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Decomposition of Sodium Tetraphenylborate

by

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SUMMARY

The chemical decomposition of aqueous alkaline solutions of sodium tetraphenylborate (NaTPB) has been investigated. The focus of the investigation is on the determination of additives and/or variables which influence NaTPB decomposition. Copper(II) ions, solution temperature, and solution pH (hydroxide ion concentration) have all been demonstrated to affect NaTPB stability. Their relationship with each other and the stability of NaTPB is presented. In additional work, the elimination of oxygen from the reaction environment did not prevent NaTPB decomposition in the presence of copper(II) ions, but did, however, affect the course of decomposition.

INTRODUCTION

NaTPB is a specialty chemical required for the In Tank Precipitation Process (ITP).[1,2] It precipitates cesium, aiding in the decontamination of high level radioactive waste solutions. It is to be obtained as an aqueous solution having a composition of 0.55 ± 0.05 M NaTPB and 0.10 M NaOH.[3] Of serious concern, however, was the observation that upon production, the NaTPB showed varying degrees of stability.[4,5,6] This led to an investigation into the causes and prevention of NaTPB decomposition.

Decomposition of NaTPB can occur in acidic solutions through acid hydrolysis.[7] In strongly basic solutions, NaTPB is generally considered to be quite stable.[8] However, certain components or conditions were found to be capable of decomposing NaTPB under basic conditions. These include copper(II), light, and temperature. Similarly, several components were previously tested and found to be inert to NaTPB (Appendix A). One particular additive, hydrogen peroxide, was determined to react

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stoichiometrically with tetraphenylborate (TPB^-) but did not catalytically decompose TPB^-. This document describes work aimed at providing ~~a~~ better understanding into the relationship of copper(II), solution temperature, and solution pH to NaTPB stability.

DISCUSSION

Experimental Method and Details

The method employed for decomposition testing of NaTPB solutions was incubation under controlled conditions. This was achieved by introducing additives into aqueous alkaline solutions of NaTPB and subjecting the NaTPB solutions to controlled environmental conditions (eg. temperature and/or nitrogen atmosphere). Long term exposures (over 30 weeks in some cases) were conducted to adequately determine the effect of the variables on the NaTPB solution's stability. Solutions were prepared from solid NaTPB. A.C.S. reagent grade NaTPB solid was purchased from the Aldrich Chemical Company with a purity greater than 99.5%.

Typical test solutions studied were 25 mL in volume with compositions of approximately 0.5 M NaTPB and 0.10 M NaOH. Components were added to the test solutions using microliter pipettes and prepared stock solutions. All test solutions, unless otherwise stated, were stored at a temperature of 65°C in a laboratory oven in the presence of oxygen. The test solutions were stored in capped polyethylene bottles, except for those used in inert atmosphere studies. Inert atmosphere studies were conducted by preparing and capping the test solutions in serum glass vials inside a nitrogen filled glove bag.

Three methods were utilized to monitor TPB^- decomposition. These were silver ion titration, pH, and visual observation. Samples were analyzed for TPB^- concentration either weekly or biweekly using a TPB^--silver ion titration method.[9] Titration analyses of solutions approaching complete decomposition often yielded unreasonable and inaccurate results. One probable source of error could be the over-titration of solutions containing little or no TPB^-. A second source of error could occur if air bubbles were introduced into the titration apparatus tubing. Both would result in excessively high TPB^- concentrations. Due to this problem, complete decomposition of TPB^- was typically verified by spot testing the NaTPB solutions with potassium chloride. Exposure of potassium ions (K^+) to TBP^- ions results in formation of a white precipitate. Thus the spot test method provides a simple and accurate way of determining if any TPB^- is still present in the test solutions.

Measurement of the solution pH was found to be another method of monitoring NaTPB-solution stability. A drop in the pH was observed immediately prior to decomposition. NaTPB-solution pH was measured using a pH meter equipped with a gel-filled combination pH electrode.

The solution appearance was also indicative of the stability of the solutions. Stable aqueous NaTPB solutions are a transparent, flesh-toned color. During the initial stages of decomposition (or instability), the solution turns a golden color. As the quantity of TPB^- that has decomposed increases, the solution turns dark red, then brown, and eventually black. Thus the stability of a solution can be easily estimated. Some exceptions were found. There were a few cases in which the solution's appearance indicated that decomposition had occurred, yet the TPB^- titration results and the other analyses proved otherwise.

Results

Three principal factors which affect the stability of NaTPB have been identified. These are 1) copper(II) ions, 2) temperature, and 3) solution pH (hydroxide ion concentration). Although all three were previously determined to affect stability, knowledge of their relationship with each other was unclear. The experiments described herein were undertaken to gain an understanding of this relationship. The effects of three other potential contaminants were also examined. Two of these, magnesium (II) and lead (II), were selected because they might be present, in some form, in the ITP process scheme. The other, chromium (VI), was selected based upon its relatively high degree of reactivity. None of these were found to affect NaTPB stability.

