

R. KIJKOWSKA\*, Z. KOWALSKI, D. PAWLOWSKA-KOZINSKA, Z. WZOREK

Institute of Inorganic Chemistry and Technology, Crakow University of Technology, Warszawska 24, 31-155 Kraków, Poland

## Quantitative Determination of Crystalline $\text{Na}_5\text{P}_3\text{O}_{10}$ –I (Form-I) in Commercial Tripolyphosphate using X-ray Diffraction Patterns

An x-ray diffraction method (XRD) for quantitative determination of the crystalline  $\text{Na}_5\text{P}_3\text{O}_{10}$ -I (Form-I) in a mixture of Form-I/Form-II was applied for commercial pentasodium tripolyphosphate analysis. The XRD pattern of the Form-I shows the unique non-overlapping  $2\theta$  peak at a position of  $\approx 21.8$  deg. and also at  $\approx 29.0$  deg. (Cu radiation). The area (integral of the intensity) under the peaks is proportional to the amount of the Form-I in the mixture covering the range up to 100 wt.%. That enables one to obtain a calibration line and to determine the amount of Form-I in the mixture of Form-I/Form-II and also in commercial pentasodium tripolyphosphate.

Commercial samples with high Form-I concentration, in case they are contaminated with sodium pyrophosphate ( $\text{Na}_4\text{P}_2\text{O}_7$ ), should be diluted with Form-II to bring the concentration of the Form-I below 50 wt.% in the analysed sample.

Keywords: X-ray diffraction, quantitative determination, tripolyphosphate

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### Introduction

Pentasodium tripolyphosphate (PST) is known to exist in three crystalline forms. They are hexahydrate  $\text{Na}_5\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$  and two anhydrous forms: high-temperature  $\text{Na}_5\text{P}_3\text{O}_{10}$  –I (Form-I) and low-temperature  $\text{Na}_5\text{P}_3\text{O}_{10}$  –II (Form-II) (DYMON et al. and VAN WAZER). The temperature of the transformation of Form-II to Form-I, depending on a heating rate, is estimated to be in the range of  $450^\circ\text{C} - 500^\circ\text{C}$ . The transition between the two anhydrous varieties, described by Van Wazer as a complex phenomenon is frequently not complete even in the material heated above  $500^\circ\text{C}$ . It is the usual case that the material heated at  $500^\circ\text{C}$  or above turns out to be a mixture of Form-I and Form-II.

Modern technology yields diversified grades of PST with different ratio of Form-I/Form-II. Phase analysis of the tripolyphosphate is a complex problem, especially quantitative determination of its anhydrous varieties. A number of chemical methods (BELL et al., NETHERTON et al., RAISTRICK et al., and WEISER et. al.) among them those applying radioactive isotope techniques (QUIMBY et al.) or anion-exchange chromatography (GRANDE et al. and KARL-KROUPA) have been developed for commercial sodium tripolyphosphate analyses. Most chemical methods do not distinguish between the two polymorphic forms. In contact with water they transform into hexahydrate  $\text{Na}_5\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$ . One of the methods

\* corresponding author: kij@chemia.pk.edu.pl

based on temperature rise measurement in a glicerine-water mixture due to rapid hydration of the Form-I has been developed at Procter and Gamble for routine determination of the ratio of Form-I to Form-II in penta sodium tripolyphosphate.

An application of x-ray diffraction method (XRD) was reported in the early fifties of the XX century by Van Wazer, Mabis and Corbridge et al. and some other authors. There are four molecules of  $\text{Na}_5\text{P}_3\text{O}_{10}$  in the unit cell of each anhydrous variety of the Form-I or Form-II. Both the forms crystallise in monoclinic modification, however, they differ in the unit cell dimensions. According to Dymon the cell parameters in [nm] are:

Form I:  $a = 1.18550$ ,  $b = 0.5363$ ,  $c = 0.53631$ ,  $\alpha$  and  $\gamma = 90.000^\circ$ ,  $\beta = 96.950^\circ$

Form II:  $a = 1.1210$ ,  $b = 0.5235$ ,  $c = 1.6030$ ,  $\alpha$  and  $\gamma = 90.000^\circ$ ,  $\beta = 93.200^\circ$

Practically these two forms are not separable. The reported by Mabis et al. XRD method was based on an introduction of MgO into a mixture as an internal standard. The intensity of the diffraction peak ( $2\theta = 21.8$ ) was determined by manual method as the difference between the intensity at the peak and at the background of the same angular position.

