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Tank 48H Phase 1 Initial Testing Using Sodium Permanganate to Decompose Tetraphenylborate: Simulant Studies with Shaker Oven and 2-L Vessel

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October 2025
SRNL-STI-2025-00583, Revision 0

srnl.gov

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Prepared for
U.S. Department of Energy

SRNL-STI-2025-00583
Revision 0

Keywords: *Tank 48, Simulant, Phase 1*

Retention: *Lifetime*

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ACKNOWLEDGEMENTS

The authors would like to express their appreciation to Terri Fellinger, Bill Holtzscheiter, Kenneth Fernandez, Charles Nash, and Tom Peters for their interest in this effort and sharing their knowledge on the topic of Tank 48H remediation. The authors would like to acknowledge the completion of sample analyses tasks by Analytical and Tank Farm Characterization group, and off-gas set-up tasks handled by Jake Wall, Matthew Williams, and Grayson Walker. The authors would also like to thank Jared Riffle and Ingrid Lehman-Andino for their support in nuclear magnetic resonance measurements.

EXECUTIVE SUMMARY

Tank 48H currently holds legacy material including organic tetraphenylborate (TPB) compounds from the operation of the In-Tank Precipitation process. The large quantity of TPB is not compatible with the waste treatment facilities at SRS and must be removed or undergo treatment to oxidize the organic compounds before the tank can be returned to routine Tank Farm service. Tank 48H currently holds approximately 270,000 gallons of legacy material comprised of decontaminated salt solution, approximately 20,000 kilograms of TPB solids, 3,400 kilograms of sludge solids, and 1,800 kilograms of monosodium titanate (MST).

To support Phase 1 of the Tank 48H in-tank decomposition, two series of experiments were performed to investigate the decomposition of TPB with sodium permanganate using a nonradioactive Tank 48H slurry. The tests described below were designed to identify key flowsheet parameters such as temperature, required molar ratio of permanganate, viability of high pH, importance of permanganate addition rate, off-gas generation, and initial identification of reaction byproducts. Seven tests were performed at a pH of 14 with 250 mL Erlenmeyer flasks in a shaker oven for 56 days. Two tests were performed at a pH of 14 with 2-L jacketed vessels with real-time off-gas monitoring. Test variables included the molar ratio of sodium permanganate (P) to TPB (i.e., 1, 1.5, 2, 3, and 9), reaction temperature (i.e., 25 °C and 60 °C), and oxidant addition strategy (e.g., single or multi-strike). The Table below shows experimental variables for the shaker table and 2-L vessel permanganate additions and a summary of the TPB decomposition results.

Experiment Variables for Permanganate Additions and TPB Decomposition Result Summary

Test Identification	MnO_4^-:TPB Molar Ratio	Temp. (°C)	TPB Decomposition in Final Samples (%) [a]	
			Potassium	Boron
TK48-SH-60C-NOTPB	No TPB added [b]	60	NA	NA
TK48-SH-60C-BL	0	60	8.48	340
TK48-SH-60C-9	9 [c]	60	35.8	80.9
TK48-SH-60C-111	1.5 + 1.5 + 1.5 [d]	60	32.1	122
TK48-SH-60C-33	3 + 3 [e]	60	30.1	173
TK48-SH-25C-3-60C-3	3 + 3 [e]	25, 60	27.4	36.3
TK48-SH-25C-1-60C-2	1 + 2 [f]	25, 60	26.9	119
TK48-2LV-25C-1-60C-2	1 + 2 [f]	25, 60	8.89	30.1
TK48-2LV-60C-3	3	60	7.39	34.4

[a] TPB decomposition percentages were estimated by potassium and boron ICP-ES values. Boron leaching from borosilicate glass is expected and was adjusted for each reported value by subtracting the observed quantity in the TK48-SH-60C-BL sample series. Potassium nitrite from Time 0 sample was subtracted out of the potassium value received from ICP-ES.

[b] In TK48-SH-60C-NOTPB, since there is no TPB, a 9 equivalence, similar to TK48-SH-60C-9, was used.

[c] 9 molar ratio represents testing an addition of 36000 gal 40 wt.% $NaMnO_4$ (i.e., six 6000-gal tanker trucks).

[d] 4.5 molar ratio was added in three strikes, 1.5 molar ratio with 7-day separation intervals.

[e] 6 molar ratio was added in two strikes, 3 molar ratio with 28-day separation intervals.

[f] 3 molar ratio was added in two strikes of 1 and 2 molar ratio with 7-day separation interval.

The conclusions from the testing are summarized below:

- TPB decomposition was monitored indirectly by measuring soluble boron and potassium. TPB analysis by HPLC yielded inconsistent results due to variations in sampling preparations, leading to its exclusion from the TPB decomposition calculations. In general, TPB decomposition (i.e., potassium concentrations) increased as a function of time, temperature, and P:TPB molar ratio.
- Multiple permanganate strikes led to more effective TPB decomposition. A similar net TPB decomposition was observed in a single strike experiment with a P:TPB of 9 and a 3-strike experiment with a combined P:TPB of 4.5.
- Higher temperatures resulted in higher decomposition rates for equivalent permanganate concentrations, and there was a clear correlation between permanganate concentration and TPB decomposition.
- Phenylboronic acid (PBA), diphenylborinic acid (2PB), phenol, and biphenyl were measured by HPLC and correlated with TPB decomposition.
- Partial nitrite destruction was observed in all experiments with TPB and permanganate. Complete oxidation of nitrite was observed without TPB.
- UV-vis results indicated that all TPB decomposition tests resulted in complete consumption of permanganate except TK48-2LV-25C-1-60C-2 and TK48-SH-60C-NOTPB.
- Gradually heating from 25 °C to 60 °C did not show an effect on decomposition of TPB, as supported by the off-gas analyses (2-L experiments), chemical analysis, and visual observations.
- Free hydroxide decreased, but the pH remained above 13 for all experiments. The potential loss of free hydroxide could be due to a reaction with the glass vessels and other side reactions.
- Benzene, at low concentrations up to ~75 ppm (i.e., from FTIR data), was observed and measured with the off-gas instrumentation during the second 2-L vessel experiment, TK48-2LV-60C-3. N_2O was also observed and measured up to ~237 ppm (i.e., from FTIR data) during the second 2-L vessel experiment, TK-48-2LV-60C-3. An unidentified peak was observed around 950-1100 cm^{-1} on the FTIR for both 2-L vessel experiments. Otherwise, no other off-gas species were observed throughout both 2-L experiments.
- Nuclear magnetic resonance (NMR) studies indicate ingrowth of multiple aqueous-soluble organic species (e.g., organic salts) over time. Signal splitting indicates that there is likely two or more aqueous-soluble aromatic species (e.g., PBA and phenol). Additional method development is needed for accurate species identification through a series of control experiments involving spiking with perceived analytes, redispersion in multiple solvents, and/or measurement at various pHs to disproportionately shift signals to resolve their identity and provide discrete integrations.
- In proton (^1H) NMR studies, the highest summation of relative integration of aromatic regions (i.e., where TPB byproducts would show up) across all test series was for Tk48-SH-60C-111 (relative integration (ReI) = 49.50) followed by TK48-SH-60C-9 (ReI = 46.78) and TK48-SH-25C-1-60C-2 (ReI = 42.69). Indicating that TK48-SH-60C-111 produced the highest quantity of soluble TPB byproducts by permanganate oxidation based on relative integrations.
- Carbon (^{13}C) and boron (^{11}B) NMR studies were conducted but no significant signals were observed outside of the expected reference (boric acid) and simulant (carbonate and oxalate) analytes for samples collected prior to Time 7. Both ^{13}C and ^{11}B NMR were collected on a single Time 56 sample (TK48-SH-60C-111) and very weak signals were observed in the carbon NMR but were nearly indistinguishable from the baseline. Additional method development could be used to enhance these resonances in ^{13}C and ^{11}B NMR through optimizing inverse gated pulse or coupling methods, cryogenic temperatures, or through sample concentration.

The results of this study demonstrated that several small permanganate additions over time may result in favorable processing conditions for Tank 48H. Although TK48-SH-60C-9 had the highest decomposition based on potassium, the reaction rate appeared to slow rapidly after permanganate addition. The TK48-SH-

60C-111 tests had comparable decomposition percentages and required smaller quantity additions of permanganate, which will generate less total volume of waste and may be favorable for downstream processing (e.g., lower Mn solids in an eventual Defense Waste Processing Facility (DWPF) waste stream). Favorable results were shown in test series “TK48-SH-60C-111” where multiple small strikes were performed.

Based on the results of the shaker table tests, it is recommended that the tests with the highest TPB decomposition be repeated at a larger scale utilizing a more representative slurry of Tank 48H to evaluate the extent of TPB decomposition possible with tank processing. In addition, all subsequent 2-L vessel experiments should be conducted with continuous agitation with a continuously monitored overhead mixer.

For future experiments that require analysis of species that may leach from glass in high hydroxide (e.g., boron, potassium, or silicon), it is suggested to use reaction vessels made of high-density polyethylene (HDPE), Teflon, carbon steel, or stainless steel. Quartz may be used if additional silicon from etching is not a concern. Due to the complex nature and variety of reaction pathways for TPB decomposition, it is recommended that Savannah River National Laboratory (SRNL) develop a more complex simulant based on the characterization results of the recently pulled Tank 48H sample, as outlined in the Technical Task Request (TTR) and Task Technical and Quality Assurance Plan (TTQAP). It is also recommended to perform byproduct testing (i.e., triphenylborane (3PB), 2PB, PBA, phenol, and biphenyl) with sodium permanganate to understand the kinetics and decomposition of TPB byproducts. Although favorable results were found in this study, a more complex simulant that matches the current Tank 48H chemistry would provide additional insight into the process when conducted with actual waste.

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LIST OF ABBREVIATIONS

ACTL	Aiken County Technical Laboratory
CSTF	Concentration Storage and Transfer Facilities
DOE	Department of Energy
DWPF	Defense Waste Processing Facility
FTIR	Fourier Transform Infrared Spectrometer
GC	Gas Chromatography
HPLC	High Performance Liquid Chromatography
HDPE	High-Density Polyethylene
IC	Ion Chromatography
ICP-ES	Coupled Plasma Emission Spectroscopy
IDs	Test Identification
ITP	In-Tank Precipitation
KTPB	Potassium Tetraphenylborate
LWF	Late Waste Facility
MS	Mass Spectrometer
MST	Monosodium Titanate
NaTPB	Sodium Tetraphenylborate
NMR	Nuclear Magnetic Resonance
P:TPB	Molar Ratio of Permanganate to Tetraphenylborate
ReI	Relative Integration
SRMC	Savannah River Mission Completion
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
SSCM	Standard Cubic Centimeters
SWPF	Salt Waste Processing Facility
TIC	Total Inorganic Carbon
TMSP	3-(trimethylsilyl)-2,2,3,3-tetradeuteropropionic acid sodium salt
TOC	Total Organic Carbon
TPB	Tetraphenylborate
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
UV-vis	Ultraviolet-Visible
WATERGATE	Water Suppression by Gradient Tailored Excitation

1.0 Introduction

Tank 48H at the Savannah River Site (SRS) was the main reaction tank for the In-Tank Precipitation (ITP) process where sodium tetraphenylborate (NaTPB) was added to precipitate radioactive cesium and potassium as tetraphenylborate (TPB) salts. In addition to NaTPB, monosodium titanate (MST) was added to bind strontium and lesser actinides from the salt solution. Tank 48H currently holds approximately 270,000 gallons of legacy material comprised of decontaminated salt solution, approximately 20,000 kilograms of tetraphenylborate (TPB) solids, 3,400 kilograms of sludge solids, and 1,800 kilograms of MST.[1] The original plan called for processing the TPB slurry in the ITP Facility, the Late Waste Facility (LWF), and the Defense Waste Processing Facility (DWPF). That process included concentrating the TPB salts, washing salts to reduce the nitrite concentration, decomposing the TPB to benzene, and separating the benzene from the aqueous waste.[2] The premature decomposition of the TPB in Tank 48H caused excessive benzene levels that exceeded flammability limits established for the tank. Due to the flammability risk of benzene in Tank 48H processing, any future processing by ITP with NaTPB was ceased by the Department of Energy (DOE) in 1998.

Tank 48H is strategically located at the SRS Concentration Storage and Transfer Facilities (CSTF) and is ideally positioned for optimal processing. Tank 48H is a Type IIIA tank located near other sludge and salt batch prep tanks (Tank 49H, Tank 50H, and Tank 51H), all of which support DWPF, Salt Waste Processing Facility (SWPF), and Saltstone. The preferred choice is to restore use to Tank 48H, instead of decommissioning it, as it will provide an additional avenue for sludge (or salt) batch preparation and is already interconnected with several feed and prep tanks. If in-tank destruction of TPB is successful, Tank 48H could be restored for additional CSTF use and would significantly enhance production times and reduce operational costs.

Savannah River Mission Completion (SRMC) has issued a Technical Task Request (TTR) to Savannah River National Laboratory (SRNL) to evaluate the possibility of restoring function to Tank 48H through removing TPB solids by decomposition with sodium permanganate. The TTR outlines the first of three phases for research and development activities to study TPB decomposition using sodium permanganate.[1] SRNL issued a Task Technical and Quality Assurance Plan (TTQAP) in response, which is dedicated to a detailed characterization of Tank 48H slurry and the identification of key flowsheet parameters via testing using radioactive and simulated slurries.[3]

SRNL performed scoping tests using sodium permanganate to oxidize and decompose the TPB at room temperature and 40 °C.[4] In addition, tests at 40 °C were performed at pH 6, 10, and 11 and showed a decomposition of TPB of >90% is possible after a reaction time of two weeks. Results showed that the TPB decomposition heavily favored a pH of 10, but additional experiments were recommended to be performed to ensure pH stability was achieved.[5] The findings of those scoping studies initiated the efforts described in this report. Herein, two series of experiments were performed to investigate the decomposition of TPB with sodium permanganate in simulated Tank 48H slurry. Seven tests were performed at a pH of 14 with 250 mL Erlenmeyer flasks in a shaker oven for 56 days. Two tests were performed at a pH of 14 with 2-Lvessels with real-time off-gas monitoring. Test variables include the molar ratio of sodium permanganate to tetraphenylborate (i.e., 1, 1.5, 2, 3 and 9), reaction temperature (i.e., 25 and 60 °C) and oxidant addition strategy (e.g., single or multi-strike).

2.0 Experimental Procedure

Experiments were designed considering operational conditions and constraints of implementing a permanganate strike at the CSTF. For example, temperature control of Tank 48H would be provided by operating mixing pumps for extended periods of time to increase temperature at a maximum rate of 5 °C per day, while the in-tank cooling coils help maintain the temperature upper bounds. Thus, temperature control in the laboratory experiments was provided either by an oven or by circulating heated water through a jacketed reaction vessel to replicate the projected heating rate in Tank 48H. Additionally, sodium permanganate would be supplied to the CSTF by tanker trucks with an assumed average volume of 6000 gallons per truck. Emptying one tanker truck of 40% sodium permanganate into Tank 48H would increase the initial molar ratio of permanganate to tetraphenylborate (P:TPB) in the tank by 1.5. Consequently, P:TPB ratios were designed to target multiples of 1.5 (e.g., 1.5, 3, and 9).

2.1 Simulant Preparation

A base Tank 48H simulant was developed as described in previous reports.[5] The composition, shown in Table 2-1, was adjusted to align with concentrations from a recent detailed Tank 48H characterization report.[6] Although NaTPB was added in the original ITP process, both Cs and K were precipitated as TPB salts and became insoluble. Thus, to match the insoluble nature of TPB in Tank 48H, Potassium TPB (KTPB) was utilized to achieve this goal. KTPB was prepared by the reaction of potassium nitrate and sodium TPB in deionized water and the precipitate was collected by filtration, washed with deionized water, and air dried to a constant weight. To mitigate uncertainty from subsampling insoluble KTPB from the base simulant and achieve a consistent 0.056 M concentration of KTPB across all tests, KTPB was added independently for each 250-mL and 2-L test. An image of the prepared 250-mL Erlenmeyer flasks for shaker oven tests is shown in Figure 2-1.

Figure 2-1 250-mL vessel after KTPB was added for shaker oven test. Flasks labeled from left to right:TK48-SH-25C-1-60C-2, TK48-SH-60C-33, TK48-SH-60C-111, TK48-SH-60C-9, TK48-SH-60C-BL, and TK48-SH-25C-3-60C-3.

Table 2-1 Base simulant composition.

Chemical Name	Formula	Molarity
Sodium Carbonate	Na_2CO_3	1.80
Sodium Hydroxide	NaOH	1.63
Sodium Nitrite	$NaNO_2$	0.710
Sodium Nitrate	$NaNO_3$	0.200
Potassium Nitrate	KNO_3	0.012
Sodium Oxalate	$Na_2C_2O_4$	0.017
Sodium Chloride	NaCl	0.022
Potassium Tetraphenylborate	$KC_{24}H_{20}B$	0.056

Table 2-2 Actual amounts of KTPB and $NaMnO_4$ used in the base simulant and experimental process.

Test ID	KTPB (mol)	Volume before 1st $NaMnO_4$ Addition (L)	$NaMnO_4$ 1st Addition (mol)	Volume before 2nd $NaMnO_4$ Addition (L)	$NaMnO_4$ 2nd Addition (mol)	Volume before 3rd $NaMnO_4$ Addition (L)	$NaMnO_4$ 3rd Addition (mol)
TK48-SH-25C-1-60C-2	0.008	0.140	0.008	0.134	0.015	NA	NA
TK48-SH-25C-3-60C-3	0.008	0.140	0.024	0.130	0.020	NA	NA
TK48-SH-60C-BL	0.008	NA	NA	NA	NA	NA	NA
TK48-SH-60C-NOTPB	NA	0.140	0.071	NA	NA	NA	NA
TK48-SH-60C-9	0.008	0.140	0.071	NA	NA	NA	NA
TK48-SH-60C-111	0.008	0.140	0.012	0.133	0.011	0.123	0.010
TK48-SH-60C-33	0.008	0.140	0.024	0.121	0.022	NA	NA
TK48-2LV-25C-1-60C-2	0.084	1.5	0.084	1.4	0.167	NA	NA
TK48-2LV-60C-3	0.084	1.5	0.252	NA	NA	NA	NA

NA = Not Applicable

2.2 Experimental Apparatus and Parameters

2.2.1 Shaker Oven Experiments

All seven shaker oven experiments were performed simultaneously in 250-mL Erlenmeyer glass flasks with 150 mL of base simulant. The shaker oven was used to ensure constant temperature and mixing. The flasks were agitated and heated to a temperature of 60 °C for a period of 56 days. TK48-SH-25C-1-60C-2 and TK48-SH-25C-3-60C-3 started heating at 25 °C, increasing 5 °C per day, until 60 °C was achieved (i.e., 7 days to reach 60 °C). As described in Section 2.0, the solution was heated at this rate due to the maximum estimated heating rate when mixing with tank pumps. When required, a solution of 40 wt% sodium permanganate was added instantaneously to the reaction vessels using a transfer pipette.

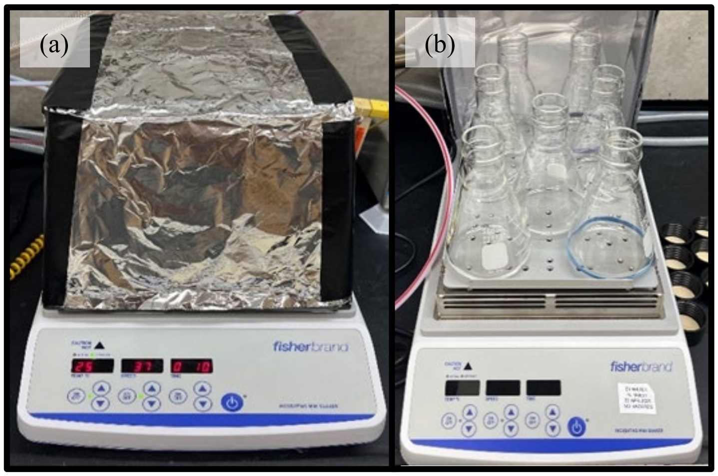


Figure 2-2 Shaker oven setup: Image (a) indicates the shaker oven covered in aluminum foil to minimize light exposure. Image (b) indicates the setup of the Erlenmeyer flasks inside the shaker oven.

The experiment parameters for all seven tests are as follows:

- Initial simulant mass: ~150 mL (~192 g)
- Reaction vessel: 250-mL Erlenmeyer glass flask
- Temperature: 25 and 60 °C (increased at 5 °C per day)
- Slurry pH: ~14
- Sodium permanganate concentration: 40 wt% (3.9 M)
- Sodium permanganate addition rate: Instantaneous
- Mixing and temperature control: shaker oven
- Reaction duration: 8 weeks (56 days)

Due to the possibility of radical formation from UV radiation, which would not be present in real Tank 48H processing, the shaker oven was covered with aluminum foil to minimize light exposure as much as possible. When removing subsamples for characterization, the cover was removed, samples were quickly collected, and then the 250-mL vessels were returned to the covered shaker oven. A thermocouple was placed in the back of the oven to ensure the shaker table oven was holding temperature throughout the experiment. The phenolic caps of the Erlenmeyer flasks were modified to include a small hole to prevent over-pressurization. Tape was placed over the hole to mitigate evaporative loss throughout the two-month experiment.

Table 2-3 provides information on test identifications (IDs), molar ratio of permanganate to TPB, and sampling intervals for the duration of the shaker oven experiments. Sample intervals are based on the timing of the initial addition of sodium permanganate. All samples were quenched with three molar equivalents of sodium sulfite shortly after being pulled to reduce unreacted permanganate and stop any additional reactions. When no permanganate is added, reaction time commenced when heating is initiated.

Table 2-3 Shaker oven experiment variables and sampling intervals.

Test ID	MnO_4^-:TPB Molar Ratio	Sampling Intervals (days)
TK48-SH-60C-NOTPB	No TPB added [a]	0, 1, 7, 14, 56 [b]
TK48-SH-60C-BL	0	0, 1, 3, 4, 5, 6, 7, 14, 56
TK48-SH-60C-9	9 [c]	0, 1, 7, 14, 56
TK48-SH-60C-111	1.5 + 1.5 + 1.5 [d]	0, 1, 7, 14, 28, 56
TK48-SH-60C-33	3 + 3 [e]	0, 1, 28, 56
TK48-SH-25C-3-60C-3	3 + 3 [e]	0, 1, 7, 28, 56
TK48-SH-25C-1-60C-2	1 + 2 [f]	0, 1, 7, 14, 56

[a] In TK48-SH-60C-NOTPB studies, since there is no TPB, the added ratio of MnO_4^- is 9.

[b] In addition to the listed samples, five samples were collected in 1 hour intervals after $NaMnO_4$ addition.

[c] 9 molar ratio represents testing an addition of 36000 gal 40% $NaMnO_4$ (i.e., six 6000-gallon tanker trucks).

[d] 4.5 molar ratio was added in three strikes of 1.5 molar ratio with 7-day separation intervals.

[e] 6 molar ratio was added in two strikes of 3 molar ratio with 28 day separation intervals.

[f] 3 molar ratio was added in two strikes of 1 and 2 molar ratio with 7-day separation interval.

The purpose for each test is described in greater detail below:

- TK48-SH-60C-NOTPB – This test was performed on the base simulant composition, shown in Table 2-1, without TPB to observe side reactions of permanganate with the salt solution. Permanganate was added at a molar ratio of 9 at 60 °C, which is similar to the molar ratio of TK48-SH-60C-9. A Time 0 sample was taken before permanganate was added. One-hour samples were taken for the first five hours and then followed the sampling interval shown in Table 2-3**.**

- TK48SH-60C-BL – This test was performed on the base simulant composition with KTPB, but no added permanganate. The sample was heated to 60 °C to determine the effect of TPB hydrolysis and decouple any observed TPB destruction from the oxidation reaction with permanganate. This test was also used as background generation for B, and K in TPB decomposition calculations.

- TK48-SH-60C-9 – Sodium permanganate was added to the base simulant composition to achieve a permanganate to TPB molar ratio (P:TPB) of 9:1 at 60 °C. This corresponds to the volume of 40% sodium permanganate in six 6000-gallon tanker trucks (i.e., 36000 gallons). The goal was to determine the effect of an increased permanganate strike on the TPB destruction reaction.

- TK48-SH-60C-111 – This test simulated one tanker truck equivalent of permanganate added to Tank 48H per week over three weeks. Each scaled 6000 gallon volume would contribute a P:TPB of 1.5:1 for a final molar ratio of 4.5:1

- TK48-SH-60C-33 – Two permanganate strikes were performed with the first strike at a P:TPB of 3:1. 28 days after the initial 3:1 strike an additional 3:1 strike was performed and allowed to react for an additional 28 days. Both strikes were performed at 60 °C.

- TK48-SH-25C-3-60C-3 – Two permanganate strikes were performed with the first 3:1 P:TPB strike at room temperature. The temperature was then increased approximately 5 °C per day until a temperature of 60 °C was achieved. The 60 °C temperature was maintained for the remainder of the test. 28 days after the initial 3:1 strike an additional 3:1 strike was performed at 60 °C and allowed to react for an additional 28 days.

- TK48-SH-25C-1-60C-2 – Two permanganate strikes were performed with the first 1:1 P:TPB strike at room temperature. The temperature was then increased approximately 5 °C per day until a temperature of 60 °C was achieved. After the 60 °C temperature was achieved the second strike (2:1 P:TPB) was performed. The 60 °C temperature was maintained for the remainder of the test.

2.2.2 2-L Vessel Experiments

Two 2-L vessel experiments were performed in a 2-L borosilicate glass jacketed vessel with 1.5 L of base simulant. The 2-L borosilicate glass jacketed vessel was equipped with a borosilicate lid and held together with a vessel clamp. Temperature control was provided by circulating heated water through the jacketed reaction vessel. The lid of the vessel was equipped with seven Ultra-Torr fittings connected to Teflon fittings. The Ultra-Torr Teflon fittings were used to introduce: 1) a gas supply line, the purge gas was comprised of air and krypton, to provide a purge throughout the experiment, 2) an off-gas line to carry the gas through the reflux condenser and the off-gas equipment, 3) an Inconel-clad type-T thermocouple for continuous temperature monitoring, 4) a reflux line to return condensate water to the vessel, 5) a Luer lock valve to add permanganate to ensure the vessel headspace was not compromised, 6) a metal sampler to pull representative sample throughout the experiment to ensure the vessel headspace was not compromised, and 7) the UV-vis probe. Mixing at 450 rpm was achieved using a 3 inch Teflon stir bar for both experiments. During the first experiment (i.e., TK48-2LV-25C-1-60C-2), adequate mixing was not achieved as TPB was observed floating on the surface. To ensure floating solids were incorporated into the bulk solution, an overhead mixer was included for the second experiment (in addition to a stir bar). In practice, the overhead mixer was active during the day, but not used when the vessel was unattended (e.g., nights and weekends). The 2-L water jacketed vessel was covered with aluminum foil to minimize light exposure as much as possible. Figure 2-4 shows the set-up used for both 2-L vessel experiments.

The purge gases, comprised of compressed air and high purity krypton, were provided using MKS controllers. An appropriate purge rate was chosen based on the 2-L vessel headspace available (i.e., 3 headspace turnovers required for full gas replacement) with the goal to completely flush the headspace every 9 hours. The purge rate of compressed air was set at 4.06 sccm and the krypton blended at a concentration of 11%. Due to a low air purge rate selected (i.e., 4.06 sccm) and a flow controller for Kr of 0.500 sccm, the krypton concentration blend was 11%. A leak check was performed after ensuring all vessel ports were closed with the associated equipment and the purge rate was set on the MKS. To mitigate water loss during the two week experiment, a reflux condenser connected to a recirculating chiller set at 5 °C was used to allow the condensate to drain back into the vessel.

After the gas exited the hood, off-gas was carried first to an Inficon MicroGC where a small fraction of the off-gas was pulled for Gas Chromatography (GC) analysis. The remainder of the off-gas was carried to the Extrel Mass Spectrometer (MS) and Fourier-Transform Infrared (FTIR) spectrometer. Following the analyses, the off-gas was carried into the Aiken County Technical Laboratory (ACTL) ventilation system. Figure 2-3 shows a schematic of the 2-L water jacketed vessel apparatus sketch used for off-gas equipment.

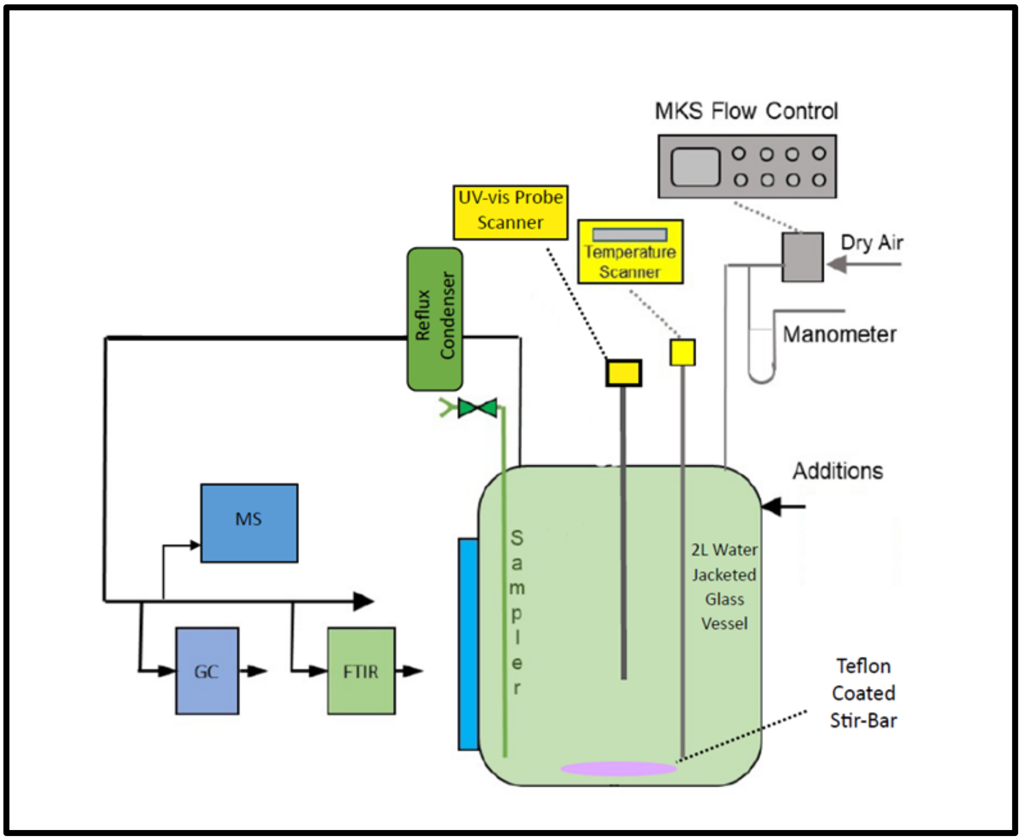


Figure 2-3 Schematic of 2-L water jacketed vessel apparatus.

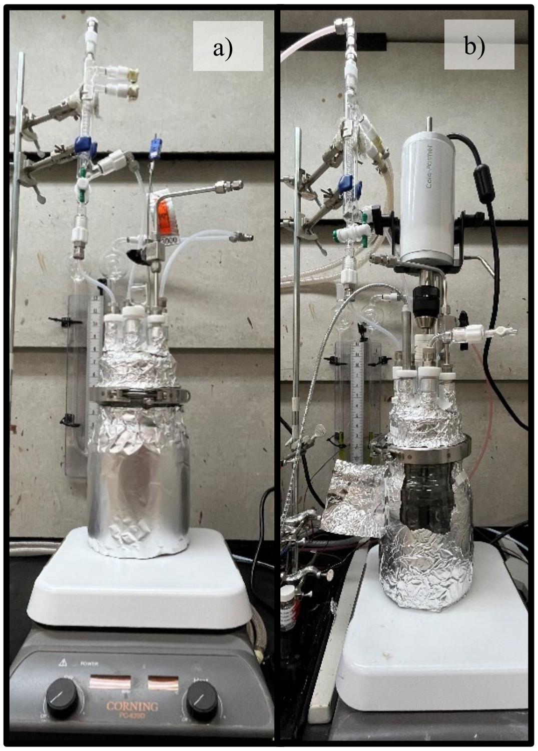


Figure 2-4 2-L vessel setup: a) shows TK48-2LV-25C-1-60C-2 and b) shows TK48-2LV-60C-3.

The experiment parameters for the two experiments are as follows:

- Initial simulant volume: 1.5 L
- Reaction vessel: 2-L borosilicate glass jacketed vessel
- Target purge rate: 4.06 sccm with a krypton tracer
- Purge gas composition: air (dried, CO_2-free)
- Mixer speed: Teflon coated stir bar/overhead mixer; vortex maintained
- Temperature: started at 25 °C and heated up to 60 °C (5 °C per day)
- Slurry pH: ~14
- Sodium permanganate concentration: 40 wt% (3.9 M)
- Oxidant addition rate: Instantaneous
- Mixing and temperature control: Stir bar/overhead mixer
- Reaction duration for each test: 2 weeks (14 days)

Table 2-4 shows the initial 2-L vessel test variables and sampling intervals. Sample intervals are based on the timing of the initial addition of sodium permanganate. All samples were quenched with sodium sulfite shortly after being pulled to remove unreacted permanganate and stop any additional reactions.

Table 2-4 2-L vessel experiment variables and sampling intervals.

Test ID	MnO_4^-: TPB Molar Ratio	Sampling Intervals (days)
TK48-2LV-25C-1-60C-2	1 + 2[a]	0, 1, 3, 4, 5, 6, 7, 14
TK48-2LV-60C-3	3	0, 1, 7, 10

[a] 3 molar ratio was added in two strikes of 1 and 2 molar ratio with 7-day separation intervals.

The purpose of each test is described in greater detail below:

- TK48-2LV-25C-1-60C-2 – Two permanganate strikes were performed with the first 1:1 P:TPB strike at room temperature. The temperature was then increased approximately 5 °C per day until 60 °C was achieved. After 60 °C has been achieved the second 2:1 strike was performed. The 60 °C temperature was maintained for the remainder of the test. The sample intervals marked as Time 0, 1, 3, 4, 5, and 6 were taken before the vessel reached 60 °C, with an increase in temperature of 5 °C per day.

- TK48-2LV-60C-3 – Sodium permanganate was added to the base simulant composition to achieve P:TPB of 3:1 at 60 °C. The vessel was heated up to 60 °C the first day and did not increase in temperature 5 °C per day. Once the vessel was set to 60 °C, the vessel was left to heat without permanganate for 4 days. This was to determine if heating had an impact on the decomposition of TPB. After permanganate addition, sampling intervals 1, 7, and 10 days followed.

2.3 Sample Analysis

2.3.1 Chemical Analysis

Table 2-5 provides information on the analytical methodology and the target analytes for the shaker oven experiments and the 2-L vessel experiments. Prior to analysis, filtrate samples were filtered with a 0.45 µm syringe filter.

Table 2-5 Analytical methods performed for target analytes.

Analytical Method	Sample Type	Target Analytes
ICP-ES	Filtrate	B, K
TIC/TOC [a]	Filtrate	Total Inorganic/Total Organic Carbon
T_Base_OH_OTHER_BASE_EXC_CO3	Filtrate	Free OH^-
HPLC	Slurry	TPB, 3PB, 2PB, 1TB, Phenol, Biphenyl
IC Anions [b]	Filtrate	Nitrite/Nitrate

[a] TIC/TOC was only measured for the Time 0, Time 14 and Time 56 sampling intervals.

[b] The full suite of anions was measured in addition to the nitrite and nitrate.

2.3.2 UV-Vis Analysis

UV-vis analysis was performed on all shaker oven samples shown in Table 2-3 and Table 2-4 with a PerkinElmer Lambda850 spectrometer. Note that an *in-situ* UV-vis probe was employed in 2-L vessel tests and the high concentration of permanganate saturated the UV-vis detector and caused absorbance values above the detection limits (i.e., the samples are too dark to observe without direct dilution). For shaker oven tests, where dilution of aliquots was possible, approximately 3 mL of the unquenched samples were removed for measurements on a steady state UV-vis spectrometer. This data was used to determine the ratio of dissolved manganese species relative to the total amount of dissolved permanganate at multiple sampling intervals.

Each of the aliquots were filtered with a 0.45-µm filter to remove solids (primarily MnO_2), and a portion of the aliquot was diluted to 10 mL with 1.630 M sodium hydroxide in a volumetric flask before performing the measurement. Various dilutions were used as needed for the final absorbance values to fall within the ideal range for measurement, often ranging from 10 – 60 µL of filtered sample added before diluting with sodium hydroxide. In several late-stage experiments, samples were not diluted due to the total conversion of permanganate and manganate to MnO_2 and the resulting weaker absorptions in the spectra.

To quantify the concentrations of manganate species left in solution, a calibration curve of permanganate in sodium hydroxide was initiated by mixing a stock solution of 10 mM sodium permanganate in 1.630 M sodium hydroxide, and then further diluting it to match the range of absorbances measured in the samples. Seven dilutions ranging from 0.02 – 0.50 mM permanganate were measured in triplicate, giving absorbances from 0.02 – 0.72 for the 607 nm band (corresponding to manganate). A direct relationship between permanganate concentration and this peak formed a trend line with a high correlation coefficient (R^2 = 0.9957). This allowed for the quantification of permanganate from the peak values in the measured UV-vis spectra.