Effect of Copper

Normal NaTPB solutions (0.5 M NaTPB and 0.1 M OH^-), at 65°C, are relatively stable over a long period of time. However, the addition of 10 ppm Cu(II) ions to this solution results in the decomposition of the NaTPB in less than three weeks. Experiments have shown that under these reaction conditions, initial Cu(II) concentrations of 0.1 to 100 ppm will initiate decomposition. Lower Cu(II) concentrations may also result in decomposition given enough time. A NaTPB solution, with a 0.05 ppm Cu(II) concentration, began to show initial signs of decomposition in about 12 weeks. A drop in solution pH along with a gradual change in solution color was observed. After 25 weeks, the solution pH had dropped to 10.5 and the solution color was black, however, the NaTPB concentration remained near 0.5 molar.

Solutions containing larger concentrations of Cu(II) ions have an increased rate of decomposition. This is shown by the results listed in Table I and can be seen graphically in Figure 1. One anomaly observed in this data is that the solution containing the largest Cu(II) concentration (100 ppm) decomposed at a slightly slower rate than the 10 ppm Cu(II) solutions. This can best be explained by the observation that within the 100 ppm test solution, a substantial portion of the Cu(II) precipitates out of solution. This leaves a smaller concentration of Cu(II) remaining in solution, whereas the 10 ppm Cu(II) solution remains supersaturated and no precipitation occurs. Consequently, the 10 ppm Cu(II) solution ultimately results in a larger Cu(II)

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concentration in solution. The actual Cu(II)-ion concentration in solution is under investigation at the present time. Preliminary results indicate less than 0.5 ppm Cu(II) remains in solution, independent of the initial concentration of Cu(II).

Temperature Dependence

The rate of copper-induced decomposition is temperature dependent. Solutions similar to those reported above, containing initial concentrations of Cu(II) ions of 0.1 to 100 ppm, failed to decompose in more than thirty weeks at room temperature (23 ± 2°C). Data are listed in Table II. It is interesting to note that only the 10 ppm Cu(II)-containing solution has shown any signs of instability. In that particular case, the solution has gradually turned a gold-brown color and the solution pH has dropped to 10.7. However, the NaTPB concentration has remained near 0.5 molar. A substantial portion of the Cu(II) precipitated out of the solutions containing larger concentrations of Cu(II) (30 and 100 ppm). Based upon this information, NaTPB solutions which contain Cu(II) would be expected to remain stable for at least 6 to 8 months at room temperature.

Solution pH Dependence

There is a trend of stabilizing NaTPB solutions with larger concentrations of OH^-. Observation of these and old NaTPB solutions indicates that the TPB^- concentration may remain constant for several weeks and/or years before rapidly decomposing in a short period of time. This suggests an autocatalytic mechanism. Solution pH has proven to be a useful way of following the stability of TPB^-. Careful monitoring of Cu(II)-containing test solutions reveals that the solution pH decreases from approximately 13.0 to 11.0 just prior to TPB^- decomposition. This is presented graphically in Figure 2 for tests at 65°C and in Figure 3 for tests at room temperature. This finding suggests a way of predicting impending decomposition.

NaTPB test solutions (0.5 M) containing OH^- concentrations ranging from 0 to 0.5 M were tested at 65°C both with and without Cu(II) (10.0 ppm) to examine the significance of the solution pH. Stability data obtained on these test solutions are listed in Table III and are plotted in Figure 4. Solutions containing Cu(II) in conjunction with OH^- concentrations of 0.01 M or less decomposed completely and rapidly ($\leq$ 6 days). Similarly their counterparts without Cu(II) decomposed rapidly ($\leq$ 6 days), but failed to completely decompose as evidenced by potassium ion spot testing. Unfortunately, all of these lower pH-non Cu(II)-containing solutions were unable to be titrated accurately thereafter. This made quantification of the extent of decomposition impossible. The NaTPB test solution containing Cu(II) and 0.5 molar OH^- took over 4 weeks to decompose. Use of large concentrations of hydroxide, such as 0.5 M, affects the TPB^- titration method giving erratic results.

The observation of delayed decomposition in solutions containing elevated OH^- concentrations prompted further testing. The addition of excess OH^- to a Cu(II)-induced decomposing solution produced a significant finding. In the experiment, a Cu(II)-containing NaTPB solution was determined to be on the verge of decomposition three days after its preparation. An aliquot of the solution was withdrawn at that time and placed in a separate container. Concentrated NaOH(aq) was then added to the original decomposing solution to raise its pH back to 13.0. The unadjusted aliquot proceeded to decompose over the next four days. The original solution, which had been pH adjusted, remained relatively stable for an additional six weeks. This observation suggests periodically increasing the pH may help to stabilize solutions which are determined to be susceptible to decomposition.

The decreased OH^- concentration studies produced another interesting observation. A NaTPB solution containing 0.001 M OH^- along with 10 ppm Fe(III), in place of Cu(II), remained stable over an eight week time period. This result is in contrast to the rapid decomposition observed when both Cu(II) was the additive in the solution and when no additive was present in the solution. The reason for this difference in stability remains a mystery. Data representing the latter two experiments are contained in Table IV.

