

## ANALYSIS OF COMMERCIAL POLYPHOSPHATES BY THIN-LAYER CHROMATOGRAPHY

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**Abstract.** Analysis procedures of  $\text{Na}_5\text{P}_3\text{O}_{10}$  (STPh) and  $(\text{NaPO}_3)_n$  (SPPh) were investigated. The effect of solvent systems on separation quality and determination accuracy were studied. Suitable components of solvents were found: for the separation of polyphosphate anions – acetone, trichloroacetic acid, and water; for the separation of cyclophosphate anions – methyl-ethyl ketone, water, dimethylformamide, and isopropanol. Procedures were developed for determination of phosphate additives in STPh and SPPh. For all procedures limits and accuracy of determination were found. The limit of separation and determination for  $\text{PO}_4^{3-}$  and  $(\text{PO}_3^-)_3$  was 0.04–0.06%  $\text{P}_2\text{O}_5$  and for  $\text{P}_2\text{O}_7^{4-}$ , 0.08–0.10%  $\text{P}_2\text{O}_5$ . Typical accuracy of  $\text{PO}_4^{3-}$  and  $(\text{PO}_3^-)_3$  determination at the content range of 0.10–0.30%  $\text{P}_2\text{O}_5$  was up to  $\pm 25\%$ ; at 2.0–8.0%  $\text{P}_2\text{O}_5$ , up to  $\pm 4.0\%$ . Determination accuracy of  $\text{P}_2\text{O}_7^{4-}$  at the content range of 0.80–1.0%  $\text{P}_2\text{O}_5$  was up to  $\pm 10\%$ ; at 4.6–8.2%, up to  $\pm 2.5\%$ .

**Key words:** polyphosphates, separation, determination.

### INTRODUCTION

All chemical analysis methods of mixtures of condensed phosphates require that the different forms of phosphates should first be separated from one another. After that it is possible to determine the quantity of each phosphate form. Qualitative and quantitative analysis of mixtures of condensed phosphates can be made by chromatographic and precipitation methods. Selective precipitation by means of organic bases was studied by Ebel et al. [1]. As only mono-, di-, tri-, tricyclo-, and tetracyclophosphate anions were formed, precipitation of different anions from mixtures was not selective enough and the method has not found use in practice. Better results were achieved by ion-exchange chromatography [2]. By means of this method each constituent of a mixture of mono-, di-, tri-, tricyclo-, and tetracyclophosphates of about equal concentration can be separated and determined. Separation of small amounts of different anions from large amounts of anions was not achieved. Paper and thin-layer chromatography,

which are until now the best methods for analysis of mixtures of condensed phosphates, were studied thoroughly by Grunze & Thilo [3] and Rössel [4-6]. Procedures of quantitative analysis of phosphate mixtures are described in [6]. Analysis results of one sample of sodium phosphate glass and one sample of sodium triphosphate are given. Constituent accuracy of each phosphate is presented, but the method of its determination is not described.

In practice analysis of mixtures of various phosphate forms is needed for the determination of phosphate additives in commercial sodium triphosphate (STPh) and sodium polyphosphate (SPPh). It is needed for controlling the manufacture and testing of products and in investigations of the chemistry and mechanism of reactions between STPh or SPPh and other substances. In this paper the main results of an investigation of the separation of condensed phosphate anions by thin-layer chromatography and determination by spectroscopic methods are presented.

## EXPERIMENTAL

Hand-made thin layer plates measuring  $200 \times 200 \times 4$  mm and  $100 \times 200 \times 4$  mm and vertical developing procedure were used. The thin layer with a thickness of 0.14-0.18 mm was prepared on the glass plates using microcrystalline cellulose and maize starch as binder (cellulose and starch mass ratio was 16:1). The inside dimensions of tanks were  $225 \times 225 \times 75$  mm. Spots of phosphates were detected by spraying two solutions with the following composition.

