

Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

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Results of the Scoping Tests for Tank 48H Simulant Destruction

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December 2019
SRNL-STI-2019-00711, Revision 0



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Printed in the United States of America

**Prepared for
U.S. Department of Energy**

Keywords: *Tank 48H, TPB*

Retention: *Permanent*

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EXECUTIVE SUMMARY

Previous Savannah River National Laboratory (SRNL) testing examined the destruction of sodium glycolate using sodium permanganate.ⁱ The results of these tests were successful enough such that the Department of Energy (DOE) provided funding for a small set of scoping tests with the intent to determine if the tetraphenylborate content of Tank 48H would be amenable to the same type of destruction. Five scoping tests have been performed, under caustic conditions, with an eye towards in-tank destruction. From these tests SRNL has identified a set of conditions (pH 11, slow addition of permanganate solution) that indicate (at least partial) destruction of insoluble tetraphenylborate does occur under mild conditions. Furthermore, gas-phase analysis found no definitive indication of benzene generation. Additional testing should identify a comprehensive set of conditions to use this method for Tank 48H content destruction in the field, as well as provide a better understanding of the underlying chemistry.

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LIST OF ABBREVIATIONS

AD	Analytical Development
DOE	Department of Energy
DWPF	Defense Waste Processing Facility
FTIR	Fourier Transform Infrared Spectroscopy (spectrometer)
GC	Gas Chromatography (chromatograph)
HPLC	High Performance Liquid Chromatography
IC-A	Ion Chromatography Anions
ICPES	Inductively Coupled Plasma Emission Spectroscopy
ITP	In-Tank Precipitation
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TPB	tetraphenylborate

1.0 Introduction

Tank 48H currently holds legacy material containing organic tetraphenylborate (TPB) compounds from the operation of the In-Tank Precipitation (ITP) process. The TPB was added during the ITP process to remove soluble cesium, but excessive benzene generation curtailed this treatment method. The contents of Tank 48H are not compatible with the waste treatment facilities at the Savannah River Site (SRS) since the organic content and the associated flammability issues pose a challenge to the salt processing and sludge processing facilities within the liquid waste system. Tank 48H currently contains ~250,000 gallons of alkaline slurry with approximately 26,000 kg of potassium and cesium tetraphenylborate.

In 2011-2012 Savannah River National Laboratory (SRNL) demonstrated TPB destruction in lab scale tests using hydrogen peroxide.ⁱⁱ More recently, experiments have been performed to investigate oxidative destruction of organics in simulated Defense Waste Processing Facility (DWPF) Recycle.ⁱ Complete destruction of glycolate was observed using sodium permanganate or hydrogen peroxide in as little as a few hours.

Recently, DOE provided funding for scoping tests to examine if TPB in Tank 48H simulant can be destroyed using the same general set of conditions as used in the recent glycolate destruction work. A limited set of reactions were proposed in a Run Plan,^{iii,iv} including one test with off-gas analysis for benzene. The goal of the scoping tests was to determine a set of conditions with an eye towards in-tank destruction that could effectively destroy the organic content of Tank 48H and return it to general service.

2.0 Experimental Procedure

In 2015, a sample of Tank 48H slurry was delivered to SRNL for analysis.^v This set of analyses is used as a basis for a simple Tank 48H simulant recipe shown in Table 1. The simulant for this work was prepared by adding reagents from top to bottom order diluted with DI water to a 500 mL volume, with the additional control of confirming the pH was above 10 before nitrite addition.

Table 1. Basic Simulant Composition (500 mL)

Compound	Added Mass (g)
NaNO ₃	5.58
KNO ₃	3.55
Na ₂ CO ₃	53
NaOH	34.2
NaAlO ₂ *H ₂ O	4.9
NaNO ₂	21.33
NaTPB	10.31

We note that the sodium carbonate took a few hours to dissolve.

Table 2. Target Concentrations in the Simulant

Compound	Target (M)
Na ⁺	4.62
K ⁺	0.01
TPB (as KTPB)	0.0603
carbonate	1
nitrate	0.202
nitrite	0.618
Free hydroxide	1.7

The simulant as prepared is a high pH salt solution, with a precipitated KTPB suspension as defined in Table 2.

A limited set of scoping tests was envisioned. Results, lessons, observations, and customer input from one test were used to modify the conditions performed at later times. For example, the customer requested a test at pH 14 to simulant a direct test under tank conditions. By the end of this work, five tests were performed at various conditions as described in Table 3. Temperature was not controlled but varied between 19-26 °C.