Mechanistic Copper Work

Copper is an ideal additive to use in NaTPB decomposition studies. NaTPB solutions initially seemed to decompose at random. This made the system difficult to study. The discovery that Cu(II) was a decomposition catalyst allowed other additives and components to be tested on more predictable NaTPB solutions. NaTPB could now be expected to decompose in a given amount of time. This predictability has allowed additional work, aimed at understanding the decomposition mechanism, to be conducted.

One mechanistic theory associated with NaTPB decomposition is that Cu(II) might be producing an intermediate complex *in situ* which is capable of reacting with NaTPB. The intermediate might be more reactive with another compound than it would be with NaTPB if this were occurring. Decomposition of NaTPB could be prevented if this were true. Fe(III) was tested as an additive in conjunction with Cu(II)-containing NaTPB solutions based upon this idea and the previous observation of increased stability with an Fe(III) additive in low OH^- solutions. Unfortunately, no NaTPB stabilization was gained in this experiment. In fact, NaTPB decomposed at a slightly enhanced rate. The presence of Cu(II) in this experiment determines the fate of the NaTPB and the Fe(III) has little affect on the stability process.

The idea of an intermediate being produced *in situ*, which could cause the decomposition of NaTPB, was further tested by adding a 5.0 mL aliquot of a previously decomposed NaTPB solution to an otherwise stable NaTPB solution. The 5.0 mL aliquot was determined to contain enough Cu(II) to produce an approximately 0.03 ppm Cu(II) resulting solution. No sign of decomposition occurred in eighteen weeks. This suggests that no intermediate capable of initiating decomposition was present in the aliquot. Data representing the above cases are listed in Table V.

Effect of Oxygen

Eliminating oxygen does not prevent the decomposition of NaTPB in the presence of Cu(II) ions. However, it does affect the course of the decomposition. This was observed in an experiment in which Cu(II)-containing NaTPB solutions were prepared in the absence of oxygen. It was thought that copper was reacting with oxygen to produce an intermediate complex which could decompose NaTPB. Therefore, if oxygen was removed from the solution environment, NaTPB decomposition could be prevented. In order to minimize the chance of exposing the test solutions to oxygen, TPB^- titration analysis was conducted only when the solutions' daily appearance was observed to change. Unexpectedly, decomposition did occur. However, several properties associated with the decomposition were different from what normally is observed when decomposition occurs in the presence of oxygen. These differences are summarized in Table VI.

The most noticeable difference observed when comparing the two decomposed solutions was that no change in the solution color occurred during decomposition in the absence of oxygen. An organic layer formed on the surface of the aqueous solution along with the formation of a white crystalline precipitate. Titration analysis of the aqueous portion of the solution indicated that no TPB^- was present. The pH of the aqueous portion was determined to be approximately 12. Analysis of the organic layer by liquid chromatography identified benzene as the primary component along with smaller amounts of biphenyl, terphenyl, and a few unidentified compounds. No phenol or phenylboronic acid was observed in the organic layer.

Comparatively, decomposition of NaTPB in the presence of oxygen results in the solution turning a dark brown-black color. No organic layer or precipitate is usually observed. The solution pH drops to approximately 11. Finally, phenol and phenylboronic acid are produced as well as benzene, biphenyl, and other benzene ring derivatives.

These differences in the two decomposition processes suggest that oxygen does not play a role in the initial steps of decomposition. However, it is involved in a secondary reaction with the intermediate complexes produced during the initial stages of decomposition.

Magnesium (II), Chromium (VI), and Lead (II)

The presence of Mg(II), Pb(II), or Cr(VI) does not cause NaTPB to decompose. Normal NaTPB solutions (0.5 M NaTPB and 0.1 M OH^-)

containing either Mg(II) or Pb(II) were tested at 65°C. They remained relatively stable over an eight week period, as evidenced by their solution pH and TPB^- titration data listed in Table VII. Similar test solutions containing Cr(VI) remained equally stable and are similarly reported in Table VII.

CONCLUSIONS

It has been shown that copper concentrations as low as 0.10 ppm can result in the decomposition of NaTPB solutions at 65°C. However, the NaTPB solutions appear to be stable for at least 6 to 8 months when held at room temperature (23°C). The stability can be enhanced by the addition of hydroxide to the solution. Decomposition was not initiated or accelerated by the presence of intermediates generated *in situ* and is not prevented by the elimination of oxygen from the NaTPB solution environment. The decomposition mechanism is affected by the atmosphere under which it is stored. Both pH and visual appearance as well as silver ion titration were found to be effective methods of monitoring the decomposition.

Additional decomposition studies at 40°C are underway. These should help provide an increased capability for predicting the stability of actual NaTPB solutions containing Cu(II) at temperatures above room temperature. This data will be documented in a later report.

