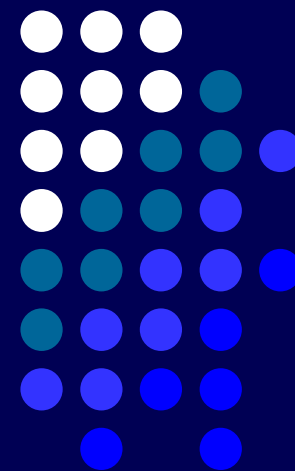
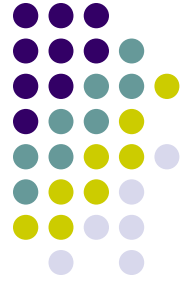


The Study of Polyphosphate Hydrolysis Using ^{31}P NMR

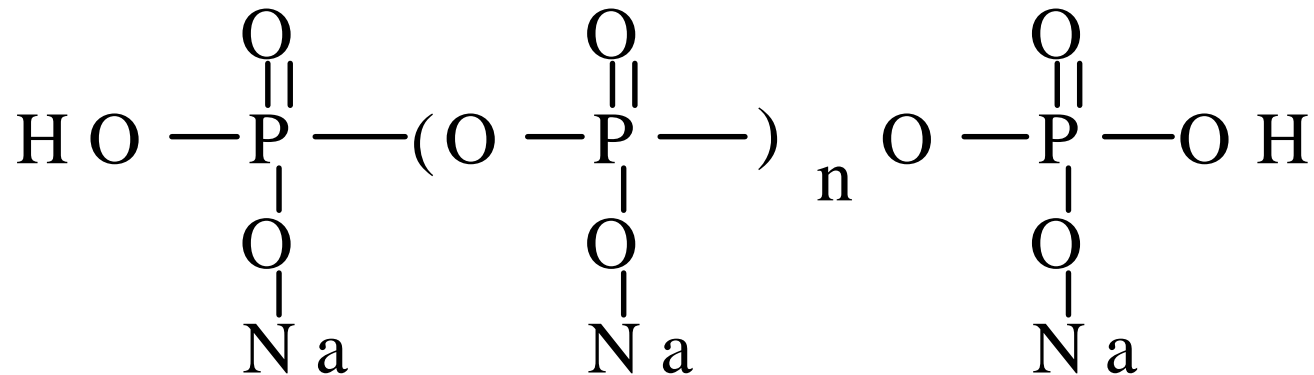
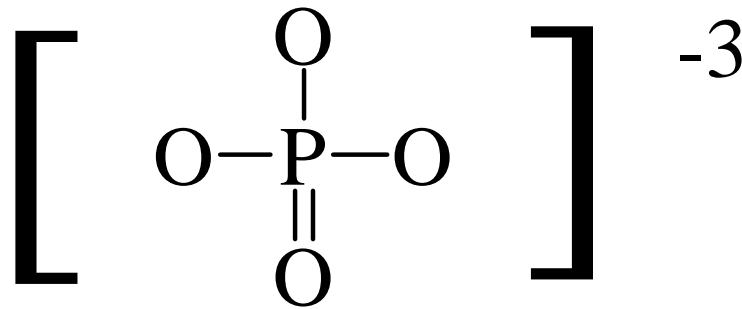
Kenneth Robertson
Austin Peay State University
Clarksville, TN

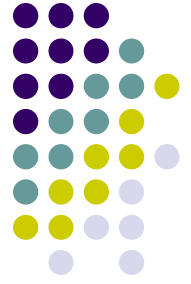




INTRODUCTION

I Orthophosphates and Polyphosphates

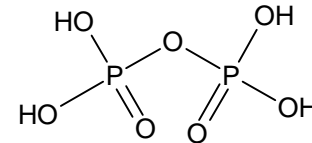




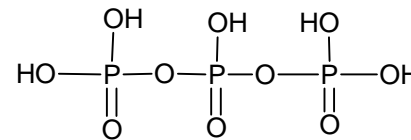
INTRODUCTION

I Several examples of polyphosphates

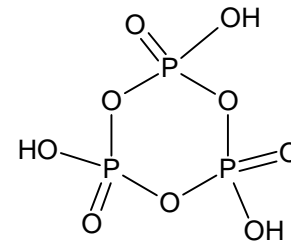
I Pyrophosphate -



I Tripolyphosphate -



I Trimetaphosphate -



I Hexametaphosphate – 16-20 P atoms in a chain

INTRODUCTION



- | Used in paint strippers, soft drinks, toothpaste, and baking powder
- | Phosphates are added to municipal water systems to prevent corrosion in pipes
- | Polyphosphates hydrolyze into orthophosphates over time
- | Little published literature concerning kinetics of the degradation



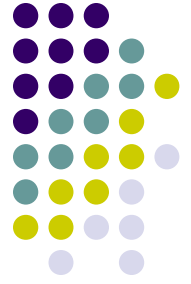
INTRODUCTION

- | ^{31}P NMR used to monitor polyphosphate hydrolysis
- | NMR can provide:
 - | Qualitative data: Peaks in ^{31}P NMR spectra
 - | Quantitative data: Areas under peaks in ^{31}P NMR spectra



INTRODUCTION - NMR

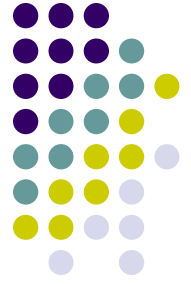
- | NMR data collected in previous research contained variability and lacked reproducibility
- | External reference standard of orthophosphate used in an attempt to improve data
- | Areas of phosphate peaks were normalized to standard's peak area
- | Normalized and unnormalized data were compared to evaluate validity



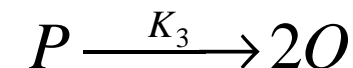
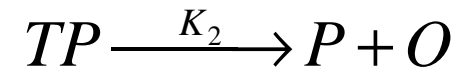
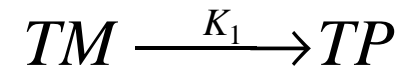
INTRODUCTION - Kinetics

- | Rate law of hydrolysis is an important area of study
- | Most researchers agree that polyphosphate hydrolysis is a first-order process.
- | If reaction is first-order, then the phosphate chain or ring is split randomly.
- | Using steady-state approximation, equations can be derived for kinetic modeling
- | Trimetaphosphate hydrolysis will be used as an example to derive equations

INTRODUCTION - Kinetics



I Trimeta degradation is a three step process



I The first order rate law is integrated to obtain an expression for the trimeta concentration

$$\frac{d[TM]}{dt} = -k_1[TM]$$

$$\int_{[TM]_0}^{[TM]} \frac{d[TM]}{[TM]} = \int_0^t -k_1 dt$$

$$[TM] = [TM]_0 e^{-k_1 t}$$

INTRODUCTION - Kinetics



- Orthophosphate is produced through two mechanisms
- Assuming steady-state approximation...
- Expression for orthophosphate concentration

$$\frac{d[O]}{dt} = 2k_3[P] + k_2[TP]$$

$$\frac{d[TP]}{dt} = 0 = k_1[TM] - k_2[TP]$$

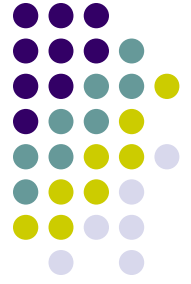
$$[TP] = \frac{k_1}{k_2}[TM] \quad \text{and}$$

$$\frac{d[P]}{dt} = 0 = k_2[TP] - k_3[P]$$

$$[P] = \frac{k_2}{k_3}[TP]$$

$$\frac{d[O]}{dt} = 3k_1[TM]$$

INTRODUCTION - Kinetics



- I The first order rate law for orthophosphate is integrated to obtain an expression for orthophosphate concentration