### I. solution:

1. Sodium molybdate, cr. ( $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ )	40 g
2. Ammonium nitrate ( $\text{NH}_4\text{NO}_3$ )	50 g
3. Water	$900 \text{ cm}^3$
4. Nitric acid ( $\rho = 1.40 \text{ g cm}^{-3}$ )	$100 \text{ cm}^3$

### II. solution:

1. Sodium pyrosulphite ( $\text{Na}_2\text{S}_2\text{O}_5$ )	300 g
2. Sodium sulphite ( $\text{Na}_2\text{SO}_3$ )	10 g
3. Metol [ $(\text{CH}_3\text{NHC}_6\text{H}_4\text{OH})_2 \cdot \text{H}_2\text{SO}_4$ ]	2 g
4. Water	$1000 \text{ cm}^3$

For the determination of the quantity of phosphate anions separated from STPh and SPPh their spots were scraped into a  $100 \text{ cm}^3$  conical flask, where cellulose was completely decomposed (burnt) by means of perchloric acid. In the solution formed and transferred into a volumetric flask, the quantity of  $\text{P}_2\text{O}_5$  was determined spectrophotometrically by phosphorus-molybdenum blue complex procedure, and adsorption was measured at 830 nm. In developing solvents and conditions for making an artificial mixture of solutions of pure  $\text{KH}_2\text{PO}_4$ ,  $\text{Na}_4\text{P}_2\text{O}_7$ ,  $\text{Na}_5\text{P}_3\text{O}_{10}$ ,  $(\text{NaPO}_3)_3$ , and  $(\text{NaPO}_3)_4$ , where the content of  $\text{P}_2\text{O}_5$  in each anion was  $4-6 \mu\text{g mm}^{-1}$ , solutions of commercial  $\text{Na}_5\text{P}_3\text{O}_{10}$  (2.000 g in a  $25 \text{ cm}^3$  volumetric

flask) and  $(\text{NaPO}_3)_n$  (1.000 g in a 25 cm<sup>3</sup> volumetric flask) were used. The sample solution was transferred to the thin layer with a micropipette with a volume of 2–5 mm<sup>3</sup> one or more times. In the latter case phosphates were concentrated in starting spots before developing. For the investigation of determination accuracy only one sample solution was transferred to a 200 × 200 mm plate on the starting line.

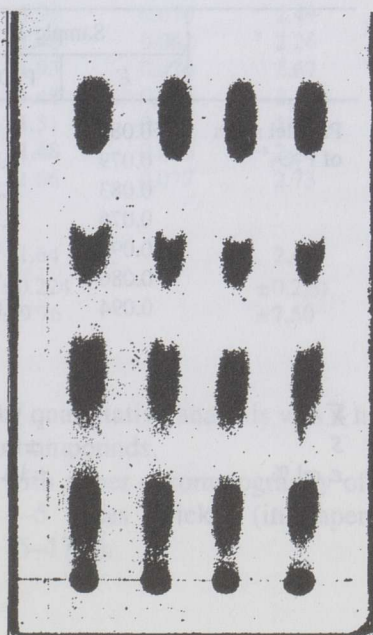
## THE MAIN RESULTS

Compositions of the solvents worked out are presented in Table 1.

**Table 1.** Composition of solvents developed and used for the separation of condensed phosphate anions

Reagent, cm <sup>3</sup>	Number of solvent							
	1	2	3	4	5	6	7	8
Acetone	68	66	63	60	68	68	68	—
Trichloroacetic acid (20%)	25	25	25	25	32	30	28	—
Water	7	9	12	20	—	2	4	39.0
Ammonium (25%)	0.3	0.3	0.3	0.3	0.3	0.3	0.3	1.0
Dimethylformamide	—	—	—	—	—	—	—	20
2-Propanol	—	—	—	—	—	—	—	20
Methyl ethyl ketone	—	—	—	—	—	—	—	20

It was found that for samples with the same concentration of each phosphate form solvent No. 1 was the most suitable one (Fig. 1). For SPPh analysis the best separation was achieved by solvents Nos. 3 and 4. Solvents Nos. 1 and 2 were suitable for quantitative determination of  $\text{PO}_4^{3-}$  and  $\text{P}_2\text{O}_7^{4-}$  in  $\text{Na}_5\text{P}_3\text{O}_{10}$  (Fig. 2). As the production and use of STPh and SPPh are the largest among sodium condensed phosphates the determination accuracy of additive phosphates in these products was studied. Accuracy was calculated by the usual procedure [7]. Typical results are presented in Tables 2–4.