QUALITY ASSURANCE

All work was conducted in accordance with the SRL Quality Assurance Program. Data are recorded in Laboratory Notebook WSRC-NB-89-11, pp. 3-84. Salt solutions were prepared from reagent grade chemicals. TPB^- titration analyses were performed by the DWPT Analytical Laboratory at TNX. A sloped calibration of the pH meter was conducted prior to its use each day.

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TABLE I. Effect of Cu(II) Concentration on NaTPB Stability at 65°C

	NaTPB-Solution Molarity and pH											
	0.00 ppm Cu(II)		0.00 ppm Cu(II)		0.00 ppm Cu(II)		0.05 ppm Cu(II)		0.10 ppm Cu(II)		0.10 ppm Cu(II)	
Time (weeks)	NaTPB (M)	pH	NaTPB (M)	pH	NaTPB (M)	pH	NaTPB (M)	pH	NaTPB (M)	pH	NaTPB (M)	pH
1	0.50	--	0.50	--	0.50	12.9	0.45	12.9	0.50	--	0.49	12.8
2	0.48	--	0.51	--	0.51	12.8	--	--	0.48	--	--	--
3	0.50	12.8	0.50	13.0	0.52	12.8	--	--	0.49	13.0	--	--
4	0.50	12.8	0.51	12.8	0.54	12.8	0.49	12.8	0.49	12.8	--	12.8
5	--	--	--	--	--	--	--	--	0.50	13.1	0.53	--
6	0.56	12.7	0.57	12.7	--	12.5	--	--	--	10.7	--	--
7	--	--	--	--	0.59	12.9	--	--	--	--	--	--
8	0.62	12.7	0.62	12.7	0.64	12.7	0.50	--	0.59	10.7	0.47	--
9							--	--			0.16	11.0
10							--	--			< 0.01	10.7
11							--	--				
12							0.51	12.7				
15							0.53	12.4				
17							0.51	11.3				
18							--	10.9				
19							0.47	10.9				
22							0.49	10.4				
25							--	10.5				

TABLE I. (continued from above)

	NaTPB-Solution Molarity and pH											
	0.50 ppm Cu(II)		1.00 ppm Cu(II)		10. ppm Cu(II)		10. ppm Cu(II)		30. ppm Cu(II)		100. ppm Cu(II)	
Time (weeks)[a]	NaTPB (M)	pH	NaTPB (M)	pH	NaTPB (M)	pH	NaTPB (M)	pH	NaTPB (M)	pH	NaTPB (M)	pH
1	--	--	--	--	--	--	0.49	12.9	0.46	--	0.47	--
2	--	--	--	--	--	--	0.49	12.5	--	--	0.46	--
3	--	10.9	< 0.01	10.9	< 0.01	11.0	< 0.01	10.9	< 0.01	11.1	--	13.0
4	0.46	10.7									< 0.01	10.8
5	< 0.01	--										

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[a] All solutions containing 0.50 ppm Cu(II) or greater decomposed in 5 weeks or less.

TABLE II. Effect of Cu(II) Concentration on NaTPB Stability at Room Temperature

Time (weeks)	NaTPB-Solution Molarity and pH							
	0.00 ppm Cu(II)		0.00 ppm Cu(II)		0.10 ppm Cu(II)		0.50 ppm Cu(II)	
	NaTPB (M)	pH	NaTPB (M)	pH	NaTPB (M)	pH	NaTPB (M)	pH
1	0.48	--	0.46	--	0.48	--	0.45	--
2	--	--	0.46	--	0.49	--	0.47	--
3	0.50	12.8	0.47	13.0	0.47	13.2	0.46	13.2
4	0.48	12.9	0.48	12.8	0.48	12.9	0.47	12.8
6	0.48	12.7	0.48	12.6	0.47	12.8	0.47	12.7
8	0.48	12.6	0.48	12.6	0.49	12.7	0.48	12.6
16	0.51	12.9	0.47	12.9	0.53	12.9	0.48	12.9
19	--	--	--	--	--	--	--	--
21	--	--	--	--	--	--	--	--
22	--	12.9	--	12.9	--	12.8	--	12.8
25	0.49	12.9	0.49	12.9	0.49	12.8	0.46	12.8
28	--		--	--	--	--	--	--
30	--		--	--	--	--	--	--
32	--	12.7	--	12.8	--	12.8	--	12.6

TABLE II. (continued from above)

Time (weeks)	NaTPB-Solution Molarity and pH							
	1.00 ppm Cu(II)		10. ppm Cu(II)		30. ppm Cu(II)		100. ppm Cu(II)	
	NaTPB (M)	pH	NaTPB (M)	pH	NaTPB (M)	pH	NaTPB (M)	pH
1	0.44	--	0.48	--	0.48	--	0.44	--
2	0.45	--	--	--	0.47	--	0.46	--
3	0.46	13.2	0.47	13.2	0.47	13.2	0.46	13.2
4	0.46	12.8	0.48	12.8	0.48	12.8	0.47	12.8
6	0.46	12.7	0.48	12.7	0.48	12.7	0.46	12.8
8	0.47	12.6	0.48	12.6	0.47	12.6	0.46	12.6
16	0.47	12.8	0.48	12.6	0.51	12.8	0.45	12.8
19	--	--	0.44	12.4	--	--	--	--
21	--	--	0.45	12.2	--	--	--	--
22	--	12.7	0.45	12.1	--	12.7	--	12.8
25	0.45	12.6	0.46	11.9	0.47	12.7	0.47	12.7
28	--	12.6	0.52	11.3	--	12.7	--	12.7
30	--	--	--	10.7	--	--	--	--
32	--	12.3	0.51	10.7	--	12.5	--	12.6