Table 3. Experiment Matrix

Test	pH	Oxidant	Oxidant:TPB M Ratio
1	11 (NaHCO ₃)	9.8M H ₂ O ₂	15.7
2	12 (H ₃ BO ₃)	1M NaMnO ₄	3.15
3	11 (pre-adjusted)	1M NaMnO ₄	3.45
4	14 (no adjustment)	1M NaMnO ₄	5.57
5	11 (pre-adjusted)	1M NaMnO ₄	6.88

In the pH column, the chemical used to adjust the pH is noted. The pH adjustment was performed before addition of the NaTPB to avoid hydrolysis reactions. “Pre-adjusted” indicates that the salt solution was prepared as if nitric acid was used to neutralize the NaOH in a 1:1 ratio emulated by substituting an equimolar amount of NaNO₃ for the NaOH. pH was measured by both pH strip and pH probe.

Each test used 500 mL (except Test #5 which used 1000 mL) of the Tank 48H simulant in a 2L glass reactor. Agitation was provided by a magnetic stirrer. The oxidant was added slowly via a syringe pump. The ~12 mL samples were pulled from the reaction vessel at ~1 cm from the bottom, about halfway from the center to the wall, and were quenched with ~0.25 g of sodium sulfite to destroy any residual permanganate. Sub-samples to be analyzed via Inductively Coupled Plasma

Emission Spectroscopy (ICPES) and Ion Chromatography (IC-A) were filtered with a 0.45 μm syringe filter, while samples for High Performance Liquid Chromatography (HPLC) were not filtered but pulled ~ 1 cm from the bottom of the vessel with vigorous mixing.

Specific details of each experiment are provided in the results section.

2.1 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60 (Design Check).^{vi} This work is Scoping/Non-Baseline class. For SRNL documents, the extent and type of review using the SRNL Technical Report Design Checklist is outlined in WSRC-IM-2002-00011, Rev. 2.^{vii} Records for this work are contained in electronic notebook.^{viii}

3.0 Results and Discussion

3.1 Acidification Concerns

Most of the tests required a reaction pH below that of the initial pH of 14 (strong caustic). The 2012 workⁱⁱ mostly used strong nitric acid to reduce the pH before the addition of the oxidant. However, use of the nitric acid had the side effect of generating benzene and was likely responsible for generating the observed biphenyl, as well as nitrated organic byproducts. Limited studies at the end of that period showed that using milder acids such as formic or phosphoric produced less benzene. At the time SRNL proposed using even milder acidification strategies to prevent benzene formation, but the work scope terminated early.

Thus, while the acidification of the simulant is not the direct focus of this work, it is inevitably linked to it. While we did not have the time or funding to separately study various acidification schemes, we varied the agent of acidification throughout these tests to gain insights.

In the third and fifth test, the acidification question was avoided all together by preparing the simulant as if the free hydroxide had all reacted away with nitric acid, and we replaced the NaOH with an equimolar amount of NaNO_3 .

3.2 Test #1

Test #1 used 30 wt % H_2O_2 as the oxidant and was intended to roughly duplicate previous tests performed in 2012. The main difference between this test and past efforts was the change from an added copper catalyst to an added iron catalyst, to avoid adding metals to the solution that would interact badly in the DWPF melter. To this end, 500 mg/L of Fe (III) was added in the form of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as the catalyst. The simulant with the TPB slurry present, was pH adjusted with solid NaHCO_3 . It was noted that the bicarbonate may not have dissolved cleanly (the white KTPB suspension prevented a clear visual observation), but the pH was adjusted to approximately 11 after stirring for several hours.

Before the start of the H₂O₂ addition, a time 0 sample was taken of the white suspension. The H₂O₂ was then added at a nominal rate of 0.4 mL/hour, 24 hours/day for 5 days. Addition of the H₂O₂ did not provide for large visual changes, although the solution had a light orange-brown tint and by the end the test. Samples were removed once per day (except on the weekend). At the end of the 7 days, a total of 48.3 mL of the H₂O₂ had been added (a weekend of no H₂O₂ addition took place after the first day of the test). A final sample was then removed and the time 0 and final sample were analyzed via ICPES. The final sample was also analyzed via IC-A. The final values reported in Table 4 are corrected for dilution (multiplied by 1.10) due to the additions of the H₂O₂ (this is an approximation and does not consider gaseous losses from H₂O₂ decomposition).

