate content in the samples and they can be accounted for by the variations in the raw materials used and conditions for thermal condensation of orthophosphate during the manufacture of triphosphate by different manufacturers. In all the determinations, the results obtained by the known method[6] are lower than the results obtained by the described method. This is also in agreement with the yield obtainable (98–99.5%) by the reported method.[6]

Estimation of pyrophosphate. Under the optimum conditions recommended for the precipitation of pyrophosphate, it was found that the present method gives a yield of 99.5% which is in contrast to a maximum yield of 93% obtainable by the known method. The absence of phosphate in the filtrate in all the precipitation experiments by the present method confirmed the completion of precipitation. Generally, commercial samples of pyrophosphate do not contain triphosphate or any other polyphosphates. However, a series of experiments were conducted to study the effect of triphosphate up to 30%, in the determination of pyrophosphate by the described method (Table 9). It is observed that with up to 5% of triphosphate, the yields were as expected. Furthermore, it was found that in the presence of 10, 20 and 30% of triphosphate, the yields were unrealistic, over 100%. Above 30% of triphosphate, the precipitate was sticky in nature at room temperature, which upon cooling to 10°C turned solid. The present method was also applied to the determination of pyrophosphate in sodium acidpyrophosphate ($Na_2H_2P_2O_7$) prepared by a standard method.[36] The results were found to be good. The replicate experiments showed the purity to be 99.4–99.8%.

Determination of triphosphate in commercial detergent powders. The present method was utilized for the determination of triphosphate in premier detergent powders of Indian origin. Detergent powders, in general, are complex and multicomponent systems. The samples for the analysis were prepared by dissolving the detergent powder in 95% ethanol to remove anionic detergent. The alcohol insoluble phosphates were then dissolved in water and used for the estimation.[1] Determinations were made in triplicate for each sample, employing the known and the described methods (Table 10). It is observed that the results of both the methods are in good agreement.

Table 8. Analysis of orthophosphoric acid and its salts by the present method

Sample	Purity of sample obtained (in wt%) 1	2	3	4	5	6	Mean dev. (%)	Standard dev. (%)
H_3PO_4 (85.0%)	84.8	84.8	84.9	85.3	84.6	84.9	0.15	0.25
$NaH_2PO_42H_2O$	99.9	99.8	99.6	99.6	100.0	100.1	0.16	0.21
Na_2HPO_4	100.1	99.7	99.5	99.9	100.0	99.6	0.20	0.24
$Na_3PO_412H_2O$	100.1	100.2	100.0	99.9	99.8	100.1	0.11	0.15
KH_2PO_4	100.0	100.5	100.3	100.3	100.4	100.2	0.15	0.19
$(NH_4)_2HPO_4$	99.7	99.9	99.5	100.2	99.9	100.0	0.17	0.25

Table 9. Effect of triphosphate in the estimation of pyrophosphate

Sample number	Pyrophosphate taken (*mg*)	Triphosphate added (*mg*)	In the mixture Pyrophosphate (%)	In the mixture Triphosphate (%)	Found* Mean (%)
1	125.00	Nil	100.0	0.0	99.4
2	121.87	3.12	97.5	2.5	99.8
3	118.75	6.25	95.0	5.0	99.8
4	112.50	12.50	90.0	10.0	100.9
5	100.00	25.00	80.0	20.0	102.3
6	87.50	37.50	70.0	30.0	†

*Calculated as $[Co(en)_2HP_2O_7]4H_2O$.

†The yield could not be accurately determined owing to the sticky nature of the precipitate.

Table 10. Comparison of the present method with the known method for the determination of triphosphate in commercial detergent powders

	Triphosphate content							
	Reported method[6]				This method			
Manufacturer's code number	I (%)	II (%)	III (%)	Mean (%)	I (%)	II (%)	III (%)	Mean (%)
A	19.9	20.9	20.1	20.3	20.6	21.3	20.2	20.7
B	27.9	27.9	27.0	27.6	28.5	27.5	27.3	27.8
C	16.8	18.9	18.0	17.9	18.2	16.9	17.0	17.4

Determination of orthophosphate in commercial matrices. For this purpose, some commercial tricalcium and dicalcium phosphates were taken. Since these are water insoluble, acid extract of these samples were used for the estimation. It was found that calcium severely interferes. At the optimum pH, precipitation of calcium phosphate occurs preferentially over the precipitation of $[Co(en)_2PO_4]$, resulting in a mixture of both the precipitates. Masking of calcium by EDTA followed by precipitation of the phosphate complex by acidified solution of (carbonato)bis(ethylenediamine)cobalt(III) chloride did not give the desired results.