TABLE III. Effect of Hydroxide Concentration on NaTPB Stability at 65°C

	NaTPB-Solution Molarity and pH									
	0.5 M NaOH		0.10 M NaOH				0.01 M NaOH			
	10. ppm Cu(II)		0.00 ppm Cu(II)		10. ppm Cu(II)		0.00 ppm Cu(II)		10. ppm Cu(II)	
Time (weeks)	NaTPB (M)	pH	NaTPB (M)	pH	NaTPB (M)	pH	NaTPB (M)	pH	NaTPB (M)	pH
1	0.32	13.4	0.50	13.4	0.48	13.2	0.48	11.0	< 0.01	10.9
2	0.48	13.4	0.51	12.8	0.49	12.5	0.48	10.2		
3	--	12.9	0.52	12.8	< 0.01	10.9	0.50	--		
4	--	12.7	0.54	12.8			0.40	10.1		
6	< 0.01	--	--	12.5			0.39	10.1		
7			0.59	12.9			0.39	--		
8			0.64	12.7			0.39	--		

TABLE III. (continued from above)

	NaTPB-Solution Molarity and pH									
	0.001 M NaOH				0.0001 M NaOH		No NaOH			
	0.00 ppm Cu(II)		10. ppm Cu(II)		0.00 ppm Cu(II)		0.00 ppm Cu(II)		10. ppm Cu(II)	
Time (weeks)	NaTPB (M)	pH	NaTPB (M)	pH	NaTPB (M)	pH	NaTPB (M)	pH	NaTPB (M)	pH
1	NCD[a]	10.8	< 0.01	10.9	NCD	10.8	NCD	10.7	< 0.01	10.9
2										
3										
4										
6										
7										
8										

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[a] NCD indicates the NaTPB solution has not completely decomposed but also not able to be titrated.

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TABLE IV. Mechanistic pH Studies at 65°C

		NaTPB-Solution Molarity and pH					
		NaTPB solution containing 10 ppm Cu(II) divided into two portions on day 3				0.0001 M NaOH 10. ppm Fe(III)	
		Excess NaOH added on day 3		No NaOH added on day 3			
Time (weeks)		NaTPB (M)	pH	NaTPB (M)	pH	NaTPB (M)	pH
1	day 1	--	12.7	--	12.7	--	--
	day 3	--	12.3	--	12.3	--	--
	day 7	--	12.9	< 0.01	10.8	0.50	9.7
2		--	12.8			0.46	9.6
3		--	--			--	--
4		0.46	12.5			0.46	9.9
6		0.49	12.6			0.48	10.1
7		< 0.01	12.5			--	--
8						0.49	10.3

TABLE V. Mechanistic Copper Studies at 65°C

	NaTPB-Solution Molarity and pH							
	NaTPB solution containing 10. ppm Cu(II) and the listed quantity of Fe(III)						25 mL NaTPB solution containing 5 mL of decomposed AFF sample #267	
	10. ppm Fe(III)		30. ppm Fe(III)		100. ppm Fe(III)		0.03 ppm Cu(II)[a]	
Time (weeks)	NaTPB (M)	pH	NaTPB (M)	pH	NaTPB (M)	pH	NaTPB (M)	pH
1	--	--	0.28	--	0.46	--	0.48	13.0
2	< 0.01	--	< 0.01	--	< 0.01	--	--	13.1
3		11.1		11.1		11.1	0.48	13.1
4							0.50	13.2
6							0.54	13.1
7							--	--
9							0.57	13.0
12							0.53	13.0
15							0.48	12.8
18							--	12.7

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[a] Cu(II) concentration in the solution is based on the measured copper concentration of AFF sample #267.