Table 4. Test #1 Time 0 and Final ICPES and IC-A Results.

Analyte	Time 0 (M)	Final (M)
Al	<3.35E-05	1.66E-04
B	9.72E-03	1.07E-02
Fe	5.27E-05	7.60E-05
K	5.87E-02	5.20E-02
Na	4.65E+00	4.72E+00
formate	<i>0</i>	2.58E-03
nitrite	<i>6.18E-01</i>	5.34E-01
nitrate	<i>2.02E-01</i>	1.98E-01
oxalate	<i>0</i>	1.73E-03

Values in italics are calculated values. The 1 σ analytical uncertainties for the results are 10%.

The TPB most easily degrades via boron-carbon bond breakage, which liberates free potassium and boron (via more soluble TPB-fragments) into solution. Therefore, a good indication of reaction is the ingrowth of boron and potassium in the ICPES results. Significant ingrowth of boron and potassium (Table 4) was not observed and, therefore, from the ICPES results we have no indication of a reaction. We also see a slight ingrowth of formate and oxalate, neither of which were intentionally added to the simulant. These two species are possible indicators of a very slight degradation of TPB; either during the test or as an impurity in the starting reagent. As a confirmation, we conducted an unquantified High Performance Liquid Chromatography (HPLC) analysis for TPB; this analysis initially provided a result outside the calibration range, but was estimated to indicate no reaction, and this was done at no charge. Therefore, it was decided not to pursue a further analysis by this method.

One matter of concern is the free potassium in solution at time 0. While the time 0 and final potassium results did not vary significantly, if the added NaTPB completely reacted with the potassium to generate KTPB, only ~450 mg/L (~1.1E-0 M) of free potassium should remain in solution. It seems unlikely that either enough tramp potassium was introduced via other reagents, or the NaTPB source was already degraded to a serious degree. It may be that the reaction to precipitate KTPB was incomplete by the time the H₂O₂ was added, even after a day of stirring. The reaction of free potassium with NaTPB is normally quick and complete. The reasons for the lack of complete apparent reaction are unknown currently. For this reason, the addition of the TPB was changed in Test #3.

In summary, there is no indication of any appreciable TPB degradation. This lack of reaction is most likely due to the lack of a soluble iron catalyst, as evidenced by the very small iron concentration in solution by the end of the reaction (4.25 mg/L). Either more iron must be used, a lower pH to accommodate more iron must be used, or a different metal catalyst must be used if H₂O₂ is to be used as the oxidant. As permanganate was the main focus of the testing, it was decided not to pursue further H₂O₂ tests at this time.

3.3 Test #2

Test #2 used 1M NaMnO₄ as the oxidant and was intended to roughly duplicate previous tests with glycolate destruction. Higher concentrations of NaMnO₄ tend to be less soluble at room temperature and can cause line clogging issues. As the previous pH adjustment attempt using NaHCO₃ was not as simple as anticipated, the simulant, with the TPB slurry present was pH adjusted with solid boric acid (H₃BO₃), even though the boric acid would invalidate using boron as a tracer for TPB destruction. It was noted that the boric acid may not have dissolved cleanly (although the white KTPB suspension prevent a clear visual observation), but the pH reached approximately 12 after stirring for several hours. Before the start of the permanganate addition, a time 0 sample was taken (a white suspension). The permanganate was then added at a nominal rate of 0.6 mL/hour, 24 hours/day for 8 days (sometime over the weekend had no permanganate addition). Over the period of the experiment, the permanganate addition caused the solution to go green initially, then purple, and at the end, green. Brown MnO₂ solids formed within a day after time 0. Samples were removed once per day. At the end of the 8 days, a total of 95 mL of the permanganate had been added. A final sample was then removed and the time 0 and final sample were analyzed via ICPEs. The final sample was also analyzed by IC-A. The final values are corrected for dilution (multiplied by 1.19) from additions of the permanganate (this is an approximation and does not consider possible effects from phase changes). The data is shown in Table 5.

Table 5. Test #2 Time 0 and Final ICPES and IC-A Results.

Analyte	Time 0 (M)	Final (M)
Al	1.07E-01	8.77E-02
B	1.41E+00	1.41E+00
Fe	4.11E-06	<0.0000021
K	4.72E-02	4.70E-02
Na	3.94E+00	4.26E+00
Formate	0	<0.0026
Nitrite	<i>6.20E-01</i>	5.90E-01
Nitrate	<i>2.02E-01</i>	2.34E-01
oxalate	0	1.54E-02

Values in italics are calculated values. The 1σ analytical uncertainties for the results are 10%.

