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Evaluation of Chemical Additives for Glycolate Destruction in the Recycle Collection Tank

Dan Lambert, Anthony Howe, Matt Williams, Cory Trivelpiece, Gene Ramsey

February 2019

SRNL-STI-2018-00585, Revision 0

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February 2019

Prepared for the U. S. Department of Energy under contract number DE-AC09-08SR22470.

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EXECUTIVE SUMMARY

Savannah River National Laboratory (SRNL) has completed a work scope in support of the Savannah River Remediation (SRR) Nitric-Glycolic flowsheet. Glycolic acid will replace formic acid as a reducing agent in the pre-processing of High-Level Waste sludge performed at the Defense Waste Processing Facility (DWPF). Glycolic acid will perform the same function as formic acid, namely reduction of mercury and adjustment of feed rheology and melter oxidation/reduction potential, while significantly reducing the potential for hydrogen generation in DWPF processing. Development testing has demonstrated glycolic acid virtually eliminates hydrogen production in the pre-processing steps.

The Nitric-Glycolic flowsheet significantly improves DWPF's ability to address Savannah River Site's key challenge - the incorporation of effluent received from the Salt Waste Processing Facility (SWPF). SWPF will deliver significant effluent volume to DWPF, resulting in a concurrent increase in DWPF effluent returned to the Concentration, Storage and Transfer Facilities (CSTF). This work scope demonstrates that glycolate can be destroyed under the Nitric-Glycolic flowsheet prior to returning the DWPF recycle stream to CSTF.

To avoid potential flammability issues due to thermolysis of glycolate in CSTF, SRR tasked SRNL to quantify and mitigate glycolate returns via DWPF recycle stream. The development of a strategy for glycolic mitigation initiated with a system's engineering workshop. Various chemical and/or physical solutions for how to and where to destroy glycolate were considered – consistent with DWPF operational capabilities and process requirements. The workshop identified chemical oxidation of glycolate within the DWPF Recycle Collection Tank (RCT)[a] as the most promising option with sodium permanganate and Fenton's reagent (metallic ion catalyzed hydrogen peroxide) as the two most promising oxidants.

SRNL performed this testing and worked with SRR to make a downselection between Fenton's reagent and permanganate. A test matrix was generated to evaluate the impact of:

- Glycolate concentration,
- Oxidant type (sodium permanganate or Fenton's reagent),
- Oxidant strike time (rate of delivery),
- Oxidant stoichiometry,
- RCT solution temperature, and
- RCT solution pH.

Testing conditions were selected to reflect DWPF process capability and requirements. Non-prototypic concentrations of process organics were added to the process simulant to challenge the methodology and better support the downselection. Tests were conducted with discrete liquid sampling events and online offgas analysis for data generation.

For the test conditions performed and data obtained, two conclusions are drawn.

1. Sodium permanganate was clearly superior to Fenton's reagent as an oxidizing agent for destruction of glycolate in the RCT. Permanganate strikes consistently reduced glycolate concentrations from nominally 125-250 mg/L to below the target threshold of 50 mg/L. Corresponding strikes with Fenton's reagent did not successfully mitigate glycolate.

[a] The RCT collects offgas condensate from pre-processing, vitrification, and other unit operations performed in DWPF and is the singular return vessel delivering recycle effluent back to CSTF.

2. Successful permanganate mitigations of glycolate were demonstrated across broad range of RCT process conditions. These conditions include the following.
    a. RCT solution starting pH: 3-13
    b. RCT solution temperature: 15-50 ºC
    c. Oxidant strike time: 10 minutes to 2 hours
    d. Glycolate concentration: 125-250 mg/L (with exploratory testing up to 2000 mg/L)
    e. Oxidant addition amount: 100-150% stoichiometric requirement for all organics
    f. Demonstrated reaction time consistently within targeted 2-hour duration
    g. Neither appreciable hydrogen gas generation nor process vessel pressurization were observed during the testing protocols.