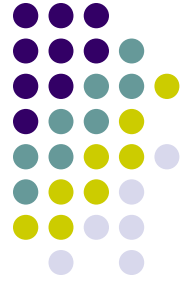
$$\frac{d[O]}{dt} = 3k_1[TM]_0 e^{-k_1 t}$$

$$\int_{[O]_0}^{[O]} d[O] = 3k_1[TM]_0 \int_0^t e^{-k_1 t} dt$$

$$[O] = 3[TM]_0 (1 - e^{-k_1 t})$$

- I By using steady-state approximation, kinetic equations for orthophosphate and polyphosphate concentrations can be derived

PROCEDURE – Sample Preparation



- | Four polyphosphates were studied:
 - | Pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$)
 - | Tripolyphosphate ($\text{Na}_5\text{P}_3\text{O}_{10}$)
 - | Trimetaphosphate ($\text{Na}_3\text{P}_3\text{O}_9$)
 - | Hexametaphosphate (16-20 P atoms in chain)

- | Solutions of each phosphate were prepared at pH's of 1 and 7

PROCEDURE – Sample Preparation



- I Deuterated solvents were used so the solvent would not interfere with the molecular spin of the sample
- I Approximately 35 mg of phosphate were added to 1 mL of deuterated water (D_2O) for every solution
- I Deuterated nitric acid (DNO_3) and deuterated sodium hydroxide ($NaOD$) were used to control pH of solution

PROCEDURE – Sample Preparation



- | External reference standards were added to all pH 1 solutions
- | Approximately 50 mg sodium orthophosphate added to 1 mL D₂O
- | pH of standard was adjusted to 9 so its peak would separate from the solution's orthophosphate peak
- | Standard was placed in NMR tube insert, which was then fit into standard NMR tube



PROCEDURE – NMR Testing

- | 250 MHz Bruker Nuclear Magnetic Resonance Spectrometer
- | Operated at P resonant frequency of 100 MHz
- | Relaxation delay – 5 seconds
- | 64 scans taken



PROCEDURE – Data Analysis



- | NMR generates FIDs
- | PCNMR for Windows used to convert FIDs to spectra
- | Spectra contained peaks that represented P atoms in different magnetic environments
- | Area under peaks proportional to number of P atoms that peak represented
- | Chemical shifts of peaks obtained from NMR spectra plotter



PROCEDURE – Data Analysis

- I Hydrolysis data was fit to first-order kinetics models using *Graphical Analysis for Windows*

- I **Polyphosphate concentration** – 1st order model:

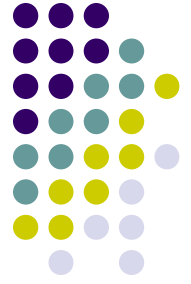
$$[poly] = [poly]_0 e^{-kt}$$

- I **Orthophosphate concentration** – consecutive 1st order reaction model:

$$[Ortho] = [A]_0 (1 - e^{-kt})$$

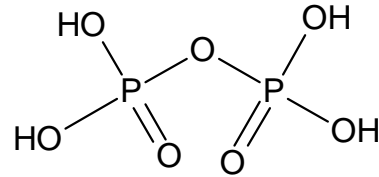
- I Areas under phosphate peaks graphed according to these models

PROCEDURE – Data Analysis

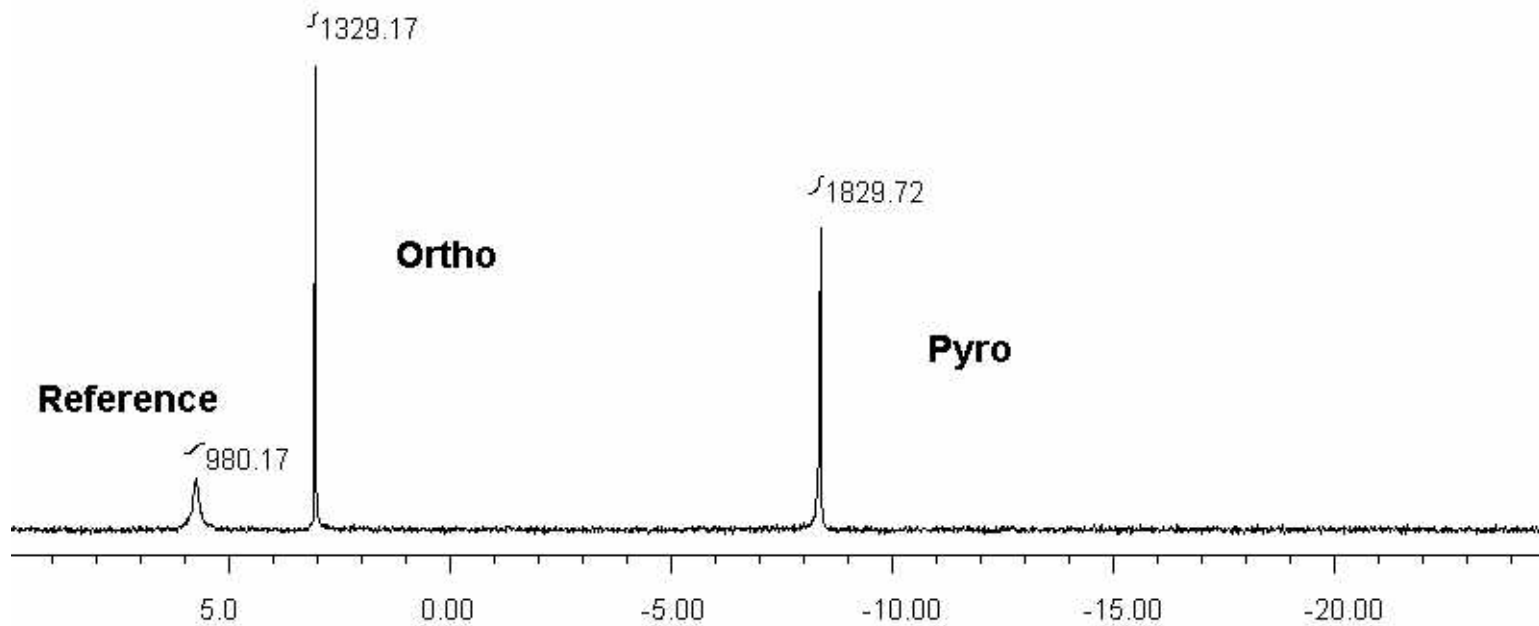


- | Rate constants (k) were produced by these models
- | 0.693 was divided by polyphosphate rate constant to determine polyphosphate half-lives
- | Error in polyphosphate rate constant calculated using linear regression