Table VI. NaTPB Solution Differences Between Air and Nitrogen Decomposition Processes

Characteristic	Presence of Oxygen	Absence of Oxygen
Color	brown-black	clear
Organic phase	no	yes
Precipitate	no	yes
Solution ph	drops to 11	drops to 12
Products	benzene phenol phenylboronic acid biphenyl others	benzene biphenyl terphenyl others

TABLE VII. Effect of Additional Additives on NaTPB-Solution Stability at 65°C

	NaTPB-Solution Molarity and pH					
Time (weeks)	10. ppm Mg(II) NaTPB (M)	pH	30. ppm Mg(II) NaTPB (M)	pH	100. ppm Mg(II) NaTPB (M)	pH
1	0.54	12.9	0.52	12.6	0.49	12.4
2	0.51	12.6	0.51	12.7	0.50	12.3
3	--	--	--	--	--	--
4	0.53	12.5	0.53	12.2	0.52	12.1
6	0.57	12.7	0.55	12.5	0.53	12.5
8	0.58	12.7	0.58	12.7	0.56	12.6

	NaTPB-Solution Molarity and pH					
Time (weeks)	10. ppm Cr(VI) NaTPB (M)	pH	30. ppm Cr(VI) NaTPB (M)	pH	100. ppm Cr(VI) NaTPB (M)	pH
1	0.48	--	0.46	--	0.48	--
2	0.50	--	0.50	--	0.49	--
3	0.49	13.2	0.49	13.2	--	13.2
4	0.51	12.9	0.51	12.9	0.50	12.8
6	0.57	12.9	0.55	12.8	0.54	12.7
8	0.60	12.7	0.60	12.6	0.57	12.7

	NaTPB-Solution Molarity and pH					
Time (weeks)	10. ppm Pb(II) NaTPB (M)	pH	30. ppm Pb(II) NaTPB (M)	pH	100. ppm Pb(II) NaTPB (M)	pH
1	0.50	--	0.49	--	0.48	--
2	0.51	--	0.51	--	0.46	--
3	0.49	13.1	0.49	13.1	--	13.2
4	0.51	12.8	0.52	12.8	0.49	12.8
6	0.57	12.8	0.55	12.7	0.55	12.8
8	0.59	12.7	0.59	12.7	0.60	12.7

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Figure 1. **Effect of Copper Concentration on NaTPB-Solution Stability at 65°C**

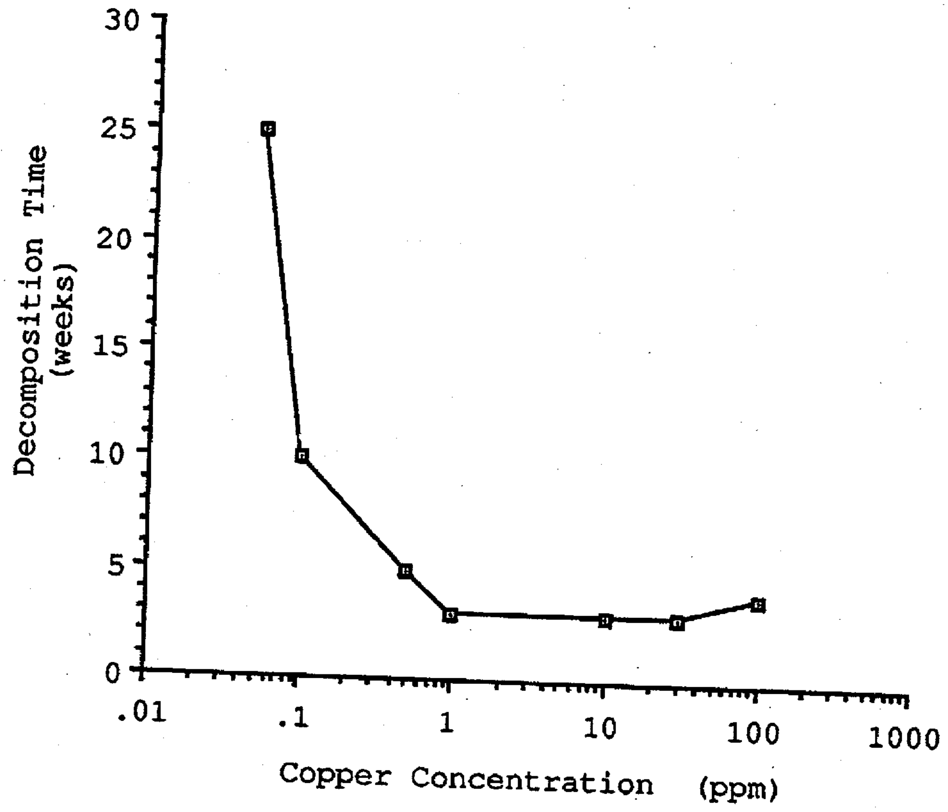

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Figure 2. Solution pH vs. Time for NaTPB Solutions with and without Copper at 65°C