The aim of the present work was to employ X-ray diffraction patterns without an internal standard for quantitative determination of Form-I in commercial Tripoli (PST) materials. The XRD equipment, available at present time, gives an opportunity to get the data on the intensity as an integral (area) under the XRD peaks ready from the computer system. We have decided to investigate whether the area of the peaks characteristic to Form-I is proportional to its amount in the mixture. If so, they would give the numbers directly applied for calibration line without an internal standard.

In case that commercial product is contaminated with some small amount of sodium pyrophosphate ( $\text{Na}_4\text{P}_2\text{O}_7$ ) its effect on Form-I determination has been also considered.

### Materials and methods

For the current investigations anhydrous  $\text{Na}_5\text{P}_3\text{O}_{10}$  -I,  $\text{Na}_5\text{P}_3\text{O}_{10}$  -II, and sodium pyrophosphate ( $\text{Na}_4\text{P}_2\text{O}_7$ ) have been prepared as standard materials by the methods described by Van Wazer. The materials were characterised by x-ray powder diffraction (XRD) and Ir spectroscopy. The XRD was acquired using Philips Xpert equipment furnished with graphite monochromator PW 1752/00 with Cu  $K_\alpha$  radiation, Ni filter, 30 Kv, 30 mA.

For quantitative determination of Form-I in industrial PST materials, calibration lines for known concentrations of Form-I have been obtained. For this purpose series of mixtures of Form-I/form-II with varying concentrations of each component over the range from 0 to 100 % were prepared from the standard materials. The unique non-overlapping peaks were chosen by examination of the XRD patterns. Areas (integrals) under the chosen XRD peaks corresponding their intensity gave numbers for the calibration lines and for the measurement of the amount of Form-I in commercial samples. The integrals were calculated automatically by XRD- computer- system.

### Results and discussion

Figure 1 shows the XRD patterns of the mixtures of the Form- I/Form-II. The Form-I exhibits a unique non-overlapping diffraction peak at a reasonable intensity at  $2\theta$  value close

to  $21.8^\circ$  the one, that Mabis et al. exploited for the quantitative analysis, and another one at  $2\Theta = 29.0^\circ$ . The latter has been additionally included in the present work. The intensity of the peaks is increasing with an increase of the amount of Form-I in the investigated mixtures. The data on the integral of the peaks can be approximated to a straight line by linear regression presented in table 1. The experimental points and the calibration lines (regression line) for  $2\Theta \approx 21.8^\circ$  and  $2\Theta \approx 29.0$  are presented in figures 2 and 3.

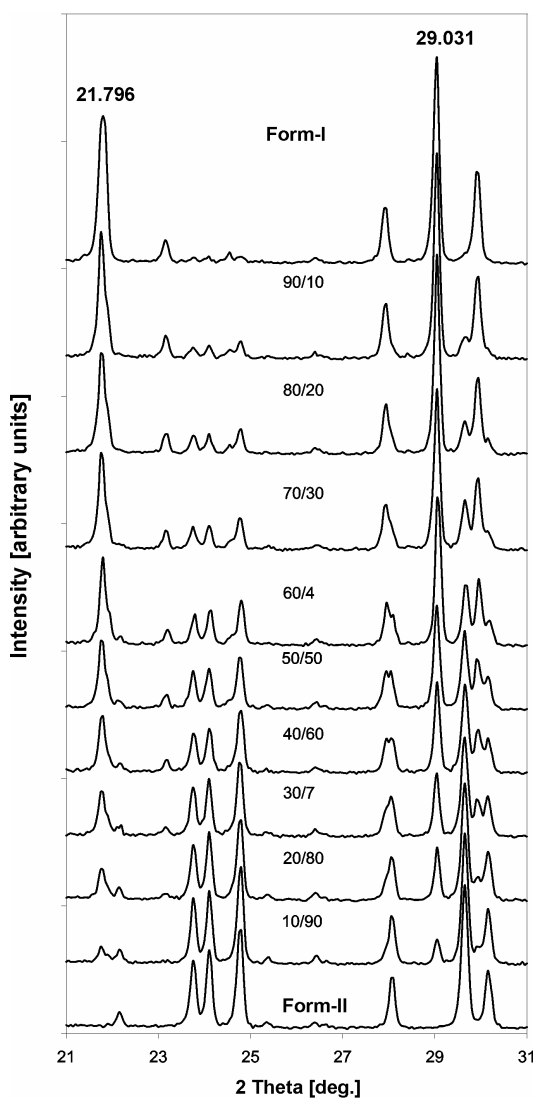
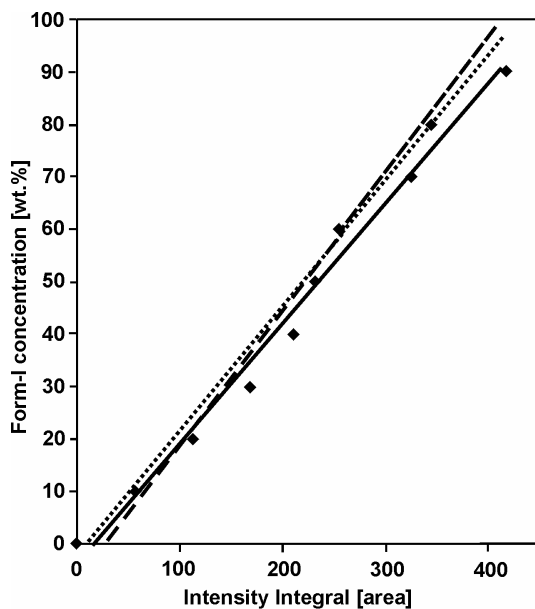