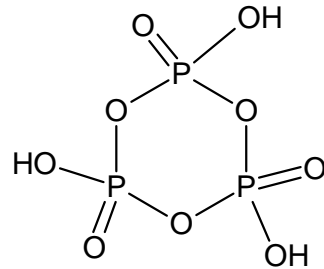
SPECTRA



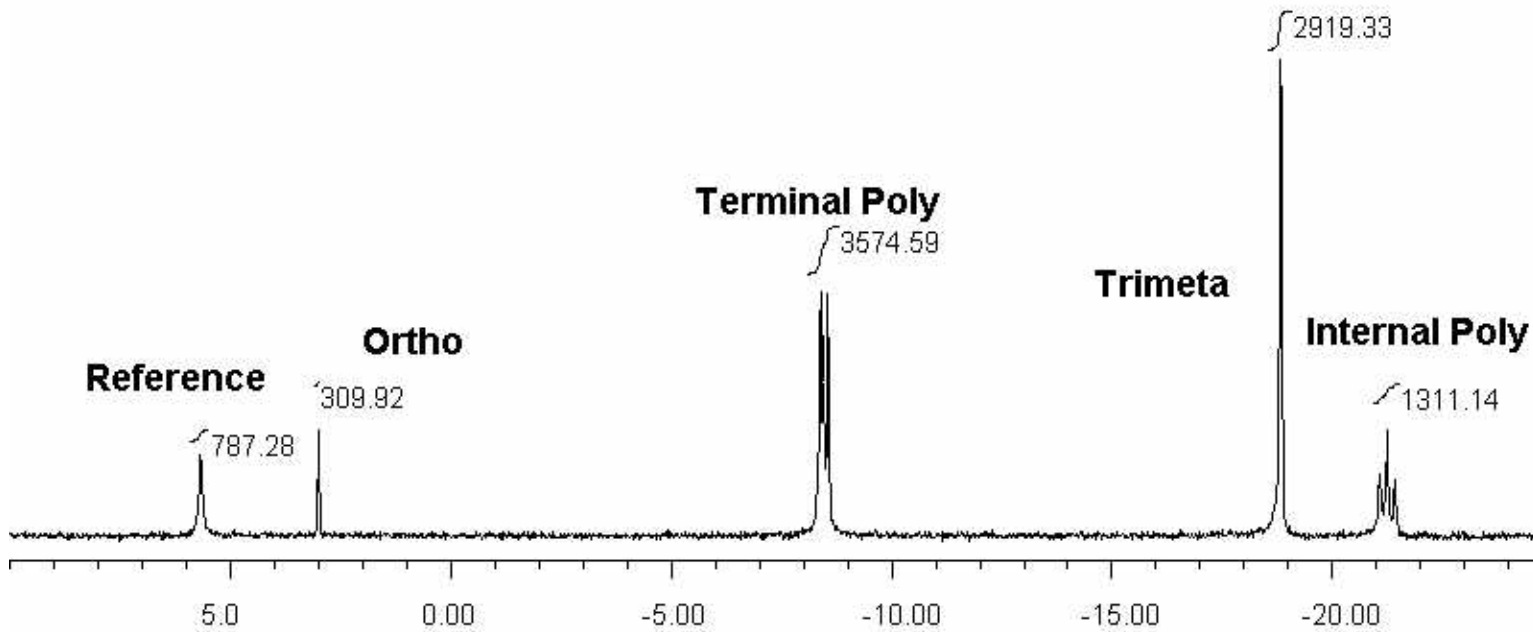
Pyrophosphate - pH 0.96
30 Hours



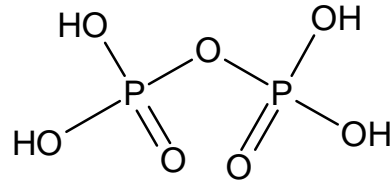
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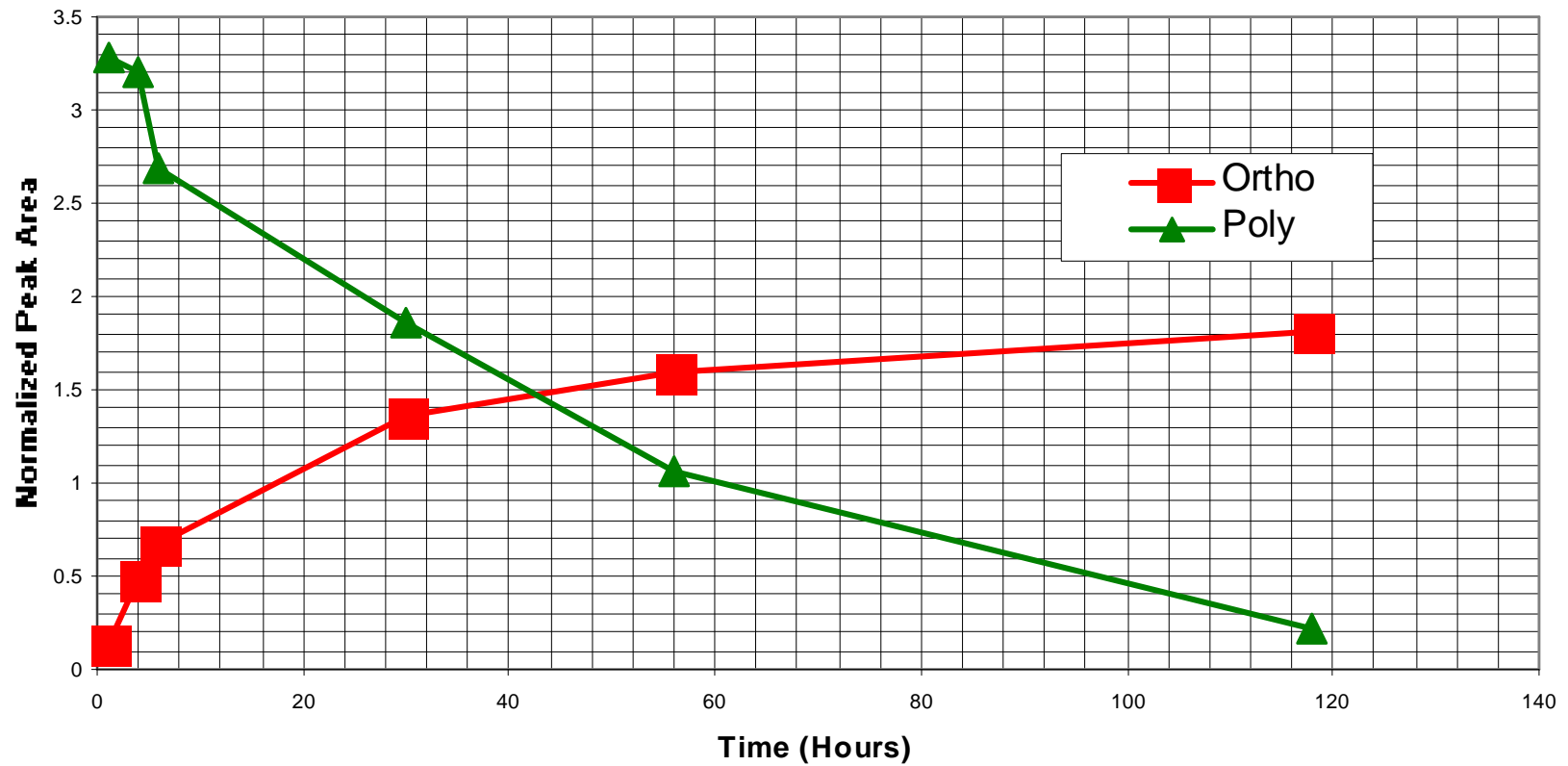
Trimetaphosphate - pH 1.03
2 Hours