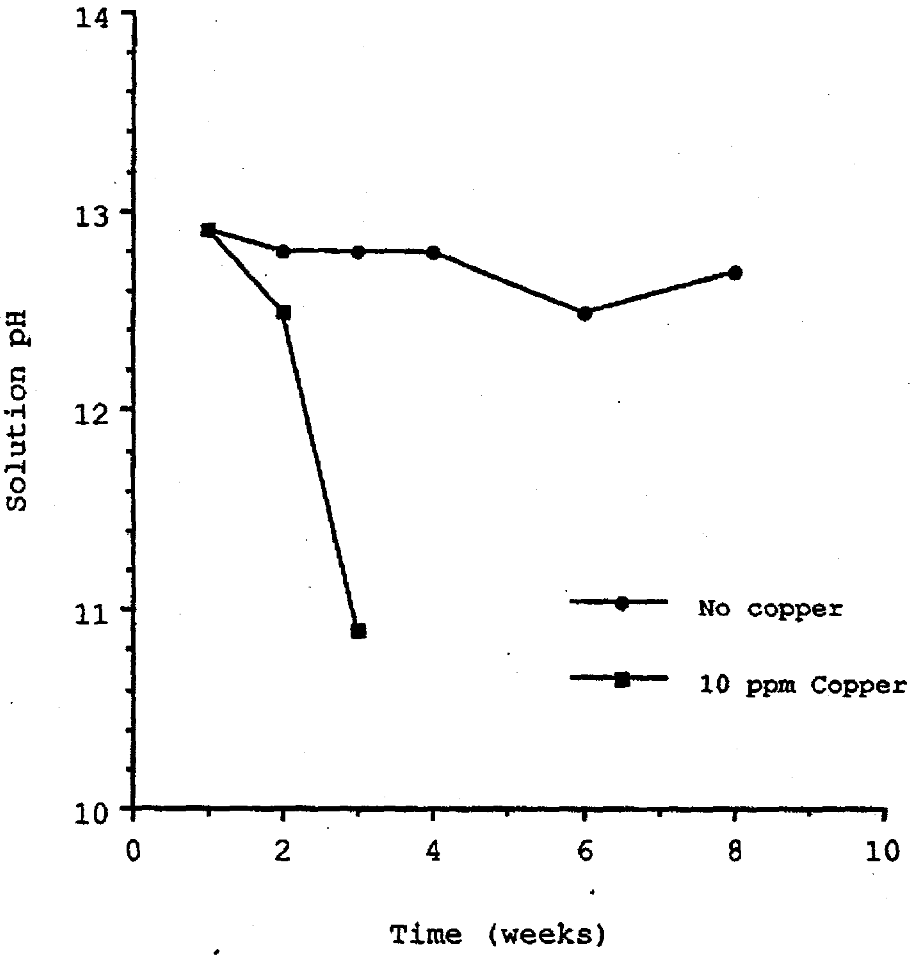

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Figure 3. Solution pH vs. Time for a 10 ppm Copper-Containing NaTPB Solution at Room Temperature