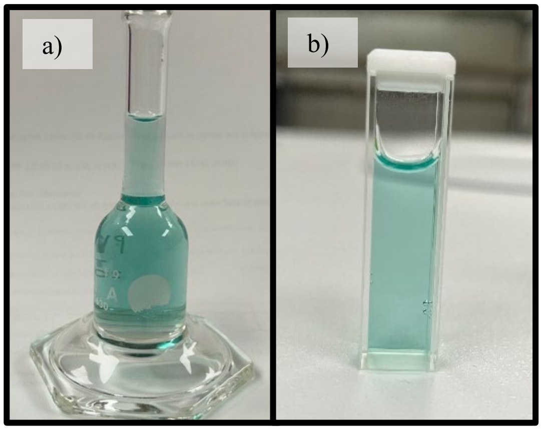


Figure 2-5 a) Image shows the simulant sample after being diluted with sodium hydroxide for UV-vis measurements. b) Indicates the diluted sample in the cuvette.

2.3.3 NMR Analysis

^{1}H nuclear magnetic resonance (NMR) measurements were performed on a Bruker 500 MHz ASCEND® Spectrometer. Liquid samples were filtered prior to all measurements and all spectra were collected at 299.0 K. A co-axial methodology was used to prepare samples without direct dilution in an effort to maintain the maximum possible signal-to-noise ratio. In this method, 400 µL of filtrate was added to a glass Wilmad® Precision NMR sample tube of 5.0 mm outer diameter combined with a stem coaxial insert (WGS-5BL, outer diameter = 2.0 mm, stem height = 55 mm) containing 50 µL of a locking solvent with reference analyte (10 mM 3-(trimethylsilyl)-2,2,3,3-tetradeuteropropionic acid sodium salt (TMSP) in D_2O or 100 mM boric acid in D_2O). Deuterium oxide is used to lock the magnet on a known signal (deuterium) and prevent drift in the magnetic field. TMSP was selected as an axis-calibration reference where the associated signal (9H-singlet) was referenced to 0.0 ppm. Boric acid was used as an integration reference for ^{11}B NMR but spectra were not calibrated to the peak position (approx. 19 ppm) since its resonance may be dependent on its local environment (e.g., in highly concentrated salt solutions). The ^{11}B signal for boric acid appears at approximately 19 ppm in all collected spectra. An image of the coaxial-tube configuration and sample loaded using a 22-mm sample depth gauge is shown in Figure 2-6.

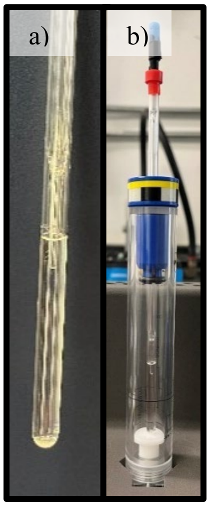


Figure 2-6 a) Image of NMR coaxial tube configuration containing simulant sample (outer) and TMSP in D_2O reference (inner) and b) sample tube loading into blue sample spinner using a 22-mm sample depth gauge.

Four types of NMR experiments were performed on simulant samples and a summary of the method development can be found in Appendix B. A summary of water suppression method development is shown in Figure B-1. First, a standard ^1H NMR method was collected for all samples and a large water signal at 5.1 ppm was present in all aqueous samples. The spectral overlap of a broad water signal with signals of interest in the aromatic region impacts the integration values and can cause peaks to be missed on the shoulders of the broad signal. Thus, a WATERGATE (Water Suppression by Gradient Tailored Excitation) method was applied in separate experiments to suppress the large water signal at 5.1 ppm in the aqueous samples. This method relies on applying a gradient spin echo technique to separate the water magnetization (by diffusing it with two gradients) from other signals.[7,8] A hard 90-degree pulse is applied to magnetize the water followed by a 2-millisecond gradient pulse (a sine-shaped gradient of 50 mT m^{-1} was applied to diffuse it). Lastly, a train of pulses set at different angles acts as a 180-degree pulse for everything else in the sample except for water. Additionally, ^{13}C NMR spectra were collected using a ^{13}C inverse-gated method which reduces the impact of the nuclear Overhauser effect (compared to standard decoupled ^{13}C-NMR methods) leading to disproportionate signal-enhancement by enabling decoupling only during acquisition periods. ^{11}B spectra were obtained using standard decoupling methods and the reported ^{11}B spectra were referenced with an inner-coaxial insert containing 50 µL of a 100 mM boric acid solution in D_2O. To verify the boron-containing standard concentration, ICP-ES was applied and shows a final boron concentration of 99.45 mM (5% RSD, n = 2). The TMSP and organic byproduct standards were prepared at a target of 10 mM with identical methods in analytical glassware but were not further verified (shown in Figure B-2 through Figure B-4). ^1H (standard method and WATERGATE), ^{11}B, and ^{13}C NMR spectra and a discussion of results can be found in Section 3.1.4 and Appendix B.

Table 2-6 List of NMR experiments, analyzed nuclei, and sample identification matrix.

Sample Identification	^{1}H, Time Interval	^{11}B, Time Interval	^{13}C, Time Interval
TK48-2LV-60C-3	0, 1, 7, 10	– –	– –
TK48-2LV-25C-1-60C-2	0, 1, 3, 4, 5, 6, 7, 14	0, 1, 3, 4, 5, 6, 7	0, 1, 3, 4, 5, 6, 7
TK48-SH-25C-1-60C-2	1, 7, 56	1, 7	1, 7
TK48-SH-25C-3-60C-3	1, 7, 56	1, 7	1, 7
TK48-SH-60C-9	1, 56	1	1
TK48-SH-60C-33	1, 56	1	1
TK48-SH-60C-111	1, 56	1, 56	1, 56
TK48-SH-60C-BL	1, 3, 5, 7, 56	1, 3, 4, 5, 6, 7	1, 3, 4, 5, 6, 7
TK48-SH-60C-NOTPB	1, 56	1	– –

2.3.4 Off-Gas Analysis

GC analysis was provided by an Inficon Micro GC, equipped with a MolSieve 5Å column and a PoraPlot Q column (both used Ar carrier gas). A 120 second isothermal method was used to adequately separate H_2, N_2, O_2, Kr, CH_4, CO_2, and N_2O. GC sampling occurred approximately every 10 minutes during the experiment. The GC was calibrated before and after every experiment with a calibration gas composed of 50 ppm H_2, 101 ppm CH_4, 0.99% CO_2, 0.505% N_2O, 0.508% Kr, and air.

Mass Spectrometer (MS) analysis was provided by an Extrel Core MS. The sampling capability of the MS ran from 8 seconds per reading for the first experiment, TK48-2LV-25C-1-60C-2, to 5 minutes per reading for the second experiment, TK48-2LV-60C-3. Data collection time intervals were extended during the second run due to excessive data logging on the instrument. H_2, N_2, O_2, Kr, CH_4, CO_2, and N_2O responses were calibrated using separate calibration gases. Additionally, the MS employed a scanning feature, allowing the occasional collection of raw mass spectrometry data to investigate for unidentified gases.

Fourier Transform Infrared Spectrometer (FTIR) analysis was provided by an MKS FTIR Spectrometer. The FTIR was able to measure N_2O, NO, NO_2, CO_2, NH_3, and CH_4 using literature libraries of example spectra as a basis for calibration. C_6H_6 was calibrated on the FTIR with a calibrated benzene gas (i.e., benzene concentration of 0.02%, 10 ppm, 20.01 ppm, and 50 ppm in balanced Nitrogen). The FTIR was also able to visually show unknown observed peaks throughout the experiments. Unknown observed peaks can be compared to the library spectra to offer possible identities for new species. Table 2-7 lists the species of gases observed in both the 2-L Tank 48H simulant experiments and identifies the analytical techniques used to quantify each molecule.

Table 2-7 Gas species by analytical technique.

Gas of Interest	GC A Column	GC B Column	MS	FTIR
	Carrier Gas: Argon	Carrier Gas: Argon	N/A	N/A
H_2	X		X	
CO_2		X	X	X
CO				X
NO			X	X
NO_2			X	X
N_2	X		X	
N_2O		X		X
O_2	X		X	
Kr	X		X	
NH_3				X
CH_4	X			X
C_6H_6			X	X

2.4 Quality Assurance

This work was requested via a TTR and directed by a TTQAP[1,3] Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2. The functional classification requested for this work is Safety Class. In accordance with Manual E7, Procedure 3.60, a technical review of the contents of this report has been performed to ensure consistency and accuracy. Per Manual E7, Procedure 2.60, a Design Verification, at a minimum, must be performed for work supporting a Safety Class functional classification. Analytical methods conform with Measurement Systems and Equipment (MS&E) and Measuring and Test Equipment (M&TE) program requirements. Data is recorded in the SRNL electronic laboratory notebook system as experiment ID: K6349-00614-11.[9]

2.5 Visual Observation

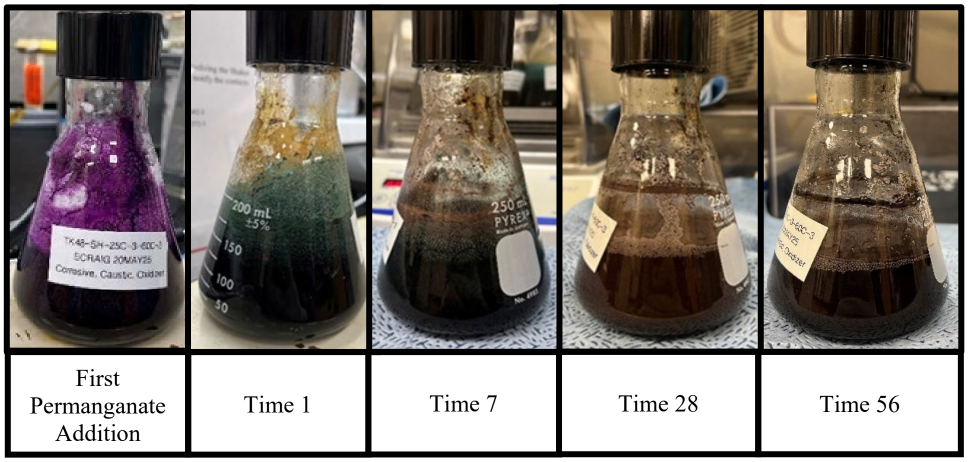
Distinct colors existed for many of the relevant species in the KTPB base simulant experiments with the permanganate added. Relevant colors include: KTPB (foamy white solids), manganese dioxide (black/brown solids), manganese (VI) oxide (green solution), and permanganate (purple solution). A visual depiction of the experiment's sample interval times (Table 2-3 and Table 2-4 indicate the sample interval times) for the shaker table experiments and the 2-L vessel experiments are shown in Figure 2-7 through Figure 2-14, and Figure 2-16. The addition of KTPB to the base simulant solutions resulted in a white, foamy solution with the solids floating to the top of the solution. After the addition of permanganate, deviations in color were noted between the simulants.

2.5.1 Shaker Oven Experiments

Experiments Tk48-SH-25C-1-60C-2 and TK48-SH-25C-3-60C-3 color changed to manganese (VI) by Time 1 (i.e., from purple to green) and still had a tint of green by Time 7. This indicated that striking initially at 25 °C and gradually heating to 60 °C did not consume permanganate at a higher rate. Instead, it was observed that starting at 60 °C accelerated the consumption of permanganate. For the rest of the shaker table experiments the permanganate changed to manganese (VI) by Time 1 (i.e., green) and by the next sampling evolution at Time 7 all permanganate and manganate appear to have been converted to manganese dioxide (brown suspended solids). The formation of manganese dioxide in the experiments indicated that all the permanganate had fully reacted.

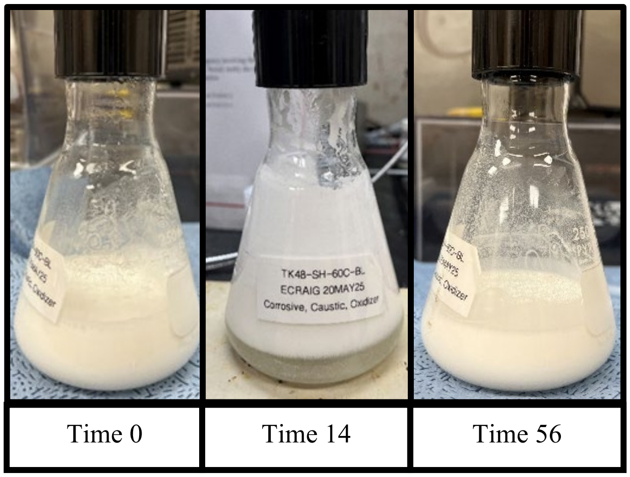
First Permanganate Addition | Time 1 | Time 8 | Time 14 | Time 56

Figure 2-7 Visual observations of TK48-SH-25C-1-60C-2. The second permanganate addition occurred 24 hours before Time 8. A purple band on the exterior of the flask prevented the glass from rubbing against each other.



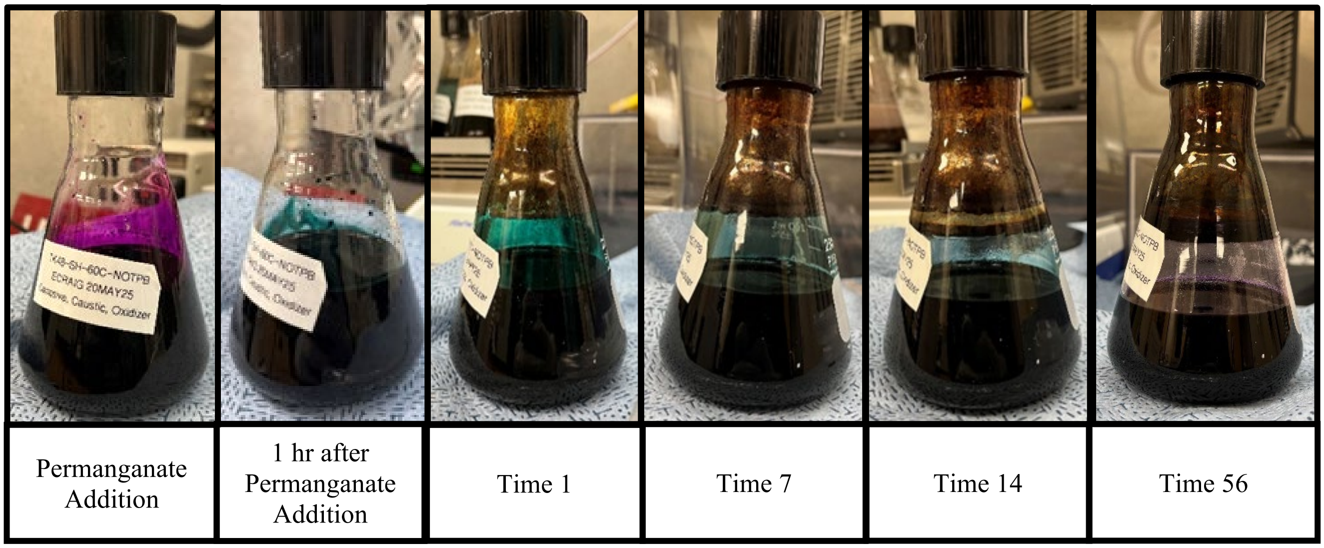
First Permanganate Addition | Time 1 | Time 7 | Time 28 | Time 56

Figure 2-8 Visual observations of TK48-SH-25C-3-60C-3. The second permanganate addition occurred immediately after Time 28.



Time 0 | Time 14 | Time 56

Figure 2-9 Visual observations of TK48-SH-60C-BL.



Permanganate Addition | 1 hr after Permanganate Addition | Time 1 | Time 7 | Time 14 | Time 56

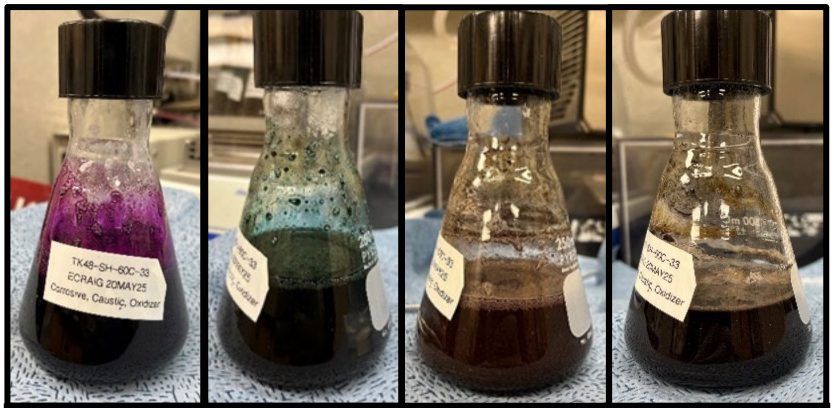
Figure 2-10 Visual observations of TK48-SH-60C-NOTPB.

Permanganate Addition	Time 1	Time 7	Time 14	Time 56

Figure 2-11 Visual observations of TK48-SH-60C-9.

First Permanganate Addition	Time 1	Time 7	Time 14	Time 28	Time 56

Figure 2-12 Visual observations for TK48-SH-60C-111. The second permanganate addition occurred immediately after Time 7. Third permanganate addition occurred immediately after Time 14.



First Permanganate Addition

Time 1

Time 28

Time 56

Figure 2-13 Visual observations for TK48-SH-60C-33. The second permanganate addition occurred immediately after Time 28.

2.5.2 2 L Vessel Experiments

At the start of the TK48-2LV-25C-1-60C-2 experiment, Time 0 indicated an abundance of KTPB foam sitting on top of the slurry. This foam was never able to be reincorporated with the slurry due to insufficient agitation. Previous experiments have shown that foam is typical in simulant solutions containing KTPB.[10] After the addition of permanganate, 24 hours later, the sample at Time 1 appeared to have largely converted permanganate to manganate based on the green color of the solution. The slurry appears to have stayed as manganate-bearing (i.e., green) until after Time 7.

At the start of the TK48-2LV-60C-3 experiment, Time 0 showed minimal foam present on the surface of the slurry. During this experiment a more efficient agitator was used and allowed the foam to mix into the simulant. After the addition of permanganate, 24 hours later, Time 1 manganate had been observed. By Time 7, manganese dioxide, which was indicated by the appearance of brown solids, had been observed. The formation of manganese dioxide in the experiments indicated that all the permanganate had fully reacted. Additionally, it was observed that starting temperature of 60 °C accelerated the consumption of permanganate and increased the rate of reaction.

At the end of both 2-L vessel experiments, crystals were observed on the interior surface of the lid and vessel. TK48-2LV-60C-3 had noticeably more crystals form on the lid. This could be due to the improved agitation during the experiment, which allowed for decomposition of TPB. The crystals were removed and kept in a glass jar for analysis. Based on visual observations, the crystals could be biphenyl, as the crystals have been known to form in past experiments.[11] Additional analyses would be needed to verify the crystals identity. Note that crystals were not observed in shaker oven testing, presumably due to condensate build-up on the caps of the 250-mL Erlenmeyer flasks or absence of purge flow that might induce crystallization.

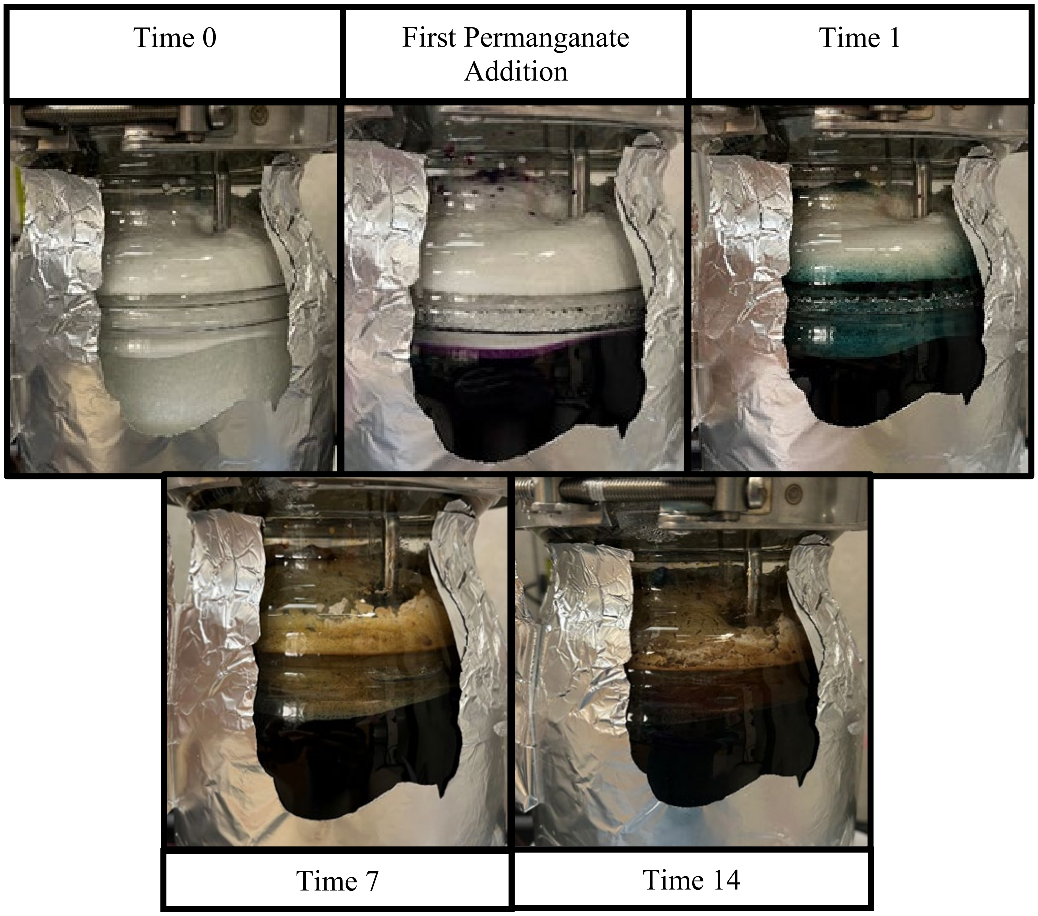


Figure 2-14 Visual observations for TK48-2LV-25C-1-60C-2.

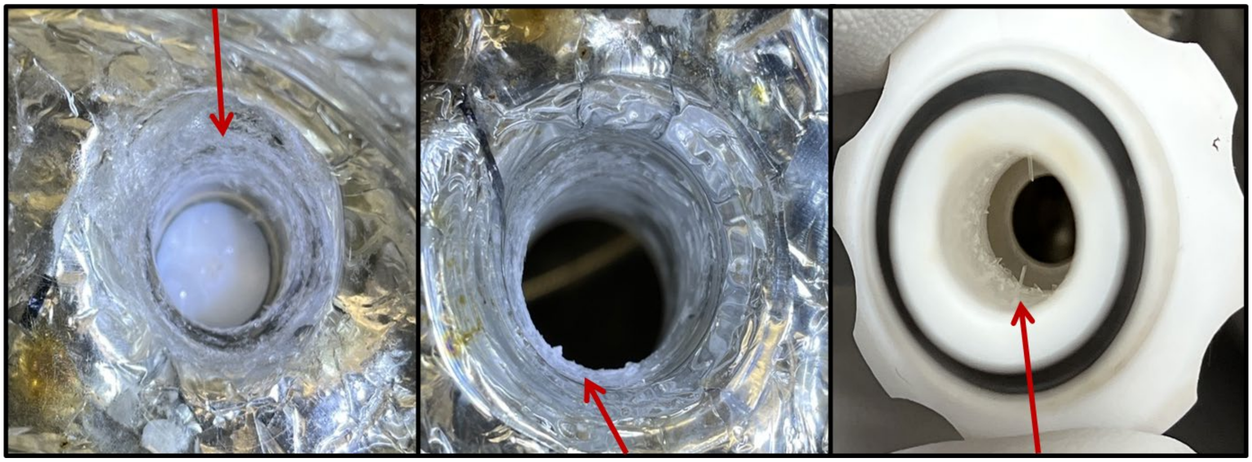
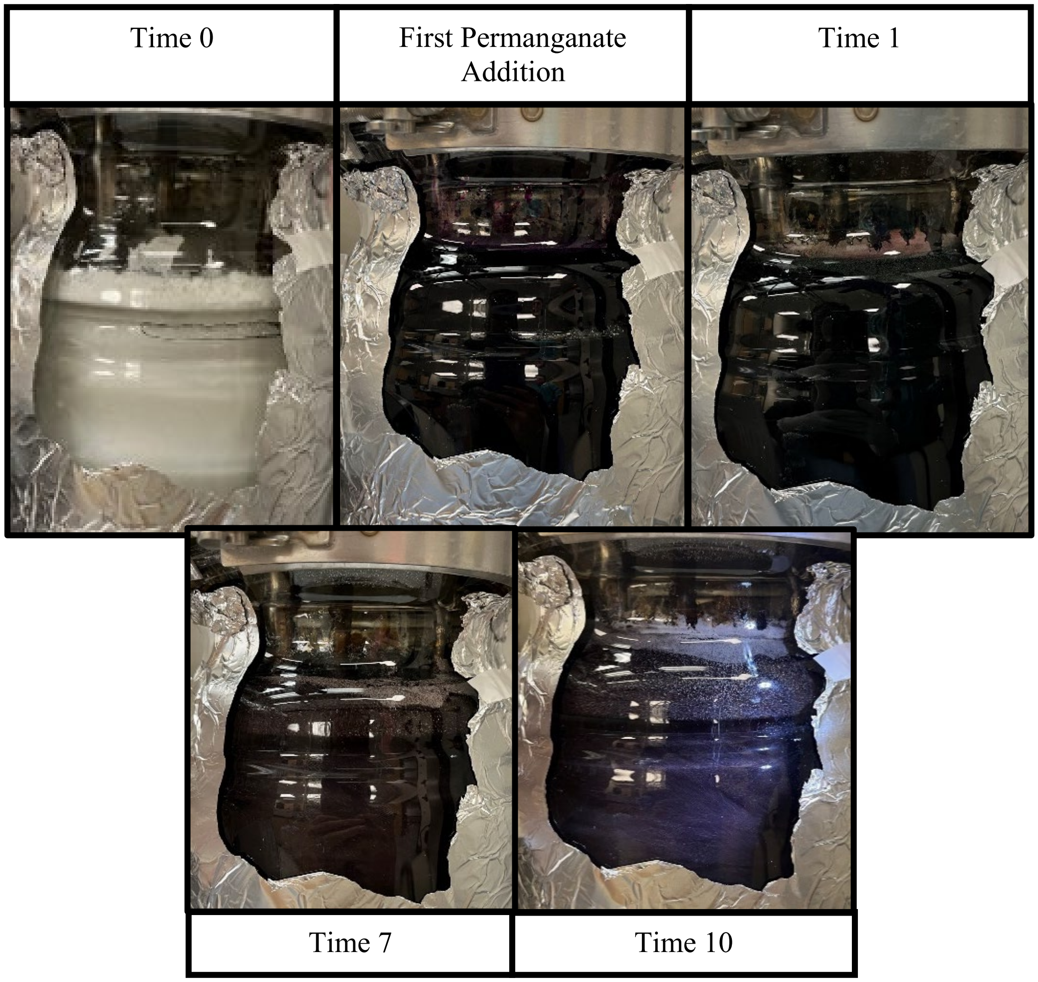


Figure 2-15 Visual observations, indicated by the red arrows, of crystals forming on the lid and inside the Teflon fitting leading to the reflux condenser for TK48-2LV-25C-1-60C-2.



Time 0

First Permanganate Addition

Time 1

Time 7

Time 10

Figure 2-16 Visual observations for TK48-2LV-60C-3.

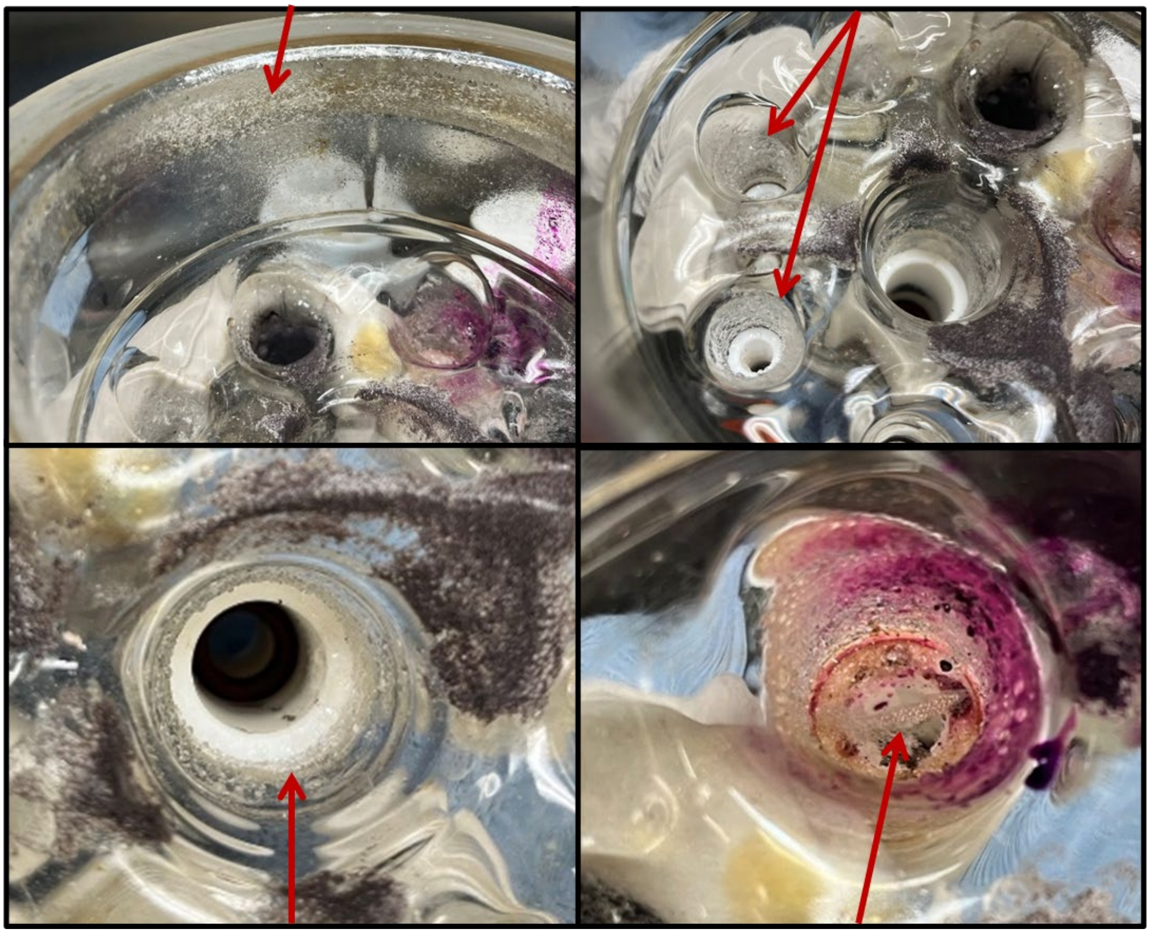


Figure 2-17 Visual observations, indicated by the red arrows, of crystals forming on the lid and vessel for TK48-2LV-60C-3. The permanganate was introduced through the port that is coated in purple.

3.0 Results and Discussion

3.1.1 Proposed Reaction Mechanisms

A balanced equation for the oxidation reaction of TPB with permanganate is proposed in Equation (1) below. For simplicity, this equation assumes the terminal products are carbon dioxide and water, yet previous reports indicate the reaction does not progress to give those reaction products under basic conditions. Instead, the reaction generates more phenol/phenoxide with a distribution of phenyl borate intermediates (3PB, 2PB, and 1PB) in the breakdown chain.[12]

$$22MnO_4^- + BC_{24}H_{20}^- + 31OH^- = 24CO_2 + 22MnO_2 + B(OH)_3 + 24H_2O \qquad (1)$$

In the range of pH 3–12, permanganate will oxidize nitrite, which results in the generation of manganese dioxide solids and nitrate as shown in Equation (2) below. In addition, this reaction will generate 2 mols of hydroxide from every 3 mols of nitrite reacted. Assuming 100% conversion of the 0.71 M nitrite in the Tank 48H base simulant to nitrate, hydroxide content would increase by 0.42 M. In the absence of carbonate, 0.42 M hydroxide would increase the simulant pH to >13, essentially nearing the hydrolysis constant of water.

$$2MnO_4^- + 3NO_2^- + H_2O = 2MnO_2 + 3NO_3^- + 2OH^- \quad (2)$$

3.1.2 Chemical Composition Results

Table 3-1 and Table 3-2 present the ICP-ES results for the 2-L vessel and shaker oven experiments, respectively. Detected analytes included aluminum, boron, barium, iron, potassium, sodium, and silicon. Other analytes were below the detection limit and not reported. Sodium concentration is a function of the salts included in the Tank 48H base simulant, sodium permanganate additions, and sodium sulfite used to quench unreacted permanganate. Al, B, K and Si concentrations increased over time in all experiments consistent with caustic etching of the borosilicate glass vessel. A fraction of the B and K ingrowth can also be attributed to TPB decomposition. The decomposition of TPB to a soluble species makes boron detectable in the analysis. Potassium can also be used as an indirect indicator of TPB decomposition, as TPB forms a complex with potassium that become insoluble in filtrate samples. When KTPB is decomposed, potassium is liberated and becomes detectable in the filtrate. However, an increase in potassium does not necessarily indicate complete phenyl borate destruction, as it does not provide information about TPB byproducts. For B and K to provide meaningful approximations of TPB decomposition, other sources of B and K need to be considered. Significant quantities of B and K originated from the borosilicate glass reactor vessels, and K is a component of the base simulant. Having no other sources of B or K, the reaction with no permanganate additions (i.e., TK48-SH-60C-BL) was used to determine a background for B and K ingrowth from the glass vessel. This background was then subtracted from analogous measurements to calculate B and K resulting from TPB decomposition. Potassium concentrations measured in "Time 0" samples were used to account for KNO_3 present in the base simulant. All reported ICP-ES data for shaker oven samples had the boron content of a matching blank sample subtracted to account for glass leaching (e.g., Time 1 sample would subtract data from Time 1 blank, but Time 56 sample would subtract data from Time 56 blank). A blank experiment was not performed on the 2-liter vessel experiments (i.e., blank, with no permanganate addition to the simulant), and thus, TK48-2LV-25C-1-60C-2 and TK48-2LV-60C-3 are reported as their measured values.

Table 3-3 (Calculation of TPB decomposition is shown in Appendix A) reveals that TPB decomposition, monitored by potassium content (i.e., filtrate), showed potassium-based decomposition ranging from 7.39% to 35.8% by the end of the last sample intervals pulled for each experiment. Gradually heating from 25°C to 60 °C had a minimal impact on TPB decomposition. Once 60 °C was obtained it was indicated that the rate of reaction increased. In experiment TK48-SH-60C-9, the decomposition of TPB at Time 1 was determined to be 24%. By Time 56, the decomposition of TPB by potassium levels had increased to 35.8%, which indicated the highest TPB decomposition by potassium. The TK48-SH-60C-111 sample indicated that with each 1.5 equivalents of permanganate added, decomposition of TPB increased, reaching as high as 32.1% for potassium. Comparatively, TK48-SH-60C-9 displayed an 11.7% increase in decomposition from Time 1 to Time 56, whereas TK48-SH-60C-111 showed a more significant increase of 30.2% from Time 1 to Time 56. The increased TPB decomposition of TK48-SH-60C-111 is likely due to the permanganate multi-strike addition; when added in small quantities it was able to react with the target reagent (i.e., TPB) instead of reagents in the simulant (e.g., sodium nitrite). The Time 56 samples for boron-based decomposition yielded inconclusive results and showed very high levels of decomposition. This suggests that glass leaching persists even after accounting for the blank samples. The 2-L vessel experiment TK48-2LV-60C-3 had better TPB decomposition than the first 2-L experiment based on potassium at 7.39% and based on boron at 34.4%. Note that the TK48-2LV-60C-3 did not run for a full two weeks after permanganate addition (Maintained at 60 °C for four days without permanganate to observe the results of TPB decomposition during heating) and would have potentially shown higher results if left to run the full two weeks. Higher temperatures resulted in higher decomposition rates for equivalent permanganate concentrations, and there was a clear correlation between permanganate concentration and TPB decomposition.

Table 3-4 shows ion chromatography (IC) anion results from the shaker oven and 2-L vessel experiments. The concentrations of chloride, a spectator ion, were similar for all measurements and provide confidence in subsampling and measurement. Oxalate concentrations remained similar for all experiments, except TK48-SH-60C-9 where oxalate was below detection limits. The appearance of sulfate is due to the use of sodium sulfite to quench unreacted permanganate. In all experiments with added permanganate, nitrite decreased with a proportional increase in nitrate. No nitrite destruction was observed in reactions without permanganate, suggesting a reaction of permanganate with nitrite as in Equation (2). As expected, complete oxidation of nitrite was observed in the reaction without TPB (i.e., TK48-SH-60C-NOTPB). Visual observations and UV-vis analyses (Section 2.3.2) confirmed that all permanganate was consumed in the reactions, suggesting permanganate that did not react with nitrite participated in a competing reaction with TPB.

Results of HPLC analysis of TPB and byproducts from shaker oven and 2-L vessel experiments are found in Table 3-5. TPB measurements were inconsistent with the added masses of KTPB, and fluctuations in measured concentration indicated inconsistencies in sample preparations. Representative sample pulls for slurry samples are difficult to pull, due to the TPB floating. Across all experiments the analytes of 4-phenylphenol, 2-phenylphenol, p-terphenyl, and m-terphenyl were below the detection limit of 50 mg/L. The HPLC method did indicate the in-growth of byproducts over time, particularly in experiments TK48-SH-60C-9, TK48-SH-60C-111, TK48-SH-25C-3-60C-3, and TK48-2LV-60C-3. This indicates that TPB decomposition is taking place.