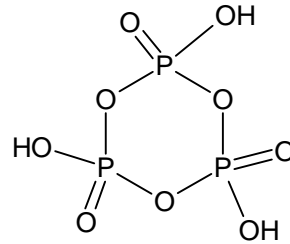
HYDROLYSIS GRAPHS – pH 1



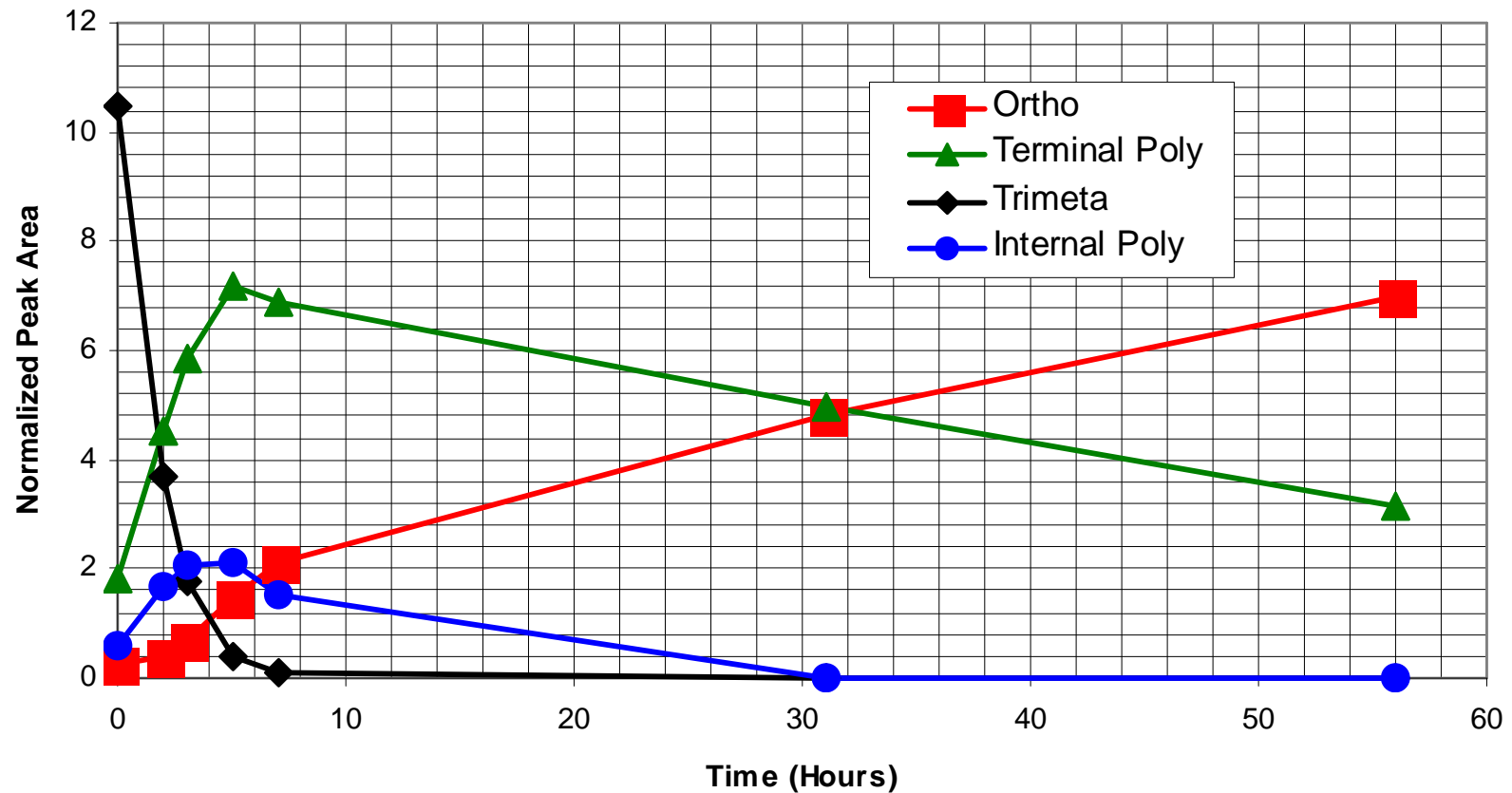
Pyrophosphate - pH 0.96 - Normalized



HYDROLYSIS GRAPHS – pH 1



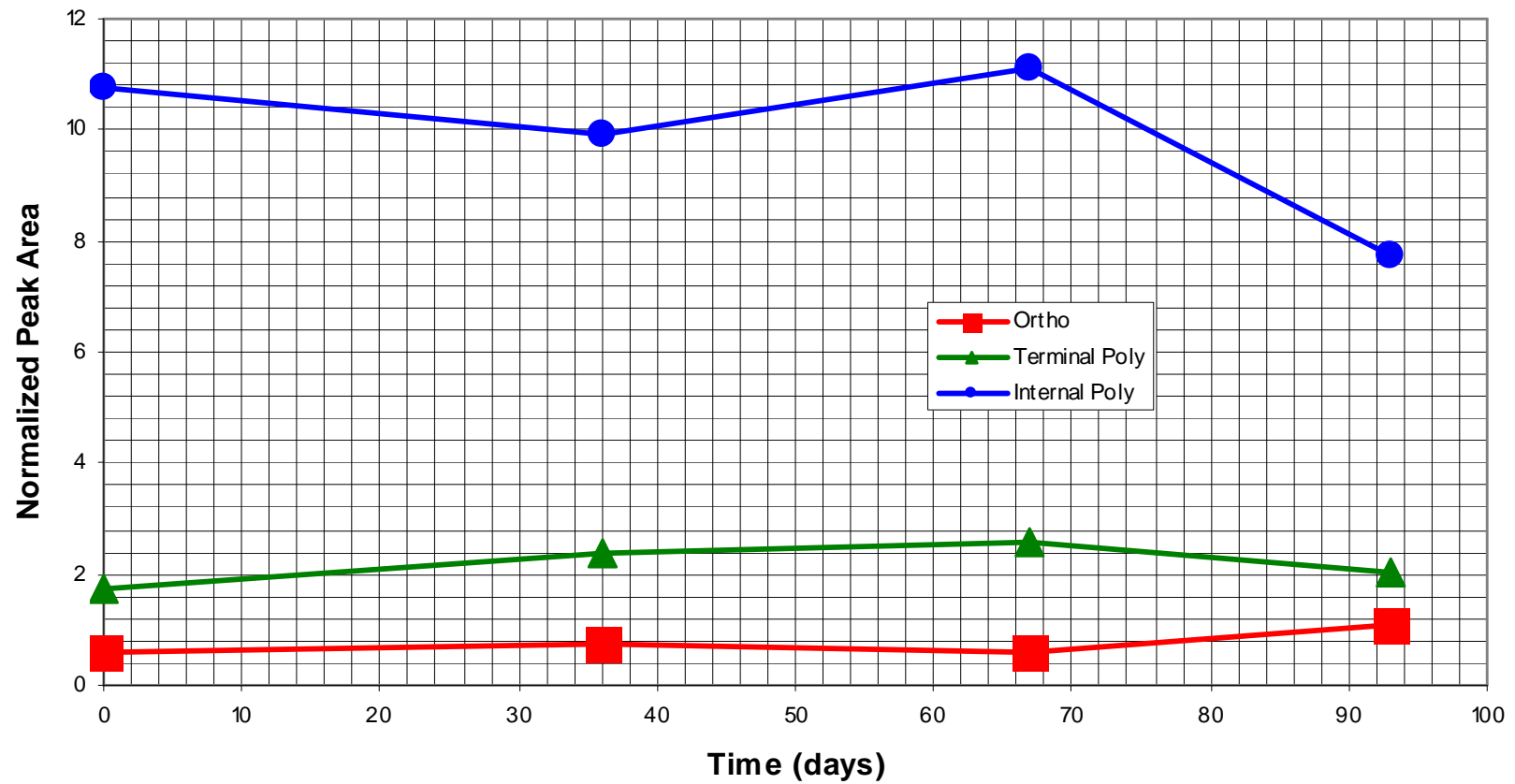
Trimetaphosphate - pH 1.03 - Normalized



HYDROLYSIS GRAPHS – pH 7