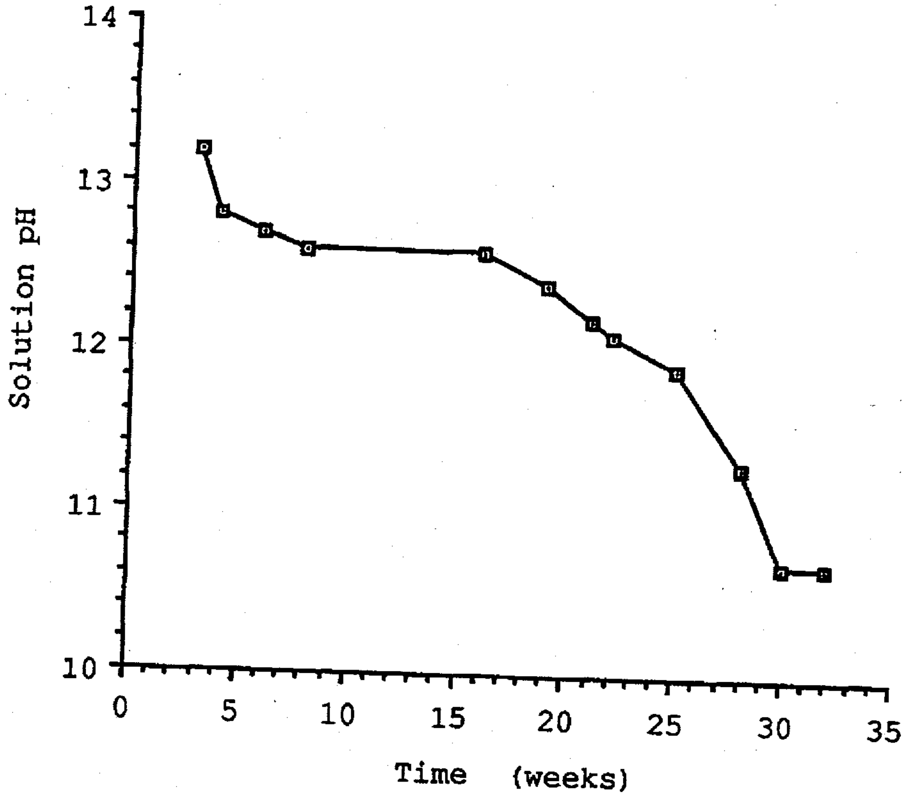

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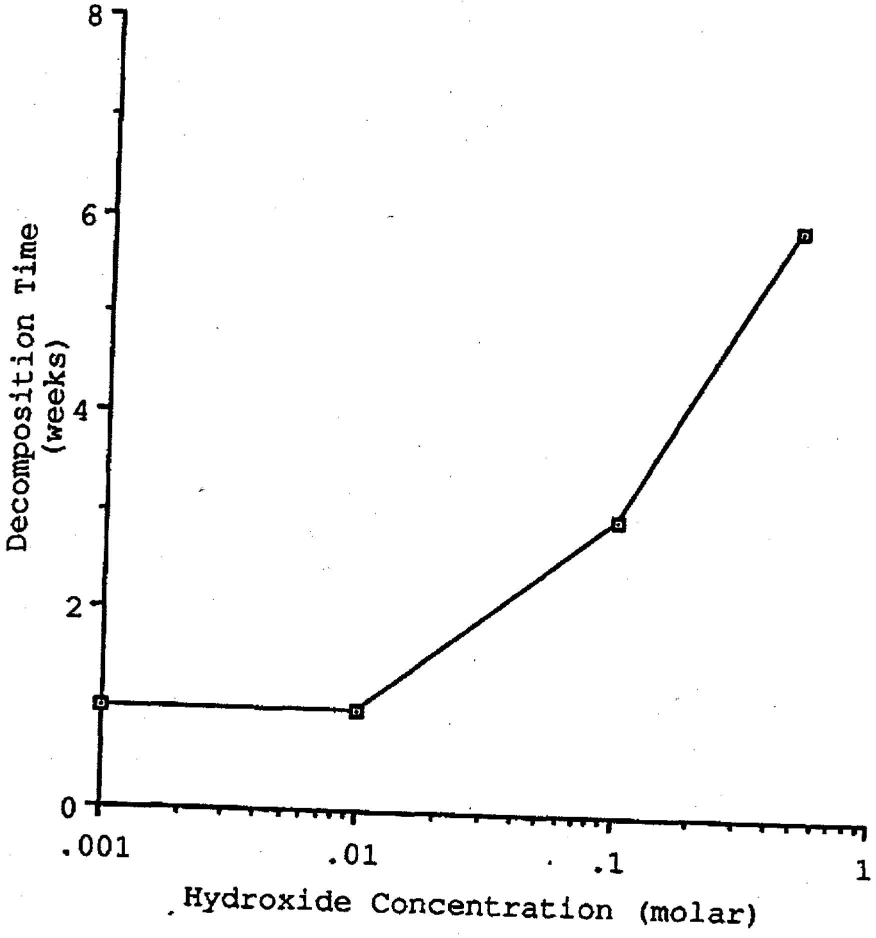
Figure 4. Decomposition Time of Copper-Containing NaTPB Solutions with Varying Hydroxide Ion Concentrations at 65°C



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Appendix A
Preliminary Experiments on Sodium Tetraphenylborate Stability

Preliminary experiments on the stability of 0.5 molar sodium tetraphenylborate solutions were performed by D. D. Walker and recorded in laboratory notebook DPSTN-4749, pp 88-97, and WSRC-NB-89-148, pp 4-9. The experimental procedure was similar to that reported here. All solutions contained 0.10 (±.01) molar free NaOH and 0.50 (±.03) molar sodium tetraphenylborate initially. The sodium tetraphenylborate was high purity (99+%) reagent grade. The metal salts used were all nitrates. Solutions (25 mL) were placed in capped polyethylene bottles (50 mL) under air and stored in an incubator at 65°C (±1°C). Each week for eight weeks the samples were removed from the incubator, cooled to room temperature, and a portion removed for analysis.

Table A-1 lists the results of these tests. Within the ranges tested, only one component, Cu(II), appeared to cause decomposition within eight weeks. The samples with 10, 30, and 100 ppm Cu were repeated and the time required for decomposition to occur was found to vary by several weeks. The last three samples listed, which had a portion of already-decomposed solution added to them, contained Cu(II) in very small amounts. The estimated copper contents are shown.

Table A-1
Results of Preliminary Experiments

Variable	Concentration	Observations
polyethylene	--	no decomposition
glass	--	no decomposition
Nitrate ion	200 ppm	no decomposition
Zn(II)	10, 30, 100 ppm	no decomposition
Cr(II)	10, 30, 100 ppm	no decomposition
Hg(II)	10, 30, 100 ppm	no decomposition
Cu(II)	10 ppm	decomposed in < 1 week
	30 ppm	decomposed in 1-7 weeks
	100 ppm	decomposed in 2-8 weeks
phenol	500, 1500, 3000 ppm	no decomposition
sodium phenylborate (phenylboric acid, disodium salt)	500, 1500, 3000 ppm	no decomposition
Sodium tetraborate (borax)	500, 1500, 3000 ppm	no decomposition
Hydrogen peroxide	1200, 3600, 12000 ppm	no decomposition
Decomposed NaTPB solution	4,000 ppm (0.04 ppm Cu)	no decomposition
	20,000 ppm (0.2 ppm Cu)	decomposed in 7-8 weeks
	60,000 ppm (0.6 ppm Cu)	decomposed slowly in 1-4 weeks