Table 3-7 shows the free hydroxide and TIC/TOC filtrate results for the shaker oven and 2-L vessel experiments. In general, the concentration of free hydroxide decreased as a function of time with added permanganate consistent with Equation (1). Free hydroxide was relatively unchanged in the control sample (with no added permanganate) and TK48-2LV-25C-1-60C-2 indicating minimal TPB decomposition.

Table 3-1 ICP-ES filtrate results reported in mg/L for 2-L vessel experiments.

	Al	B	Ba	Fe	K	Na	Si
TK48-2LV-25C-1-60C-2 Time 0	25.5	24.5	8.78	2.24	473	124000	244
TK48-2LV-25C-1-60C-2 Time 1	7.20	11.6	2.80	2.08	471	128000	71.6
TK48-2LV-25C-1-60C-2 Time 3	7.54	13.1	2.62	2.02	481	130000	88.0
TK48-2LV-25C-1-60C-2 Time 4	8.96	16.0	2.90	2.16	475	130000	110
TK48-2LV-25C-1-60C-2 Time 5	10.4	19.5	2.76	2.14	472	131000	146
TK48-2LV-25C-1-60C-2 Time 6	12.3	27.9	2.66	2.16	479	132000	205
TK48-2LV-25C-1-60C-2 Time 7	16.3	42.0	2.92	2.30	476	131000	304
TK48-2LV-25C-1-60C-2 Time 14	44.0	182	2.32	1.82	669	140000	1140
TK48-2LV-60C-3 Time 0	15.7	21.7	5.40	3.96	454	133000	143
TK48-2LV-60C-3 Time 1	32.7	79.2	6.00	4.60	548	140000	528
TK48-2LV-60C-3 Time 7	52.5	170	4.88	3.68	606	138000	1180
TK48-2LV-60C-3 Time 10	63.3	208	4.62	3.58	617	134000	1490

Table 3-2 ICP-ES filtrate results reported in mg/L for shaker oven experiments.

	Al	B	Ba	Fe	K	Na	Si
TK48-SH-25C-1-60C-2 Time 0	33.7	29.2	9.56	2.84	417	126000	310
TK48-SH-25C-1-60C-2 Time 1	30.1	25.7	2.62	1.90	444	134000	276
TK48-SH-25C-1-60C-2 Time 8	64.0	169	3.08	2.20	596	161000	1190
TK48-SH-25C-1-60C-2 Time 14	117	421	1.72	1.28	767	147000	3070
TK48-SH-25C-1-60C-2 Time 56	288	2780	<1.22	<0.648	1010	143000	24200
TK48-SH-25C-3-60C-3 Time 0	20.3	19.8	7.94	1.54	466	123000	195
TK48-SH-25C-3-60C-3 Time 1	33.4	32.2	3.38	2.56	559	134000	290
TK48-SH-25C-3-60C-3 Time 7	50.1	123	2.60	1.98	605	144000	869
TK48-SH-25C-3-60C-3 Time 28	54.1	1110	8.74	6.06	784	142000	9450
TK48-SH-25C-3-60C-3 Time 56	153	2280	<1.22	<0.648	1070	154000	18500
TK48-SH-60C-BL Time 0	20.3	19.4	8.44	1.66	478	125000	195
TK48-SH-60C-BL Time 1	30.6	29.7	9.98	2.28	473	122000	303
TK48-SH-60C-BL Time 3	23.3	24.0	8.20	1.82	469	124000	252
TK48-SH-60C-BL Time 4	25.6	29.6	8.18	1.74	464	125000	300
TK48-SH-60C-BL Time 5	33.5	44.3	8.42	2.32	462	125000	430
TK48-SH-60C-BL Time 6	32.6	53.4	7.68	1.98	463	124000	510
TK48-SH-60C-BL Time 7	40.6	80.4	7.04	1.90	458	126000	758
TK48-SH-60C-BL Time 14	128	329	6.32	3.48	490	129000	3080
TK48-SH-60C-BL Time 56	197	2060	18	5.5	665	126000	18800
TK48-SH-60C-NOTPB Time 0	19.8	18.3	9.26	1.88	465	129000	192
TK48-SH-60C-NOTPB Time 1	57.9	141	4.02	3.08	675	171000	1090
TK48-SH-60C-NOTPB Time 7	103	433	3.00	2.58	716	165000	3470
TK48-SH-60C-NOTPB Time 14	21.5	885	3.88	3.32	761	163000	6950
TK48-SH-60C-NOTPB Time 56	86.2	3200	<1.22	<0.648	982	156000	27900
TK48-SH-60C-9 Time 0	19.4	19.0	8.60	1.62	451	127000	193
TK48-SH-60C-9 Time 1	56.8	220	5.82	4.86	982	165000	974
TK48-SH-60C-9 Time 7	93.0	500	2.46	1.88	1080	160000	2980
TK48-SH-60C-9 Time 14	21.7	888	2.84	2.56	1110	162000	6040
TK48-SH-60C-9 Time 56	246	2550	<1.22	<0.648	1240	152000	21100
TK48-SH-60C-111 Time 0	20.8	23.0	8.50	1.80	443	125000	206
TK48-SH-60C-111 Time 1	50.3	109	2.86	2.28	486	139000	900
TK48-SH-60C-111 Time 7	82.4	325	2.58	2.00	624	136000	2530
TK48-SH-60C-111 Time 14	23.6	688	3.00	2.46	833	146000	5140
TK48-SH-60C-111 Time 28	82.0	1490	8.38	5.94	1030	149000	11800
TK48-SH-60C-111 Time 56	238	2800	<1.22	<0.648	1150	153000	23200
TK48-SH-60C-33 Time 0	23.1	24.4	8.70	2.00	476	126000	224
TK48-SH-60C-33 Time 1	55.7	152	2.74	2.16	617	144000	1100
TK48-SH-60C-33 Time 28	140	1940	8.56	6.06	902	138000	16800
TK48-SH-60C-33 Time 56	254	3110	<1.22	<0.648	1140	150000	25200

Table 3-3 TPB decomposition from ICP-ES measurements of potassium and boron.[a]

	Measured K (mol/L) [b]	TPB Decomposition (%) from K	Measured B (mol/L) [c]	TPB Decomposition (%) from B
TK48-SH-25C-1-60C-2 Time 0	0.000	0.00	0.001	1.62
TK48-SH-25C-1-60C-2 Time 1	0.001	1.22	0.000	-0.66
TK48-SH-25C-1-60C-2 Time 8	0.005	8.12	0.008	14.6
TK48-SH-25C-1-60C-2 Time 14	0.009	15.9	0.009	15.2
TK48-SH-25C-1-60C-2 Time 56	0.015	26.9	0.067	119
TK48-SH-25C-3-60C-3 Time 0	0.000	0.00	0.000	0.066
TK48-SH-25C-3-60C-3 Time 1	0.002	4.22	0.000	0.413
TK48-SH-25C-3-60C-3 Time 7	0.004	6.31	0.004	7.036
TK48-SH-25C-3-60C-3 Time 28	0.008	14.4	NA	NA
TK48-SH-25C-3-60C-3 Time 56	0.015	27.4	0.020	36.3
TK48-SH-60C-9 Time 0	0.000	0.00	0.000	-0.07
TK48-SH-60C-9 Time 1	0.014	24.1	0.018	31.4
TK48-SH-60C-9 Time 7	0.016	28.5	0.039	69.4
TK48-SH-60C-9 Time 14	0.017	29.9	0.052	92.3
TK48-SH-60C-9 Time 56	0.020	35.8	0.045	80.9
TK48-SH-60C-111 Time 0	0.00	0.00	0.000	0.59
TK48-SH-60C-111 Time 1	0.001	1.95	0.007	13.1
TK48-SH-60C-111 Time 7	0.005	8.21	0.023	40.4
TK48-SH-60C-111 Time 14	0.010	17.7	0.003	59.3
TK48-SH-60C-111 Time 28	0.015	26.6	NA	NA
TK48-SH-60C-111 Time 56	0.018	32.1	0.259	122
TK48-SH-60C-33 Time 0	0.000	0.00	0.000	0.83
TK48-SH-60C-33 Time 1	0.004	6.40	0.011	20.2
TK48-SH-60C-33 Time 28	0.011	19.3	NA	NA
TK48-SH-60C-33 Time 56	0.017	30.1	0.097	173
TK48-2LV-25C-1-60C-2 Time 0	0.000	0.00	0.002	4.05
TK48-2LV-25C-1-60C-2 Time 1	0.000	-0.09	0.001	2.00
TK48-2LV-25C-1-60C-2 Time 3	0.000	0.36	0.001	2.20
TK48-2LV-25C-1-60C-2 Time 4	0.000	0.09	0.001	2.60
TK48-2LV-25C-1-60C-2 Time 5	0.000	-0.05	0.002	3.20
TK48-2LV-25C-1-60C-2 Time 6	0.000	0.27	0.003	4.60
TK48-2LV-25C-1-60C-2 Time 7	0.000	0.14	0.004	6.90
TK48-2LV-25C-1-60C-2 Time 14	0.005	8.89	0.017	30.1
TK48-2LV-60C-3 Time 0	0.000	0.00	0.002	3.58
TK48-2LV-60C-3 Time 1	0.002	4.36	0.007	13.1
TK48-2LV-60C-3 Time 7	0.004	6.89	0.016	28.1
TK48-2LV-60C-3 Time 10	0.004	7.39	0.019	34.4

[a] Calculation example TPB decomposition from K and B are performed in Appendix A.

[b] Measured K in Time 0 samples was subtracted from all samples to account for KNO_3.

[c] The BL experiment was subtracted from all experiments, except for TK48-2LV-25C-1-60C-2, and TK48-2LV-60C-3 to account for glass leaching.

NA = Not applicable, a Time 28 Blank sample was not pulled and could not be subtracted out of the measured B.

Table 3-4 IC anions filtrate results reported in mol/L for shaker oven and 2 L-vessel experiments.

	Chloride	Nitrite	Nitrate	Sulfate	Oxalate
TK48-SH-25C-1-60C-2 Time 0	0.021	0.698	0.260	<0.00104	0.009
TK48-SH-25C-1-60C-2 Time 1	0.020	0.654	0.282	0.213	0.008
TK48-SH-25C-1-60C-2 Time 8	0.020	0.504	0.410	0.198	0.005
TK48-SH-25C-1-60C-2 Time 14	0.021	0.504	0.424	0.070	0.007
TK48-SH-25C-3-60C-3 Time 0	0.021	0.700	0.271	<0.00104	0.009
TK48-SH-25C-3-60C-3 Time 1	0.021	0.591	0.352	0.199	0.009
TK48-SH-25C-3-60C-3 Time 7	0.021	0.489	0.458	0.101	0.008
TK48-SH-25C-3-60C-3 Time 28	0.021	0.478	0.687	0.064	0.012
TK48-SH-60C-BL Time 0	0.021	0.674	0.269	<0.00104	0.008
TK48-SH-60C-BL Time 1	0.021	0.687	0.273	<0.00104	0.009
TK48-SH-60C-BL Time 3	0.021	0.683	0.274	<0.00104	0.009
TK48-SH-60C-BL Time 4	0.021	0.698	0.279	<0.00104	0.009
TK48-SH-60C-BL Time 5	0.021	0.685	0.279	<0.00104	0.009
TK48-SH-60C-BL Time 6	0.021	0.702	0.282	<0.00104	0.009
TK48-SH-60C-BL Time 7	0.021	0.698	0.285	<0.00104	0.009
TK48-SH-60C-BL Time 14	0.021	0.704	0.294	<0.00104	0.010
TK48-SH-60C-NOTPB Time 0	0.021	0.702	0.266	<0.00104	0.008
TK48-SH-60C-NOTPB Time 1	0.021	0.115	0.768	0.982	0.008
TK48-SH-60C-NOTPB Time 7	0.022	0.004	0.952	0.177	0.009
TK48-SH-60C-NOTPB Time 14	0.022	<0.002	1.053	0.160	0.010
TK48-SH-60C-9 Time 0	0.022	0.733	0.295	<0.00104	0.009
TK48-SH-60C-9 Time 1	0.021	0.190	0.700	0.449	<0.00114
TK48-SH-60C-9 Time 7	0.021	0.148	0.729	0.012	<0.00114
TK48-SH-60C-9 Time 14	0.021	0.148	0.731	0.130	<0.00114
TK48-SH-60C-111 Time 0	0.020	0.678	0.264	<0.00104	0.008
TK48-SH-60C-111 Time 1	0.020	0.596	0.340	0.377	0.011
TK48-SH-60C-111 Time 7	0.021	0.591	0.353	0.150	0.011
TK48-SH-60C-111 Time 14	0.021	0.502	0.418	0.086	0.010
TK48-SH-60C-111 Time 28	0.021	0.502	0.418	0.086	0.010
TK48-SH-60C-33 Time 0	0.021	0.696	0.284	<0.00104	0.008
TK48-SH-60C-33 Time 1	0.021	0.506	0.435	0.134	0.010
TK48-SH-60C-33 Time 28	0.021	0.500	0.682	0.045	0.017
TK48-2LV-25C-1-60C-2 Time 0	0.020	0.672	0.269	<0.00104	0.008
TK48-2LV-25C-1-60C-2 Time 1	0.021	0.648	0.297	0.099	0.008
TK48-2LV-25C-1-60C-2 Time 3	0.021	0.654	0.308	0.105	0.008
TK48-2LV-25C-1-60C-2 Time 4	0.021	0.646	0.324	0.128	0.009
TK48-2LV-25C-1-60C-2 Time 5	0.021	0.643	0.329	0.130	0.009
TK48-2LV-25C-1-60C-2 Time 6	0.021	0.654	0.337	0.104	0.009
TK48-2LV-25C-1-60C-2 Time 7	0.021	0.637	0.345	0.101	0.009
TK48-2LV-25C-1-60C-2 Time 14	0.0022	0.476	0.481	0.062	0.009
TK48-2LV-60C-3 Time 0	0.020	0.693	0.495	<0.00104	0.008
TK48-2LV-60C-3 Time 1	0.020	0.513	0.623	0.125	0.008
TK48-2LV-60C-3 Time 7	0.021	0.461	0.681	0.056	0.009
TK48-2LV-60C-3 Time 10	0.021	0.467	0.706	0.064	0.010

Table 3-5 HPLC slurry analysis of TPB and byproducts in mg/L for shaker oven and 2-L vessel experiments.

	TPB	3PB	2PB	PBA	Phenol	Biphenyl
TK48-SH-25C-1-60C-2 Time 0	2680	<40	<80	<50	<50	<50
TK48-SH-25C-1-60C-2 Time 8	1030	<40	<80	<50	<50	<50
TK48-SH-25C-1-60C-2 Time 14	480	<40	<80	<50	<50	<50
TK48-SH-25C-3-60C-3 Time 0	2975	<40	<80	<50	<50	<50
TK48-SH-25C-3-60C-3 Time 28	11300	<40	173	300	109	<50
TK48-SH-60C-BL Time 0	3740	<40	<80	<50	<50	<50
TK48-SH-60C-BL Time 1	9920	<40	<80	<50	<50	<50
TK48-SH-60C-BL Time 3	9220	<40	<80	<50	<50	<50
TK48-SH-60C-BL Time 4	8940	<40	45.8	<50	<50	<50
TK48-SH-60C-BL Time 5	5980	<40	<80	<50	<50	<50
TK48-SH-60C-BL Time 6	9160	<40	<80	<50	<50	<50
TK48-SH-60C-BL Time 7	13700	<40	<80	<50	<50	<50
TK48-SH-60C-BL Time 14	15966	<40	<80	<50	<50	<50
TK48-SH-60C-9 Time 0	1810	<40	<80	<50	<50	<50
TK48-SH-60C-9 Time 14	3180	<40	134	<50	<50	<50
TK48-SH-60C-111 Time 0	9580	<40	<80	<50	<50	<50
TK48-SH-60C-111 Time 14	5480	<40	<80	612	160	61.6
TK48-SH-60C-33 Time 0	4650	<40	<80	<50	<50	<50
TK48-SH-60C-33 Time 28	7680	<40	<80	<50	<50	<50
TK48-2LV-25C-1-60C-2 Time 3	2866	<40	<80	<50	<50	<50
TK48-2LV-25C-1-60C-2 Time 4	3441	<40	<80	<50	<50	<50
TK48-2LV-25C-1-60C-2 Time 5	3175	<40	<80	<50	<50	<50
TK48-2LV-25C-1-60C-2 Time 6	3008	<40	<80	<50	<50	<50
TK48-2LV-25C-1-60C-2 Time 7	2980	<40	<80	<50	<50	<50
TK48-2LV-25C-1-60C-2 Time 14	<200	<40	<80	<50	<50	<50
TK48-2LV-60C-3 Time 0	1066	<40	<80	<50	<50	<50
TK48-2LV-60C-3 Time 1	12241	<40	<80	69.6	110	156
TK48-2LV-60C-3 Time 7	9433	<40	<80	232	90.8	186
TK48-2LV-60C-3 Time 10	5300	<40	<80	183	120	123

Table 3-6 HPLC analysis for TK48-SH-60C-111 Filtrate of TPB and byproducts in mg/L

	TPB	3PB	2PB	PBA	Phenol	Biphenyl
TK48-SH-60C-111 Time 56	<30	<30	<30	622	130	<30

Table 3-7 Free hydroxide and TIC/TOC results for shaker oven and 2-L vessel experiments.

	Free OH (M)	TIC (µg C/mL)	TOC (µg C/mL)
TK48-SH-25C-1-60C-2 Time 0	1.18	20260	353
TK48-SH-25C-1-60C-2 Time 1	1.22	NM	NM
TK48-SH-25C-1-60C-2 Time 8	1.12	NM	NM
TK48-SH-25C-1-60C-2 Time 14	1.01	17000	882
TK48-SH-25C-3-60C-3 Time 0	1.20	18700	396
TK48-SH-25C-3-60C-3 Time 1	1.22	NM	NM
TK48-SH-25C-3-60C-3 Time 7	1.19	NM	NM
TK48-SH-25C-3-60C-3 Time 28	0.771	NM	NM
TK48-SH-60C-BL Time 0	1.22	17100	326
TK48-SH-60C-BL Time 1	1.21	NM	NM
TK48-SH-60C-BL Time 3	1.13	NM	NM
TK48-SH-60C-BL Time 4	1.18	NM	NM
TK48-SH-60C-BL Time 5	1.13	NM	NM
TK48-SH-60C-BL Time 6	1.15	NM	NM
TK48-SH-60C-BL Time 7	1.20	NM	NM
TK48-SH-60C-BL Time 14	1.07	17300	392
TK48-SH-60C-NOTPB Time 0	1.24	17100	315
TK48-SH-60C-NOTPB Time 1	1.25	NM	NM
TK48-SH-60C-NOTPB Time 7	1.09	NM	NM
TK48-SH-60C-NOTPB Time 14	0.71	17000	326
TK48-SH-60C-9 Time 0	1.22	15900	914
TK48-SH-60C-9 Time 1	1.12	NM	NM
TK48-SH-60C-9 Time 7	0.965	NM	NM
TK48-SH-60C-9 Time 14	0.732	NM	NM
TK48-SH-60C-111 Time 0	1.22	16600	324
TK48-SH-60C-111 Time 1	1.19	NM	NM
TK48-SH-60C-111 Time 7	1.10	NM	NM
TK48-SH-60C-111 Time 14	0.940	NM	NM
TK48-SH-60C-111 Time 28	0.705	16900	928
TK48-SH-60C-33 Time 0	1.18	NM	NM
TK48-SH-60C-33 Time 1	1.2	NM	NM
TK48-SH-60C-33 Time 28	0.493	NM	NM
TK48-2LV-25C-1-60C-2 Time 0	1.22	17300	321
TK48-2LV-25C-1-60C-2 Time 1	1.23	NM	NM
TK48-2LV-25C-1-60C-2 Time 3	1.23	NM	NM
TK48-2LV-25C-1-60C-2 Time 4	1.19	NM	NM
TK48-2LV-25C-1-60C-2 Time 5	1.25	NM	NM
TK48-2LV-25C-1-60C-2 Time 6	1.23	NM	NM
TK48-2LV-25C-1-60C-2 Time 7	1.23	NM	NM
TK48-2LV-25C-1-60C-2 Time 14	1.22	16400	643
TK48-2LV-60C-3 Time 0	1.23	NM	NM
TK48-2LV-60C-3 Time 1	1.27	NM	NM
TK48-2LV-60C-3 Time 7	1.18	NM	NM
TK48-2LV-60C-3 Time 10	1.16	NM	NM

NM = Not Measured

3.1.3 UV-Vis Results

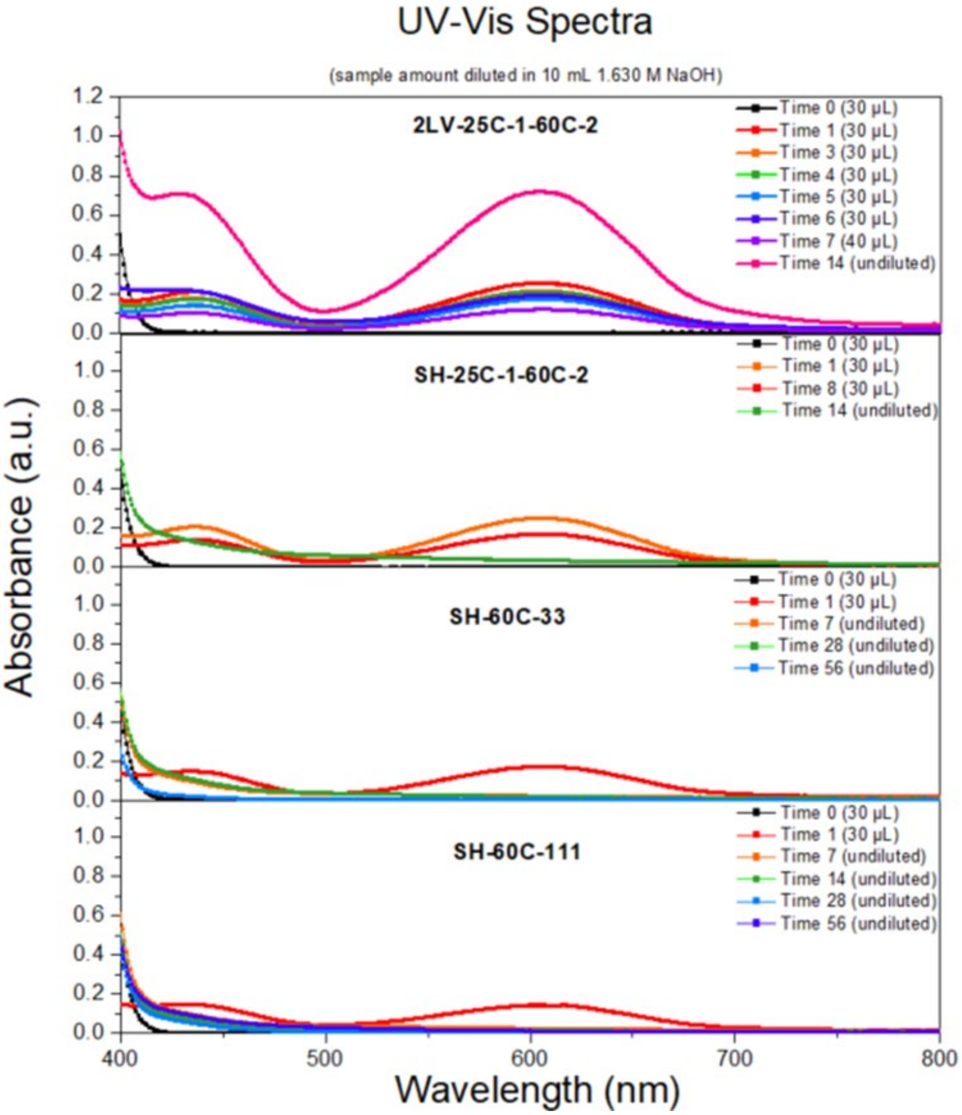


Figure 3-1 UV-vis spectra of manganate species over time for shaker table and 2 L-vessel experiments.

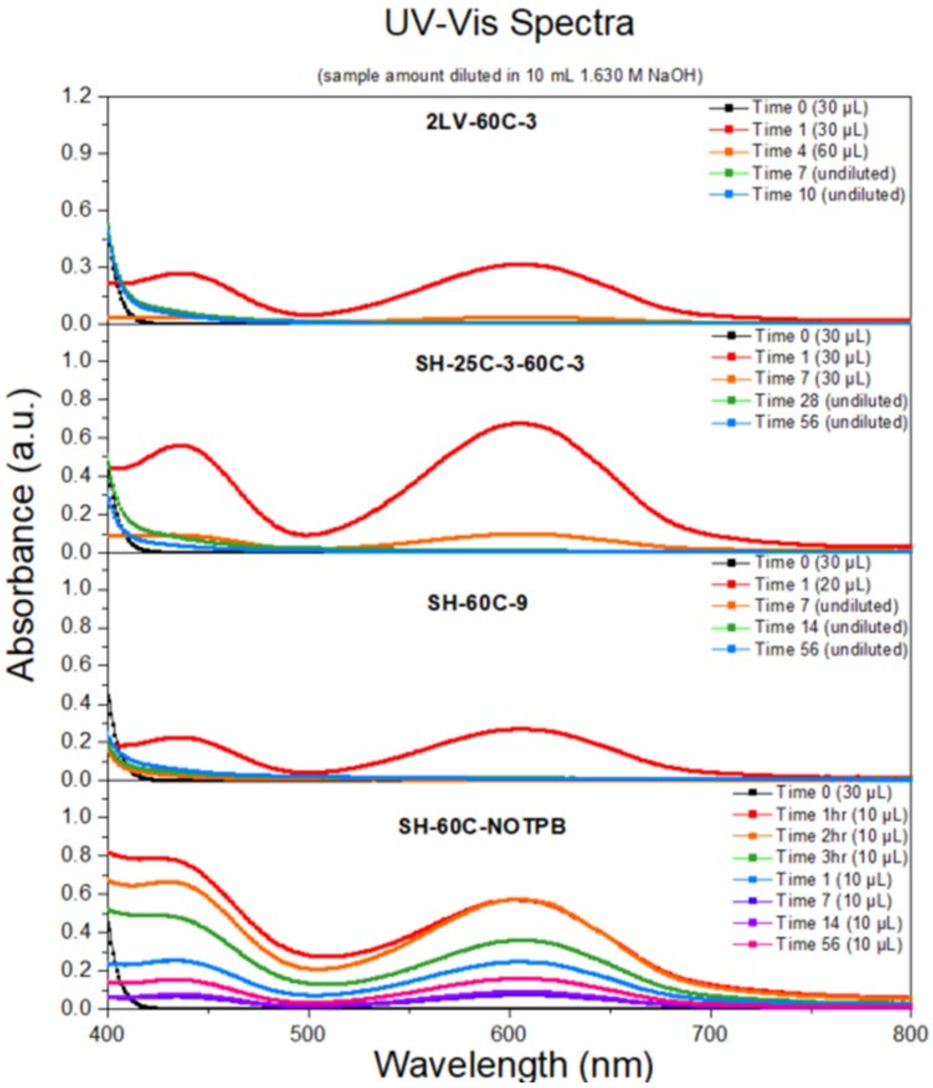


Figure 3-2 UV-vis spectra of manganate species over time for shaker table and 2 L-vessel experiments.

Results of UV-vis spectroscopy are shown above in Figure 3-1 and Figure 3-2. The spectra were truncated to the region of interest, primarily displaying two absorbance bands around 607 nm (manganate, MnO_4^{2-}) and 437 nm (unreacted permanganate, MnO_4^{-}). Oxidation of permanganate to manganate is clearly observed by the characteristic higher wavelength (and lower intensity) bands seen in our results, centered at 607 nm. Further oxidation to hypomanganate (MnO_4^{3-}) would display an extremely weak signal around 670 nm and was not observed in filtered solutions of red-brown manganese oxide solids (MnO_2). Time zero samples taken before permanganate addition provide a clear baseline with no interfering data. Since concentration of permanganate directly correlates to absorbance intensity in this region, a calibration curve was prepared to translate the spectra to a quantitative expression of permanganate oxidation and concentration decay over time in solution, as seen in Figure 3-3. Note that samples were pulled before permanganate strikes and thus no sharp increase in signal is shown after additions.

While the first sample after sodium permanganate addition in all but one of the experiments was taken at Time 1 (24 hours after sodium permanganate addition), the “NOTPB” test shows that there is a remarkable reactivity within the first 24-hour period due to nitrite oxidation. A theoretical point immediately after permanganate additions can be considered based on the equivalent molar ratio of sodium permanganate added at each interval. Each “equivalent” corresponds to 56 mM TPB and thus would spike the solution to the 56 mM level, shown by the permanganate absorbance. While TPB is not the only organic compound present, nor the only species responsible for permanganate oxidation, some conclusions can be made from the suite of UV-vis studies. First, the rate of oxidation can be correlated to increased concentrations of added permanganate, though complex reactions and lack of repeated trials leaves this open to interpretation. Second, notably, the time to complete reaction in all cases is less than 2 weeks except for the NOTPB trial, which never fully reacted (i.e., nitrite oxidation was completed). Third, this is a good indicator of overall reaction time, as well as confirmation that the TPB and permanganate contribute to a reaction that consumes the difference in measured permanganate between the two trials of 9 equivalent additions (with and without TPB). Further studies of reaction rate and mechanism would require replicate testing and benefit from a smaller delay during sampling at the beginning of the test, where the majority of the permanganate reactivity occurs.

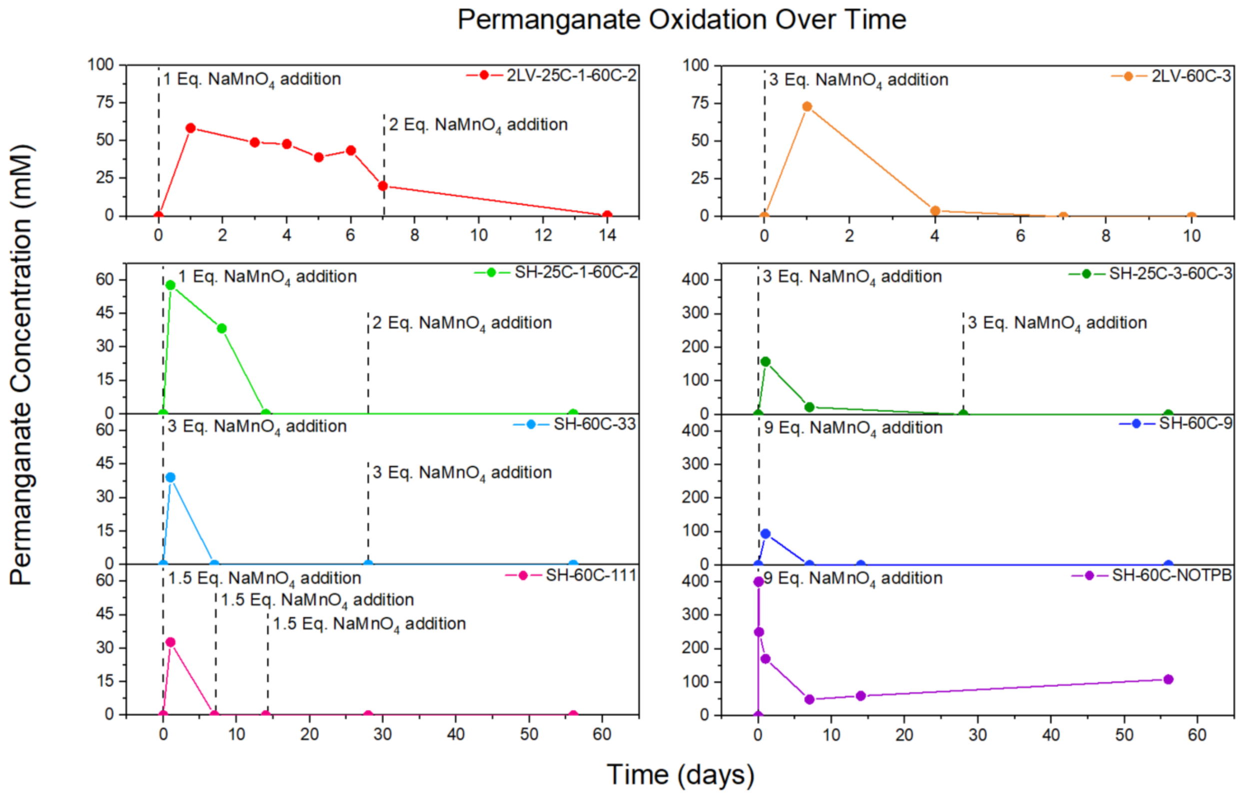


Figure 3-3 Permanganate oxidation over time for shaker table and 2 L vessel experiments.

3.1.4 NMR Results

Initial method development for ^1H (standard method and WATERGATE), inverse-gated ^{13}C, and decoupled ^{11}B NMR, described in Appendix B, has led to a general understanding of measuring aqueous solutions with a high pH and multiple salts present while observing organic resonances and not diluting the samples through co-axial insert methodology. Upon completion of these initial method development tests, a series of samples (described in Table 2-6) were collected with the P3919GP (4.9 ppm offset frequency) and proton methods at 64-scans to average each. Signals are labeled based on Figure 3-4 and the corresponding signal in each subsequent table is noted with its integration value and peak identification. The spectra of each test series are shown in Figure 3-5 through Figure 3-12 for water suppression and Figure B-5 through Figure B-13 for standard proton. The NMR data is visually scaled to observe the growth of signals, but relative integration values are included as tables below each test series to compare between test series (Table 3-8 through Table 3-15 for water suppression and Table B-1 through Table B-9 for standard proton). Figure B-14 shows the water suppression NMR spectrum of TK48-SH-60C-NOTPB, containing no aromatic signals, with relative integrations shown in Table B-10. The TMSP integration was always calibrated as a 9H singlet in the range of −0.01 – 0.01 ppm, due to the singlet splitting electronic nature of the protons and nine protons in the three methyl functionalities on the silyl group. This TMSP peak is used as an integration reference that scales all other integrations (i.e., relative integrations). If a signal is noted as "low signal-to-noise (low s/n)," there are weakly-observed peaks in the baseline but are not useful for any meaningful integration due to low intensity. The chemical shifts are noted in ppm.

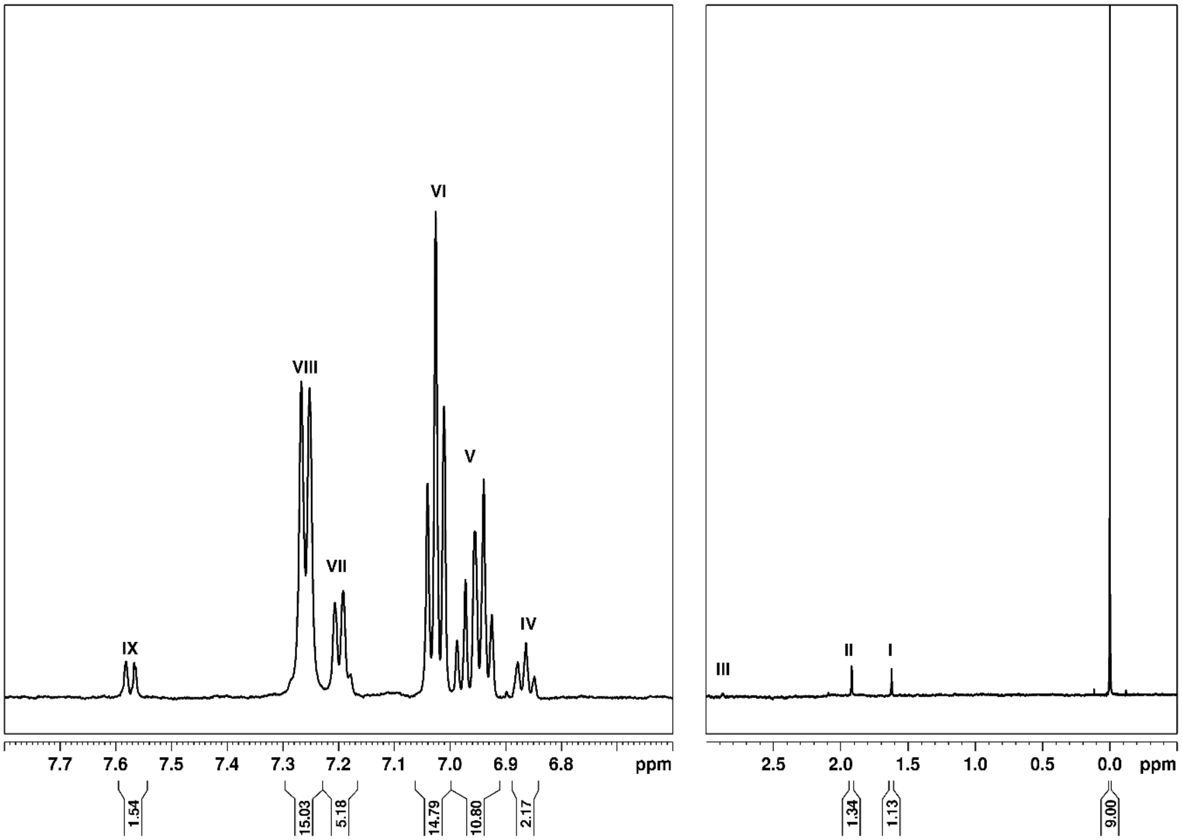


Figure 3-4 Labeled peak identification reference for NMR spectra integrations in integration tables and discussion.