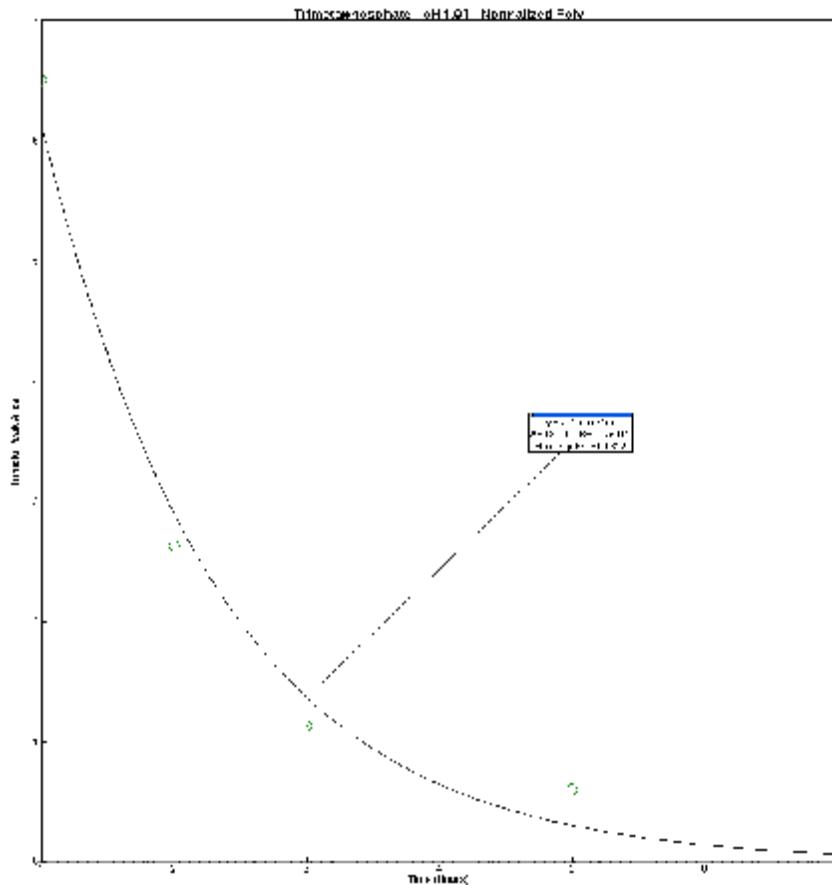
Hexametaphosphate - pH 6.80 - Normalized



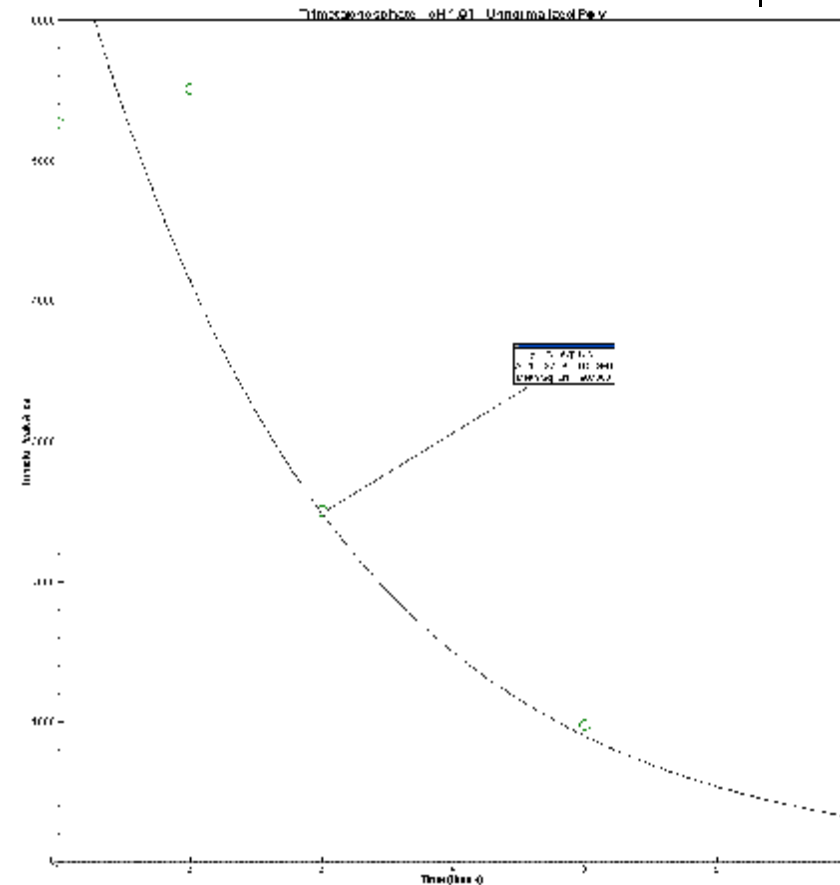
TRIMETA – POLY CURVE-FITS

Normalized

Unnormalized



$k=7.5 \times 10^{-1} \text{ 1/hr}$

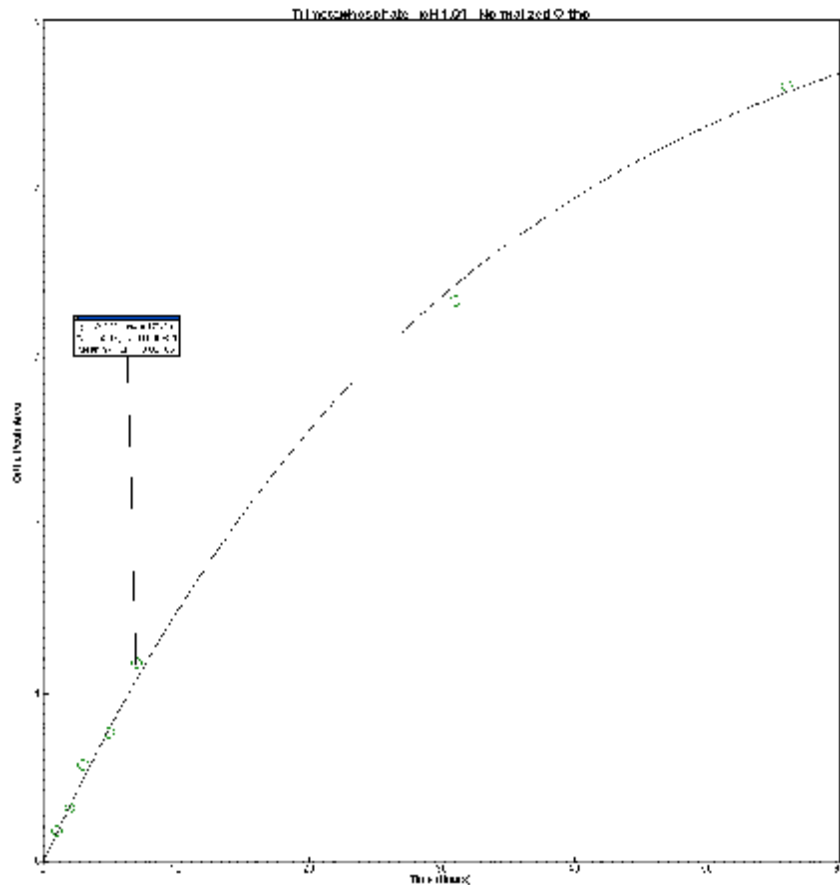
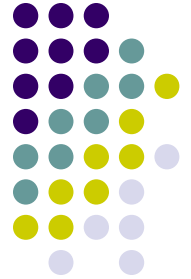