A qualitative summary of the testing trends for the sodium permanganate testing is included in Figure 1 below. No summary was prepared for Fenton's reagent testing due to the poor destruction efficiencies.

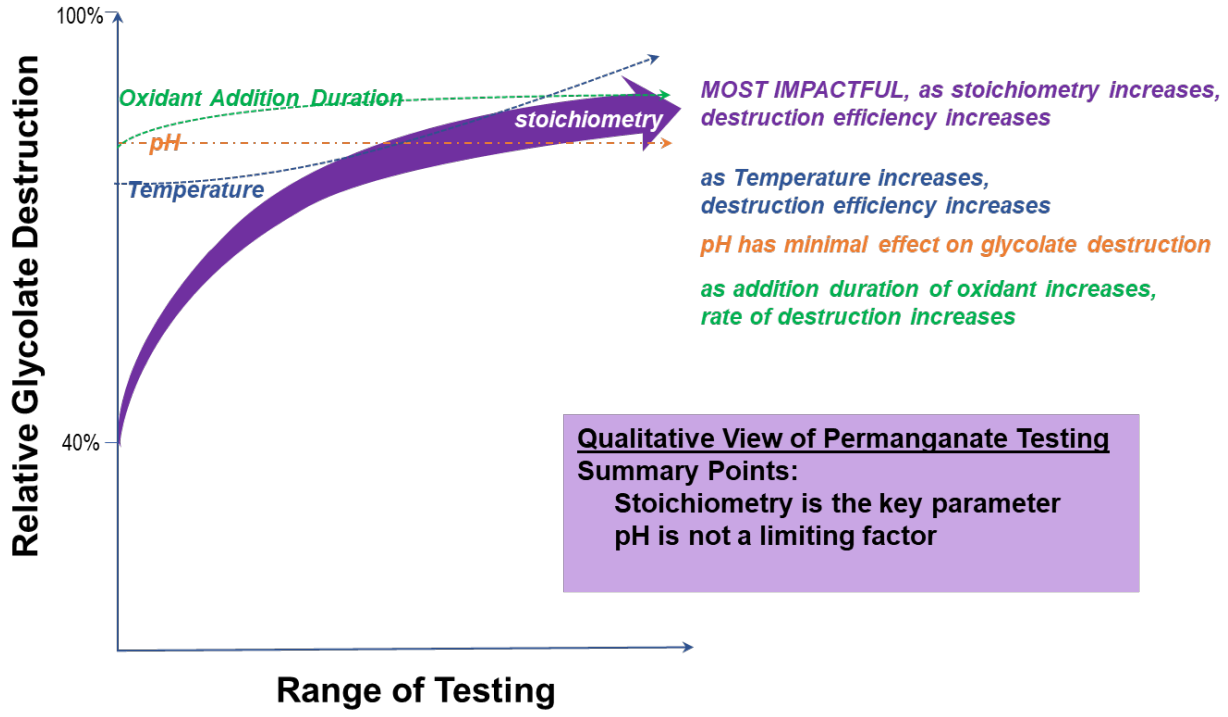


Figure 1. Graphical Summary of Key Testing Parameters for Glycolate Destruction by Sodium Permanganate Oxidation

SRNL, in conjunction with SRR, is continuing the glycolate mitigation development effort. Future activities will include protocol testing intended to clearly define strike parameters for engineering and operational implementation, off-normal testing for remediating foam-over conditions and testing at larger scale or with actual waste. Materials corrosion phenomena (Appendix A) will be evaluated and quantification of expected manganese oxide mass transfer to CSTF via glycolate mitigation operations will be defined.