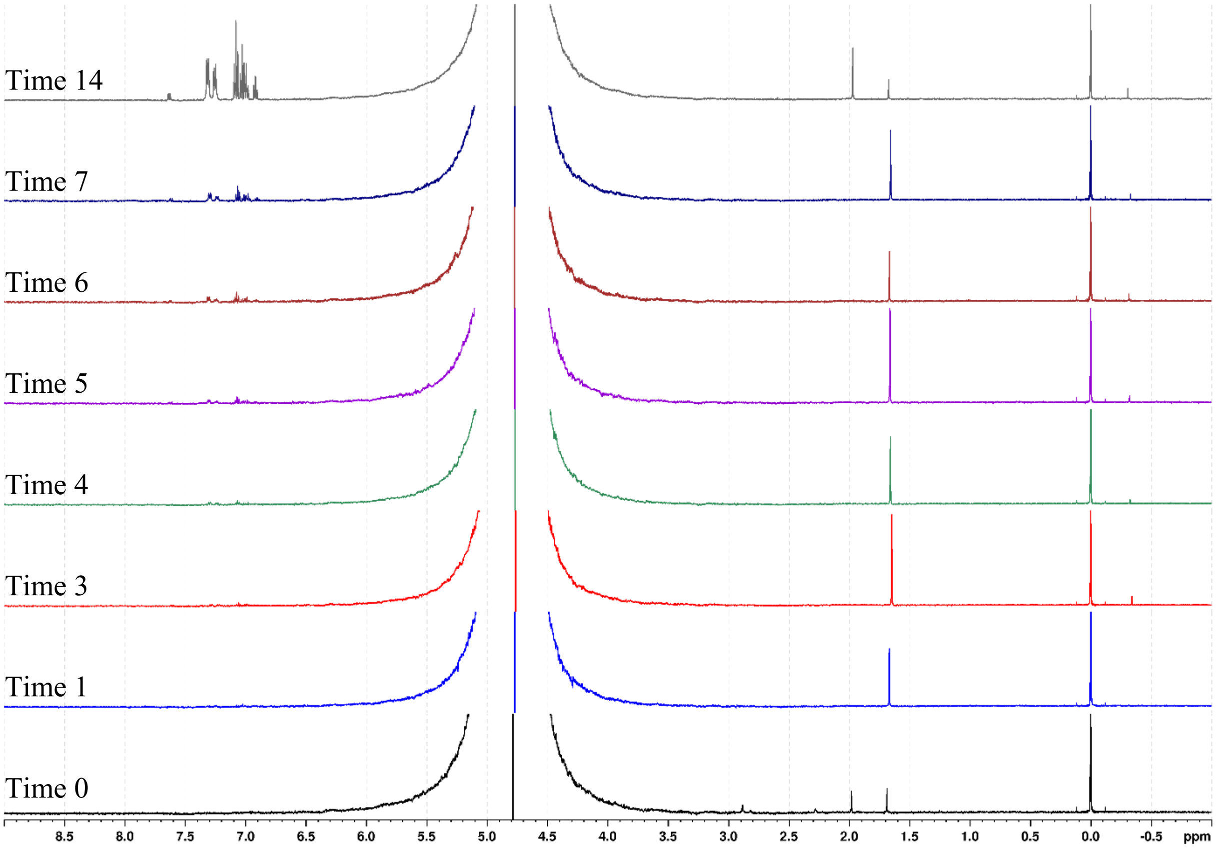


Figure 3-5 ^{1}H NMR spectra of TK48-2LV-25C-1-60C-2 test series using P3919GP WATERGATE method. Samples were axis calibrated to 0.0 ppm with TMSP/D_2O reference. The black, blue, red, green, purple, maroon, navy, and grey spectra correspond to Time 0, Time 1, Time 3, Time 4, Time 5, Time 6, Time 7, and Time 14, respectively (listed from bottom to top). The absence of signal between ~5.3 and 4.5 ppm is due to the high intensity water signal exceeding the Y-axis scaling.

Table 3-8 Relative integration (ReI) and chemical shift (in ppm) values of signals standardized to the 9H singlet signal for TMSP for TK48-2LV-25C-1-60C-2 (P3919GP WATERGATE method).

Time	I ReI, ppm	II ReI, ppm	III ReI, ppm	IV ReI, ppm	V ReI, ppm	VI ReI, ppm	VII ReI, ppm	VIII ReI, ppm	IX ReI, ppm
0	0.85, 1.69	0.90, 1.98	0.94, 2.89	low s/n	low s/n	low s/n	low s/n	low s/n	low s/n
1	1.87, 1.67	– –	– –	low s/n	low s/n	low s/n	low s/n	low s/n	low s/n
3	3.20, 1.65	– –	– –	low s/n	low s/n	low s/n	low s/n	low s/n	low s/n
4	2.26, 1.66	– –	– –	low s/n	low s/n	low s/n	low s/n	low s/n	low s/n
5	3.12, 1.66	– –	– –	low s/n	low s/n	low s/n	low s/n	low s/n	low s/n
6	1.67, 1.66	– –	– –	low s/n	low s/n	low s/n	low s/n	low s/n	low s/n
7	2.47, 1.66	– –	– –	0.81, 6.90	1.56, 6.99	1.34, 7.07	0.92, 7.24	1.48, 7.30	0.51, 7.62
14	0.81, 1.67	– –	– –	2.42, 6.92	7.46, 7.01	6.19, 7.08	4.72, 7.25	5.94, 7.32	0.81, 7.63

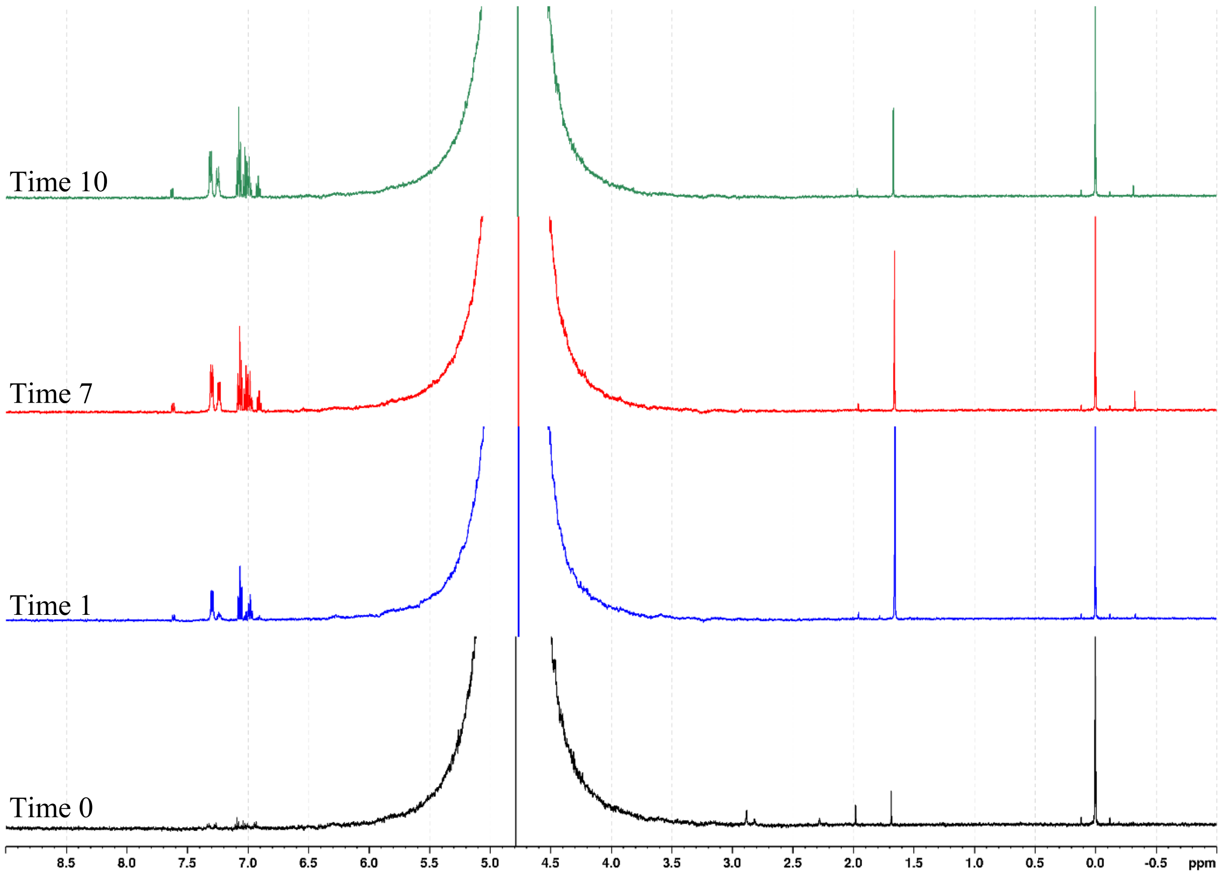


Figure 3-6 ^{1}H NMR spectra of TK48-2LV-60C-3 test series using P3919GP WATERGATE method. Samples were axis calibrated to 0.0 ppm with TMSP/D_2O reference. The black, blue, red, and green spectra correspond to Time 0, Time 1, Time 7, and Time 10, respectively (listed from bottom to top). The absence of signal between ~5.3 and 4.5 ppm is due to the high intensity water signal exceeding the Y-axis scaling.

Table 3-9 Relative integration (ReI) and chemical shift (in ppm) values of signals standardized to the 9H singlet signal for TMSP for TK48-2LV-60C-3 (P3919GP WATERGATE).

Time	I	II	III	IV	V	VI	VII	VIII	IX
	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm
0	0.84, 1.69	– –	– –	low s/n	low s/n	low s/n	low s/n	low s/n	low s/n
1	6.33, 1.65	– –	– –	0.58, 6.90	2.27, 6.99	2.79, 7.07	1.02, 7.24	2.70, 7.30	0.51, 7.61
7	3.22, 1.65	– –	– –	1.40, 6.91	4.37, 7.00	3.96, 7.07	2.76, 7.24	3.86, 7.30	0.62, 7.62
10	1.51, 1.67	– –	– –	1.31, 6.91	4.19, 7.01	3.90, 7.08	2.56, 7.25	3.76, 7.31	0.63, 7.63

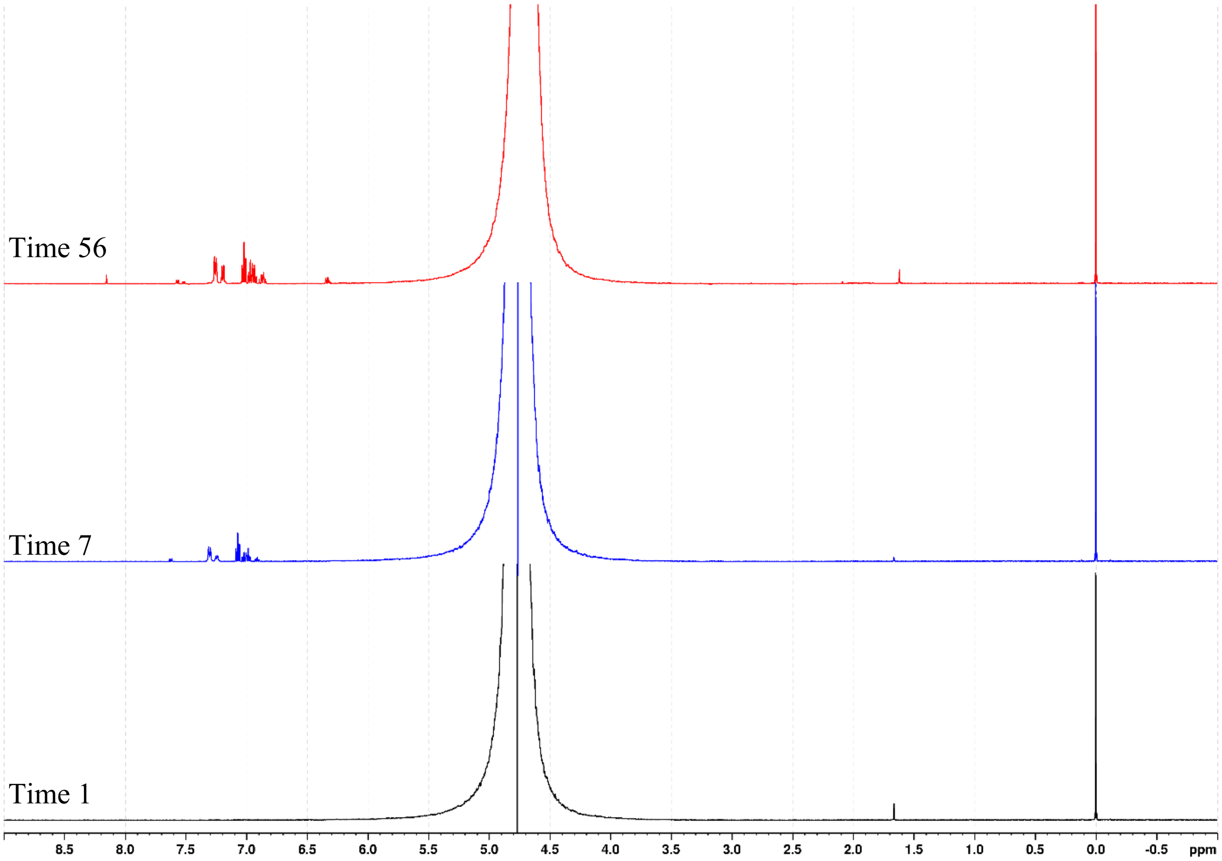


Figure 3-7 ^{1}H NMR spectra of TK48-SH-25C-1-60C-2 test series using P3919GP WATERGATE method. Samples were axis calibrated to 0.0 ppm with TMSP/D_2O reference. The black, blue, and red spectra correspond to Time 1, Time 7, and Time 56, respectively (listed from bottom to top). The absence of signal between ~5.3 and 4.5 ppm is due to the high intensity water signal exceeding the Y-axis scaling.

Table 3-10 Relative integration (ReI) and chemical shift (in ppm) values of signals standardized to the 9H singlet signal for TMSP for TK48-SH-25C-1-60C-2 (P3919GP WATERGATE).

Time	I ReI, ppm	II ReI, ppm	III ReI, ppm	IV ReI, ppm	V ReI, ppm	VI ReI, ppm	VII ReI, ppm	VIII ReI, ppm	IX ReI, ppm
1	1.67, 1.66	– –	– –	low s/n	low s/n	low s/n	low s/n	low s/n	low s/n
7	0.55, 1.66	– –	– –	1.27, 6.91	4.84, 7.00	5.46, 7.07	2.69, 7.25	5.45, 7.31	0.81, 7.62
56	1.20, 1.62	0.49, 2.09	– –	4.34, 6.87	10.17, 6.95	9.82, 7.03	6.56, 7.19	10.67, 7.26	1.13, 7.57

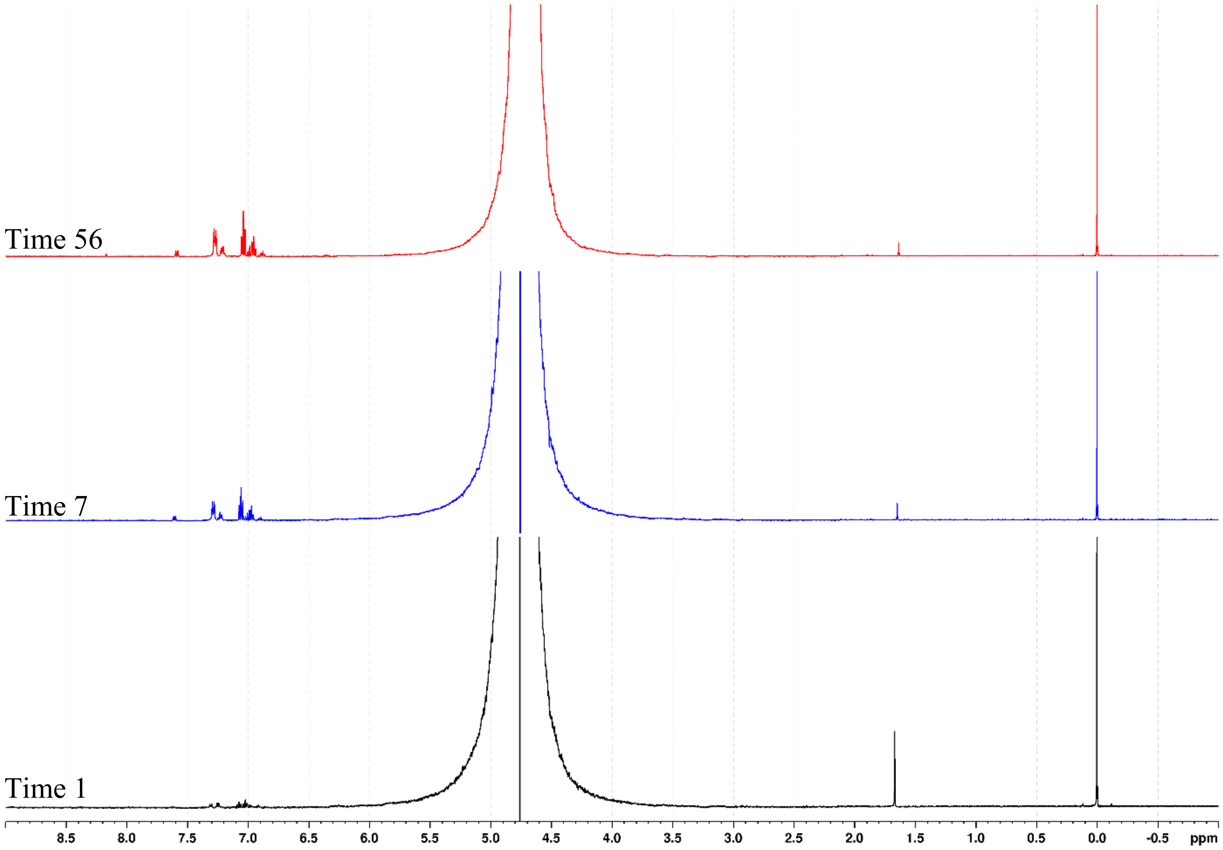


Figure 3-8 ^{1}H NMR spectra of TK48-SH-25C-3-60C-3 test series using P3919GP WATERGATE method. Samples were axis calibrated to 0.0 ppm with TMSP/D_2O reference. The black, blue and red spectra correspond to Time 1, Time 7, and Time 56, respectively (listed from bottom to top). The absence of signal between ~5.3 and 4.5 ppm is due to the high intensity water signal exceeding the Y-axis scaling.

Table 3-11 Relative integration (ReI) and chemical shift (in ppm) values of signals standardized to the 9H singlet signal for TMSP for TK48-SH-25C-3-60C-3 (P3919GP WATERGATE).

Time	I	II	III	IV	V	VI	VII	VIII	IX
	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm
1	2.51, 1.67	– –	– –	low s/n	low s/n	low s/n	low s/n	low s/n	low s/n
7	1.15, 1.65	– –	– –	1.01, 6.90	3.62, 6.97	4.50, 7.06	2.02, 7.23	4.59, 7.29	0.97, 7.61
56	1.55, 1.63	– –	– –	1.75, 6.88	6.94, 6.97	9.90, 7.04	4.06, 7.21	10.41, 7.28	1.58, 7.59

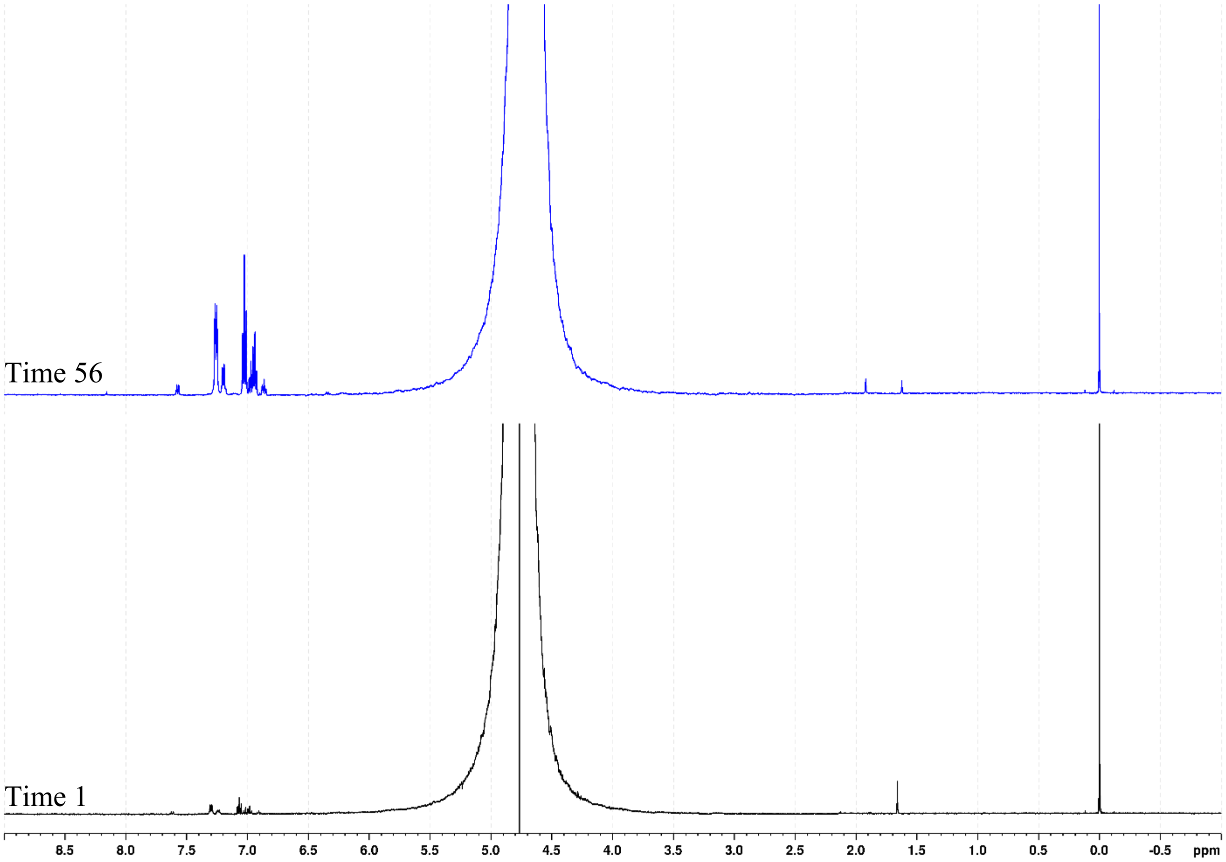


Figure 3-9 ^{1}H NMR spectra of TK48-SH-60C-111 test series using P3919GP WATERGATE method. Samples were axis calibrated to 0.0 ppm with TMSP/D_2O reference. The black and blue spectra correspond to Time 1 and Time 56, respectively (listed from bottom to top). The absence of signal between ~5.3 and 4.5 ppm is due to the high intensity water signal exceeding the Y-axis scaling.

Table 3-12 Relative integration (ReI) and chemical shift (in ppm) values of signals standardized to the 9H singlet signal for TMSP for TK48-SH-60C-111 (P3919GP WATERGATE).

Time	I	II	III	IV	V	VI	VII	VIII	IX
	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm
1	1.71, 1.66	– –	– –	0.80, 6.90	2.11, 7.00	1.91, 7.07	1.11, 7.24	2.05, 7.30	0.46, 7.62
56	1.13, 1.63	1.34, 1.92	– –	2.17, 6.86	10.80, 6.95	14.79, 7.03	5.18, 7.20	15.03, 7.26	1.54, 7.57

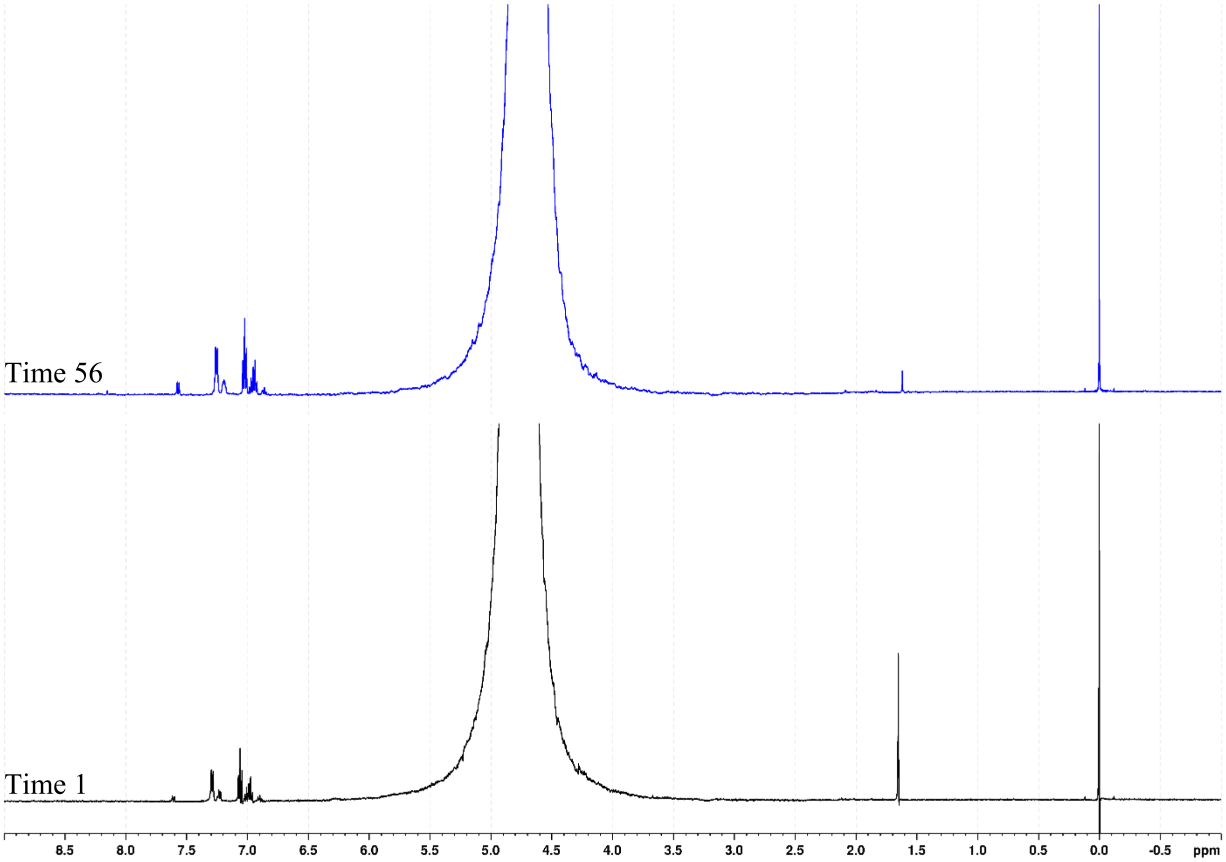


Figure 3-10 ^{1}H NMR spectra of TK48-SH-60C-33 test series using P3919GP WATERGATE method. Samples were axis calibrated to 0.0 ppm with TMSP/D_2O reference. The black and blue spectra correspond to Time 1 and Time 56, respectively (listed from bottom to top). The absence of signal between ~5.3 and 4.5 ppm is due to the high intensity water signal exceeding the Y-axis scaling.

Table 3-13 Relative integration (ReI) and chemical shift (in ppm) values of signals standardized to the 9H singlet signal for TMSP for TK48-SH-60C-33 (P3919GP WATERGATE). Note that signals are poorly phased and thus ReI and ppm are marked as n/a.

Time	I ReI, ppm	II ReI, ppm	III ReI, ppm	IV ReI, ppm	V ReI, ppm	VI ReI, ppm	VII ReI, ppm	VIII ReI, ppm	IX ReI, ppm
1	n/a	– –	– –	n/a	n/a	n/a	n/a	n/a	n/a
56	1.72, 1.62	– –	– –	1.21, 6.86	4.81, 6.96	6.45, 7.03	2.81, 7.19	6.75, 7.26	1.29, 7.57

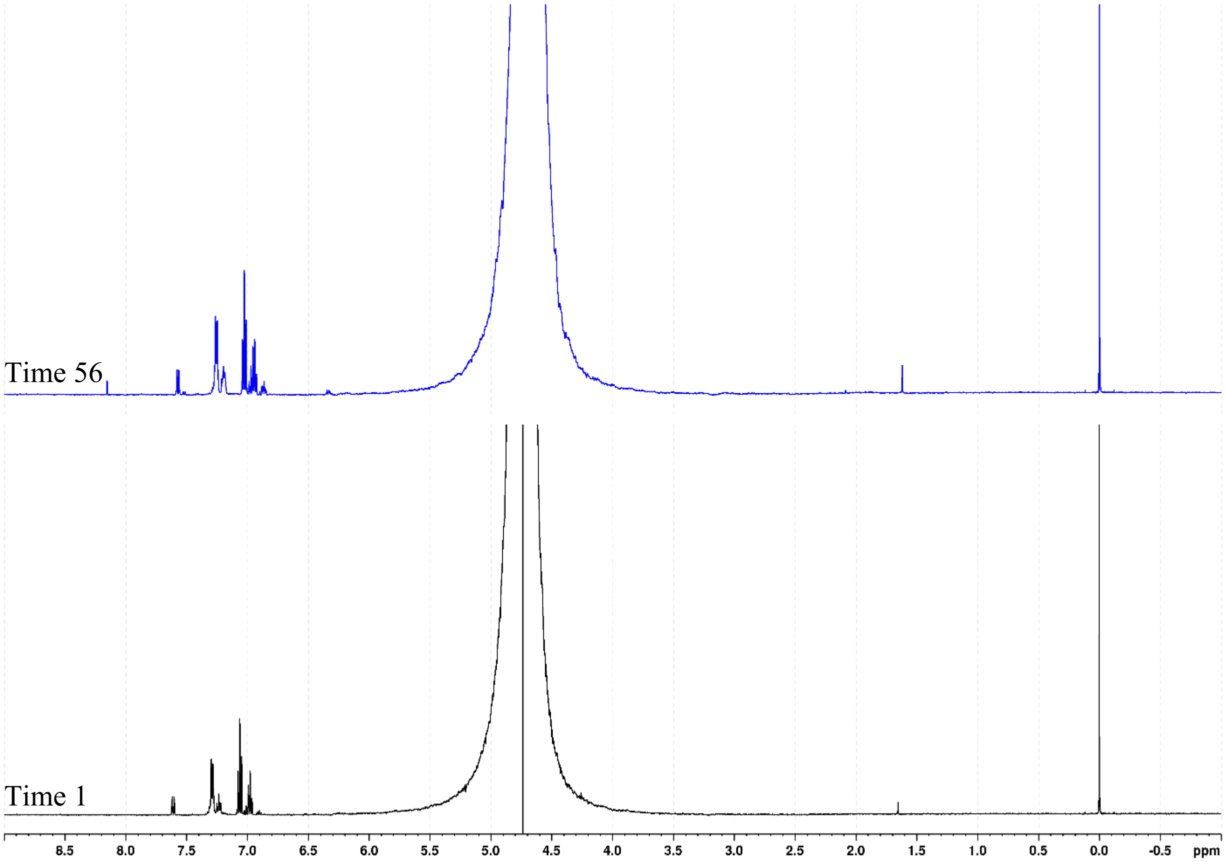


Figure 3-11 ^{1}H NMR spectra of TK48-SH-60C-9 test series using P3919GP WATERGATE method. Samples were axis calibrated to 0.0 ppm with TMSP/D_2O reference. The black and blue spectra correspond to Time 1 and Time 56, respectively (listed from bottom to top). The absence of signal between ~5.3 and 4.5 ppm is due to the high intensity water signal exceeding the Y-axis scaling.

Table 3-14 Relative integration (ReI) and chemical shift (in ppm) values of signals standardized to the 9H singlet signal for TMSP for TK48-SH-60C-9 (P3919GP WATERGATE).

Time	I	II	III	IV	V	VI	VII	VIII	IX
	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm
1	0.61, 1.65	– –	– –	0.95, 6.90	6.47, 6.98	10.64, 7.06	3.92, 7.24	10.55, 7.29	2.52, 7.61
56	1.52, 1.62	– –	– –	2.29, 6.87	8.77, 6.96	12.25, 7.03	6.09, 7.19	14.40, 7.27	2.97, 7.58

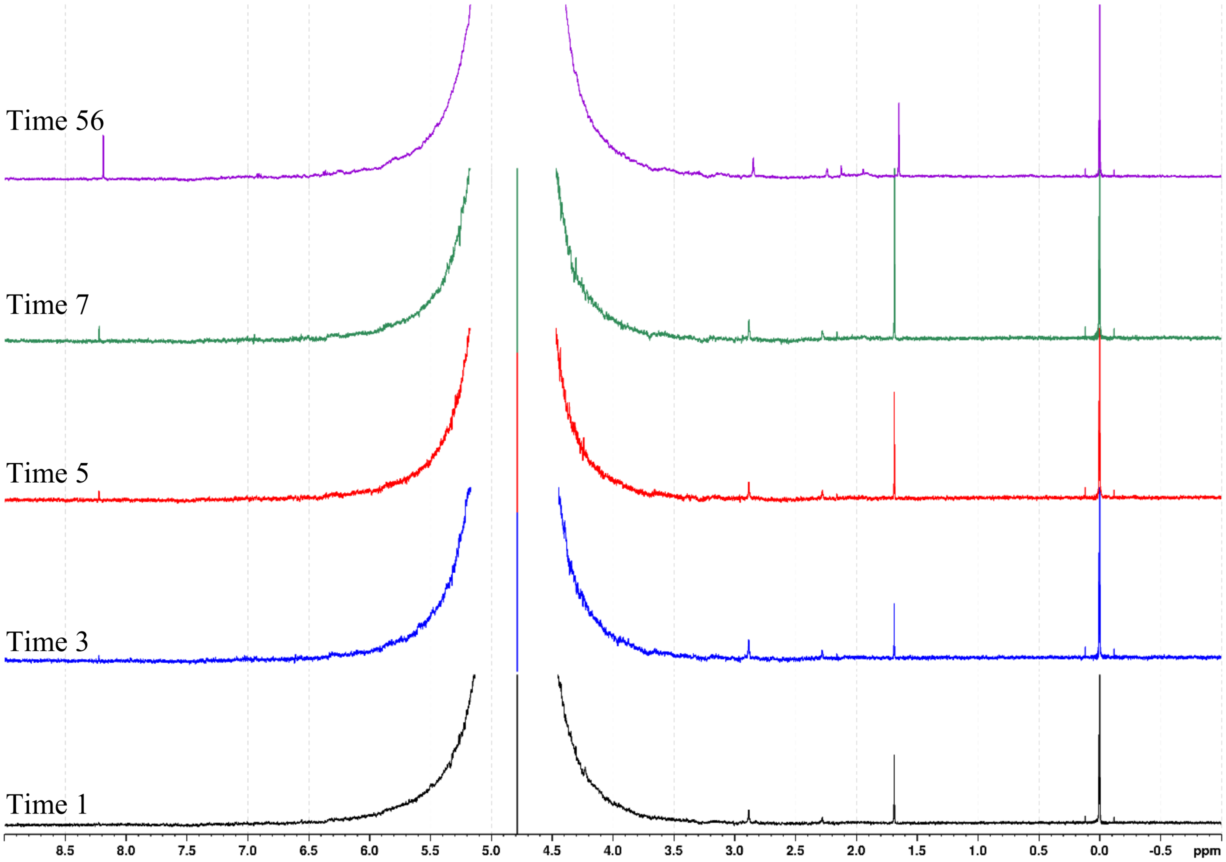


Figure 3-12 ^{1}H NMR spectra of TK48-SH-60C-BL test series using P3919GP WATERGATE method. Samples were axis calibrated to 0.0 ppm with TMSP/D_2O reference. The black, blue, red, green, and purple spectra correspond to Time 1, Time 3, Time 5, Time 7, and Time 56, respectively (listed from bottom to top). The absence of signal between ~5.3 and 4.5 ppm is due to the high intensity water signal exceeding the Y-axis scaling.

Table 3-15 Relative integration (ReI) and chemical shift (in ppm) values of signals standardized to the 9H singlet signal for TMSP for TK48-SH-60C-BL (P3919GP WATERGATE).

Time	I ReI, ppm	II ReI, ppm	III ReI, ppm	IV ReI, ppm	V ReI, ppm	VI ReI, ppm	VII ReI, ppm	VIII ReI, ppm	IX ReI, ppm
1	1.54, 1.69	0.86, 2.28	1.41, 2.88	– –	– –	– –	– –	– –	– –
3	0.58, 1.69	0.64, 2.29	0.90, 2.89	– –	– –	– –	– –	– –	– –
5	1.24, 1.69	0.63, 2.28	1.18, 2.88	– –	– –	– –	– –	– –	– –
7	2.22, 1.68	0.57, 2.28	0.90, 2.88	– –	– –	– –	– –	– –	– –
56	1.50, 1.65	0.64, 1.94	1.26, 2.85	– –	– –	– –	– –	– –	– –

Several comparisons and conclusions can be made from the results of the initial NMR experiments. In particular, a comparison of all samples at Time-56 was made to look at the relative intensity of samples under each shaker oven and 2-L vessel condition. These results are shown in Figure 3-13 (full spectrum), Figure 3-14 (aromatic region from 6.0 – 9.0 ppm), and Table 3-16 (integration values).