$k=5.1 \times 10^{-1} \text{ 1/hr}$

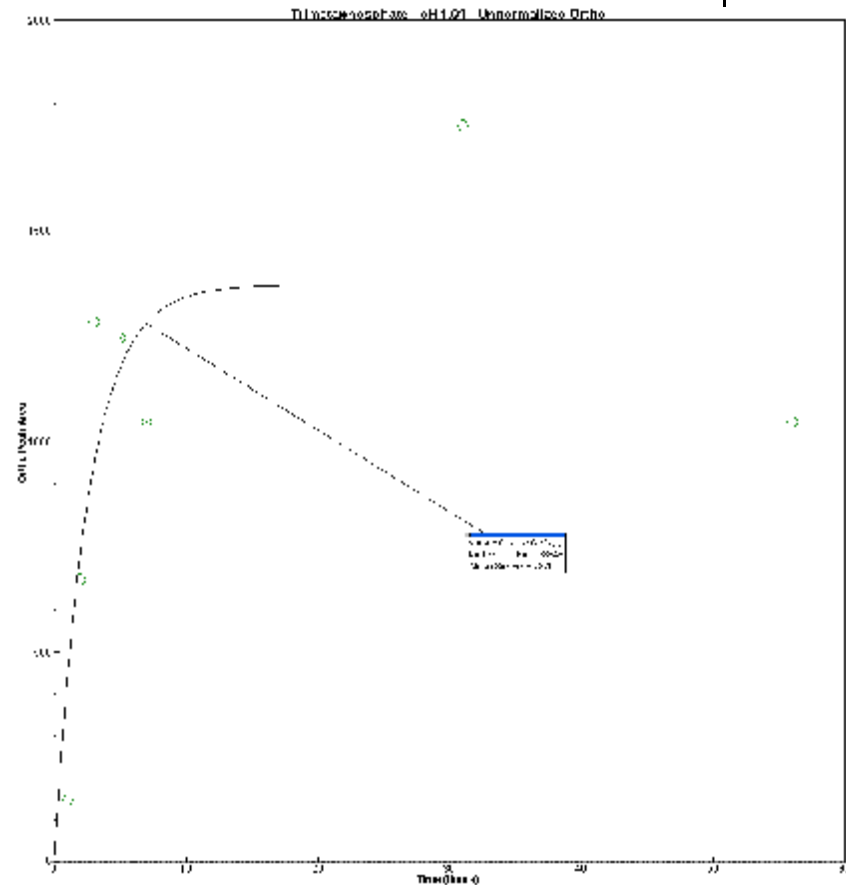
TRIMETA - ORTHO CURVE-FITS

Normalized

Unnormalized



$$k=3.1 \times 10^{-2} \text{ 1/hr}$$



$$k=3.9 \times 10^{-1} \text{ 1/hr}$$

Average 1st Order Rate Constants and Half-Lives for Polyphosphate Hydrolyses



Polyphosphates	pH ± 0.2	Poly 1 st Order Rate Constants	Half-Lives	Overall 1 st Order Rate Constants
Na-Pyrophosphate	7	10^{-3} / day	<1000 days	10^{-1} / day
Na-Tripolyphosphate	7	10^{-3} / day	<1000 days	10^{-1} / day
Na-Trimetaphosphate	7	Too much variability to model data		10^{-3} / day
Na- Hexametaphosphate	7	10^{-3} / day	<1000 days	10^{-2} / day
NORMALIZED				
Na- Pyrophosphate	1	2.3×10^{-2} / hr	30 hr	3.9×10^{-2} / hr
Na- Tripolyphosphate	1	3.2×10^{-2} / hr	22 hr	1.1×10^{-2} / hr
Na- Trimetaphosphate	1	$70. \times 10^{-2}$ / hr	1 hr	3.3×10^{-2} / hr
Na- Hexametaphosphate	1	2.7×10^{-2} / hr	26 hr	2.6×10^{-2} / hr
UNNORMALIZED				
Na- Pyrophosphate	1	2.7×10^{-2} / hr	26 hr	12×10^{-2} / hr
Na- Tripolyphosphate	1	3.2×10^{-2} / hr	22 hr	7.2×10^{-2} / hr
Na- Trimetaphosphate	1	55×10^{-2} / hr	1 hr	44×10^{-2} / hr
Na- Hexametaphosphate	1	4.2×10^{-2} / hr	17 hr	7.8×10^{-2} / hr

Average Errors in Polyphosphate Rate Constants



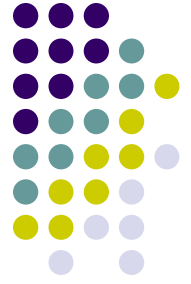
Polyphosphate	<i>Normalized Polyphosphate</i>		<i>Unnormalized Polyphosphate</i>	
	Rate Constant (1/hr)	Error (1/hr)	Rate Constant (1/hr)	Error (1/hr)
Pyrophosphate – pH 1	2.3×10^{-2}	0.1×10^{-2}	2.7×10^{-2}	0.2×10^{-2}
Tripolyphosphate – pH 1	3.2×10^{-2}	0.6×10^{-2}	3.2×10^{-2}	0.8×10^{-2}
Trimetaphosphate – pH 1	$70. \times 10^{-2}$	5×10^{-2}	55×10^{-2}	8×10^{-2}
Hexametaphosphate – pH 1	2.7×10^{-2}	0.2×10^{-2}	4.2×10^{-2}	0.6×10^{-2}

Errors greater for all unnormalized rate constants

Chemical Shifts of Peaks in ^{31}P NMR Spectra



Polyphosphates	pH ± 0.2	H_3PO_4 Standard Singlet	Ortho Singlet	Terminal Poly	Trimeta Singlet	Internal Poly
Pyrophosphate	7		4.0 ppm	-5.2 ppm (singlet)		
Tripolyphosphate	7		3.2 ppm	-5.7 ppm (doublet)		-19.5 ppm (triplet)
Trimetaphosphate	7		3.2 ppm	-5.5 ppm (multiple)	-19.3 ppm	
Hexametaphosphate	7		3.0 ppm	-5.5 ppm (multiple)		-19.6 ppm (multiple)
Avg. Chemical Shifts at pH 7			3.4 ppm	-5.5 ppm	-19.3 ppm	-19.6 ppm
Pyrophosphate	1	4.8 ppm	1.9 ppm	-9.3 ppm (singlet)		
Tripolyphosphate	1	4.6 ppm	2.0 ppm	-9.1 ppm (singlet)		-21.6 ppm (singlet)
Trimetaphosphate	1	4.5 ppm	1.8 ppm	-9.6 ppm (singlet)	-19.9 ppm	-22.2 ppm (singlet)
Hexametaphosphate	1	4.6 ppm	1.9 ppm	-9.5 ppm (multiple)	-19.8 ppm	-22.2 ppm (multiple)
Avg. Chemical Shifts at pH 1		4.6 ppm	1.9 ppm	-9.4 ppm	-19.9 ppm	-22.0 ppm



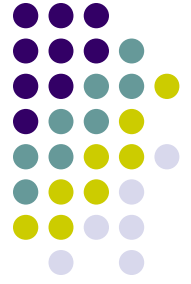
CONCLUSIONS

- | All phosphates except pyrophosphate: multi-step reactions involving intermediate breakdown products
- | **Pyrophosphate** - one-step reaction:
 - | Pyro breaks down into 2 orthos
 - | Only single-step reaction studied



CONCLUSIONS

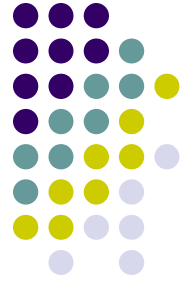
- | **Tripolyphosphate** - two step reaction:
 1. Tripoly into pyro and ortho
 2. Pyro into orthophosphate
- | **Trimetaphosphate** - three step reaction:
 1. Trimeta into tripolyphosphate
 2. Tripoly into pyro and ortho
 3. Pyro into orthophosphate
- | Trimeta ring half-life extremely small. Ring is cleaved extremely quickly to form Tripolyphosphate



CONCLUSIONS

- | **Hexametaphosphate** – multi-step process:
 - | Chain is broken down into smaller chains throughout hydrolysis until only orthophosphate is left
- | Polyphosphate hydrolyses are acid-catalyzed
- | Neutral solutions remarkably stable
- | External standard reduced variability and increased consistency
- | Chemical shifts of peaks influenced by pH. As pH decreases, chemical shifts move downfield

DISCUSSION and FUTURE WORK



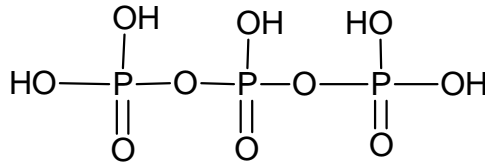
- | Since hydrolyses did not exhibit steady-state approximation properties, kinetics equations should be solved more rigorously using computer programs like Mathematica. A new curve-fitting program would also be required.
- | Possibilities of metal or enzyme catalysis
- | Commercial mixtures of ortho and polyphosphates