**Fig. 1.** Chromatograms of mono-, di-, tri-, tricyclo-, and tetracyclophosphates, obtained by solvent No. 1. Solvent front 160 mm. Developing time was 105 min and chamber temperature 5 °C.

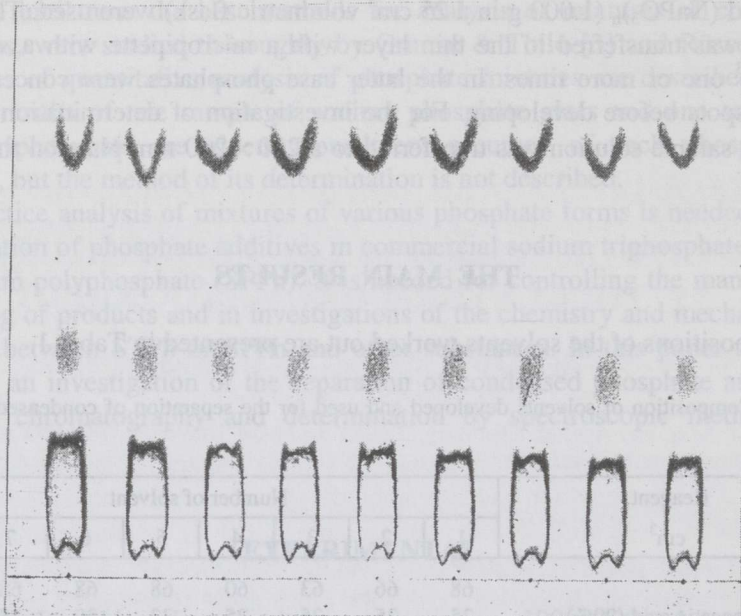


Fig. 2. Typical chromatogram of sodium triphosphate, obtained by solvent No. 7 at 5°C.

Table 2. Typical results of the determination of phosphorus content in diphosphate spots on thin-layer chromatograms

	Sample 1		Sample 2		Sample 3	
	<i>E</i>	P <sub>2</sub> O <sub>5</sub> , %	<i>E</i>	P <sub>2</sub> O <sub>5</sub> , %	<i>E</i>	P <sub>2</sub> O <sub>5</sub> , %
Parallel spots	0.084	0.86	0.224	4.59	0.243	8.12
of P <sub>2</sub> O <sub>7</sub> <sup>4-</sup>	0.079	0.80	0.207	4.91	0.228	7.65
	0.083	0.86	0.224	4.59	0.234	7.83
	0.076	0.74	0.210	4.71	0.245	8.24
	0.094	1.05	0.216	4.83	0.246	8.24
	0.086	0.92	0.220	4.59	0.250	8.36
	0.094	1.05	0.210	4.87	0.245	8.24
			0.222	4.63	0.245	8.24
					0.255	8.53
$\bar{X}$		0.89		4.75		8.18
<i>S</i>		± 0.105		± 0.153		± 0.268
$\epsilon$ , rel.%		± 10.1		± 2.53		± 2.47

**Table 3.** Typical results of the determination of phosphorus content in monophosphate spots on thin-layer chromatograms

	Sample 1		Sample 4		Sample 3	
	<i>E</i>	P <sub>2</sub> O <sub>5</sub> , %	<i>E</i>	P <sub>2</sub> O <sub>5</sub> , %	<i>E</i>	P <sub>2</sub> O <sub>5</sub> , %
Parallel spots of PO <sub>4</sub> <sup>3-</sup>	0.086	0.13	0.087	2.11	0.150	5.06
	0.091	0.14	0.084	2.02	0.158	5.30
	0.102	0.18	0.086	2.07	0.172	5.77
	0.088	0.14	0.070	1.70	0.178	6.00
	0.094	0.15	0.096	2.27	0.159	5.30
	0.079	0.10	0.080	1.94	0.168	5.65
	0.089	0.13	0.072	1.70	0.162	5.47
	0.080	0.11	0.081	1.94	0.186	6.12
			0.092	2.19	0.168	5.65
$\bar{X}$	0.14		1.99		5.59	
<i>S</i>	±0.02		±0.198		±0.345	
$\epsilon$ , rel. %	±14.3		±8.04		±4.65	