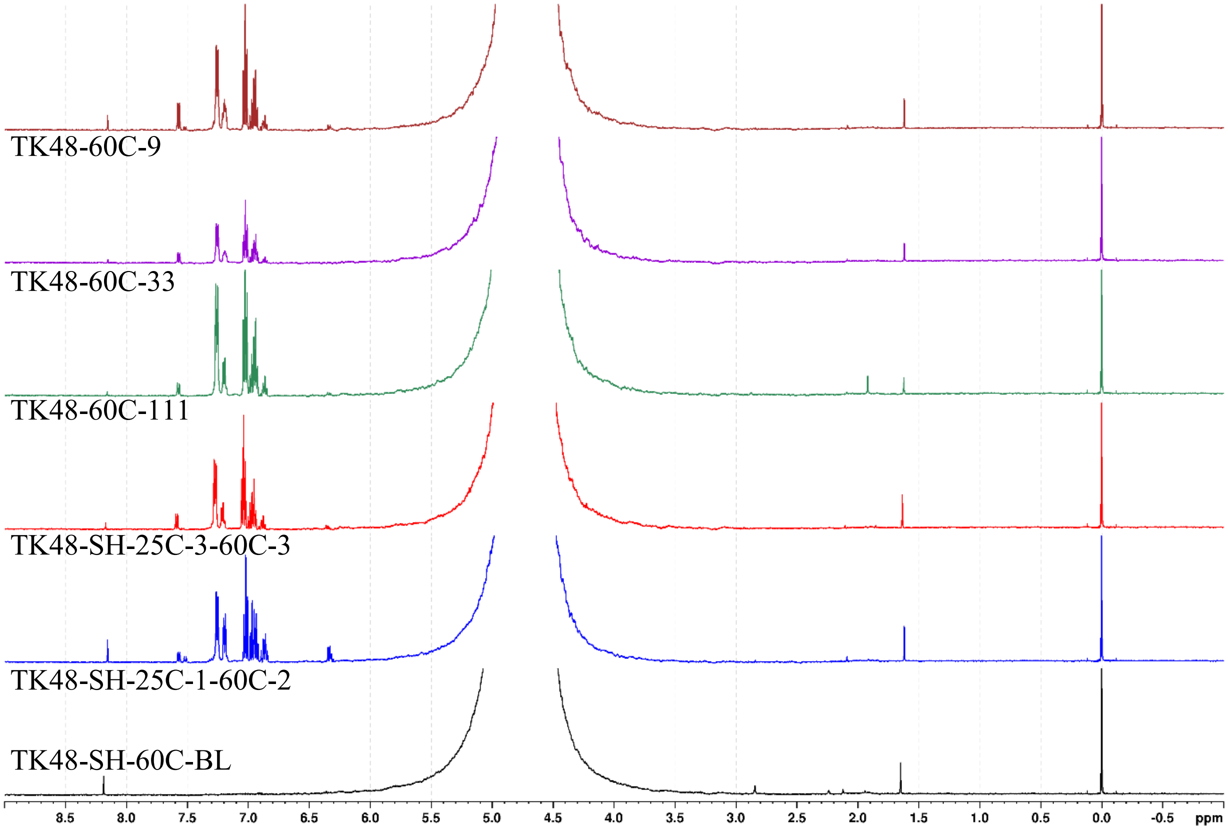


Figure 3-13 Full-region ^{1}H NMR spectra for Time 56 samples from multiple test series using P3919GP WATERGATE method. Samples were axis calibrated to 0.0 ppm with TMSP/D_2O reference. The black, blue, red, green, purple, and maroon spectra correspond to TK48-SH-60C-BL, TK48-SH-25C-1-60C-2, TK48-SH-25C-3-60C-3, TK48-SH-60C-111, TK48-SH-60C-33, and TK48-SH-60C-9, respectively (listed from bottom to top). The absence of signal between ~5.3 and 4.5 ppm is due to the high intensity water signal exceeding the Y-axis scaling.

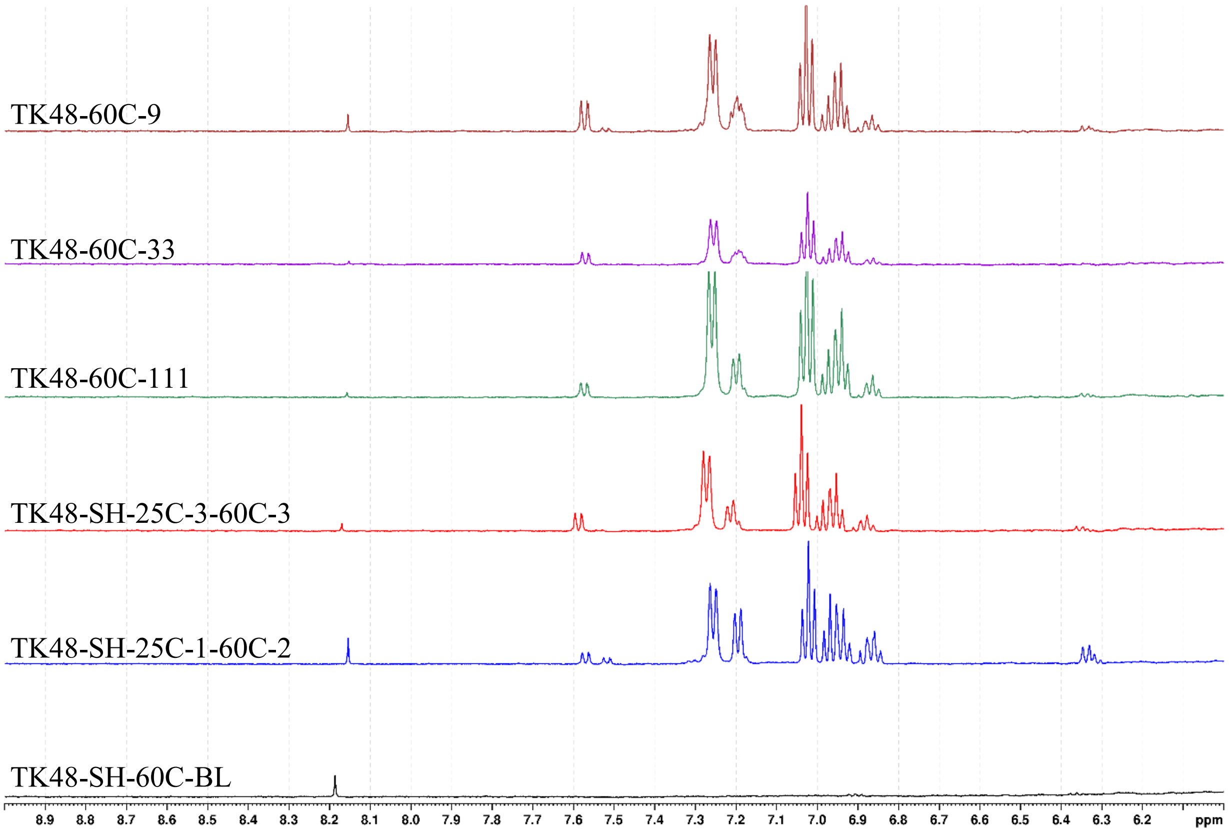


Figure 3-14 Zoomed-in ^{1}H NMR spectra for Time 56 samples from multiple test series using P3919GP WATERGATE method. Samples were axis calibrated to 0.0 ppm with TMSP/D_2O reference. The black, blue, red, green, purple, and maroon spectra correspond to TK48-SH-60C-BL, TK48-SH-25C-1-60C-2, TK48-SH-25C-3-60C-3, TK48-SH-60C-111, TK48-SH-60C-33, and TK48-SH-60C-9, respectively (listed from bottom to top).

Table 3-16 Relative integration (ReI) and chemical shift (in ppm) values of signals standardized to the 9H singlet signal for TMSP for TK48-SH-60C-BL (test 1), TK48-SH-25C-1-60C-2 (test 2), TK48-SH-25C-3-60C-3 (test 3), TK48-SH-60C-111 (test 4), TK48-SH-60C-33 (test 5), and TK48-SH-60C-9 (test 6) (P3919GP WATERGATE).

Test ID	I ReI, ppm	II ReI, ppm	III ReI, ppm	IV ReI, ppm	V ReI, ppm	VI ReI, ppm	VII ReI, ppm	VIII ReI, ppm	IX ReI, ppm
1	1.50, 1.65	0.64, 1.94	1.26, 2.85	low s/n	low s/n	low s/n	low s/n	low s/n	low s/n
2	1.20, 1.62	0.49, 2.09	– –	4.34, 6.87	10.17, 6.95	9.82, 7.03	6.56, 7.19	10.67, 7.26	1.13, 7.57
3	1.55, 1.63	– –	– –	1.75, 6.88	6.94, 6.97	9.90, 7.04	4.06, 7.21	10.41, 7.28	1.13, 7.57
4	1.13, 1.63	1.34, 1.92	– –	2.17, 6.86	10.80, 6.95	14.79, 7.03	5.18, 7.20	15.03, 7.26	1.54, 7.57
5	1.72, 1.62	– –	– –	1.21, 6.86	4.81, 6.96	6.45, 7.03	2.81, 7.19	6.75, 7.26	1.29, 7.57
6	1.52, 1.62	– –	– –	2.29, 6.87	8.77, 6.96	12.25, 7.03	6.09, 7.19	14.40, 7.27	2.97, 7.58

In the comparison of all Time 56 samples by ^{1}H NMR, the sum of aromatic relative integration values for TK48-SH-60C-111 Time 56 has the highest quantity of aromatic protons ($\sum$ ReI = 49.50), followed by TK48-SH-60C-9 ($\sum$ ReI = 46.78). Interestingly, TK48-SH-60C-33 had the lowest sum of aromatic integration values ($\sum$ ReI = 23.32). This does not necessarily mean that the reaction rate or amount of total product is less in this sample since NMR only observes the filtered liquid phase and several of the expected products will likely precipitate as they are insoluble in alkaline aqueous solutions.

In order to perform quantitative ^{1}H NMR experiments, an appropriate integral ratio should be determined due to the co-axial methodology employed. In all NMR experiments, only 50 µL of TMSP/D_2O is present in the inner co-axial stem insert whereas 400 µL of sample is loaded to the external tube. The center-of-field in the NMR magnet correlates the concentrations and not the total volumes present in the magnet. A scaling ratio must be applied using this method since it is a disproportionate amount of sample in the center of the magnetic field. In addition, the analyte identity must be determined to correspond to the number of protons associated with the respective resonance integration value. Thus, quantitative analysis cannot be performed (without several assumptions of signal identity and relative concentrations) until several control experiments are performed to separate signals in high-salt simulant samples. Because of this, conclusions are made based on summation of relative integration values in the aromatic region.

Boron (^{11}B) NMR studies were conducted but no significant signals were observed outside of the expected reference material (boric acid) appearing at 19.4 ppm, and an ingrowth of free borate (due to borosilicate leaching from glass in the high-salt and high-hydroxide simulant) appearing at 1.47 ppm. It is possible that phenyl borates are oxidized to borate rapidly, and those species would not be distinguishable from leached borate from the borosilicate reaction vessels. All ^{11}B spectra outlined in Table 2-6 are compared in Figure B-15 (TK48-SH-60C-NOTPB Time 1 and TK48-SH-60C-BL Time 1–7), Figure B-16 (TK48-SH-25C-1-60C-2 Time 1 and Time 7, TK48-SH-25-C-3-60C-3 Time 1 and Time 7, TK48-SH-60C-9 Time 1, TK48-SH-60C-33 Time 1, and TK48-SH-60C-111 Time 1 and Time 56), and Figure B-17 (TK48-2LV-25C-1-60C-2 Time 0–7).

Carbon (^{13}C) NMR studies, similar to ^{11}B, do not show strong signals (except for carbonate at 172.2 ppm and oxalate at 168.2 ppm, from the simulant) in tests ≤ Time 7. Both ^{13}C and ^{11}B NMR were collected on a single Time 56 sample (TK48-SH-60C-111). Two very weak signals at 127.3 and 130.9 ppm were observed in this ^{13}C NMR spectrum but were nearly indistinguishable from the baseline. All ^{13}C spectra outlined in Table 2-6 are compared in Figure B-18 (TK48-SH-60C-NOTPB Time 1 and TK48-SH-60C-BL Time 1–7), Figure B-19 (TK48-SH-25C-1-60C-2 Time 1 and Time 7, TK48-SH-25-C-3-60C-3 Time 1 and Time 7, TK48-SH-60C-9 Time 1, TK48-SH-60C-33 Time 1, and TK48-SH-60C-111 Time 1 and Time 56), and Figure B-20 (TK48-2LV-25C-1-60C-2 (Time 0–7). Additional method development could be used to enhance these weak resonances in ^{13}C and ^{11}B NMR through optimizing inverse gated pulse or coupling methods, cryogenic temperatures, or through sample concentration.

Some general observations were made through analyzing the resulting NMR spectra of all test series. For example, several spectra have a singlet signal at ~8.15 ppm. Although it is unlikely due to the immiscibility of benzene in water, it is possible that entrained benzene (or dissolved benzene gas) could be present. Benzene typically appears at ~7.3 ppm in deuterated organic solvents and a lock of solvation from water in a high-salt simulant sample could electronically de-shield and dramatically shift the benzene signal downfield. Additional testing is required to determine the identity of this signal. All spectra have an unidentified singlet signal at ~1.69 ppm (including the blank and NOTPB samples). Several spectra have a signal at 2.28 and 2.88 which has not been identified. It is in all TK48-SH-60C-BL samples and a few "Time 0" samples. Splitting of signals is difficult to identify due to signal overlap. For example, the signal centered at 6.95 ppm (noted as integral V in Figure 3-4) is likely two triplets implied by two unique *j*-coupling constants and disproportionate ingrowth. With additional NMR experiments (e.g., sample spiking with suspected analytes and adding various solvents to shift peaks) and other complimentary data, peak identification (and thus concentrations of each component) may be possible.

3.1.5 Off-Gas Results

Off-gas measurements were collected for the two 2-L experiments only (TK48-2LV-25C-1-60C-2 and Tk48-2LV-60C-3) and not the shaker oven experiments. GC, FTIR, and MS were used to collect data consistently for a two-week period.

In both experiments the GC PoraPlot Q column degraded over the course of the two weeks. Data is limited for N_2O and CH_4 on the GC because of the column degradation. N_2O and CH_4 were collected and analyzed on the other instrumentation to ensure data was not lost. During the 2-week experiment, the retention time of the Inficon GC began to shift. Manual peak integrations of GC data were performed instead of using instrument software, in 3-hour increments, due to retention time shifting.

Shown below in, Figure 3-15, Figure 3-16, and Figure 3-17 is the off-gas data for FTIR and MS for TK48-2LV-25C-1-60C-2. It is indicated by the very low ppm concentrations that there is no significant off-gas being produced. Heating up to 60 °C with the addition of one equivalent of permanganate did not produce any off-gas and the addition of the second equivalent of permanganate at 60 °C did not produce any off-gas. The low amounts of off-gas observed could be attributed to the inadequate mixing used for the first 2-L experiment. If sufficient mixing was obtained, it is possible that off-gas would have been produced. A large amount of noise is observed in all gas species throughout the experiment; however, this does not indicate the presence of off-gas. Figure 3-17 indicates a peak in benzene, H_2, NO, and CO_2 which was caused by a power outage and should be ignored. Off-gas instrumentation was rebooted and stable before proceeding to permanganate addition.

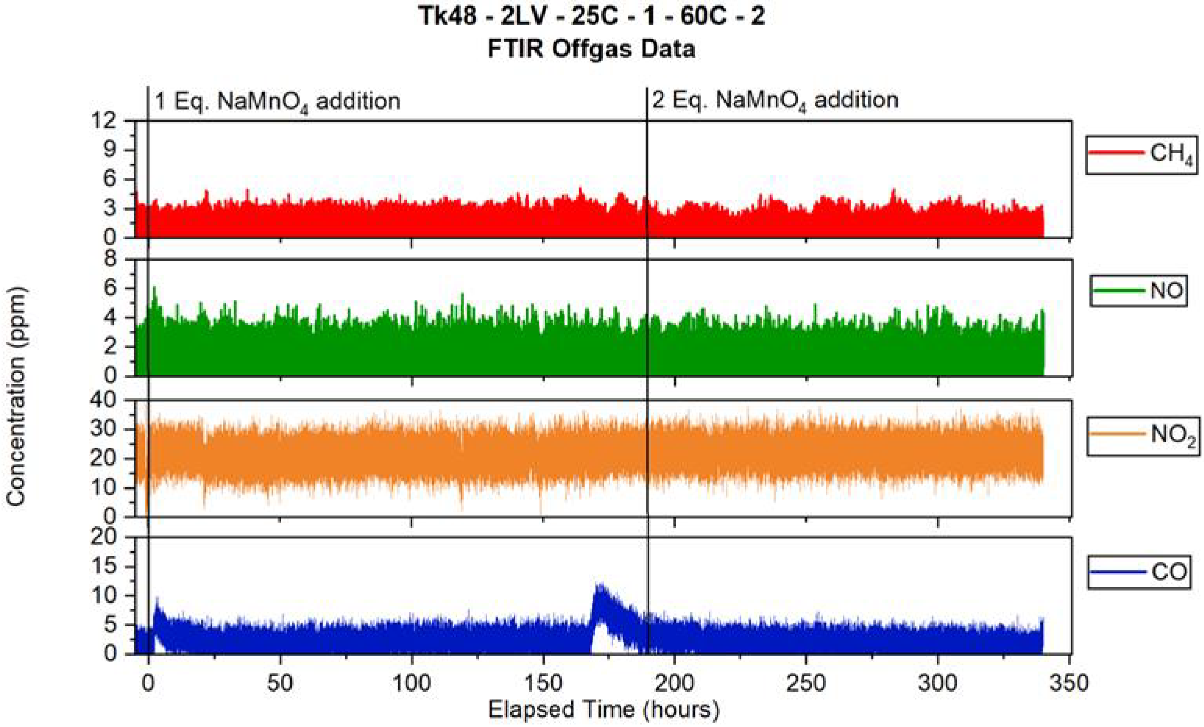


Figure 3-15 Concentration in ppm of CH_4, NO, NO_2, and CO FTIR off-gas data for TK48-2LV-25C-1-60C-2.

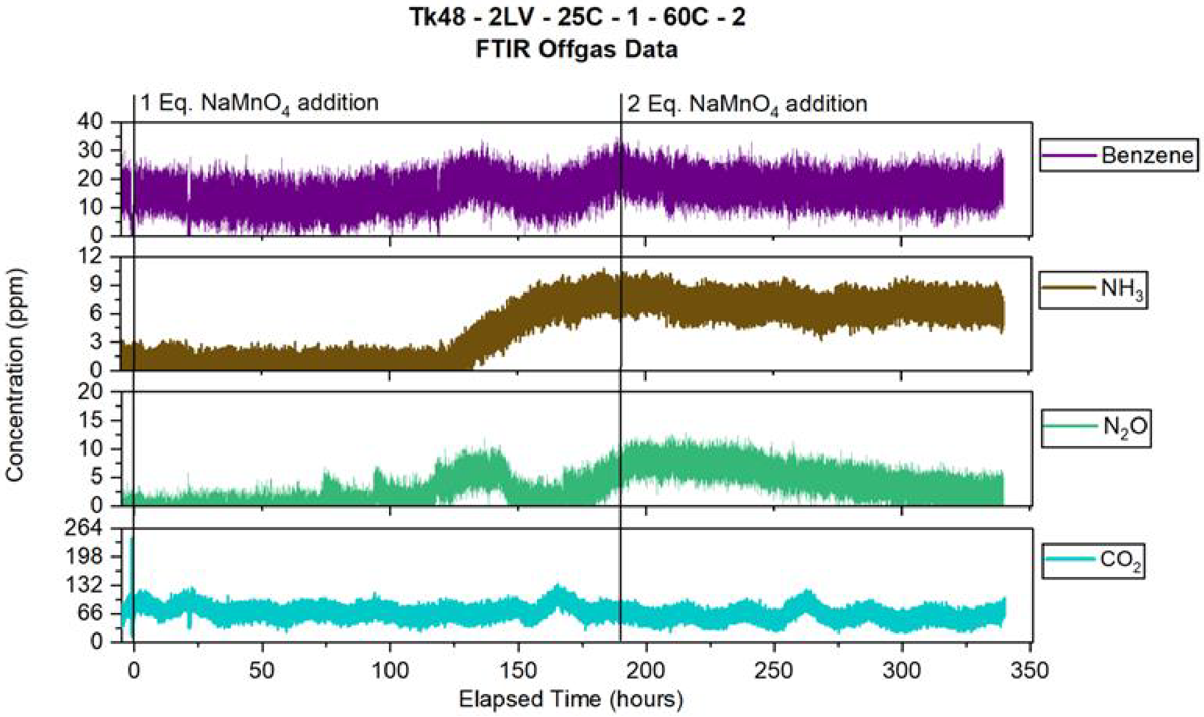


Figure 3-16 Concentration in ppm of benzene, NH_3, N_2O, and CO_2 FTIR off-gas data for TK48-2LV-25C-1-60C-2.

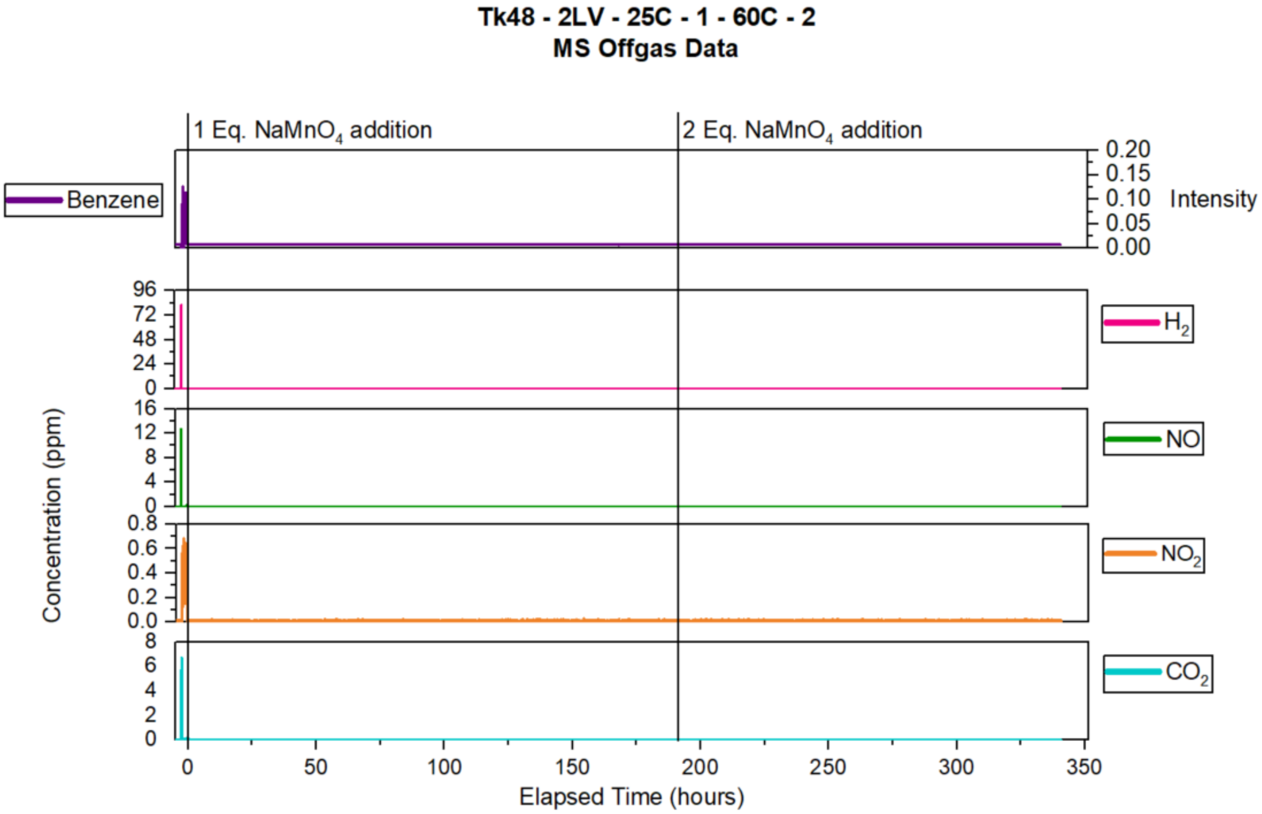


Figure 3-17 Concentration in ppm of H_2, NO, NO_2, CO_2 and intensity of benzene MS off-gas data for Tk48-2LV-25C-1-60C-2.

An unidentified peak became present and increased in intensity throughout the experiment. Figure 3-18 and Figure 3-19 show the FTIR spectrum of the unknown peak seen around 950–1100 cm^{-1}. The spectrum was compared to literature library on the FTIR software, but it was inconclusive on what the actual off-gas species was present. Additional efforts could identify the unknown peak by comparing MS data with the FTIR data but would require several calibration and control experiments to fully determine the unknown peak.

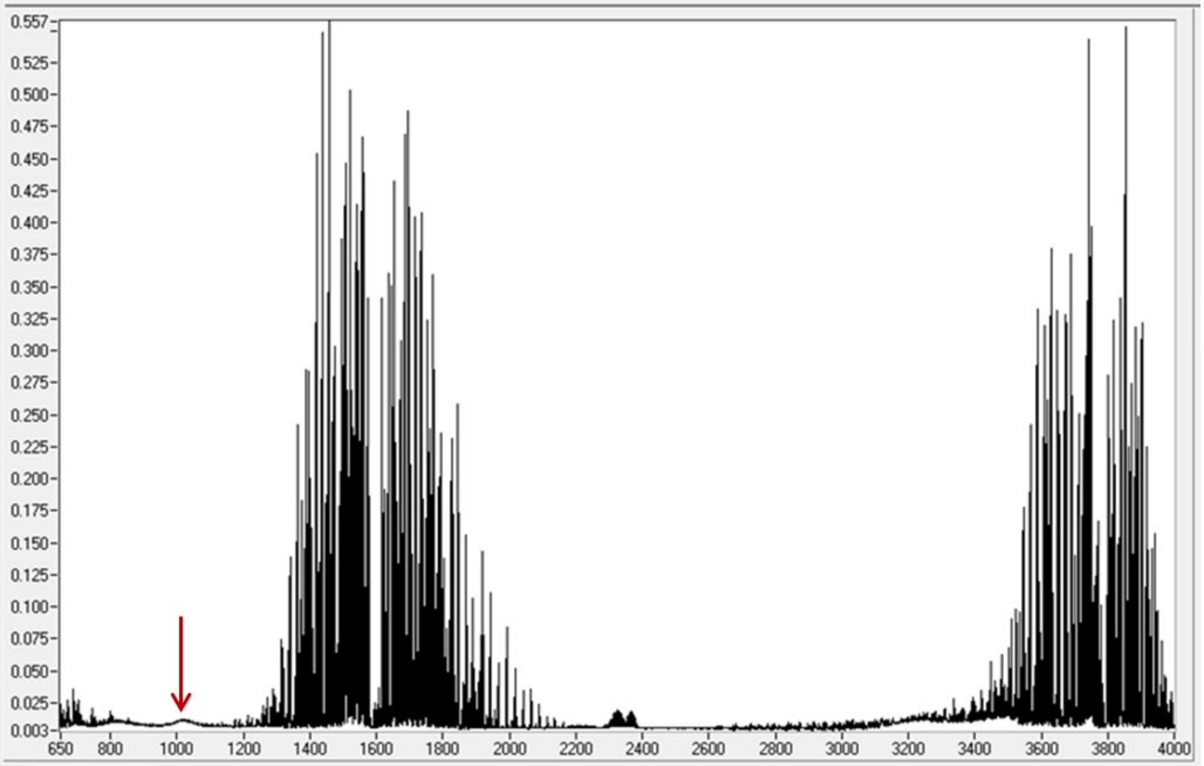


Figure 3-18 Spectrum of unknown peak, indicated by the red arrow, from FTIR present in TK48-2LV-25C-1-60C-2. Units of the X-axis are in wavenumber (cm^{-1}).

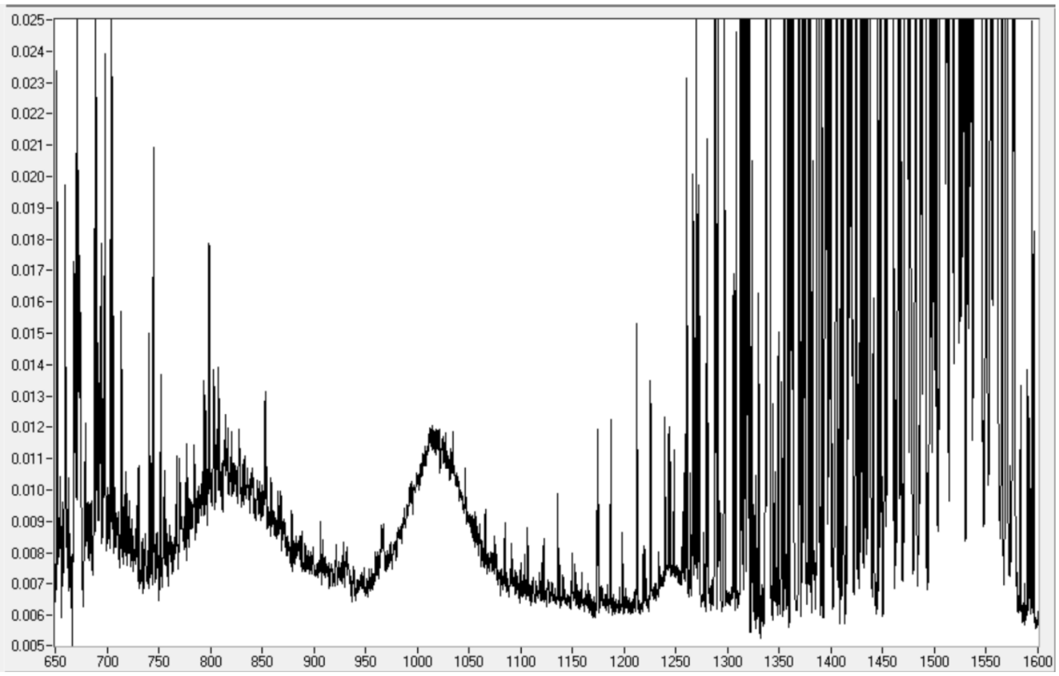


Figure 3-19 Spectrum of expanded unknown peaks from FTIR present in TK48-2LV-25C-1-60C-2. Units of the X-axis are in wavenumber (cm^{-1}).

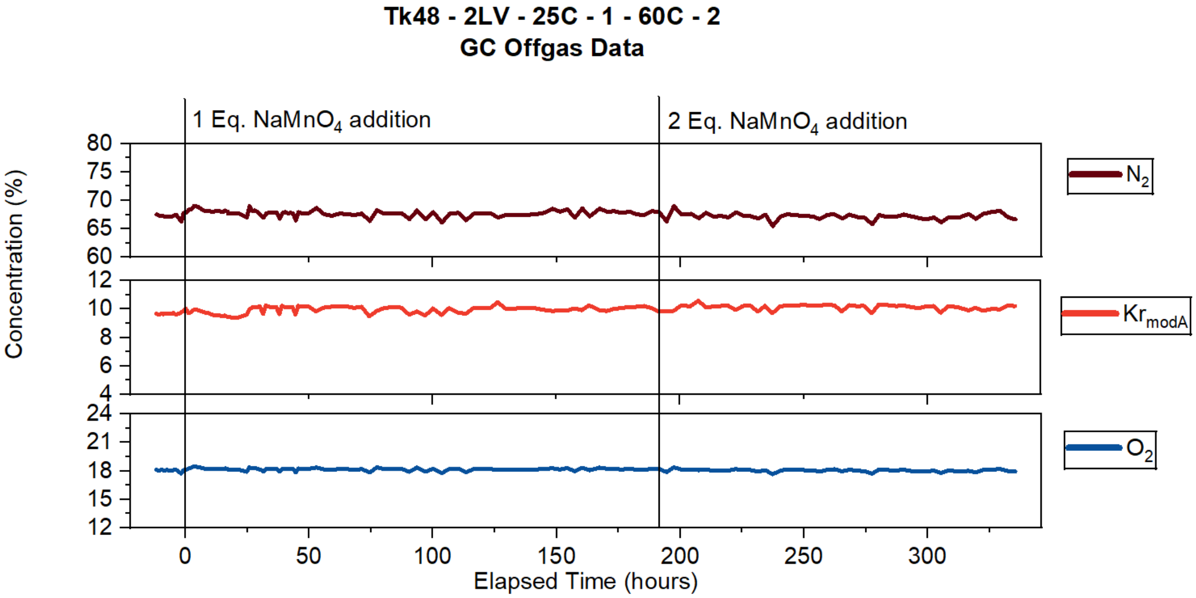


Figure 3-20 Concentration in percent of N_2, Kr (measured by the first GC module), and O_2 GC off-gas data for TK48-2LV-25C-1-60C-2.

Figure 3-20 shows the GC off-gas data collected during the first 2-L vessel experiment, TK48-2LV-25C-1-60C-2. No significant trends were measured from the Kr tracer gas, or air purge (N_2 and O_2). No notable measurements of other targeted gas species (H_2, CH_4, CO_2, or N_2O), were distinguishable from the baseline. Note that additional gases may be present but were not directly analyzed (e.g., benzene). In addition, data is limited for N_2O and CH_4 on the GC, likely due to column degradation or clogging that occurred during the experiment.

Figure 3-21, Figure 3-22, and Figure 3-23 show the off-gas data collected and graphed for the FTIR and MS for TK48-2LV-60C-3. Most of the off-gas species were very low in ppm concentration and showed no off-gas being produced. Benzene and N_2O were observed to be produced in both the FTIR and MS data. The Benzene and N_2O did not release until after the addition of permanganate. This observation suggests that TPB is decomposing, as benzene is a byproduct of TPB decomposition. Before permanganate addition the simulant was left to mix at 60 °C for around ~96 hrs. This indicated no off-gas release and hence no TPB decomposition products observed in the off-gas. This can also be supported by the chemical analysis results and visual observations that heating up to 60 °C does not have an impact on TPB decomposition.

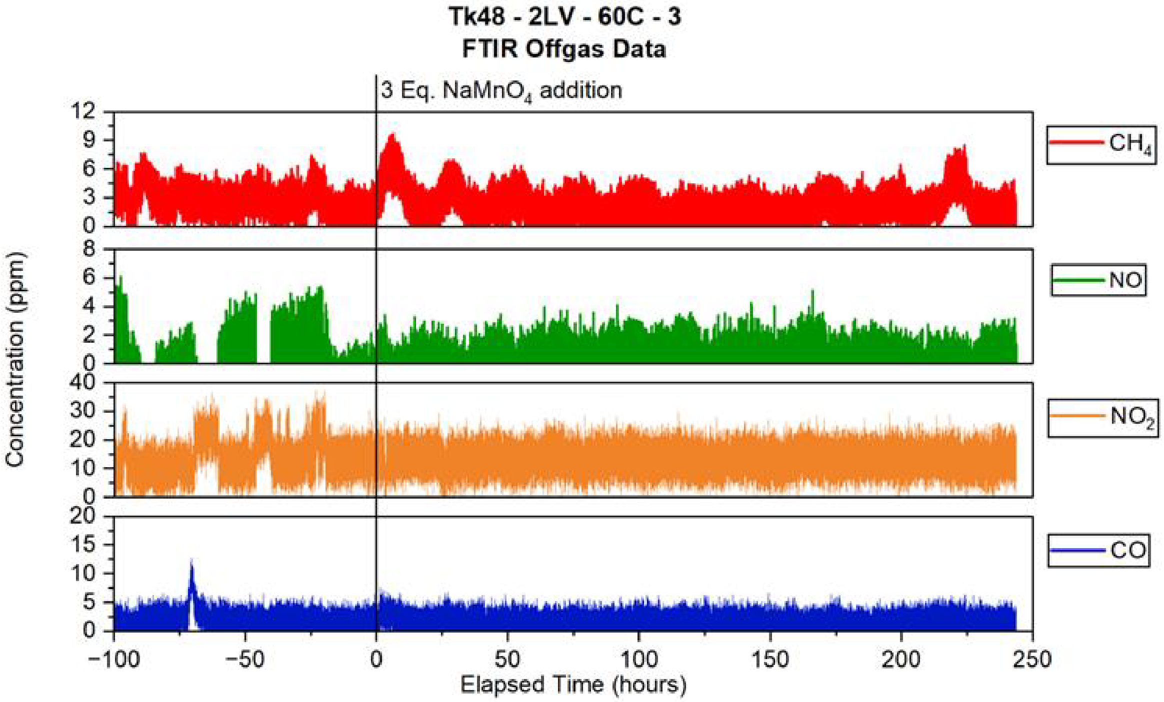


Figure 3-21 Concentration in ppm of CH_4, NO, NO_2, and CO FTIR off-gas data for Tk48-2LV-60C-3.

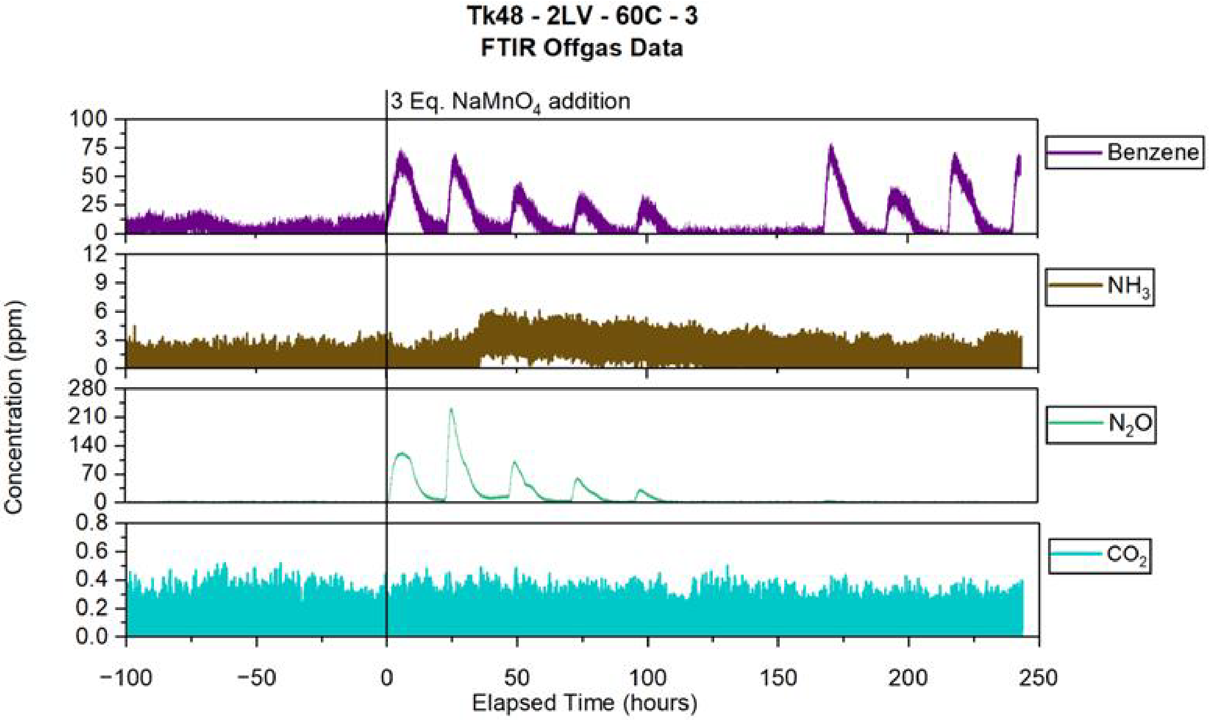


Figure 3-22 Concentration in ppm of benzene, NH_3, N_2O, and CO_2 FTIR off-gas data for TK48-2LV-60C-3.