ACKNOWLEDGEMENTS

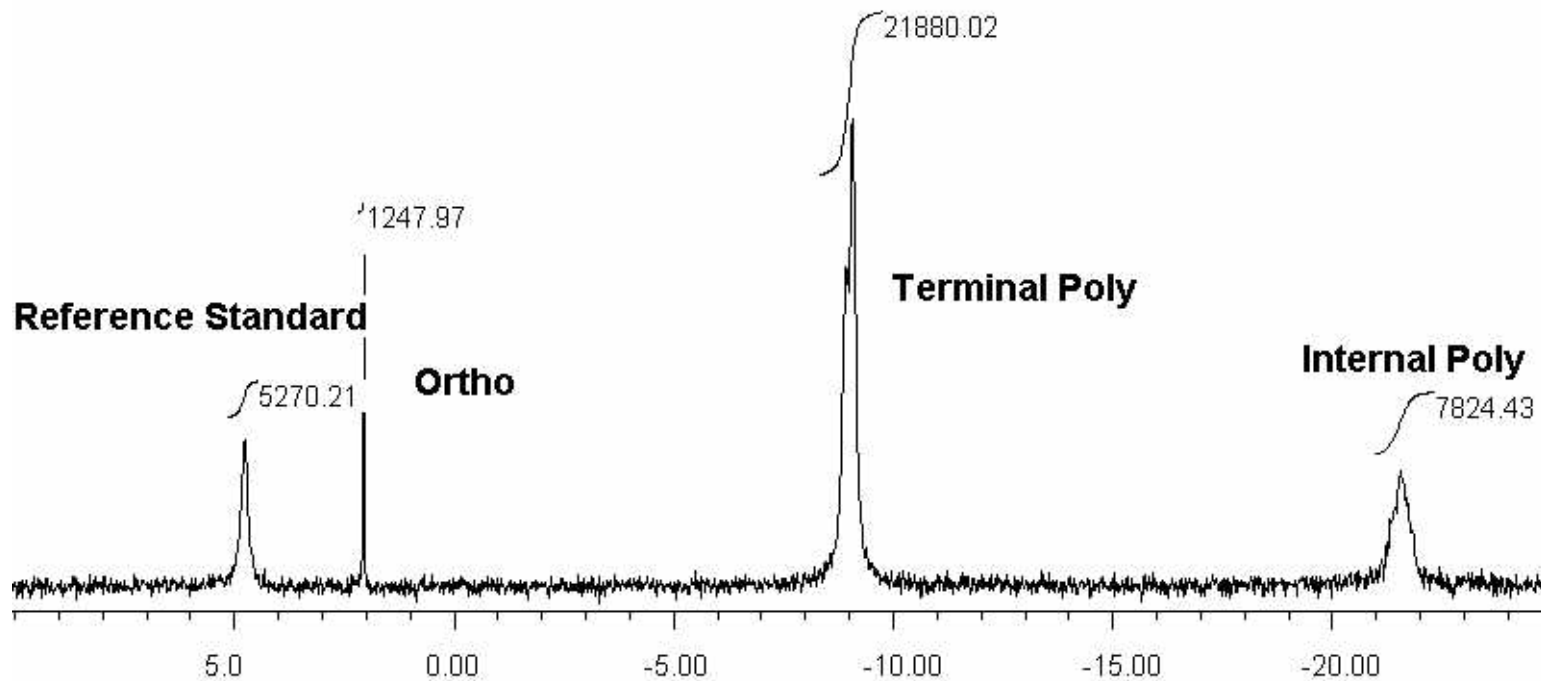


- | Dr. Ron Robertson – research advisor
- | Instrumentation and supplies provided by the Department of Chemistry at Austin Peay State University