TABLE OF CONTENTS

LIST OF TABLES x
LIST OF FIGURES xi
LIST OF ABBREVIATIONS xii
1.0 Introduction 1
2.0 Experimental Procedure and Operations 1
2.1.1 Sodium Permanganate 2
2.1.2 Fenton's Reagent 2
2.2 Experimental Design 2
2.3 Preliminary Screening Testing in 735-11A 4
2.4 Matrix Study Simulant Composition 5
2.5 Determination of Oxidant Stoichiometry 7
2.6 Experimental Apparatus and Parameters 10
2.7 Scaling 12
2.8 Offgas Analysis 12
2.9 Liquid Analyses 14
2.9.1 pH 14
2.9.2 Sampling and Analysis 14
2.10 Test Chronology 15
2.11 Quality Assurance 16
3.0 Results and Discussion 17
3.1 Duplicate Test Comparison 17
3.2 Offgas Analyses 19
3.3 Destruction of Glycolate 22
3.3.1 Impact of Oxidant on Glycolate Destruction Efficiency 22
3.3.2 Impact of Oxidant Stoichiometry on Glycolate Destruction Efficiency 23
3.3.3 Impact of Temperature on Glycolate Destruction Efficiency 25
3.3.4 Impact of Oxidant Feed Rate on Glycolate Destruction Efficiency 26
3.3.5 Impact of Starting pH on Glycolate Destruction Efficiency 27
3.3.6 Statistical Review of Data 29
3.4 Destruction of Other Organics 32
3.4.1 Organic Carbon Destruction 32
3.4.2 Formate Destruction 34
3.4.3 Oxalate Destruction 35

3.4.4 Methylmercury Destruction (Methylmercury Added to Tests 1b, 3a, 4a, 5a, and 10 Only) 36
3.4.5 Antifoam Degradation Products (Propanal, Trimethylsilanol and Hexamethyldisiloxane) 36
3.4.6 Formaldehyde Destruction 37
3.4.7 Glyoxylate Destruction 38
3.4.8 Organic Summary 38
3.5 Carbon Balance 38
3.6 Nitrogen Balance 39
3.6.1 Offgas Production of Oxides of Nitrogen 40
3.6.2 Destruction of Nitrite/Production of Nitrate 41
3.7 Recalculated Oxidant Stoichiometry 42
3.8 Solids Generation 43
3.9 Process Implications 43
4.0 Conclusions 44
5.0 Recommendations 45
6.0 References 46
Appendixes A-1

LIST OF TABLES

Table 2-1. Experimental Design for Variables of Interest 3
Table 2-2. RCT Simulant Composition (pH ~4) 6
Table 2-3. Organic Species Requested by TTR 7
Table 2-4. Oxidation State of One and Two Carbon Organics 8
Table 2-5. Proposed Reactions for Complete Oxidation to CO_2 9
Table 2-6. Analyzer Used in Quantifying Offgas Species 13
Table 2-7. Sample Frequency, Quench Method, and Analytical Plan 15
Table 2-8. Test Chronology 16
Table 3-1. Time Zero and Final Glycolate Concentration for All Tests 22
Table 3-2. Oxidant Addition Compared to Oxidant Target 24
Table 3-3. Carbon Concentration and Destruction 34
Table 3-4. Time Zero and Final Formate Concentration for All Testing 35
Table 3-5. Time Zero and Final Oxalate Concentration for All Testing 36
Table 3-6. Final Antifoam Degradation Products (Propanal, Trimethylsilanol and Hexamethyldisiloxane) 37
Table 3-7. Carbon Balance without Methylmercury 39
Table 3-8. Oxides of Nitrogen in the Offgas 41
Table 3-9. Nitrogen Balance 42
Table 3-10. Recalculated Oxidant Stoichiometry 43
Table 3-11. Comparison of Processes 44

LIST OF FIGURES

Figure 1. Graphical Summary of Key Testing Parameters for Glycolate Destruction by Sodium Permanganate Oxidation vii

Figure 2-1. DWPF Process Vessels Impacting Generation of Condensate for RCT 2

Figure 2-2. Screening Tests for Destruction of Glycolate Starting at 250 mg/L Glycolate 4