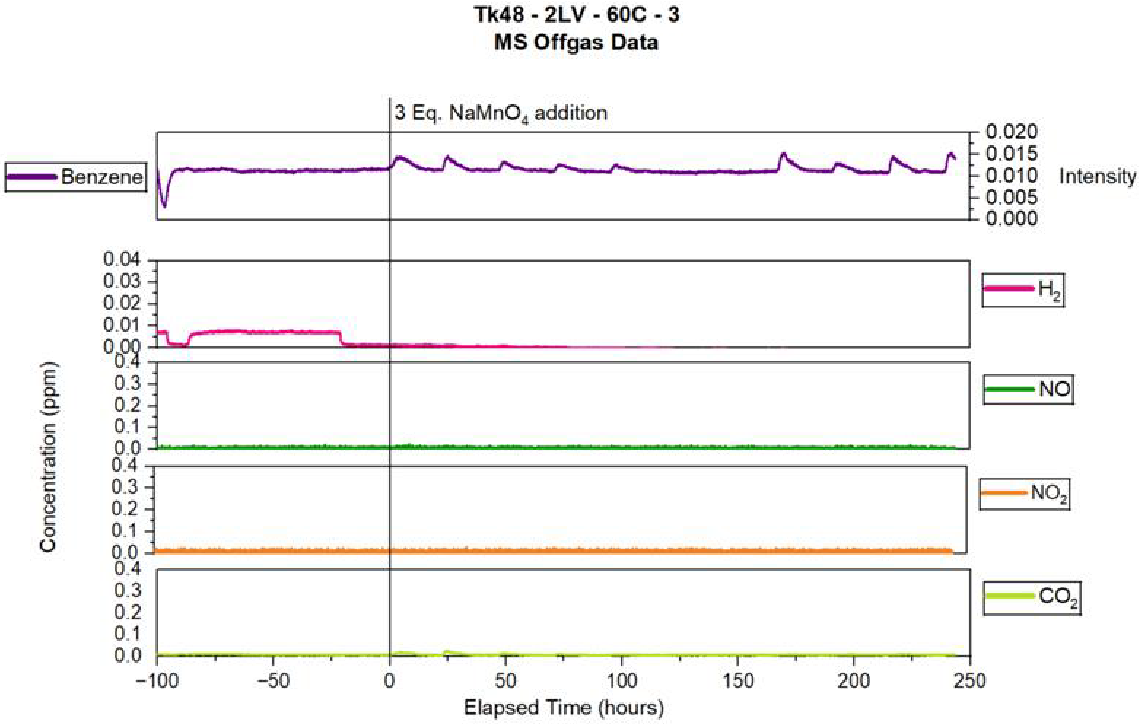


Figure 3-23 Concentration in ppm of H_2, NO, NO_2, CO_2 and intensity of benzene MS off-gas data for Tk48-2LV-60C-3.

Figure 3-24 shows that agitation (with an overhead mixer) had an impact on observable benzene and N_2O based on FTIR data. At the beginning of each day the Teflon stir bar was turned off and the overhead mixer was turned on (Table 3-17 indicated the time the stir bar was switched out with the overhead mixer). As the agitation from the overhead mixer continued throughout the day, the levels of benzene and N_2O gradually decreased and stabilized when the overhead mixer was exchanged for the Teflon stir bar at night. It is also observed that as the simulant was agitated daily, the concentration of benzene and N_2O decreased over the course of the week. This suggests that benzene and N_2O are being released from solution (or foam) due to enhanced agitation. If continuous enhanced agitation (i.e., an overhead mixer) was used, benzene concentrations would approach a static value. The same trend was not observed in N_2O after the second week of processing. This could be due to the nitrate and nitrite completing a reaction after the first week. Furthermore, while the peaks are distinct enough to confirm that there was benzene generated during this oxidation process, the noise in the benzene signal (seen by the thickness of the response before averaging) is still relatively large. These peaks also never reach the lower limit of detection included in the gas calibration methods (including measurements down to ~95 ppm), which is likely the reason the signals were not detected.

Table 3-17 Mixing schedule of when stir bar and overhead mixer were turned on and off for TK48-2LV-60C-3 (June 2025)

Method	Time	Date	Elapsed Time (h)
Stir bar	4:40 pm – 9:05 am[a]	6/11–16	-112 – 0
Overhead mixer	9:05 am – 4:00 pm[b]	6/16	0 – 7
Stir bar	4:00 pm – 7:30 am	6/16–17	7 – 22.5
Overhead mixer	7:30 am – 4:00 pm	6/17	22.5 – 31
Stir bar	4:00 pm – 7:30 am	6/17–18	31 – 46.5
Overhead mixer	7:30 am – 4:00 pm	6/18	46.5 – 55
Stir bar	4:00 pm – 7:30 am	6/18–19	55 – 70.5
Overhead mixer	7:30 am – 4:00 pm	6/19	70.5 – 79
Stir bar	4:00 pm – 7:30 am	6/19–20	79 – 94.5
Overhead mixer	7:30 am – 4:00 pm	6/20	94.5 – 103
Stir bar	4:00 pm – 7:30 am	6/20–23	103 – 166.5
Overhead mixer	7:30 am – 4:00 pm	6/23	166.5 – 182
Stir bar	4:00 pm – 7:30 am	6/23–24	182 – 197.5
Overhead mixer	7:30 am – 4:00 pm	6/24	197.5 – 206
Stir bar	4:00 pm – 7:30 am	6/17–18	206 – 214.5
Overhead mixer	7:30 am – 4:00 pm	6/24	197.5 – 206
Stir bar	4:00 pm – 7:30 am	6/24–25	206 – 214.5
Overhead mixer	7:30 am – 4:00 pm	6/25	214.5 – 230
Stir bar	4:00 pm – 7:30 am	6/25–26	230 – 238.5
Overhead mixer	7:30 am – 12:00 pm	6/26	238.5 – 243

[a] Simulant was added on 6/11
[b] Permanganate was added on 6/16

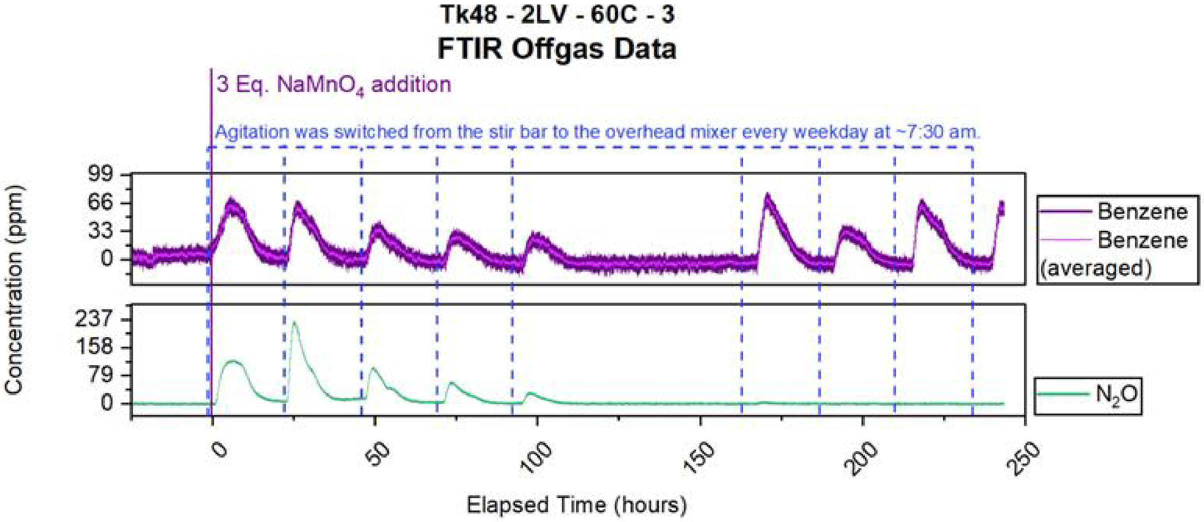


Figure 3-24 TK48-2LV-60C-3 agitation impact on benzene and N_2O.

While collecting FTIR data, an unidentified peak increased in intensity throughout the experiment, which was also observed in TK48-2LV-25C-1-60C-2. Figure 3-25 and Figure 3-26 show the FTIR spectrum of the unknown peak seen at ~950–1100 cm^{-1}. The peak intensity by the end of the run did not appear to have as high of an intensity compared to the first 2-L experiment. The unknown peak in the first run got up to ~0.012 intensity while the second 2-L vessel experiment reached ~0.005. The spectrum was compared to a literature library on the FTIR software, but it was inconclusive on what off-gas species is present. Additional efforts could identify the unknown peak by comparing MS and GC data with the FTIR data but would require several calibration and control experiments to fully determine the unknown peak.

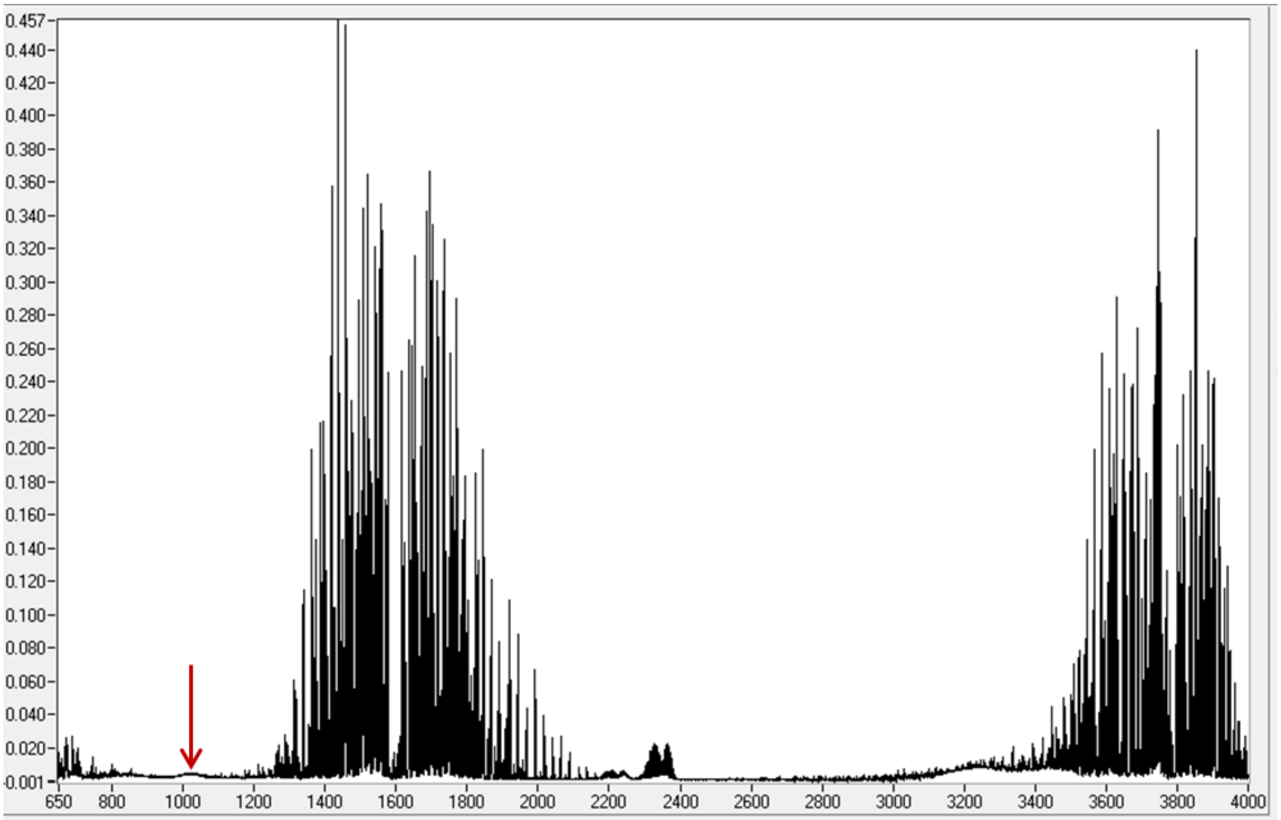


Figure 3-25 Spectrum of unknown peak, indicated by the red arrow, from FTIR present in TK48-2LV-60C-3. Units of the X-axis are in wavenumber (cm^{-1}).

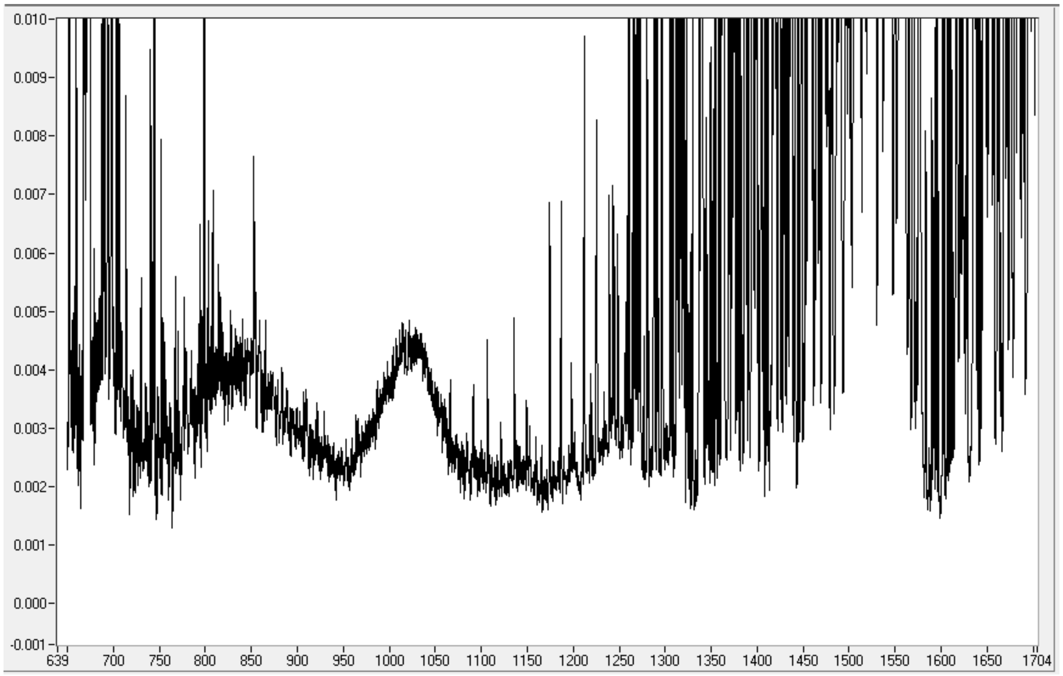


Figure 3-26 Spectrum of expanded unknown peaks from FTIR present in TK48-2LV-60C-3. Units of the X-axis are in wavenumber (cm^{-1}).

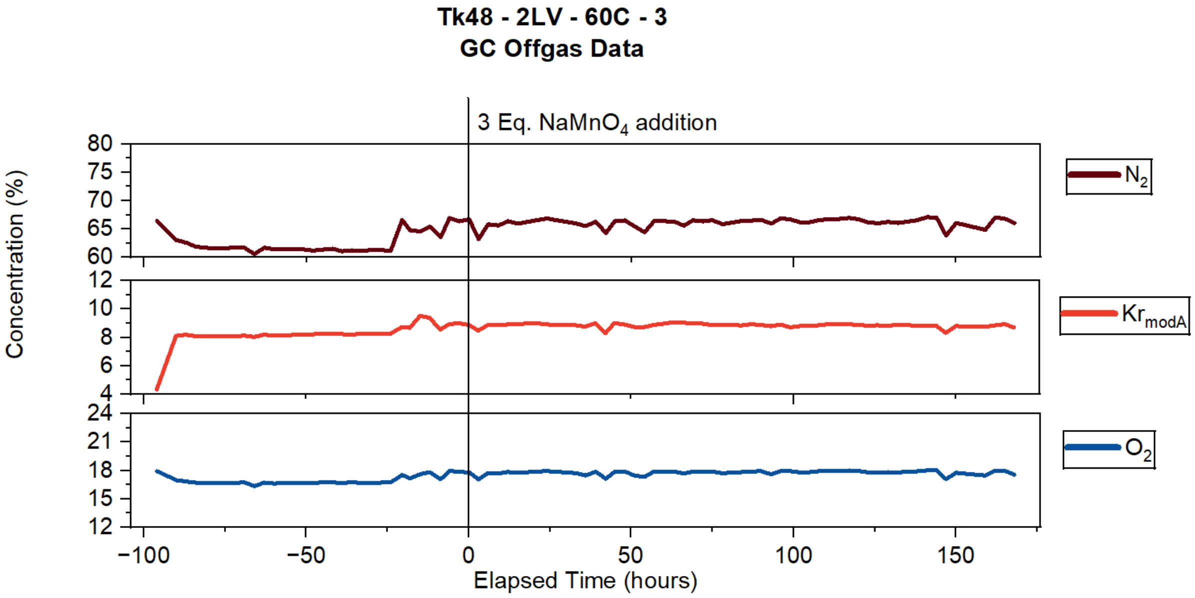


Figure 3-27 Concentration in % of N_2, Kr (measured by the first GC module), and O_2 GC off-gas data for TK48-2LV-60C-3.

Figure 3-27 shows the GC off-gas data collected during the second 2-L vessel experiment, TK48-2LV-60C-3. No significant trends were measured from the Kr tracer gas or air purge (N_2 and O_2). No notable measurements of other targeted gas species (H_2, CH_4, CO_2, or N_2O), were distinguishable from the baseline. Note that additional gases may be present but were not directly analyzed (e.g., benzene). In addition, data is limited for N_2O and CH_4 on the GC because of column degradation or clogging that occurred during the experiment.

4.0 Conclusions and Recommendations

Two series of experiments were performed to investigate the decomposition of TPB with sodium permanganate in simulated Tank 48H slurry. Seven tests were performed at a pH of 14 with 250 mL Erlenmeyer flasks in a shaker oven for 56 days. Two tests were performed at a pH of 14 with 2-L jacketed vessels with real-time off-gas monitoring. Test variables include the molar ratio of sodium permanganate to tetraphenylborate (i.e., 1, 1.5, 2, 3 and 9), reaction temperature (i.e., 25 and 60 °C) and oxidant addition strategy (e.g., single or multi-strike).

The conclusions from the testing are summarized below:

- TPB decomposition was monitored indirectly by measuring soluble boron and potassium. TPB analysis by HPLC yielded inconsistent results due to variations in sampling preparations, leading to its exclusion from the TPB decomposition calculations. In general, TPB decomposition (i.e., potassium concentrations) increased as a function of time, temperature, and P:TPB molar ratio.
- Multiple permanganate strikes led to more effective TPB decomposition. A similar net TPB decomposition was observed in a single strike experiment with a P:TPB of 9 and a 3-strike experiment with a combined P:TPB of 4.5.
- Higher temperatures resulted in higher decomposition rates for equivalent permanganate concentrations, and there was a clear correlation between permanganate concentration and TPB decomposition.

- Phenylboronic acid (PBA), diphenylborinic acid (2PB), phenol, and biphenyl were measured by HPLC and correlated with TPB decomposition.
- Partial nitrite destruction was observed in all experiments with TPB and permanganate. Complete oxidation of nitrite was observed without TPB.
- UV-vis results indicated that all TPB decomposition tests resulted in complete consumption of permanganate except TK48-2LV-25C-1-60C-2 and TK48-SH-60C-NOTPB.
- Gradually heating from 25 °C to 60 °C did not show an effect on decomposition of TPB, as supported by the off-gas analyses (2-L experiments), chemical analysis, and visual observations.
- Free hydroxide decreased, but the pH remained above 13 for all experiments. The potential loss of free hydroxide could be due to a reaction with the glass vessels and other side reactions.
- Benzene, at low concentrations up to ~75 ppm (i.e., from FTIR data), was observed and measured with the off-gas instrumentation during the second 2-L vessel experiment, TK48-2LV-60C-3. N_2O was also observed and measured up to ~237 ppm (i.e., from FTIR data) during the second 2-L vessel experiment, TK-48-2LV-60C-3. An unidentified peak was observed around 950-1100 cm^{-1} on the FTIR for both 2-L vessel experiments. Otherwise, no other off-gas species were observed throughout both 2-L experiments.
- Nuclear magnetic resonance (NMR) studies indicate ingrowth of multiple aqueous-soluble organic species (e.g., organic salts) over time. Signal splitting indicates that there is likely two or more aqueous-soluble aromatic species (e.g., PBA and phenol). Additional method development is needed for accurate species identification through a series of control experiments involving spiking with perceived analytes, redispersion in multiple solvents, and/or measurement at various pHs to disproportionately shift signals to resolve their identity and provide discrete integrations.
- In proton (^{1}H) NMR studies, the highest summation of relative integration of aromatic regions (i.e., where TPB byproducts would show up) across all test series was for Tk48-SH-60C-111 (relative integration (ReI) = 49.50) followed by TK48-SH-60C-9 (ReI = 46.78) and TK48-SH-25C-1-60C-2 (ReI = 42.69). Indicating that TK48-SH-60C-111 produced the highest quantity of soluble TPB byproducts by permanganate oxidation based on relative integrations.
- Carbon (^{13}C) and boron (^{11}B) NMR studies were conducted but no significant signals were observed outside of the expected reference (boric acid) and simulant (carbonate and oxalate) analytes for samples collected prior to Time 7. Both ^{13}C and ^{11}B NMR were collected on a single Time 56 sample (TK48-SH-60C-111) and very weak signals were observed in the carbon NMR but were nearly indistinguishable from the baseline. Additional method development could be used to enhance these resonances in ^{13}C and ^{11}B NMR through optimizing inverse gated pulse or coupling methods, cryogenic temperatures, or through sample concentration.

The results of this study demonstrated that several small permanganate additions over time may result in favorable processing conditions for Tank 48H. Although TK48-SH-60C-9 had the highest decomposition based on potassium, the reaction rate appeared to slow rapidly after permanganate addition. The TK48-SH-60C-111 tests had comparable decomposition percentages and required smaller quantity additions of permanganate, which will generate less total volume of waste and may be favorable for downstream processing (e.g., lower Mn solids in an eventual Defense Waste Processing Facility (DWPF) waste stream). Favorable results were shown in test series “TK48-SH-60C-111” where multiple small strikes were performed.

Based on the results of the shaker table tests, it is recommended that the tests with the highest TPB decomposition be repeated at a larger scale utilizing a more representative slurry of Tank 48H to evaluate the extent of TPB decomposition possible with tank processing. In addition, all subsequent 2-L vessel experiments should be conducted with continuous agitation with a continuously monitored overhead mixer.

For future experiments that require analysis of species that may leach from glass in high hydroxide (e.g., boron, potassium, or silicon), it is suggested to use reaction vessels made of high-density polyethylene (HDPE), Teflon, carbon steel, or stainless steel. Quartz may be used if additional silicon from etching is not a concern. Due to the complex nature and variety of reaction pathways for TPB decomposition, it is recommended that Savannah River National Laboratory (SRNL) develop a more complex simulant based on the characterization results of the recently pulled Tank 48H sample, as outlined in the Technical Task Request (TTR) and Task Technical and Quality Assurance Plan (TTQAP). It is also recommended to perform byproduct testing (i.e., triphenylborane (3PB), 2PB, PBA, phenol, and biphenyl) with sodium permanganate to understand the kinetics and decomposition of TPB byproducts. Although favorable results were found in this study, a more complex simulant that matches the current Tank 48H chemistry would provide additional insight into the process when conducted with actual waste.

5.0 References

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Appendix A. Calculation of TPB Decomposition (%)

Table A-1 and Table A-2 provide an example of TK48-SH-60C-9 step-by-step calculations performed from potassium and boron ICP-ES measurements to obtain TPB decomposition. Equation A-1 and A-2 show the equation used to obtain the TPB decomposition results shown in Table 3-3.

Table A-1. TPB Decomposition of filtrate from ICP-ES measurements of potassium (TK48-SH-60C-9)

	Time 0	Time 1	Time 8	Time 14	Time 56
Measured K from ICP-ES (mg/L)	451	982	1080	1110	1240
From KNO_3 (mg/L)	451	451	451	451	451
From KTPB (mg/L)[a]	0.00	531	629	659	789
From KTPB (mol/L)	0.000	0.014	0.016	0.017	0.020
TPB Added (mol/L)	0.056	0.056	0.056	0.056	0.056
TPB Decomposition (%)	0.00	24.1	28.5	29.9	35.8

[a] Potassium nitrite from Time 0 sample was subtracted out of the potassium value received from ICP-ES.

$$\frac{\boldsymbol{From\ KTPB\ (\frac{mol}{L})}}{\boldsymbol{TPB\ Added\ (\frac{mol}{L})}} * \mathbf{100} = \boldsymbol{TPB\ Decomposition}\ (\%) \qquad \text{(A-1)}$$

Table A-2. TPB Decomposition of filtrate from ICP-ES measurements of boron (TK48-SH-60C-9)

	Time 0	Time 1	Time 8	Time 14	Time 56
Measured B from ICP-ES (mg/L)	19	220	500	888	2550
Calculated B (mg/L)[a]	-0.4	191	420	559	490
Calculated B (mol/L)	0.000	0.018	0.039	0.052	0.045
TPB Added (mol/L)	0.056	0.056	0.056	0.056	0.056
TPB Decomposition (%)	-0.07	31.5	69.4	92.3	80.9

[a] The Blank sample was subtracted out of the measured B from ICP-ES. The ICP-ES Blank results are shown in **Table 3-2**.

$$\frac{\boldsymbol{Calculated\ B\ (\frac{mol}{L})}}{\boldsymbol{TPB\ Added\ (\frac{mol}{L})}} * \mathbf{100} = \boldsymbol{TPB\ Decomposition}\ (\%) \qquad \text{(A-2)}$$

Appendix B. NMR Method Development

An initial set of experiments were performed to compare proton methodology with water suppression methods. A proton spectrum was first collected on TK48-SH-25C-3-60C-3 Time 7 without water suppression as a baseline for expected peak shapes of aromatic resonances. Next, a water suppression method using pre-saturation pulses (ZGPR) was tested. These experiments showed out-of-phase signals that shift the baseline along the broad water signal and into the aromatic spectral region (i.e., 6.0 – 9.0 ppm). Following these tests, a series of P3919GP (i.e., WATERGATE)[7,8] methods were tested using various offset frequencies (O1P: 4.7, 4.9, and 5.1 ppm), and it was found that the P3919GP method using an offset frequency of 4.9 ppm provided the narrowest water signal, in-phase spectra, and lower signal-to-noise ratios. A similar method has been used previously at SRNL for high-salt samples, however, on a different instrument.[8] Thus, all water-suppression ^{1}H NMR spectra were collected using the P3919GP WATERGATE method with 64 scans averaged.

A summary of the initial water suppression methodology can be found in Figure B-1. It is important to note that the baseline in the right spectrum (P3919GP with offset frequency (O1P) set to 4.9 ppm) is flat in both regions of interest (−1.0 – 2.0 ppm, and 6.0 – 9.0 ppm) whereas the baseline is not flat in either the standard proton or ZGPR methods. Thus, all tank samples that were collected with and without water suppression were collected with the P3919GP method with a 4.9 ppm offset frequency. The sharp line in the center of the water signal for spectra collected in the P3919GP method is due to over-suppression of the water signals intensity, resulting in negative phasing, but does not alter the integrations outside of this region.

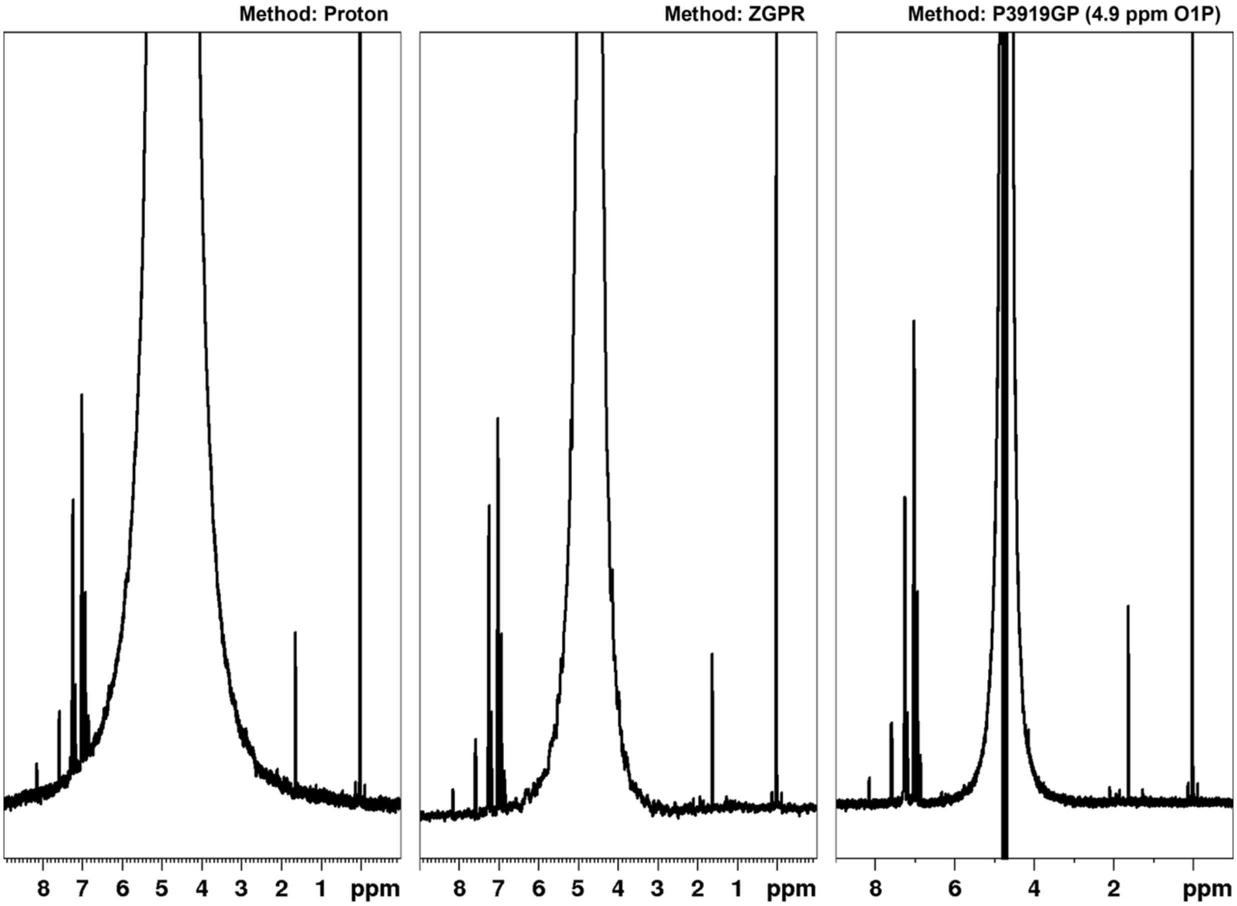

Figure B-1 ^{1}H NMR spectra of TK48-SH-25C-3-60C-3 Time 7 using three different data-collection methods: (*left*) standard proton, (*middle*) ZGPR, and (*right*) P3919GP (i.e., WATERGATE) with 4.9 ppm offset frequency.

To confirm that the determined water suppression method would not over-suppress peaks of interest in the aromatic region, a comparison of a standard proton NMR with the WATERGATE method was made. For this, an approximately 10 mM solution of sodium tetraphenylborate was prepared in deionized water. The same coaxial sample tube configuration was used for this experiment with a 10 mM TMSP/D_2O lock and reference standard coaxial insert. 400 µL of sample was loaded to the outer tube and 50 µL of lock and reference standard was added to the coaxial insert. Integration of the spectral regions in the aromatic region show consistent trends with that expected for sodium tetraphenylborate, shown in Figure B-2. The integrations are labeled with green letters corresponding to the associated protons on aromatic rings. The signals integrate to the expected values of 8H, 8H, and 4H when the isolated peak is calibrated to 8H, indicating that the carbon-bound protons of the compounds of interest (and its derivatives) are not removed via water suppression. It is important to note that acidic protons (e.g., –OH groups) will likely exchange with water and can be removed in traditional proton and water suppression methods in specific analytes like boric acid and phenylboronic acid.[13]

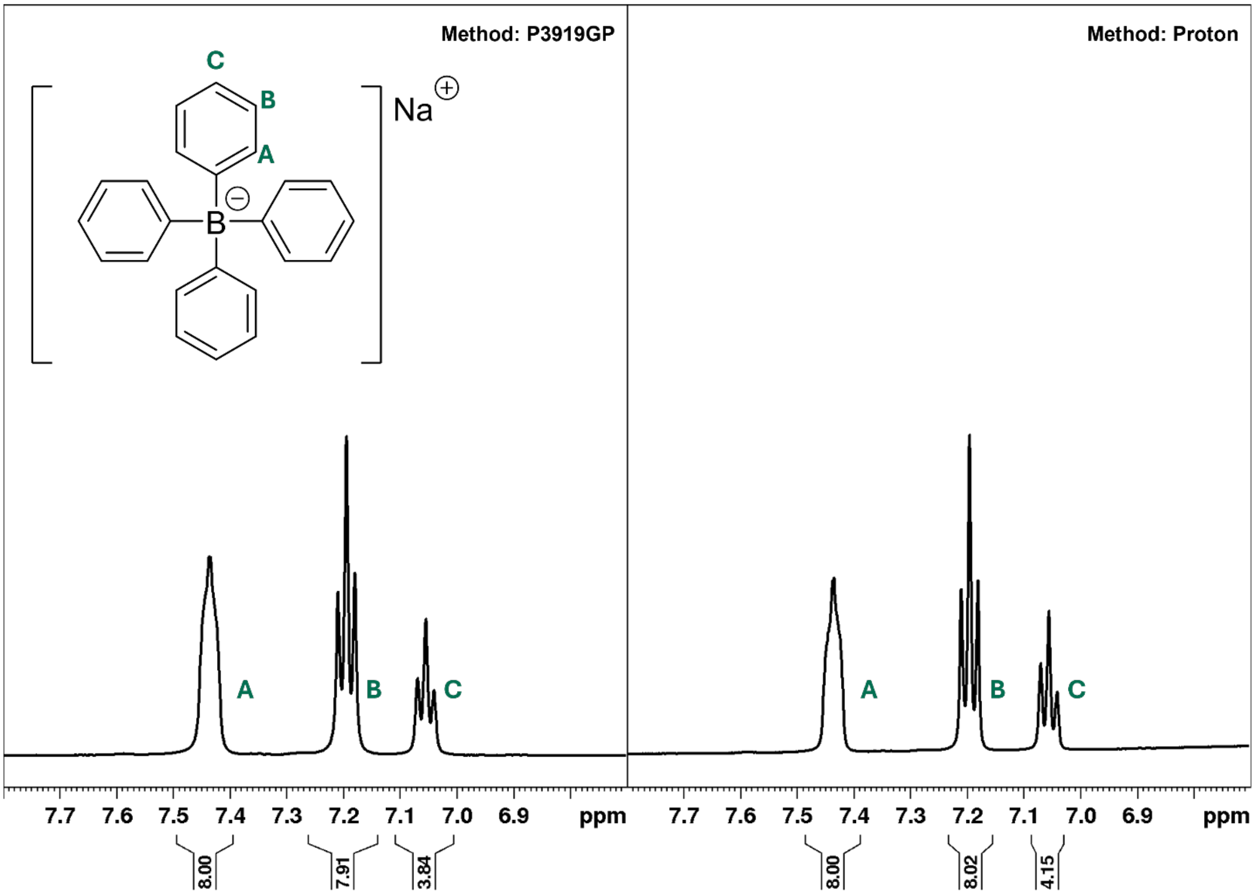

Figure B-2 ^{1}H NMR spectra of 10 mM sodium tetraphenylborate with standard proton (*left*) and P3919GP WATERGATE (*right*) methods. The integrations of each signal are shown. The corresponding proton assignments and their integrations are shown with the labeled inset of sodium tetraphenylborate.

Additional tests on phenylboronic acid in H_2O and boric acid in H_2O (both at 10 mM analyte concentration with 10 mM TMSP/D_2O locking and reference coaxial insert) were collected. Their spectra can be found in Figure B-3 and Figure B-4, respectively. Phenylboronic acid behaves as expected with identifiable resonances in the aromatic region and peak assignments were possible due to known peak splitting patterns and integration values. WATERGATE data for these standards were collected at a 5.1 ppm offset frequency and not a 4.9 ppm offset frequency, thus only the standard proton NMR (not with water suppression) are shown. In the boric acid spectrum (Figure B-4), only TMSP and water are observed, likely due to proton exchange in boric acid with water.