SPECTRA



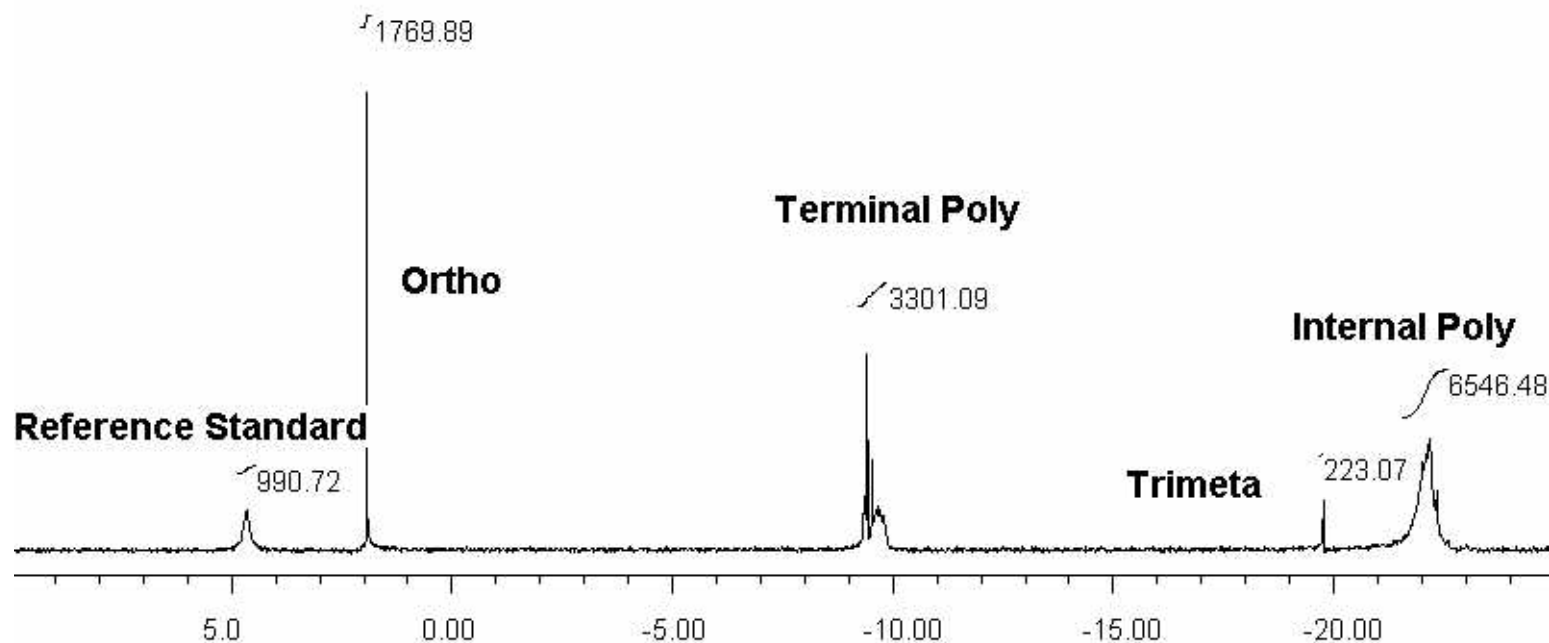
**Tripolyphosphate - pH 0.85
22 Hours**



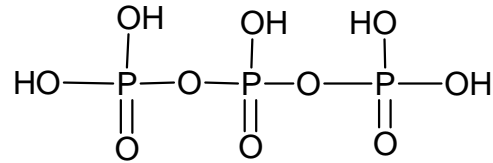
SPECTRA



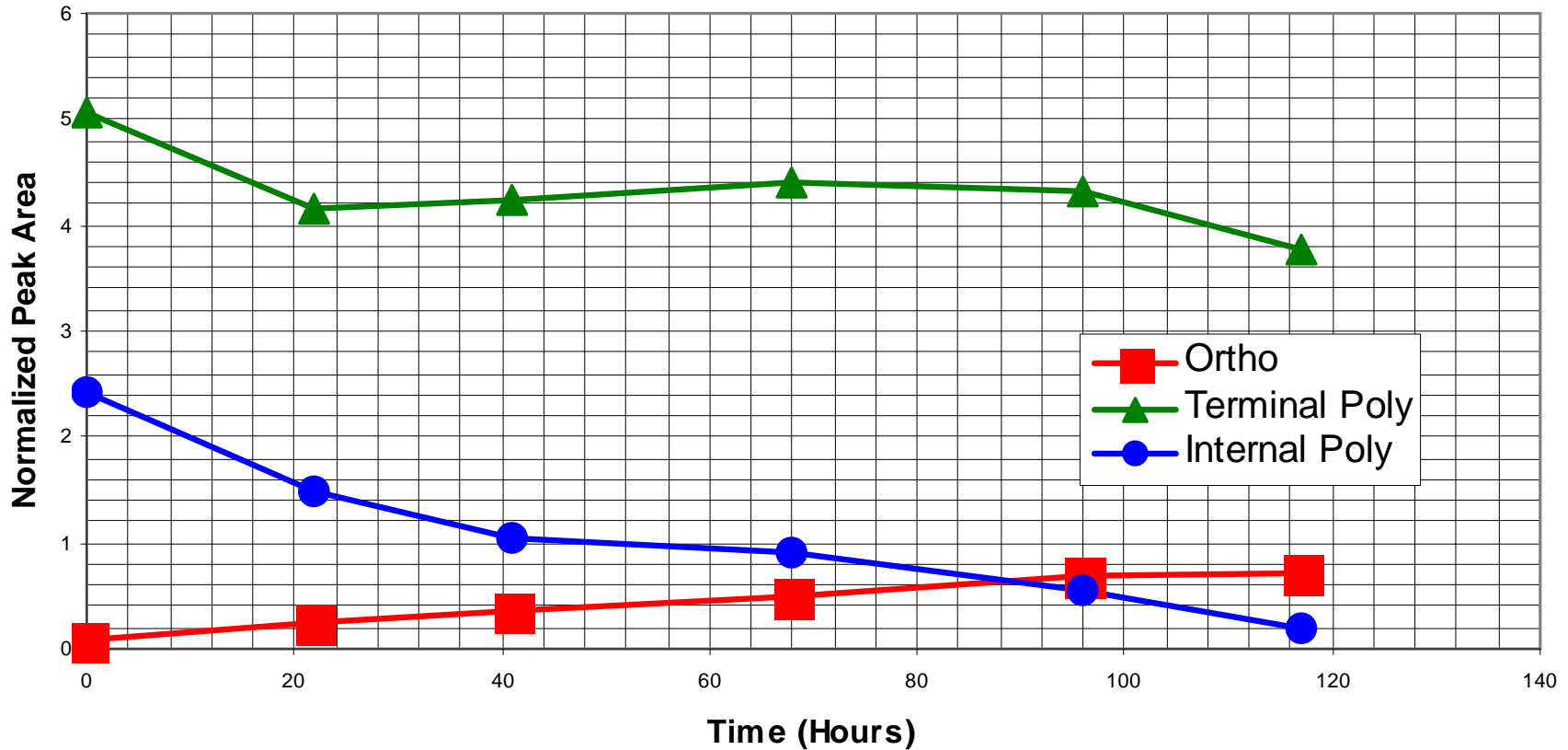
Hexametaphosphate - pH 0.93 23 Hours



HYDROLYSIS GRAPHS – pH 1



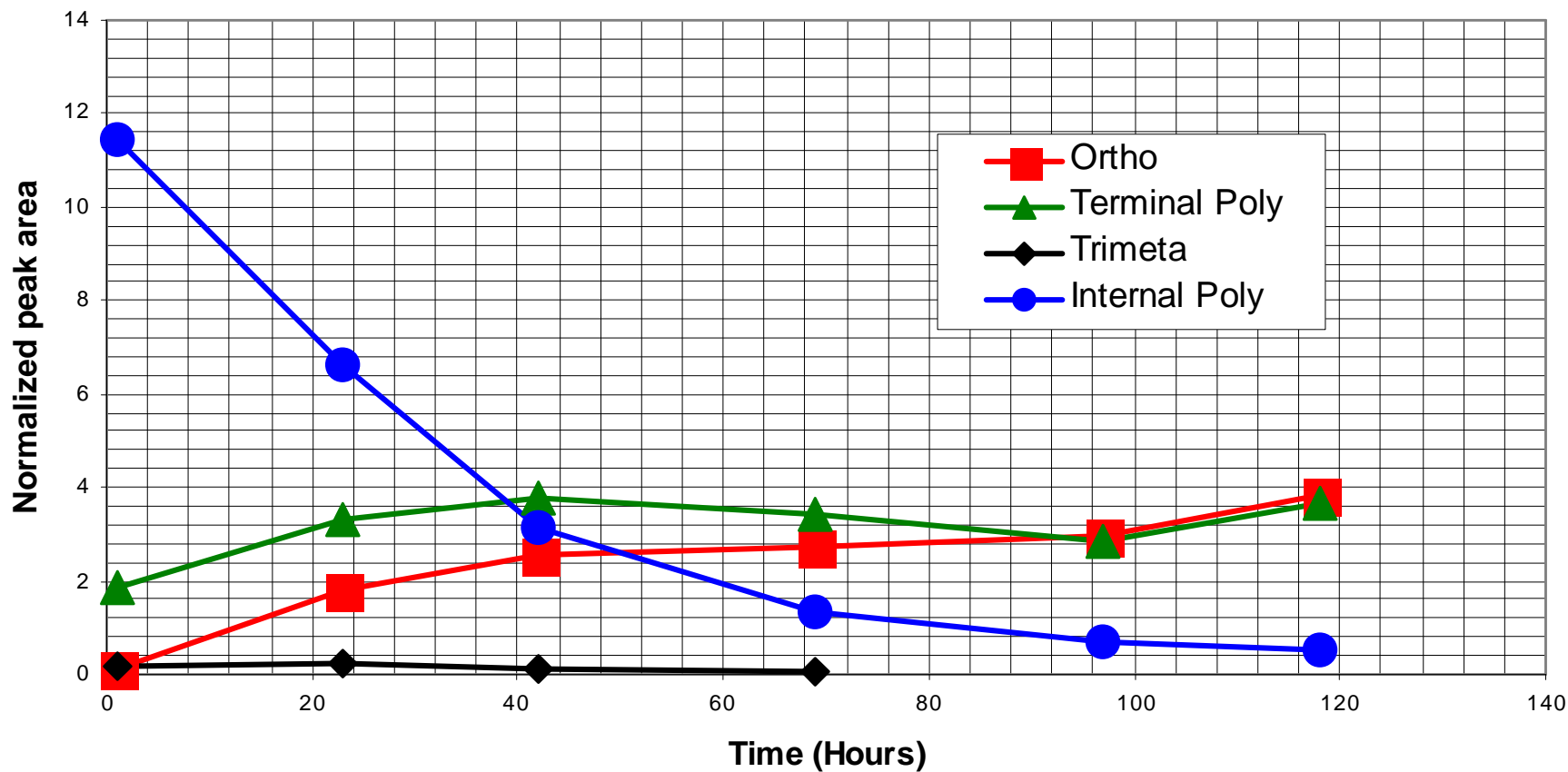
Tripolyphosphate - pH 0.85 - Normalized



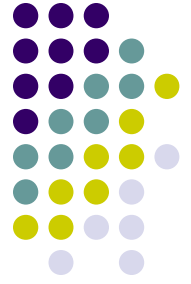
HYDROLYSIS GRAPHS – pH 1



Hexametaphosphate - pH 0.93 - Normalized



APPLICATIONS



- | Study useful to water treatment centers and consumers
- | Many phosphates are added to municipal water systems in liquid form; phosphates may be hydrolyzing before they are added to system
- | Kinetics information helps water treatment centers determine time intervals when phosphate should be added
- | Renewed public awareness for phosphate additives