One indication of a reaction is the ingrowth of boron and potassium in the ICPES results. Such increases are not observed in Table 5 and, therefore, from the ICPES results there is no indication of a reaction. The large boron content is from the boric acid pH adjustment. From the anion results we see a slight decline in nitrite and a slight increase in nitrate indicating a possible oxidation of nitrite to nitrate, although the result is not statistically significant. We also see ingrowth of oxalate (more than in Test #1), but no formate. This finding is a possible indicator of a slight degradation of TPB. As a confirmation, we conducted an unquantified HPLC analysis for TPB; this analysis initially provided a result outside the calibration range but was estimated to indicate no reaction. Therefore, it was decided not to pursue a further analysis by this method. As with the previous test, it appears the reaction to precipitate KTPB was not complete by the start of the permanganate addition.

In summary, there is no indication of any appreciable TPB degradation.

3.4 Test #3

Test #3 used 1M NaMnO₄ as in Test #2. Given that the high starting potassium results from the first two tests indicated the possibility of contamination in the NaTPB source, we procured a new bottle of NaTPB. With the issues with acidification in the previous two tests, the simulant, with the TPB slurry present was not pH adjusted but was prepared as if the NaOH had already been reacted with nitric acid by replacing the NaOH with an equimolar amount of NaNO₃. Even so, a slight pH adjustment with nitric acid was required to reach pH 11, before the addition of the NaTPB. During the salt solution preparation, during the final pH adjustment to 11, the aluminum solids would not re-dissolve and were filtered off before the addition of the NaTPB.

Before the start of the permanganate addition, an initial sample was taken at time 0. The permanganate was then added at a nominal rate of 2.4 mL/hour, 8 hours/day for 6 days, although

the test continued for 12 days total. Samples were removed once per day. At the end of the 12 days, a total of 104 mL of the permanganate solution were added. Final samples were then removed, and the final sample was analyzed by ICPES, IC-A, and HPLC. The final values shown in Table 6 are corrected for dilution (multiplied by 1.19) from additions of the permanganate (this is an approximation and does not consider possible effects from phase changes).

Table 6. Test #3 Time 0 and Final ICPES and IC-A Results.

Analyte	Time 0 (M)	Final (M)
Al	NA	NA
B	0	1.00E-02
Fe	0	<0.0000082
K	<i>1.07E-02</i>	3.89E-02
Na	<i>4.31E+00</i>	5.10E+00
formate	0	<0.0027
nitrite	<i>5.78E-01</i>	4.44E-01
nitrate	<i>1.70E+00</i>	2.00E+00
oxalate	0	2.67E-02
TPB	<i>5.64E-02</i>	2.99E-02

Values in italics are calculated values. The 1σ analytical uncertainties for the results is 10%.

Unlike the previous two tests, boron results increased in concentration suggesting up to a 18% TPB destruction, and the potassium increased suggesting up to a 50% destruction. The oxalate results (assuming that for every mole of oxalate produced, 1 mole of TPB was destroyed) suggest up to a 47% destruction of TPB. Finally, the (fully quantitative) HPLC results for TPB are the most conclusive of all and suggest a 47% destruction of TPB.

In summary, there are several indications of appreciable TPB degradation.

3.5 Test #4

Test #4 used 1M NaMnO₄ as the oxidant. The simulant, with the TPB slurry present was not pH adjusted, as the desired pH was 14. Unlike previous tests, the NaTPB was added to the salt solution itself as a prepared solution instead of a solid, in an attempt to ensure complete KTPB formation.

Before the start of the permanganate addition, a time 0 sample was taken. The permanganate was then added at a nominal rate of 4.8 mL/hour, 8 hours/day for 4 days, although the test continued for 7 days total. Samples were removed once per day. At the end of the 7 days, a total of 168 mL of the permanganate had been added. During the addition of the permanganate, the solution color turned a very intense green, and there was no visual evidence of the formation of MnO₂ solids.