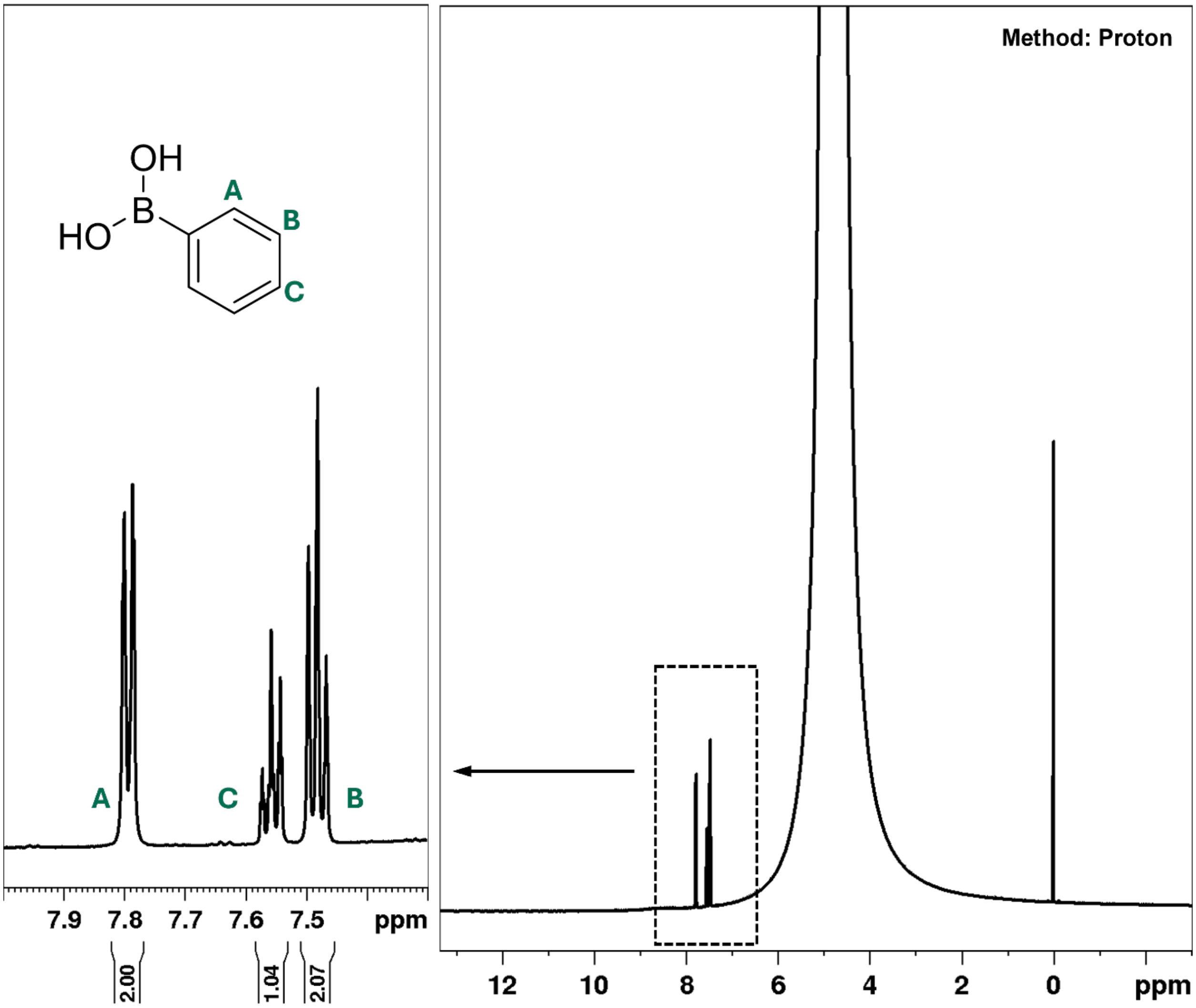

Figure B-3 ^{1}H NMR spectrum of 10 mM phenylboronic acid using the standard proton method (*right*). The aromatic region is expanded to observe the peak splitting, integrations, and identity (*left*). The corresponding proton assignments and their integrations are shown with the labeled inset of phenylboronic acid.

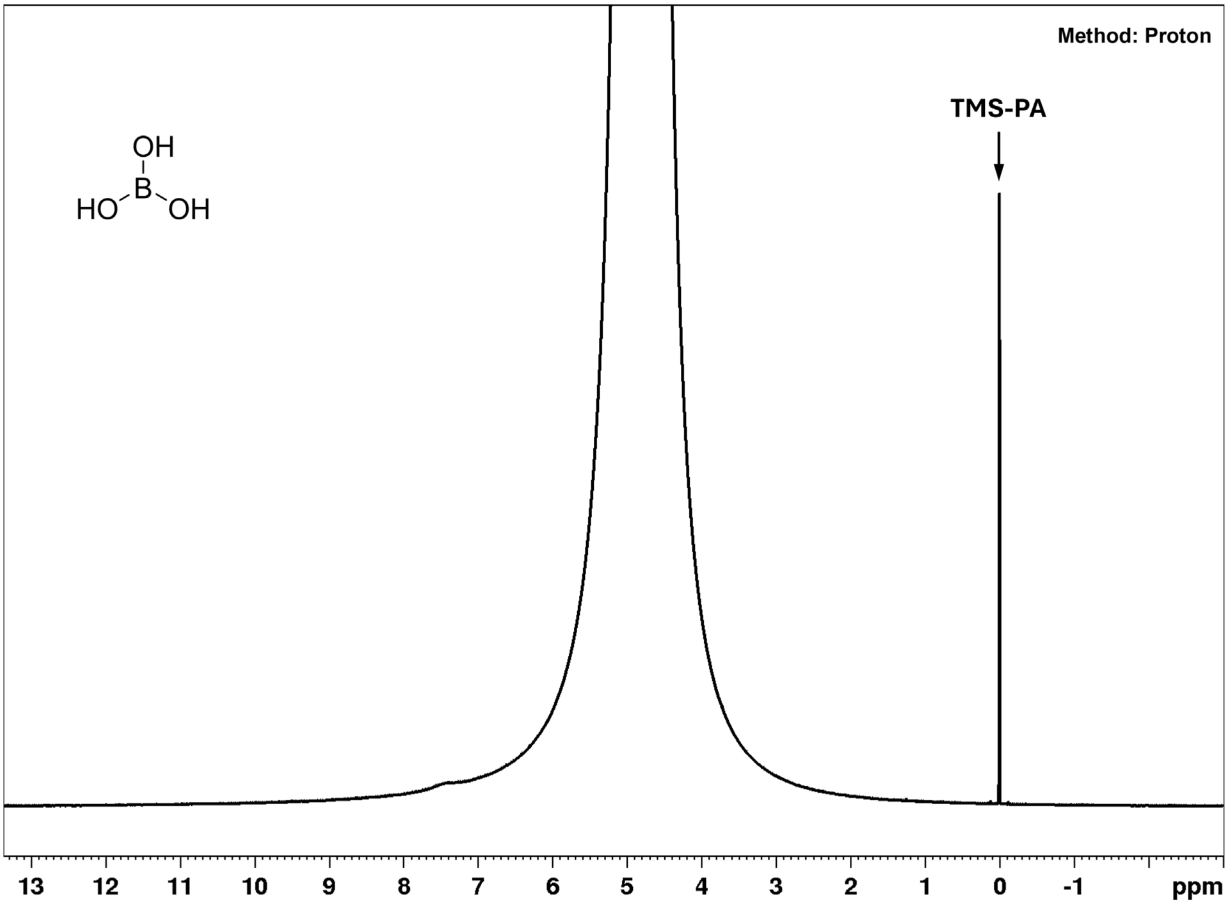

Figure B-4 ^{1}H NMR spectrum of 10 mM boric acid using the standard proton method. No additional peaks are observed other than water (centered at 4.8 ppm) and TMSP (axis-calibrated to 0.0 ppm).

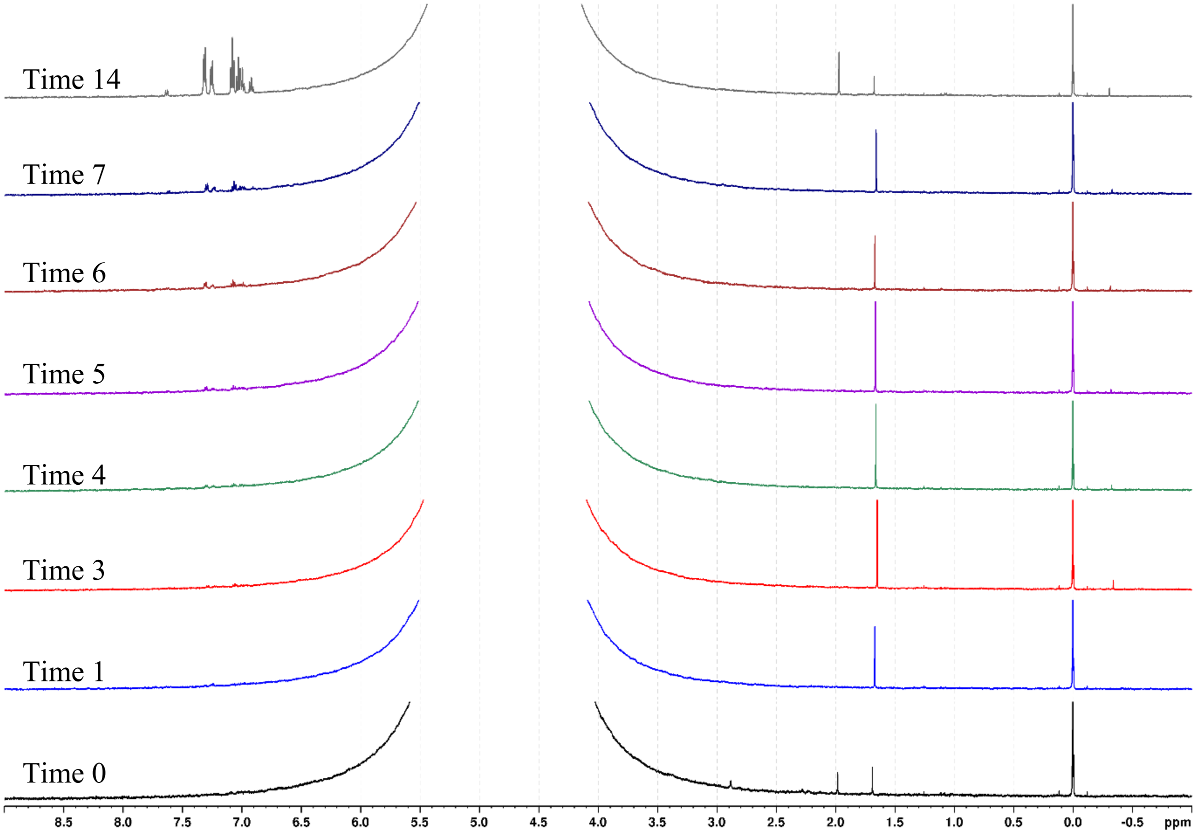

Figure B-5 ^{1}H NMR spectra of TK48-2LV-25C-1-60C-2 test series using standard proton method. Samples were axis calibrated to 0.0 ppm with TMSP/D_2O reference. The black, blue, red, green, purple, maroon, navy, and grey spectra correspond to Time 0, Time 1, Time 3, Time 4, Time 5, Time 6, Time 7, and Time 14, respectively (listed from bottom to top). The absence of signal between ~5.5 and 4.0 ppm is due to the high intensity water signal exceeding the Y-axis scaling.

Table B-1 Relative integration (ReI) and chemical shift (in ppm) values of signals standardized to the 9H singlet signal for TMSP for TK48-2LV-25C-1-60C-2 (standard ^{1}H method).

Time	I ReI, ppm	II ReI, ppm	III ReI, ppm	IV ReI, ppm	V ReI, ppm	VI ReI, ppm	VII ReI, ppm	VIII ReI, ppm	IX ReI, ppm
0	1.43, 1.69	1.54, 1.98	3.08, 2.89	low s/n	low s/n	low s/n	low s/n	low s/n	low s/n
1	1.93, 1.67	– –	– –	low s/n	low s/n	low s/n	low s/n	low s/n	low s/n
3	2.55, 1.65	– –	– –	low s/n	low s/n	low s/n	low s/n	low s/n	low s/n
4	2.52, 1.66	– –	– –	low s/n	low s/n	low s/n	low s/n	low s/n	low s/n
5	2.74, 1.66	– –	– –	low s/n	low s/n	low s/n	low s/n	low s/n	low s/n
6	1.88, 1.67	– –	– –	low s/n	low s/n	low s/n	low s/n	low s/n	low s/n
7	2.07, 1.66	– –	– –	2.08, 6.91	3.53, 6.99	2.21, 7.07	2.04, 7.24	1.77, 7.30	0.82, 7.62
14	1.25, 1.67	– –	– –	3.36, 6.92	7.81, 7.01	6.09, 7.08	4.90, 7.25	5.79, 7.32	1.22, 7.64

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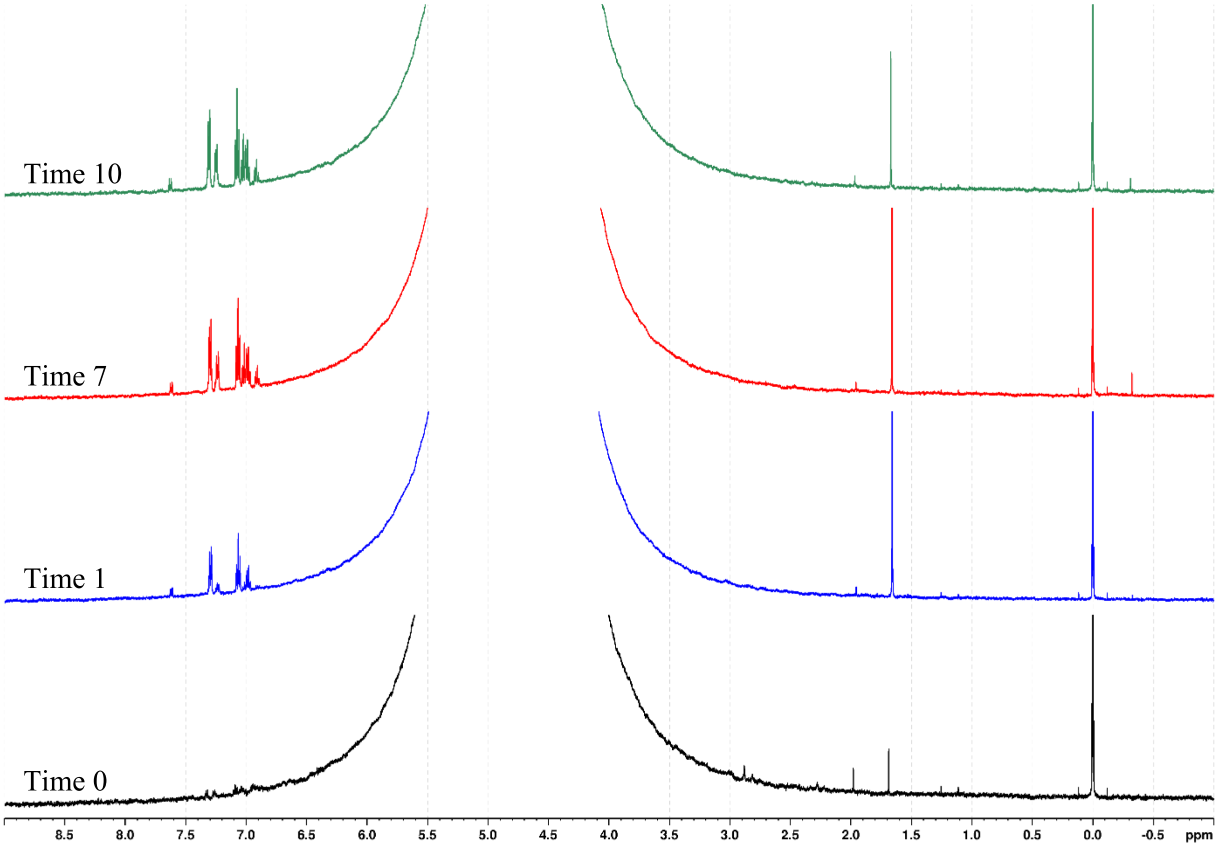

Figure B-6 ^{1}H NMR spectra of TK48-2LV-60C-3 test series using standard proton method. Samples were axis calibrated to 0.0 ppm with TMSP/D$_2$O reference. The black, blue, red, and green spectra correspond to Time 0, Time 1, Time 7, and Time 10, respectively (listed from bottom to top). The absence of signal between ~5.5 and 4.0 ppm is due to the high intensity water signal exceeding the Y-axis scaling.

Table B-2 Relative integration (ReI) and chemical shift (in ppm) values of signals standardized to the 9H singlet signal for TMSP for TK48-2LV-60C-3 (standard ^{1}H method).

Time	I ReI, ppm	II ReI, ppm	III ReI, ppm	IV ReI, ppm	V ReI, ppm	VI ReI, ppm	VII ReI, ppm	VIII ReI, ppm	IX ReI, ppm
0	0.56, 1.69	– –	– –	low s/n	low s/n	low s/n	low s/n	low s/n	low s/n
1	4.71, 1.66	– –	– –	2.46, 6.91	4.76, 6.99	3.70, 7.07	2.05, 7.24	3.30, 7.29	1.11, 7.62
7	2.43, 1.66	– –	– –	2.41, 6.91	5.54, 7.00	4.28, 7.07	3.13, 7.24	3.78, 7.30	1.10, 7.62
10	1.62, 1.67	– –	– –	2.61, 6.91	5.37, 7.01	4.14, 7.08	3.22, 7.25	4.11, 7.31	1.12, 7.63

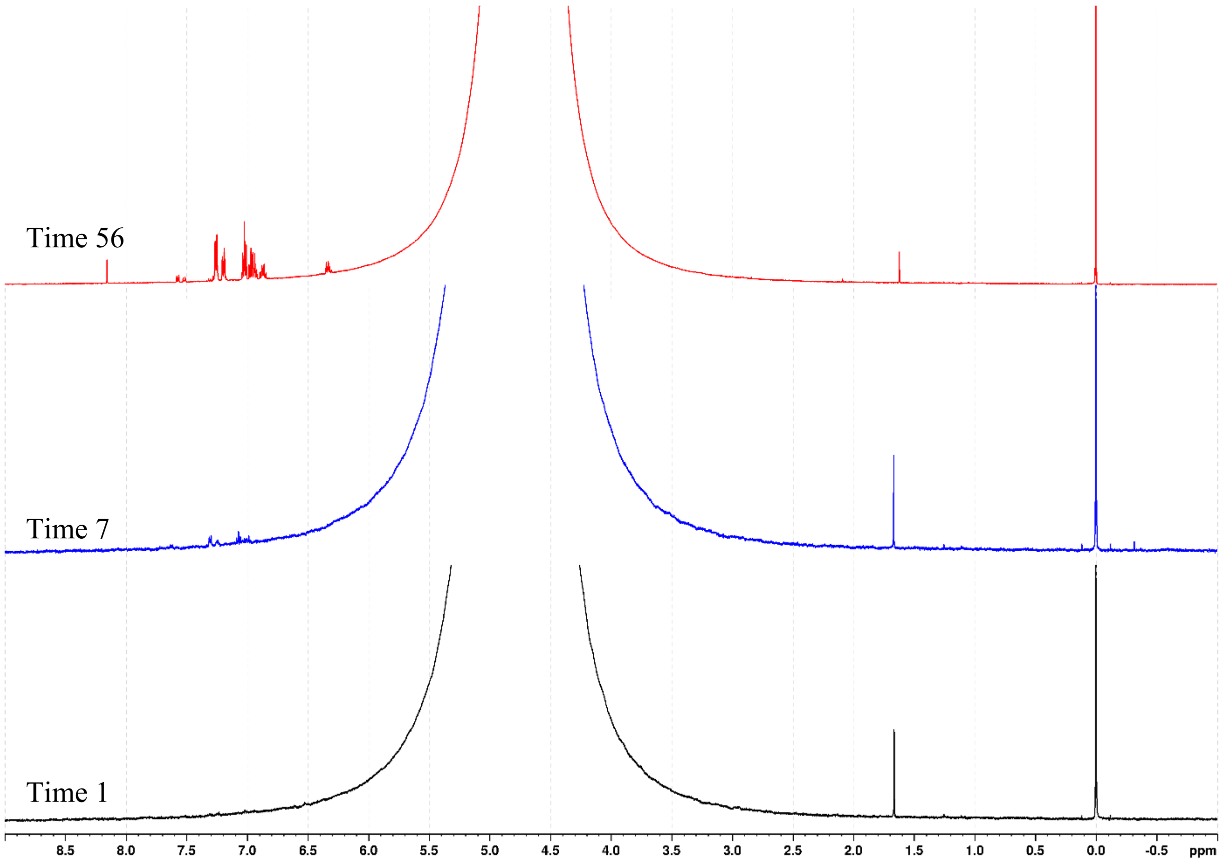

Figure B-7 ^{1}H NMR spectra of TK48-SH-25C-1-60C-2 test series using standard proton method. Samples were axis calibrated to 0.0 ppm with TMSP/D_2O reference. The black, blue, and red spectra correspond to Time 1, Time 7, and Time 56, respectively (listed from bottom to top). The absence of signal between ~5.5 and 4.0 ppm is due to the high intensity water signal exceeding the Y-axis scaling.

Table B-3 Relative integration (ReI) and chemical shift (in ppm) values of signals standardized to the 9H singlet signal for TMSP for TK48-SH-25C-1-60C-2 (standard ^{1}H method).

Time	I	II	III	IV	V	VI	VII	VIII	IX
	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm
1	1.42, 1.66	– –	– –	low s/n	low s/n	low s/n	low s/n	low s/n	low s/n
7	0.58, 1.67	– –	– –	2.65, 6.91	5.96, 7.00	5.79, 7.07	3.27, 7.24	5.35, 7.31	1.34, 7.62
56	1.75, 1.62	0.79, 2.09	– –	7.54, 6.87	11.20, 6.95	9.64, 7.02	6.81, 7.19	9.64, 7.25	2.07, 7.57

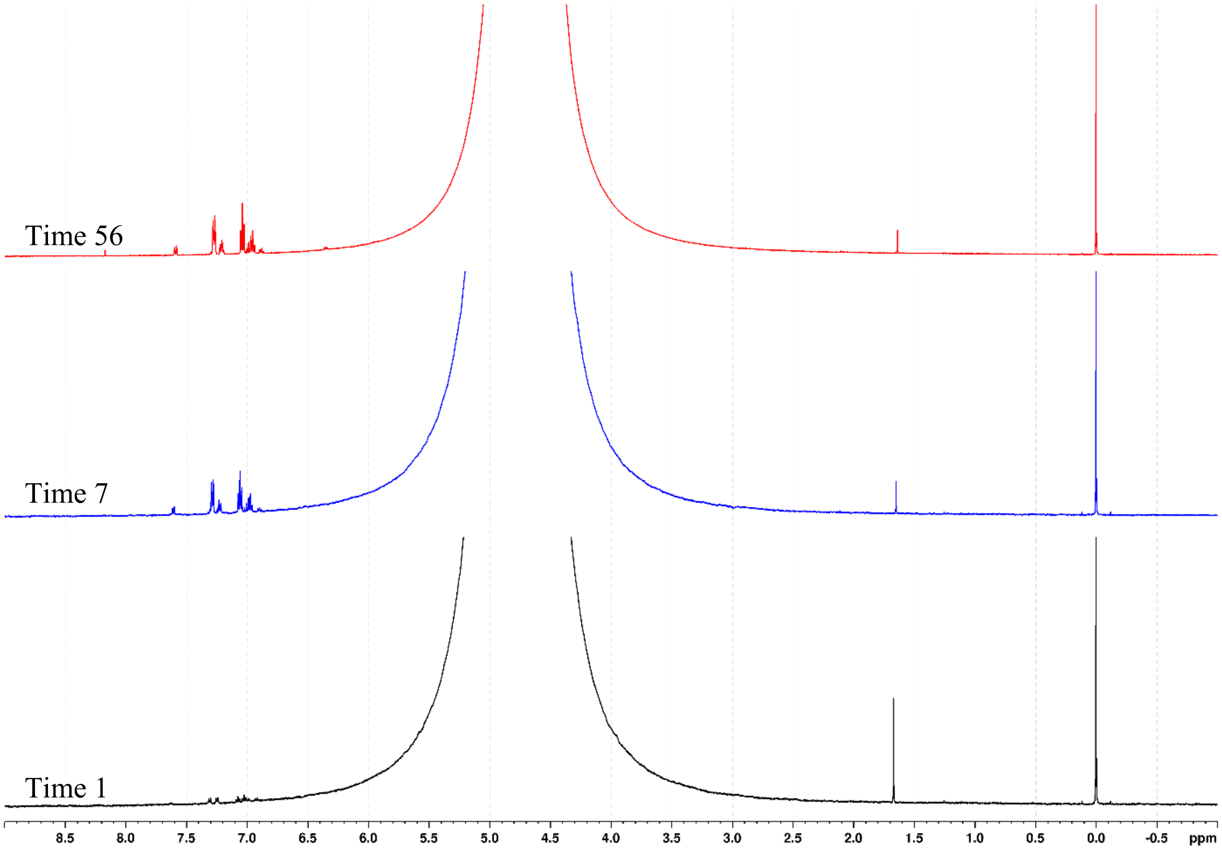

Figure B-8 ^{1}H NMR spectra of TK48-SH-25C-3-60C-3 test series using standard proton method. Samples were axis calibrated to 0.0 ppm with TMSP/D_2O reference. The black, blue, and red spectra correspond to Time 1, Time 7, and Time 56, respectively (listed from bottom to top). The absence of signal between ~5.5 and 4.0 ppm is due to the high intensity water signal exceeding the Y-axis scaling.

Table B-4 Relative integration (ReI) and chemical shift (in ppm) values of signals standardized to the 9H singlet signal for TMSP for TK48-SH-3-60C-3 (standard ^{1}H method).

Time	I ReI, ppm	II ReI, ppm	III ReI, ppm	IV ReI, ppm	V ReI, ppm	VI ReI, ppm	VII ReI, ppm	VIII ReI, ppm	IX ReI, ppm
1	2.11, 1.67	– –	– –	low s/n	low s/n	low s/n	low s/n	low s/n	low s/n
7	1.24, 1.65	– –	– –	2.16, 6.90	4.91, 6.97	4.48, 7.06	2.64, 7.23	4.23, 7.29	1.47, 7.61
56	1.88, 1.63	– –	– –	3.59, 6.89	7.87, 6.97	8.48, 7.04	4.62, 7.21	9.03, 7.27	1.95, 7.59

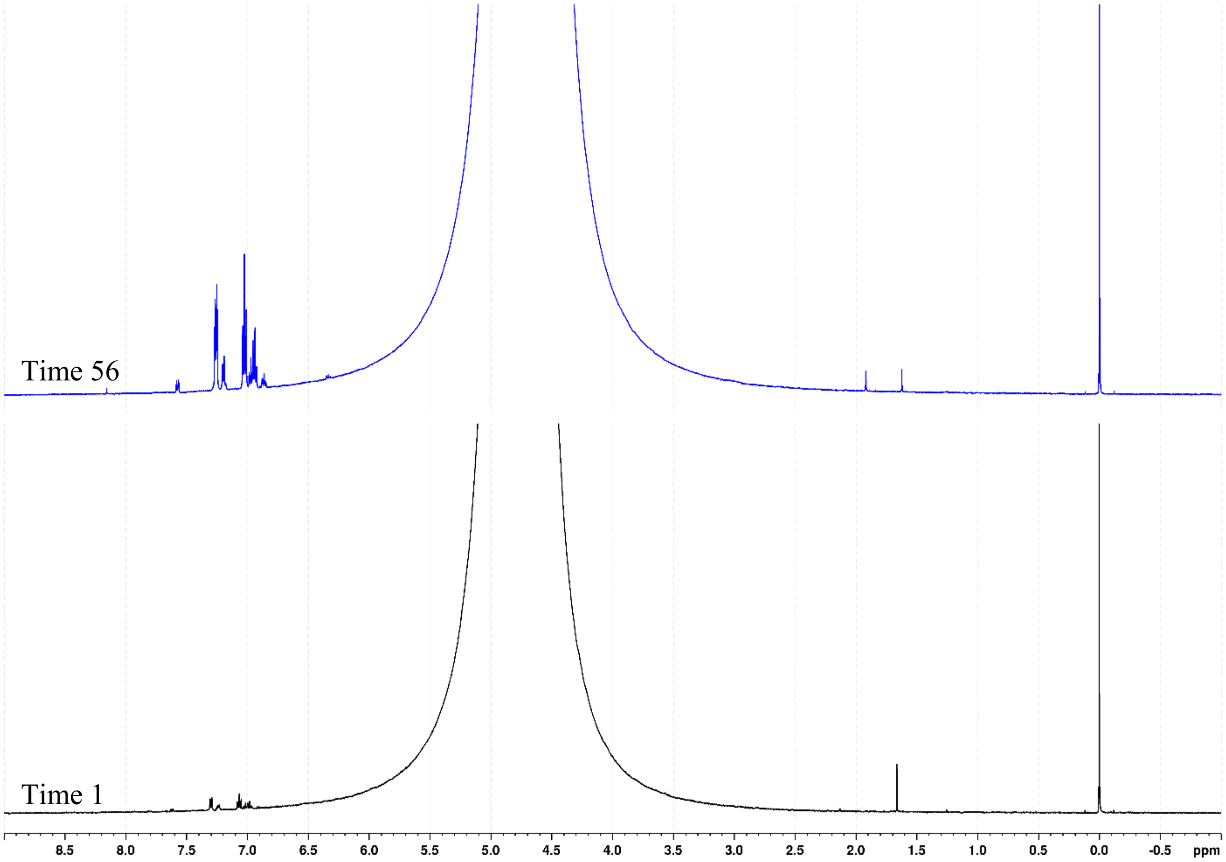

Figure B-9 ^{1}H NMR spectra of TK48-SH-60C-111 test series using standard proton method. Samples were axis calibrated to 0.0 ppm with TMSP/D_2O reference. The black and blue spectra correspond to Time 1 and Time 56, respectively (listed from bottom to top). The absence of signal between ~5.5 and 4.0 ppm is due to the high intensity water signal exceeding the Y-axis scaling.

Table B-5 Relative integration (ReI) and chemical shift (in ppm) values of signals standardized to the 9H singlet signal for TMSP for TK48-SH-60C-111 (standard ^{1}H method).

Time	I	II	III	IV	V	VI	VII	VIII	IX
	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm
1	1.77, 1.66	– –	– –	1.22, 6.92	4.36, 7.00	2.96, 7.07	2.31, 7.24	2.56, 7.30	1.12, 7.62
56	1.02, 1.62	1.57, 1.92	– –	4.18, 6.86	11.22, 6.96	12.88, 7.03	5.45, 7.19	12.72, 7.26	2.23, 7.58

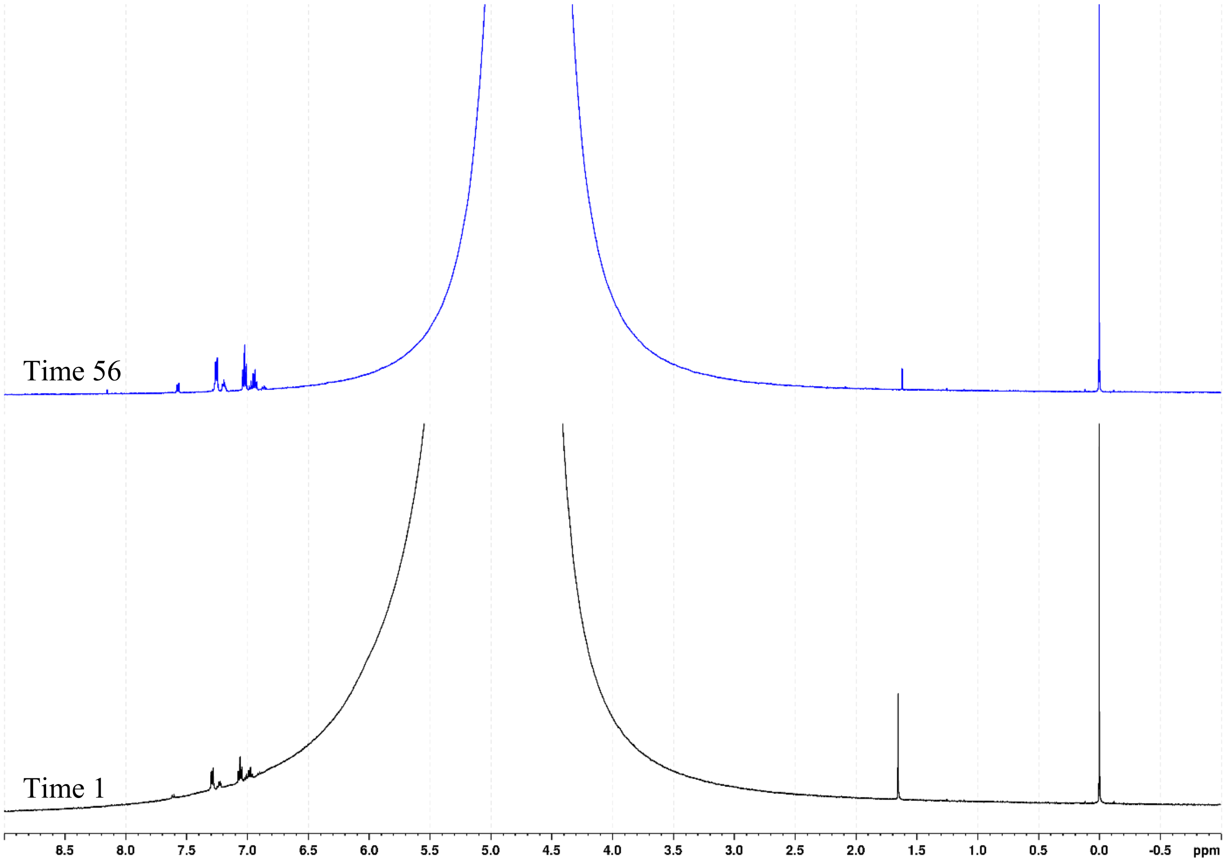

Figure B-10 ^{1}H NMR spectra of TK48-SH-60C-33 test series using standard proton method. Samples were axis calibrated to 0.0 ppm with TMSP/D_2O reference. The black and blue spectra correspond to Time 1 and Time 56, respectively (listed from bottom to top). The absence of signal between ~5.5 and 4.0 ppm is due to the high intensity water signal exceeding the Y-axis scaling.

Table B-6 Relative integration (ReI) and chemical shift (in ppm) values of signals standardized to the 9H singlet signal for TMSP for TK48-SH-60C-33 (standard ^{1}H method).

Time	I ReI, ppm	II ReI, ppm	III ReI, ppm	IV ReI, ppm	V ReI, ppm	VI ReI, ppm	VII ReI, ppm	VIII ReI, ppm	IX ReI, ppm
1	6.00, 1.65	– –	– –	7.40, 6.91	21.77, 6.99	14.11, 7.06	9.71, 7.23	11.82, 7.29	4.55, 7.61
56	1.22, 1.62	– –	– –	2.66, 6.87	6.41, 6.95	6.32, 7.03	3.68, 7.19	6.18, 7.25	2.01, 7.57

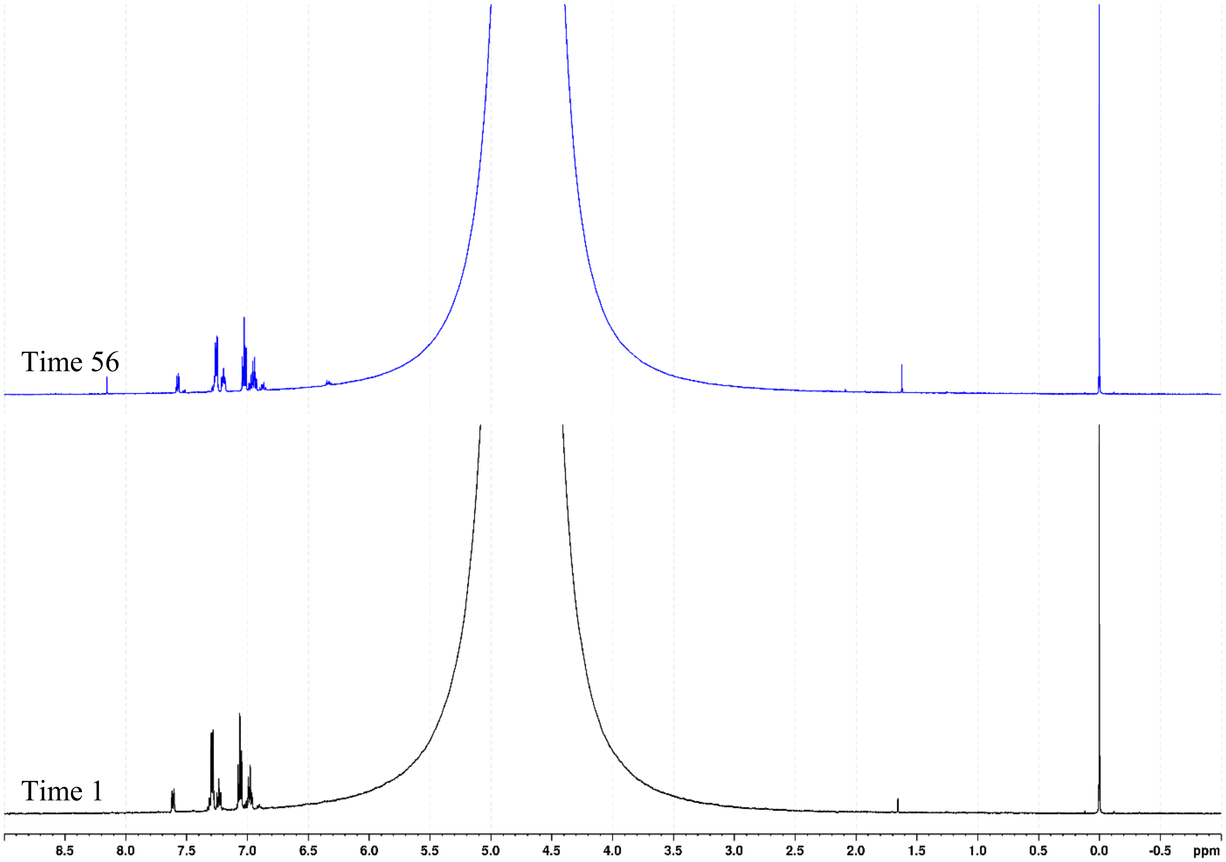

Figure B-11 ^{1}H NMR spectra of TK48-SH-60C-9 test series using standard proton method. Samples were axis calibrated to 0.0 ppm with TMSP/D_2O reference. The black and blue spectra correspond to Time 1 and Time 56, respectively (listed from bottom to top). The absence of signal between ~5.5 and 4.0 ppm is due to the high intensity water signal exceeding the Y-axis scaling.