**Table 4.** Typical results of the determination of phosphorus content in tricyclophosphate spots on thin-layer chromatograms

	Sample 5		Sample 3		Sample 2	
	<i>E</i>	P <sub>2</sub> O <sub>5</sub> , %	<i>E</i>	P <sub>2</sub> O <sub>5</sub> , %	<i>E</i>	P <sub>2</sub> O <sub>5</sub> , %
Parallel spots of (PO <sub>3</sub> ) <sub>3</sub>	0.117	0.15	0.288	1.66	0.062	2.26
	0.117	0.15	0.315	1.93	0.070	2.49
	0.128	0.17	0.260	1.48	0.062	2.26
	0.135	0.19	0.314	1.93	0.076	2.67
	0.115	0.14	0.260	1.48	0.064	2.32
	0.106	0.12	0.265	1.51	0.056	2.08
	0.111	0.14	0.260	1.48	0.066	2.36
	0.125	0.17	0.288	1.66	0.077	2.73
	0.115	0.14				
	$\bar{X}$	0.15		1.64		2.40
<i>S</i>	±0.021		±0.224		±0.220	
$\epsilon$ , rel. %	±13.3		±9.76		±7.50	

The minimum time needed for getting a result of quantitative analysis was 4 h for the determination of (PO<sub>3</sub>)<sub>3</sub> and 5.5 h for other compounds.

In conclusion we can say that in comparison with paper chromatography of condensed phosphates, the studied method is 4–5 times quicker (in paper chromatography the solvent running time alone is 15–17 h).

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## TÖÖSTUSES TOODETAVATE POLÜFOSFAATIDE ANALÜÜS ÕHUKESE KIHII KROMATOGRAAFIA ABIL

Meeme PÖLDME ja Juta PÖLDME

On antud lühike kirjandusülevaade kondenseeritud fosfaatide segude kvalitaativse ja kvantitaativse analüüsi meetodite kohta. Eksperimentaalselt on uuritud  $\text{Na}_5\text{P}_3\text{O}_{10}$  ja  $(\text{NaPO}_3)_n$  analüüsi ning määratud eluentide koostise mõju anioonide lahutamise kvaliteedile. Kõige sobivamateks eluentide komponentideks polüfosfaatide lahutamisel osutusid atsetoon, triklooretaanhape ja vesi, tsüklofosfaatide lahutamisel metüületüülketoon, vesi, dimetüülformamiid ja isopropanool.

On täpsustatud meetodikaid, mis võimaldavad lisandfosfaate määrata naatriumtrifosfaadis ja naatriumpolüfosfaadis. Kõikide fosfaatide puhul leiti määramise tundlikkus ja täpsus.  $\text{PO}_4^{3-}$  ja  $(\text{PO}_3^-)_3$  määramise piiriks on 0,04–0,06%  $\text{P}_2\text{O}_5$ ;  $\text{P}_2\text{O}_7^{4-}$  sama näitaja on 0,08–0,10%  $\text{P}_2\text{O}_5$ .  $\text{PO}_4^{3-}$  ja  $(\text{PO}_3^-)_3$  määramise täpsus  $\text{P}_2\text{O}_5$  sisalduse juures 0,10–0,30% on kuni  $\pm 25\%$ , 2,0–8,0%  $\text{P}_2\text{O}_5$  juures kuni  $\pm 4,0\%$ .  $\text{P}_2\text{O}_7^{4-}$  määramise täpsus  $\text{P}_2\text{O}_5$  sisalduse juures 0,80–1,0% on kuni  $\pm 10\%$ , sisalduse 4,6–8,2% juures kuni  $\pm 2,5\%$ .