Fig. 1. X-ray diffraction patterns of the  $\text{Na}_5\text{P}_3\text{O}_{10}$  -I (Form-I),  $\text{Na}_5\text{P}_3\text{O}_{10}$  -I (Form-II), and mixtures of the Form-I/Form-II with different weight ratio from 10/90 to 90/10 denoted in the figure.

It is worth to point out, that the measurement repeated after a year reproduced the data for the calibration line which means that the characteristics of the XRD equipment was stable giving the data at a constant level.

Table 1: Regression output for calibration lines ( $y = bx + a$ ) where  $y = \text{wt. \%}$  of Form-I in the mixture,  $x = \text{intensity integral of the XRD peaks}$ .

$2\Theta \approx 21.8 \text{ deg}$	Without $\text{Na}_4\text{P}_2\text{O}_7$	5 % $\text{Na}_4\text{P}_2\text{O}_7$	10 % $\text{Na}_4\text{P}_2\text{O}_7$
Constant (a)	-3.69	-2.60	-7.26
X Coefficient (b)	0.229	0.243	0.258
R Squared	0.985	0.993	0.977
Std. Error of Y estim.	4.0	2.8	4.9
Std. Error of (b) coef.	0.010	0.007	0.014
No of observation	10	10	10
$2\Theta \approx 29.0 \text{ deg.}$	Without $\text{Na}_4\text{P}_2\text{O}_7$	5 % $\text{Na}_4\text{P}_2\text{O}_7$	10 % $\text{Na}_4\text{P}_2\text{O}_7$
Constant (a)	0.61	-2.04	-3.57
X Coefficient (b)	0.162	0.182	0.185
R Squared	0.996	0.990	0.989
Std. Error of Y estim.	2.08	3.16	3.67
Std. Error of (b) coef.	0.004	0.007	0.007
No of observation	10	10	10

Fig. 2: Calibration line for  $\text{Na}_5\text{P}_3\text{O}_{10}$  -I (Form-I). Plot of  $\text{Na}_5\text{P}_3\text{O}_{10}$ -I content (wt.%) against area under the peak of  $2\Theta \approx 21.8^\circ$ .

◆ experimental points for calibration without  $\text{Na}_4\text{P}_2\text{O}_7$ .  
— (solid line) – regression line without  $\text{Na}_4\text{P}_2\text{O}_7$ .  
.... (dot. line) – regression line with 5 % of  $\text{Na}_4\text{P}_2\text{O}_7$ .  
- - - (dash line) – regression line with 10 % of  $\text{Na}_4\text{P}_2\text{O}_7$ .