Table B-7 Relative integration (ReI) and chemical shift (in ppm) values of signals standardized to the 9H singlet signal for TMSP for TK48-SH-60C-9 (standard ^{1}H method).

Time	I ReI, ppm	II ReI, ppm	III ReI, ppm	IV ReI, ppm	V ReI, ppm	VI ReI, ppm	VII ReI, ppm	VIII ReI, ppm	IX ReI, ppm
1	0.85, 1.66	– –	– –	2.59, 6.90	7.80, 6.99	9.58, 7.06	4.46, 7.25	9.15, 7.29	3.14, 7.61
56	1.35, 1.62	– –	– –	5.19, 6.87	9.77, 6.96	10.76, 7.03	6.46, 7.20	11.35, 7.26	3.55, 7.58

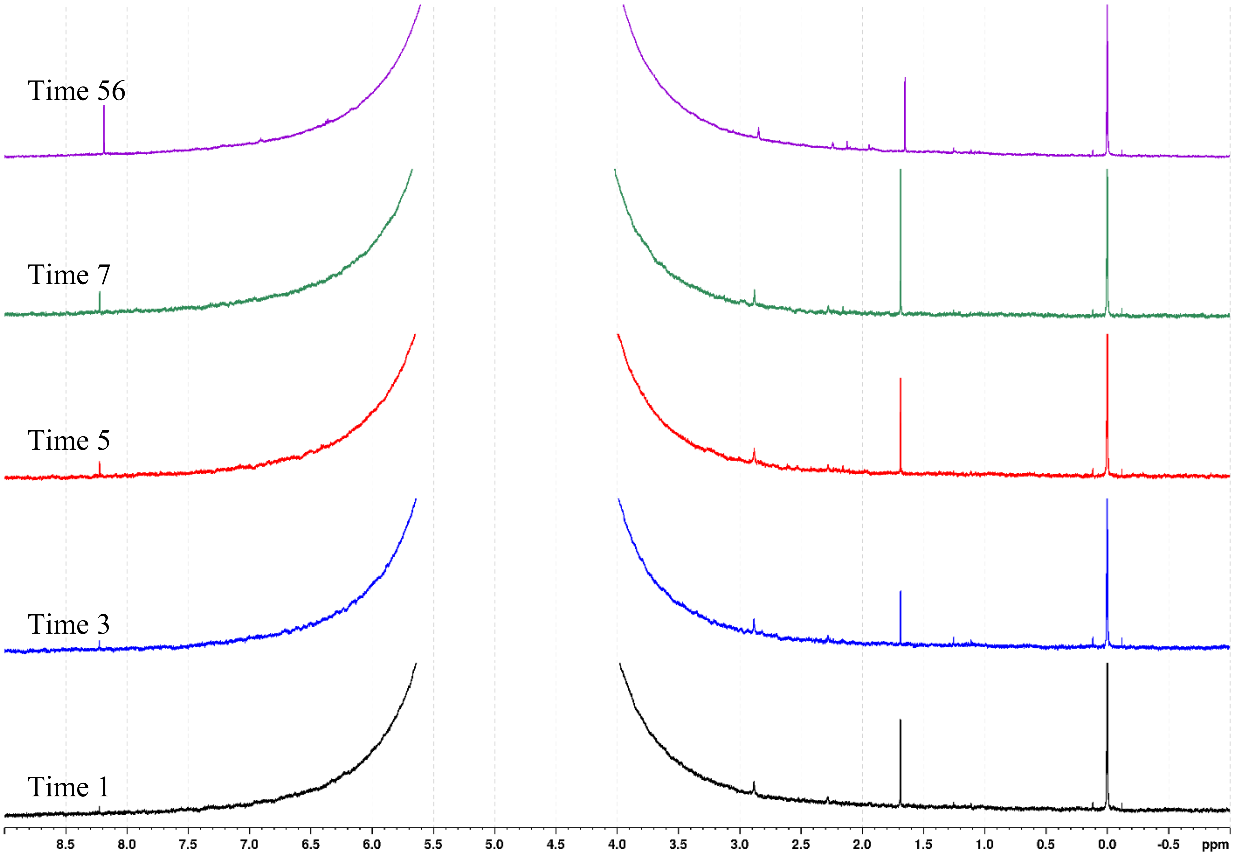

Figure B-12 ^{1}H NMR spectra of TK48-SH-60C-BL test series using standard proton method. Samples were axis calibrated to 0.0 ppm with TMSP/D_2O reference. The black, blue, red, green, and purple spectra correspond to Time 1, Time 3, Time 5, Time 7, and Time 56, respectively (listed from bottom to top). The absence of signal between ~5.5 and 4.0 ppm is due to the high intensity water signal exceeding the Y-axis scaling.

Table B-8 Relative integration (ReI) and chemical shift (in ppm) values of signals standardized to the 9H singlet signal for TMSP for TK48-SH-60C-BL (standard ^{1}H method).

Time	I	II	III	IV	V	VI	VII	VIII	IX
	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm	ReI, ppm
1	2.01, 1.69	1.56, 2.28	3.18, 2.88	– –	– –	– –	– –	– –	– –
3	0.75, 1.69	1.26, 2.28	1.72, 2.88	– –	– –	– –	– –	– –	– –
5	1.34, 1.69	0.93, 2.28	2.20, 2.88	– –	– –	– –	– –	– –	– –
7	1.67, 1.69	0.52, 2.28	1.95, 2.88	– –	– –	– –	– –	– –	– –
56	1.61, 1.65	0.96, 1.94	3.63, 2.85	– –	– –	– –	– –	– –	– –

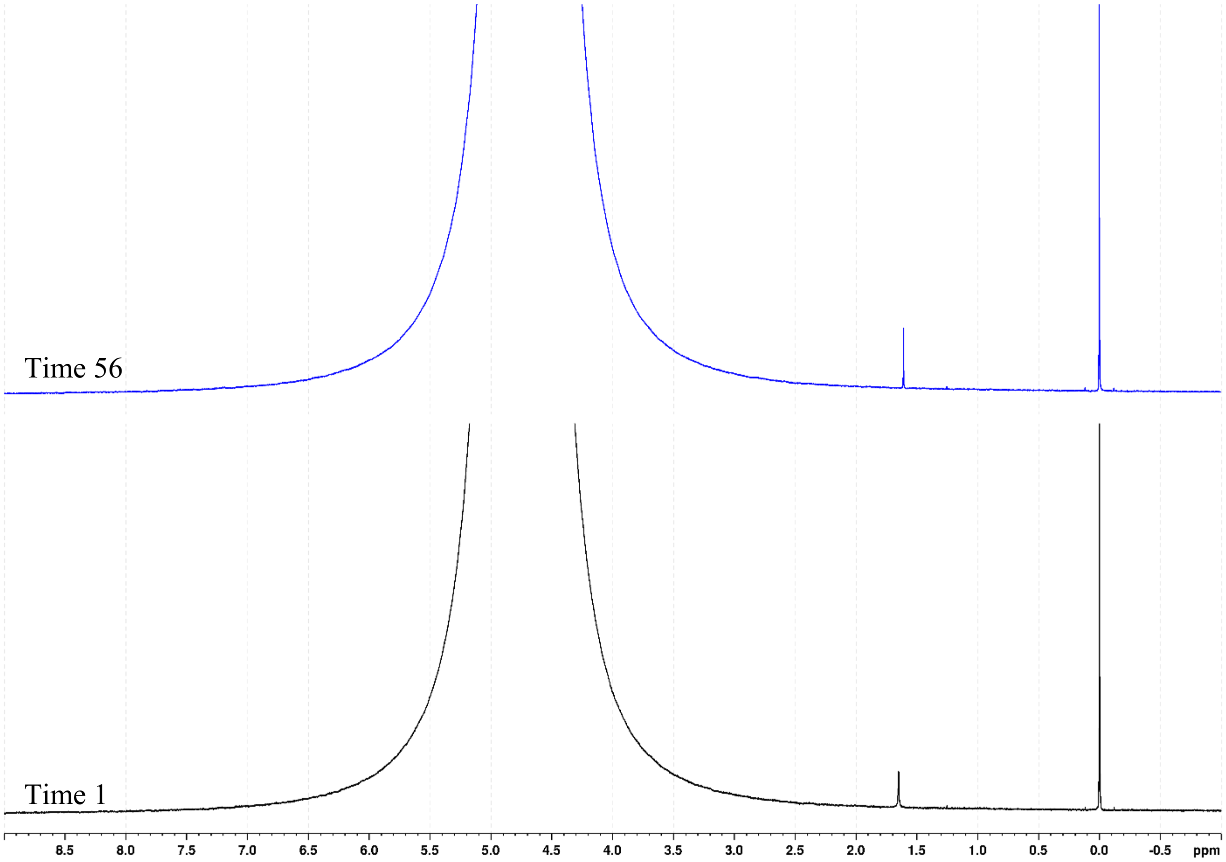

Figure B-13 ^1H NMR spectra of TK48-SH-60C-NOTPB test series using standard proton method. Samples were axis calibrated to 0.0 ppm with TMSP/D_2O reference. The black and blue spectra correspond to Time 1 and Time 56, respectively (listed from bottom to top). The absence of signal between ~5.5 and 4.0 ppm is due to the high intensity water signal exceeding the Y-axis scaling.

Table B-9 Relative integration (ReI) and chemical shift (in ppm) values of signals standardized to the 9H singlet signal for TMSP for TK48-SH-60C-NOTPB (standard ^1H method).

Time	I ReI, ppm	II ReI, ppm	III ReI, ppm	IV ReI, ppm	V ReI, ppm	VI ReI, ppm	VII ReI, ppm	VIII ReI, ppm	IX ReI, ppm
1	4.14, 1.65	– –	– –	– –	– –	– –	– –	– –	– –
56	2.73, 1.61	– –	– –	– –	– –	– –	– –	– –	– –

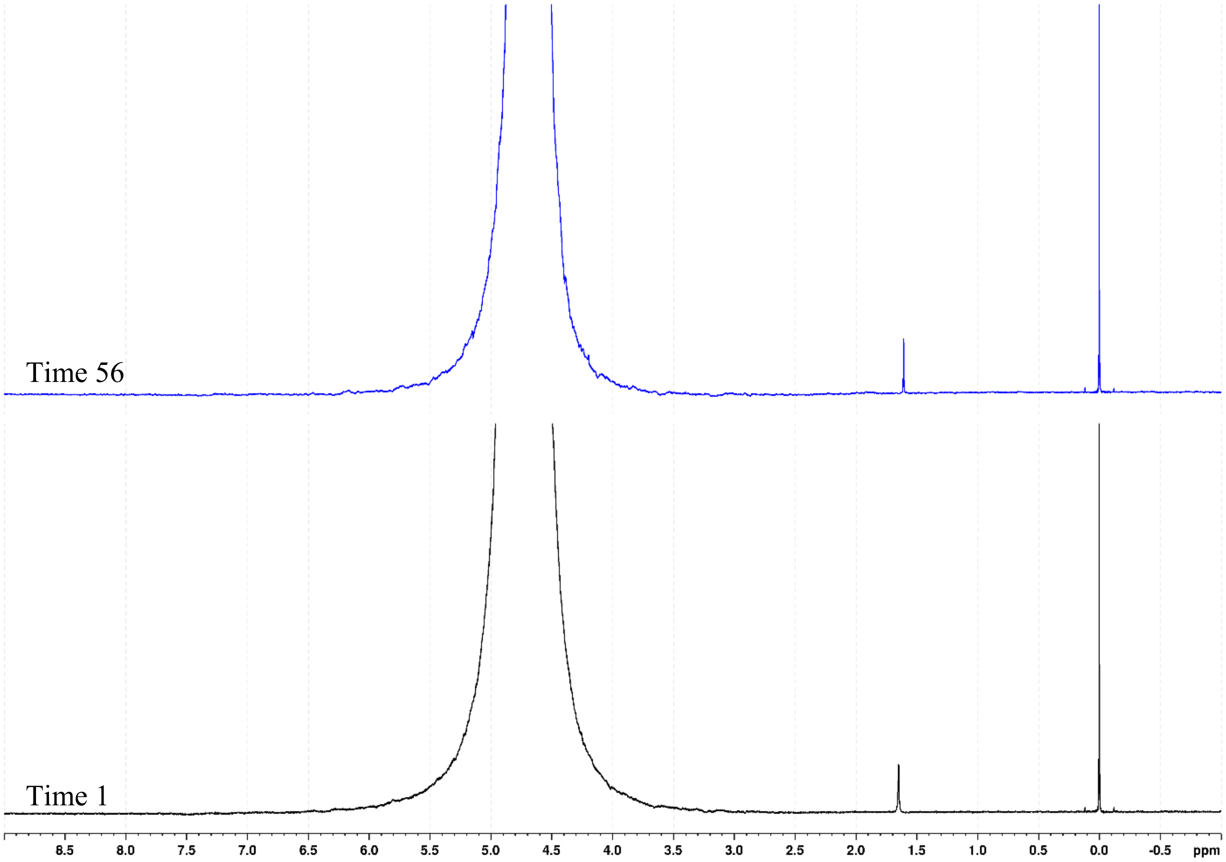

Figure B-14 ^{1}H NMR spectra of TK48-SH-60C-NOTPB test series using P3919GP WATERGATE method. Samples were axis calibrated to 0.0 ppm with TMSP/D_2O reference. The black and blue spectra correspond to Time 1 and Time 56, respectively (listed from bottom to top). The absence of signal between ~5.3 and 4.5 ppm is due to the high intensity water signal exceeding the Y-axis scaling.

Table B-10 Relative integration (ReI) and chemical shift (in ppm) values of signals standardized to the 9H singlet signal for TMSP for TK48-SH-60C-NOTPB (P3919GP WATERGATE).

Time	I ReI, ppm	II ReI, ppm	III ReI, ppm	IV ReI, ppm	V ReI, ppm	VI ReI, ppm	VII ReI, ppm	VIII ReI, ppm	IX ReI, ppm
1	3.64, 1.65	– –	– –	– –	– –	– –	– –	– –	– –
56	2.27, 1.61	– –	– –	– –	– –	– –	– –	– –	– –

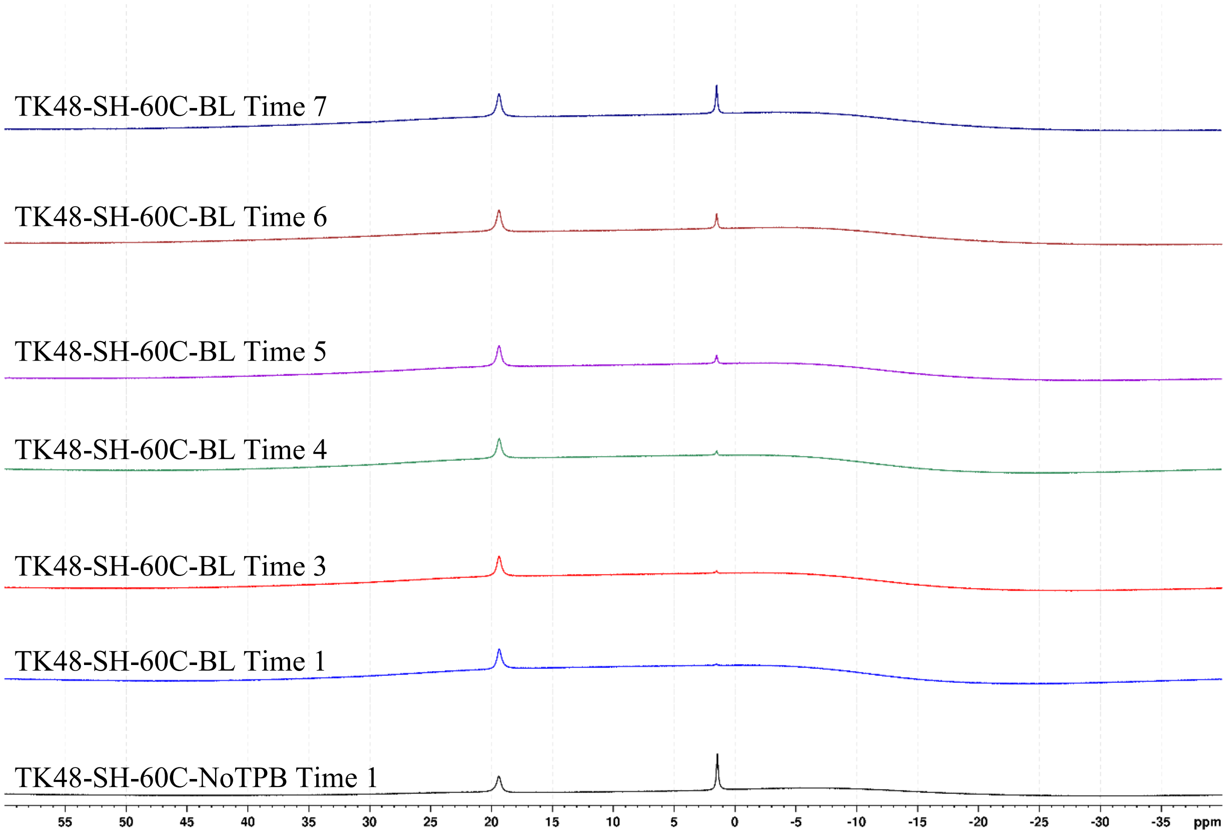

Figure B-15 ^{11}B NMR spectra (listed from bottom to top) of TK48-SH-60C-NOTPB and TK48-SH-60C-BL test series. The black, blue, red, green, purple, brown, and navy spectra correspond to TK48-SH-60C-NOTPB Time 1 and TK48-SH-60C-BL Time 1, Time 3, Time 4, Time 5, Time 6, and Time 7, respectively. Note that 11B data for TK48-SH-60C-NOTPB Time 1 was collected approximately 1 week after sample collection and thus was in contact with borosilicate glass for the same amount of time as TK-48-SH-60C-BL Time 7.

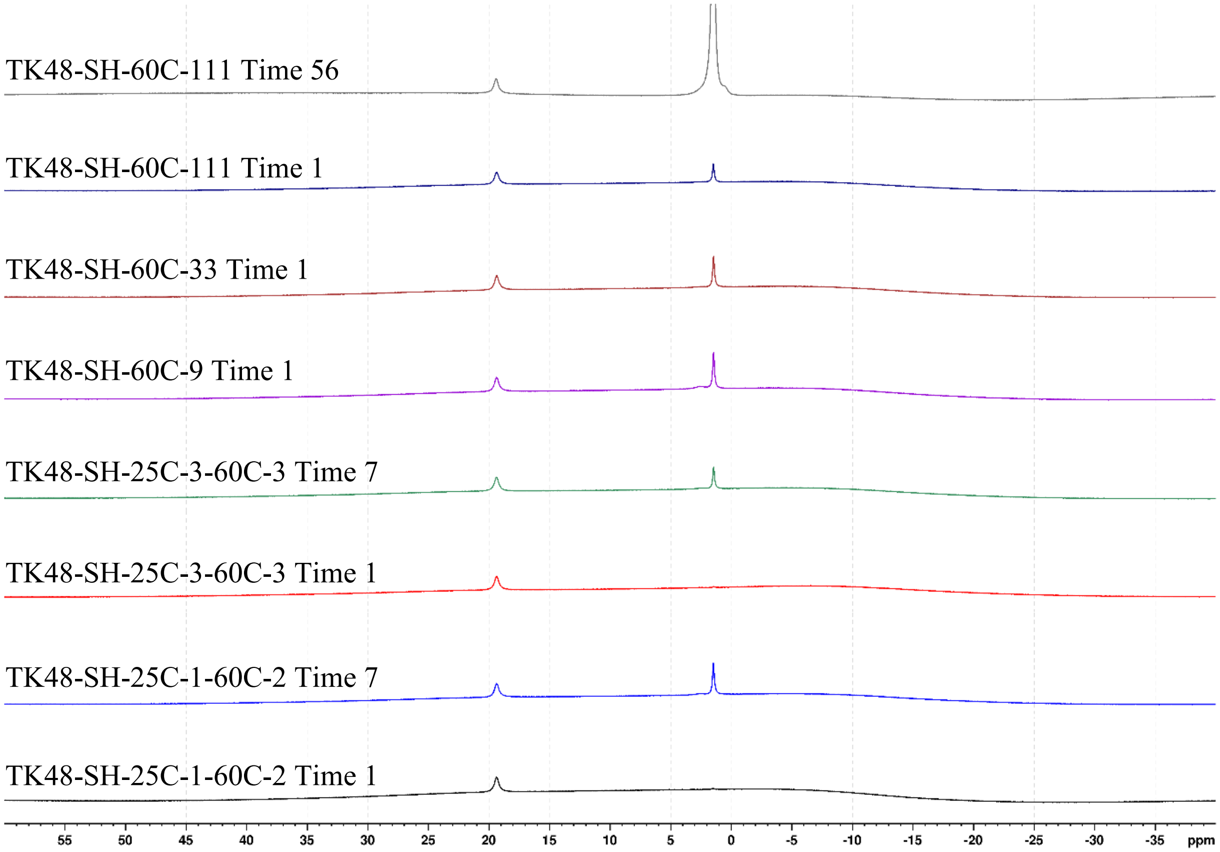

Figure B-16 ^{11}B NMR spectra (listed from bottom to top) of TK48-SH-25C-1-60C-2 Time 1 and 7, TK48-SH-25C-3-60C-3 Time 1 and 7, TK48-SH-60C-9 Time 1, TK48-SH-60C-33 Time 1, and TK-48-60C-111 Time 1 and 56. The black, blue, red, green, purple, brown, navy, and grey spectra correspond to TK48-SH-25C-1-60C-2 Time 1 and 7, TK48-SH-25C-3-60C-3 Time 1 and 7, TK48-SH-60C-9 Time 1, TK48-SH-60C-33 Time 1, and TK-48-60C-111 Time 1 and 56, respectively.

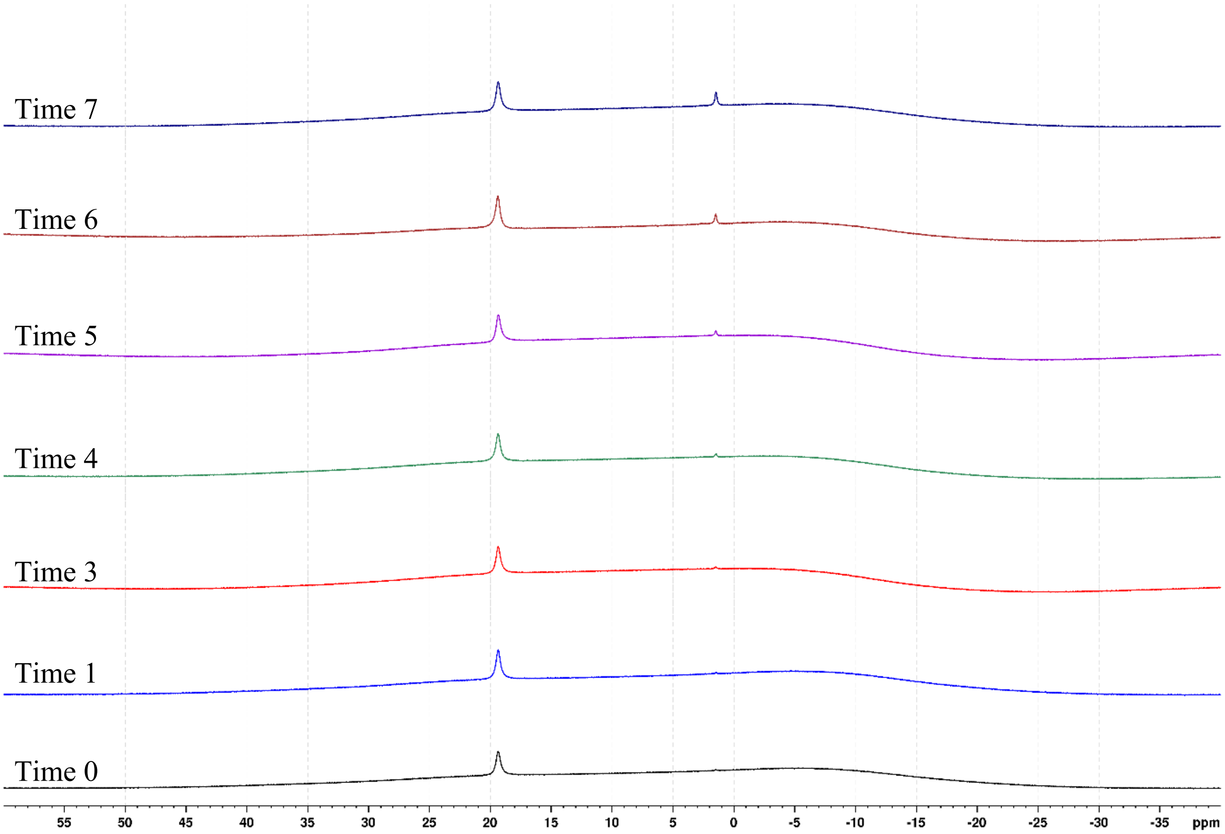

Figure B-17 ^{11}B NMR spectra (listed from bottom to top) of TK48-2LV-25C-1-60C-2 Time 0–7. The black, blue, red, green, purple, brown, and navy spectra correspond to TK48-SH-60C-NOTPB Time 1 and TK48-2LV-25C-1-60C-2 Time 0, Time 1, Time 3, Time 4, Time 5, Time 6, and Time 7, respectively.

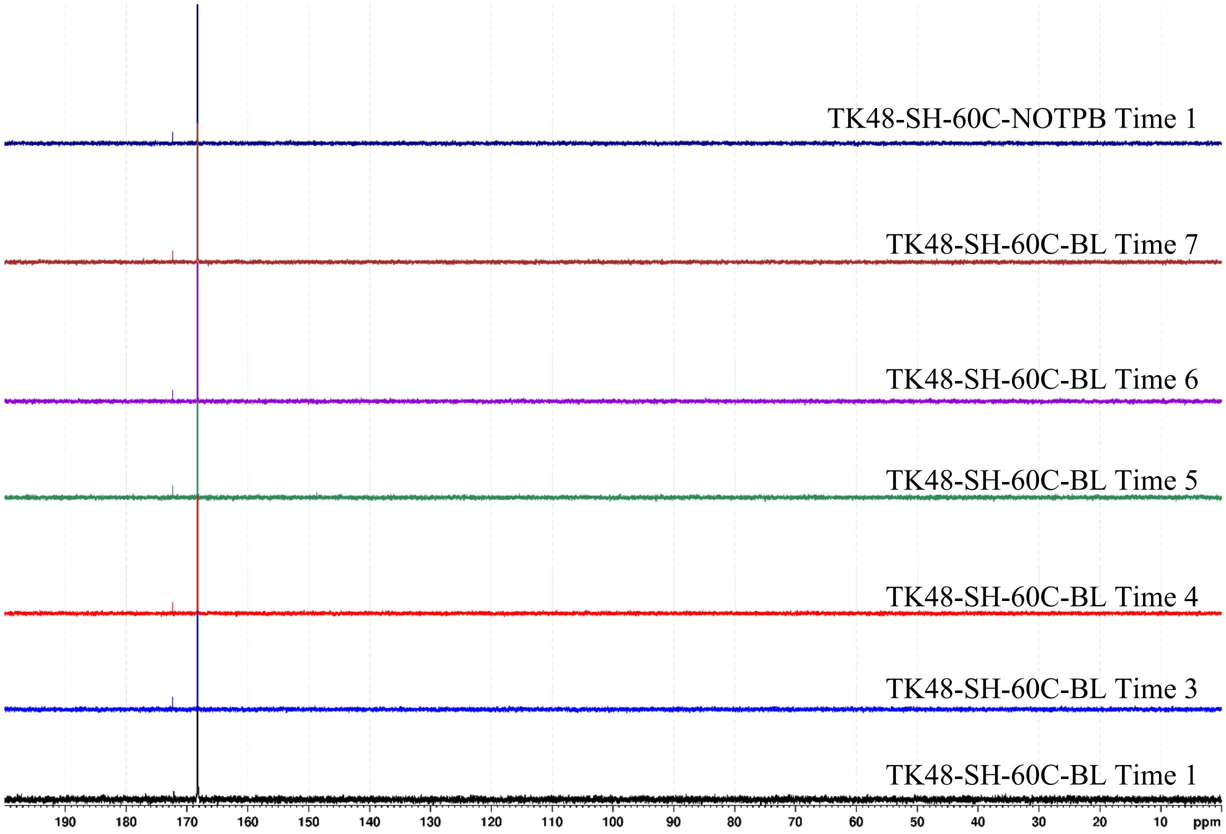

Figure B-18 ^{13}C NMR spectra (listed from bottom to top) of TK48-SH-60C-NOTPB and TK48-SH-60C-BL test series. The black, blue, red, green, purple, brown, and navy spectra correspond to TK48-SH-60C-NOTPB Time 1 and TK48-SH-60C-BL Time 1, Time 3, Time 4, Time 5, Time 6, and Time 7, respectively.

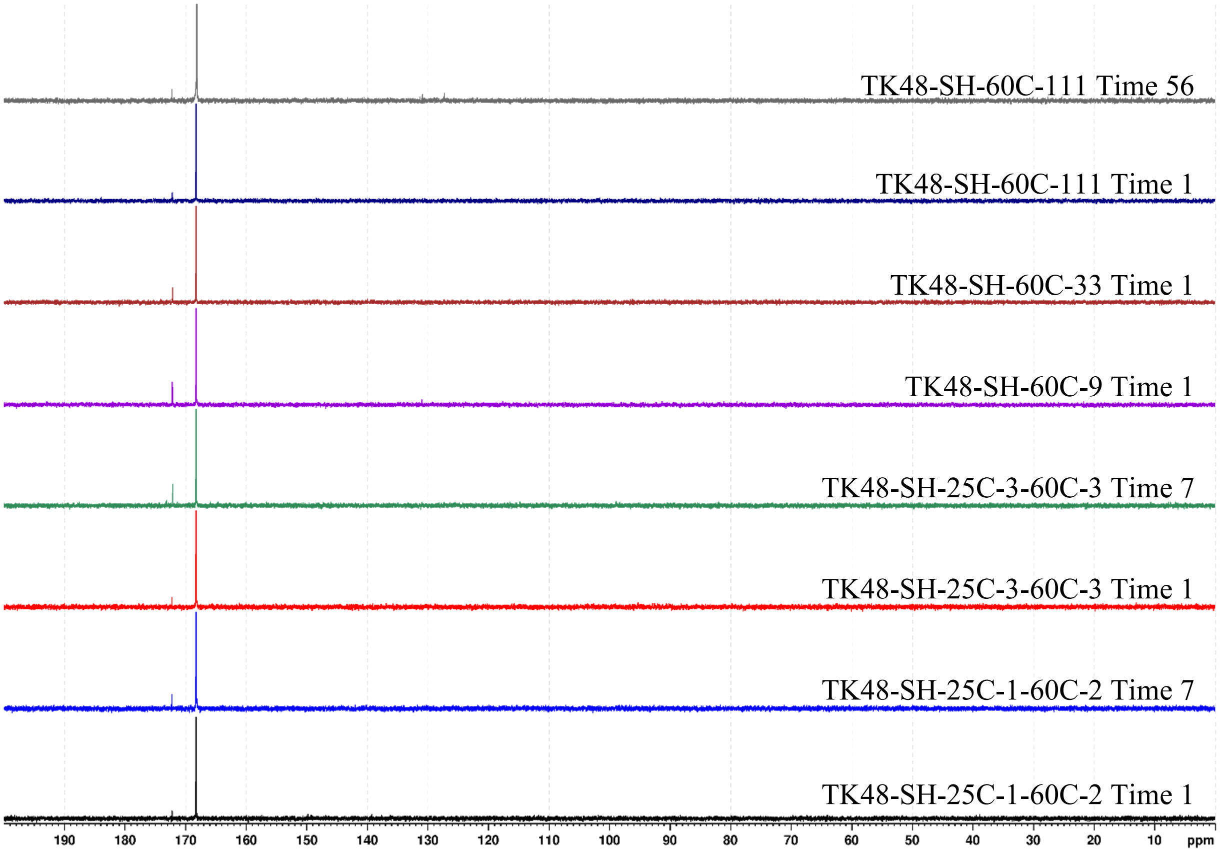

Figure B-19 ^{13}C NMR spectra (listed from bottom to top) of TK48-SH-25C-1-60C-2 Time 1 and 7, TK48-SH-25C-3-60C-3 Time 1 and 7, TK48-SH-60C-9 Time 1, TK48-SH-60C-33 Time 1, and TK-48-60C-111 Time 1 and 56. The black, blue, red, green, purple, brown, navy, and grey spectra correspond to TK48-SH-25C-1-60C-2 Time 1 and 7, TK48-SH-25C-3-60C-3 Time 1 and 7, TK48-SH-60C-9 Time 1, TK48-SH-60C-33 Time 1, and TK-48-60C-111 Time 1 and 56, respectively.

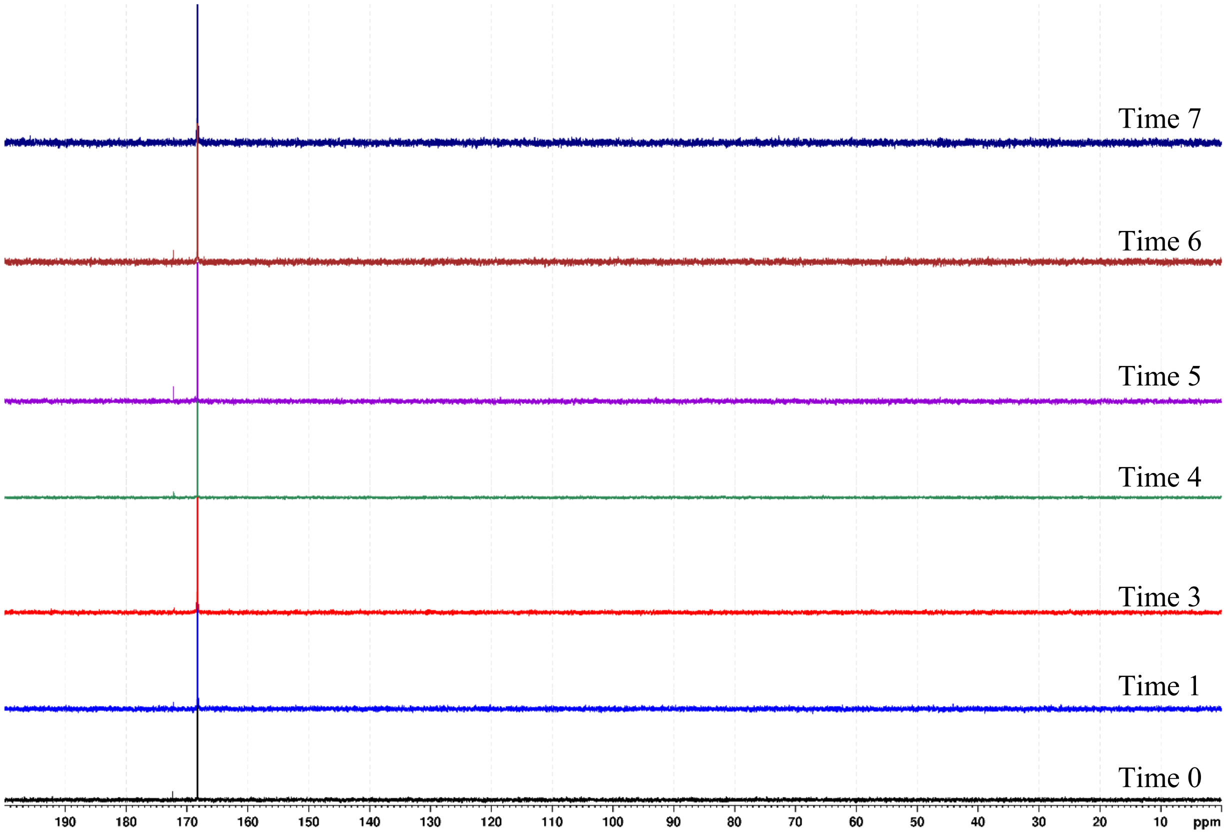

Figure B-20 ^{13}C NMR spectra (listed from bottom to top) of TK48-2LV-25C-1-60C-2 Time 0–7. The black, blue, red, green, purple, brown, and navy spectra correspond to TK48-SH-60C-NOTPB Time 1 and TK48-2LV-25C-1-60C-2 Time 0, Time 1, Time 3, Time 4, Time 5, Time 6, and Time 7, respectively.

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