Four daily samples were removed (not on the weekends). The initial and final samples were analyzed by ICPES, IC-A, and HPLC. The final values are corrected for dilution (multiplied by 1.43) from additions of the permanganate (this is an approximation and does not consider possible effects from phase changes) and some water used in attempt to sweep the foam back into solution. Unlike the previous tests we noted the appearance of TPB-laden foam. Attempts were made to sweep the foam into solution by varying the stirring rate or using small amounts of water but were not successful. Therefore, the HPLC sample for TPB was known to be biased low due to being unable to capture the solids in the foam.

Table 7. Test #4 Time 0 and Final ICPES and IC-A Results.

Analyte	Time 0 (M)	Final (M)
Al	7.93E-02	5.76E-02
B	none added	<0.0025
Fe	none added	<0.0000034
K	2.59E-02	1.90E-02
Na	4.20E+00	3.92E+00
formate	none added	<0.0016
nitrite	6.07E-01	4.16E-01
nitrate	1.89E-01	2.35E-01
oxalate	none added	<0.00081
TPB	5.64E-02	3.44E-02

The 1σ analytical uncertainties for the results are 10%.

There is no increase in boron or potassium in Table 7, and therefore from the ICPES results we have no indication of a reaction. From the anion results we see a ~31% decline in nitrite and a ~24% increase in nitrate indicating a moderate oxidation of nitrite to nitrate. The HPLC analysis for TPB seem to indicate a possible ~40% reaction but given the lack of B and K ingrowth and the fact the HPLC sample could not capture a representative amount of solids from the reaction vessel, the low TPB result should not be taken as an indication of TPB destruction. As with Tests #1 and #2, it appears the reaction to precipitate KTPB was not complete by the start of the permanganate addition, although the magnitude was less than previous.

In summary, there is no indication of any appreciable TPB degradation.

3.6 Test #5

Test #5 used 1M NaMnO₄ as the oxidant. The simulant with the TPB slurry present (using the newly procured bottle of NaTPB used in Tests #3 and #4) was not pH adjusted but prepared as if

the NaOH had reacted with nitric acid by replacing the NaOH with an equimolar amount of NaNO_3 . As with Test #4, the NaTPB was added to the salt solution itself as a prepared solution instead of a solid, in an attempt to ensure complete KTPB formation. Although very similar to Test#3, this test was at double scale (1L of simulant starting volume) and used active gas phase monitoring.

To monitor any gaseous species produced, the off-gas train included sampling by a gas chromatograph (GC) and flow through a Fourier Transform Infrared (FTIR) spectrometer. The GC was an Agilent 3000 Micro Gas Chromatograph and the FTIR was an MKS MultiGas 2030 Fourier Transform Infrared Spectrometer. The GC was set to sample the offgas stream every 5 minutes with the FTIR scanning the entire offgas stream passing through the 200 mL gas cell approximately every 8 seconds. The primary responsibility of the GC was to monitor for hydrogen while the FTIR was set up to monitor NO_x , CO_2 , and benzene along with identifying unanticipated gaseous products that may be IR-active.

Before the start of the permanganate addition, a time 0 sample was taken. The permanganate was then added at a nominal rate of 10 mL/hour, 8 hours/day for 5 days. Samples were removed once per day. At the end of the 5 days, a total of 400 mL of the permanganate had been added. Daily samples were removed. The initial and final samples were analyzed by ICPEs, IC-A, and HPLC. The final values shown in Table 8 are corrected for dilution (multiplied by 1.40) from additions of the permanganate (this is an approximation and does not consider possible effects from phase changes).

Table 8. Test #5 Time 0 and Final ICPEs and IC-A Results

Analyte	Time 0 (M)	Final (M)
Al	<2.56E-04	4.56E-02
B	<2.17E-03	6.11E-03
Fe	<8.80E-06	1.23E-05
K	1.56E-02	2.70E-02
Na	4.19E+00	5.69E+00
formate	5.20E-03	5.57E-03
nitrite	6.15E-01	2.84E-02
nitrate	1.76E+00	2.26E+00
oxalate	<1.14E-03	1.67E-02
TPB	6.37E-02	6.32E-02

The 1σ analytical uncertainties for the results are 10%.

One indication of a reaction is the ingrowth of boron and potassium in the ICPEs results. The boron results suggest up to a 11% TPB destruction, and the potassium suggests up to a 20% destruction. The oxalate results (assuming the oxalate is generated from TPB destruction in a 1:1 molar ratio) suggest up to a 29% destruction of TPB. Finally, the HPLC results for TPB indicated

no reaction at all. With the positive indicators of a reaction from the B, K and oxalate, the HPLC should also indicate a reaction. We suspect that the lack of reaction by HPLC indicates that heavy MnO_2 solids were less mobile in this test (due to the double scale, and taller reaction vessel) and tended to flocculate the TPB solids towards the bottom, which given our sampling at the bottom would pick up more solids, and therefore biasing the HPLC measurement high (less reaction).