To find out whether some reasonable amount of pyrophosphate, that sometimes is present in commercial samples affects the calibration line, series of mixtures of Form-I/Form-II with some amount of  $\text{Na}_4\text{P}_2\text{O}_7$  were also prepared. Introduction of 5 % or 10 % of  $\text{Na}_4\text{P}_2\text{O}_7$  into the mixture slightly affects the tangent of the calibration line (Fig. 2 and 3). The data obtained for the lower region of the Form-I content do not depend on the  $\text{Na}_4\text{P}_2\text{O}_7$  presence, while the data obtained in the mixtures with higher Form-I concentrations are higher than those expected to be. That phenomenon was also confirmed when commercial samples with

higher than 50 % of Form-I content were analysed. To overcome the effect of sodium pyrophosphate, the commercial samples with high content of Form-I were diluted with the Form-II to bring the Form-I content below wt. 50 % prior to the analyses. The results obtained after dilution were close to the numbers labelled by the commercial company (Table 2).

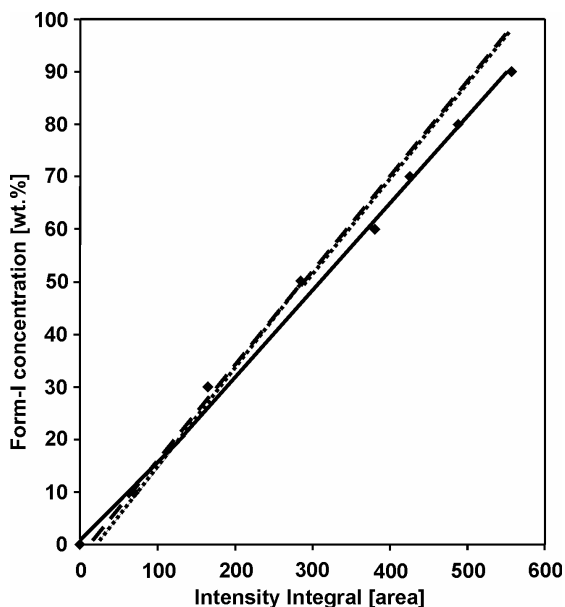


Fig. 3: Calibration line for  $\text{Na}_5\text{P}_3\text{O}_{10}$ -I (Form-I). Plot of  $\text{Na}_5\text{P}_3\text{O}_{10}$ -I content (wt.%) against area under the peak of  $2\Theta \approx 29.0^\circ$ .

- ◆ experimental points for calibration without  $\text{Na}_4\text{P}_2\text{O}_7$ .
- (solid line) – regression line without  $\text{Na}_4\text{P}_2\text{O}_7$ .
- .... (dot. line) – regression line with 5 % of  $\text{Na}_4\text{P}_2\text{O}_7$ .
- - - (dash line) – regression line with 10 % of  $\text{Na}_4\text{P}_2\text{O}_7$ .

Table 2: Wt.% of  $\text{Na}_5\text{P}_3\text{O}_9$ -I (Form-I) in commercial samples determined by calibration area under the x-ray diffraction peaks  $2\Theta \approx 21.8$  and  $2\Theta \approx 29.0$ .

	Wt % of Form-I in commercial samples				
	$2\Theta$ deg.	A2	A3	A4*	A6*
Calibration without $\text{Na}_4\text{P}_2\text{O}_7$	21.8	46.9	49.0	31.1	38.6
	29.0	43.7	47.3	31.8	38.4
Calibration with 5 % of $\text{Na}_4\text{P}_2\text{O}_7$	21.8	51.0	53.3	34.3	42.2
	29.0	46.3	50.3	32.9	40.3
Calibration with 10 % of $\text{Na}_4\text{P}_2\text{O}_7$	21.8	49.7	52.0	31.9	40.3
	29.0	45.5	49.6	31.9	39.5
Mean (wt.% of Form-I found)		47.2	50.2	32.3	39.9
Standard Dev.		2.5	2.0	1.0	1.3
Value (wt.% of Form-I) labelled by Commercial Company		46.6	50.5	31.0	39.0

\*Commercial samples diluted (1 : 1) with Form-II prior to analysis.

## Conclusion

1. The intensity of the x-ray diffraction peak  $2\Theta \approx 21.8$  or  $2\Theta \approx 29.0$  is increasing proportionally to the amount of Form-I in the mixture of Form-I and Form-II of the

pentasodium tripolyphosphate. Calibration line obtained from the data on the areas (integrals) under the above XRD-peaks enables quantitative determination of Form-I in commercial sodium tripolyphosphate.

2. An addition of 5 – 10 wt. % of sodium pyrophosphate affects the data for the higher than 50 wt.% of Form-I content in the mixture. Commercial samples with high Form-I concentration, especially contaminated with sodium pyrophosphate, should be diluted with Form-II to bring the Form-I below 50 wt.% in the analysed sample.

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