Acknowledgements—Authors wish to thank Ballarpur Industries Limited, Karwar, India, for the facilities to carry out this work. The useful advice and assistance of Dr K. S. Ramachandra is gratefully acknowledged. One of the authors (D.R.K.) is grateful to the Indian Institute of Science, for accepting him as an external registrant for the Ph.D. degree.

REFERENCES

1. H. J. Weiser Jr., *Anal. Chem.*, 1956, **28,** 477.
2. E. Karl-Kroupa, *Anal. Chem.*, 1956, **28,** 1091.
3. G. E. B. Y. Ahlijah and E. F. Mooney, *Spectrochim. Acta*, 1966, **22,** 547.
4. D. E. C. Corbridge, *J. Appl. Chem.*, 1956, **6,** 456.
5. D. E. C. Corbridge and E. J. Love, *Anal. Chem.*, 1955, **27,** 1383.
6. H. W. Mccune and G. J. Arquatte, *Anal. Chem.*, 1955, **27,** 401.
7. D. R. Kamat, V. V. Savant and D. N. Sathyanarayana, *Inorg. Chim. Acta* (1994) (submitted).
8. M. Halmann (Ed.), *Analytical Chemistry of Phosphorous Compounds.* Wiley-Interscience, New York, 1972.
9. B. Paschkes and B. Berman, *Anal. Chim. Acta*, 1961, **24,** 5.
10. IS 567-1969, IS 571-1969, IS 798-1986, Bureau of Indian Standards, New Delhi.
11. A. I. Vogel, *A Textbook of Quantitative Inorganic Analysis.* ELBS, Longmans, London, 1978.
12. R. Bennewitz and I. Taenzer, *Mikro Chim. Acta*, 1959, 853.
13. W. S. Selig, *J. Chem. Educ.*, 1985, **62,** 431.
14. L. S. Rumyantseva and I. L. Jeodovovich, *Dokl. Akad. Nauk. Uzb, SSR*, 1967, **24,** 35.
15. V. Kantere, I. E. Krasnova and G. M. Muskheli, *Otkrytiya, Izobret, Prom. Obraztsy, Tovarnye Znaki*, 1970, **47,** 131.
16. M. L. Marion, *Diss. Abstr. Int. B*, 1973, **33** (Part 1), 5706.
17. S. K. Susic, V. N. Njegovan and B. Solaja, *Z. Anal. Chem.*, 1961, **183,** 412.
18. S. R. Trivedi and G. S. Johar, *Labdev*, 1970, Part A, **8,** 19.
19. T. Takashi, H. Kazuo and K. Akinori, *Bunseki Kagaku*, 1979, **28,** 43.
20. K. Murthy, N. Krishnan and A. V. Suryanarayana, *Fresenius' Z. Anal. Chem.*, 1982, **312,** 546.
21. F. Ruf and C. R. Sem, *Geol. Commun. Nat. Malgache Geol.*, 1966, 70.
22. M. Muto, *Nippon Kagaku Zasshi*, 1964, **85,** 782.
23. J. P. Ebel, *Bull. Soc. Chim. Fr.*, 1968, 1663.
24. D. Lairon, J. Amic and H. Lafont, *J. Chromatogr.*, 1974, **88,** 183.
25. R. K. Ghatuary and A. K. Sen, *J. Indian Chem. Soc.*, 1978, **55,** 337.
26. A. Laurent and R. Bourdon, *Ann. Pharm. Fr.*, 1978, **36** (9–10), 453.

27. T. P. Mawhinney, *Anal. Lett.*, 1983, **16** (A2), 159.
28. G. D. Christian and F. J. Feldman, *Anal. Chim. Acta*, 1968, **40,** 173.
29. S. F. Lincoln and D. R. Stranks, *Aust. J. Chem.*, 1968, **21,** 37.
30. M. Linhard and G. Stim, *Z. Anorg. Chem.*, 1952, **268,** 105.
31. A. Wold and J. K. Ruff, *Inorg. Synth.*, 1973, **14,** 64.
32. W. C. Fernelius, *Inorg. Synth.*, 1946, **2,** 221.
33. J. C. Bailar, *Inorg. Synth.*, 1946, **2,** 222.
34. IS 6100-1986, Bureau of Indian Standards, New Delhi.
35. L. F. Audrieth, *Inorg. Synth.*, 1950, **3,** 103.
36. J. R. Van Wazer, *Phosphorus and Its Compounds*, Vol. 1, p. 607. Interscience, New York, 1958.