In summary, there are several liquid phase indications of appreciable TPB degradation.

For the offgas analysis, due to the high pH, most significant species (i.e., CO_2 , NO_x , etc.) expected to be present in the offgas were likely sequestered in the caustic solution. Additionally, no significant hydrogen production was observed, as measured by gas chromatography (GC). As for the identification of benzene or other unanticipated offgas species, the calibration algorithm built into the software operating the FTIR did attempt to match a small rise in the infrared spectra with the spectra for benzene (reference peak in blue), but the experimental peak (in black) was so close to background levels that no definitive claim for the presence of benzene could be made (Figure 1).

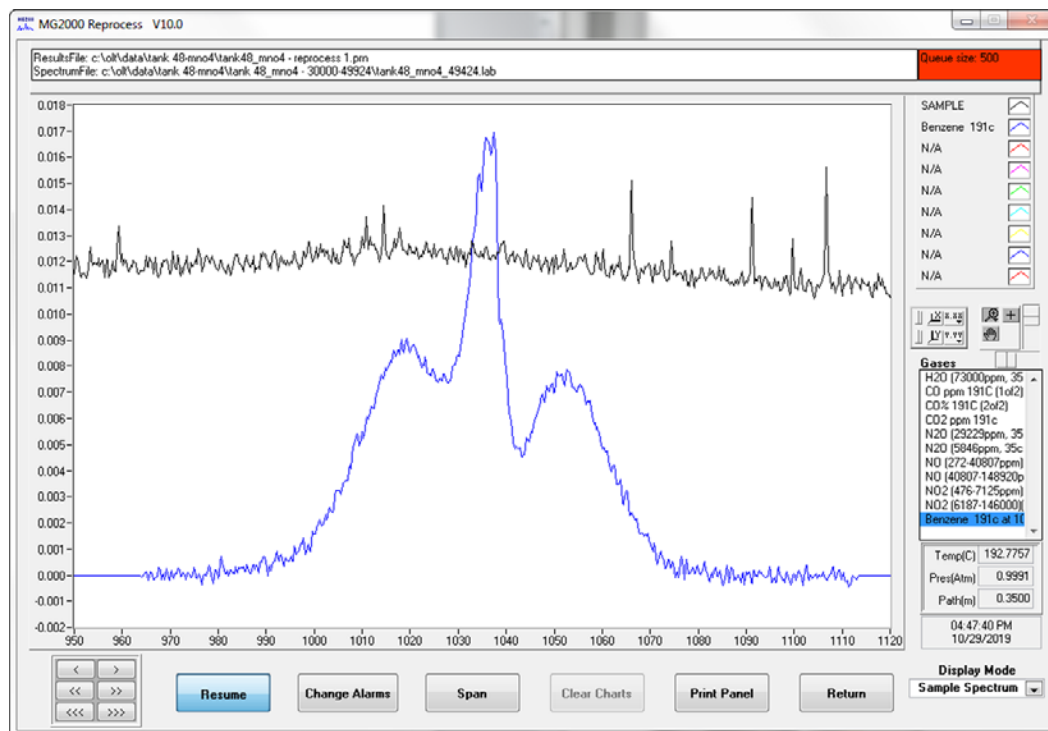


Figure 1. Comparison of Benzene calibration peak to observed FTIR spectra; black line is observed spectra; blue line is benzene calibration spectra.

In summary, there is no positive indication of flammable generation in this test.

4.0 Conclusions

Previous Savannah River National Laboratory (SRNL) testing examined the destruction of sodium glycolate using sodium permanganate. The results of these tests were successful enough such that the Department of Energy (DOE) provided funding for a small set of scoping tests to determine if the contents of Tank 48H would be amenable to the same type of destruction. Five scoping tests have been performed. From these tests SRNL has identified a set of conditions (pH 11, slow addition of permanganate) that indicate at least partial destruction of insoluble TPB is possible with Tank 48H simulant. Additional testing should identify a comprehensive set of conditions to use this method for Tank 48H content destruction in the field, as well as provide a better understanding of the underlying chemistry.

5.0 References

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