Figure 2-3. Screening Tests for Destruction of Glycolate Starting at 2000 mg/L Glycolate 5

Figure 2-4. Equipment Apparatus Sketch 11

Figure 2-5. Photo of Apparatus 12

Figure 3-1 Comparison of Duplicate Tests for Glycolate, Formate, and pH 18

Figure 3-2 Comparison of Duplicate Tests for Nitrite and Nitrate 18

Figure 3-3 Offgas Profile for pH 3 Sodium Permanganate Test 9 21

Figure 3 4 Offgas Profile for pH 13 Sodium Permanganate Test 6a 20

Figure 3-5. Impact of Oxidant Stoichiometry on Overall Glycolate Destruction 25

Figure 3-6. Impact of Temperature on Overall Glycolate Destruction 26

Figure 3-7 Impact of Oxidant Addition Time on Glycolate Destruction 27

Figure 3-8 pH Trends for Sodium Permanganate and Fenton's Reagent Testing 28

Figure 3-9. Impact of Initial pH on Overall Glycolate Destruction 29

Figure 3-10. Statistical Analysis Variability Chart of Glycolate Destroyed 30

Figure 3-11. Oxidant Stoichiometry Statistical Analysis Variability Chart of Glycolate Destroyed 31

LIST OF ABBREVIATIONS

AD	Analytical Development
CPC	Chemical Process Cell
CSTF	Concentration, Storage and Transfer Facilities
1-3 DCB	1-3 dichlorobenzene
DWPF	Defense Waste Processing Facility
FTIR	Fourier Transformed InfraRed
GC	Gas Chromatograph
HMDSO	Hexamethyldisiloxane
IC	Ion Chromatography
ICP-ES	Inductively Coupled Plasma Emission Spectroscopy
mmol	millimoles or $1/1000^{th}$ of a mole
MS	Mass Spectrometer
OGCT	Offgas Condensate Tank
ORP	Oxidation Reduction Probe
ppm_v	parts per million by volume or moles
PSAL	Process Science Analytical Laboratory
RCT	Recycle Collection Tank
SMECT	Slurry Mix Evaporator Condensate Tank
SRNL	Savannah River National Laboratory
sccm	standard cubic centimeters per minute
scfm	standard cubic feet per minute
SVOA	Semivolatile Organic Analysis
TC	Total Carbon
TIC	Total Inorganic Carbon
TMS	Trimethylsilanol
TOC	Total Organic Carbon
TTQAP	Task Technical and Quality Assurance Plan
TTR	Task Technical Request
VOA	Volatile Organic Analysis

1.0 Introduction

The chemical process flowsheet used to convert Savannah River Site (SRS) high-level waste into borosilicate glass is being modified. Glycolic acid will replace formic acid as a reducing agent in the pre-processing of sludge.[1] Glycolic acid will perform the same function as formic acid, namely reduction of mercury, adjustment of feed rheology and oxidation/reduction potential of glass. Glycolic acid has been shown superior to formic acid during chemical processing in the Sludge Receipt and Adjustment Tank (SRAT) with regards to the reduced production of hydrogen gas, the primary flammability concern, and the stability of pH during the concentration of melter feed.

This change is being implemented to improve operations within the Defense Waste Processing Facility (DWPF) and better support the Site's key challenge: the incorporation of strip effluent and monosodium titanate streams received from SWPF with sludge and subsequent feed preparation. DWPF operations include the receipt of High-Level Waste sludge and intensely radioactive process effluents, feed preparation and vitrification, and process condensate collection and return to Concentration, Storage and Transfer Facilities (CSTF). As the volume of strip effluent requiring processing significantly increases as SWPF comes on line, DWPF condensate returns to the CSTF will increase. A small concentration of glycolate, ≤120 mg/L[2] is anticipated to return to the CSTF with each batch (typical carryover from CPC or melter) of DWPF recycle. To avoid the generation of hydrogen through thermolysis in the CSTF, SRNL has been tasked to mitigate the concentration of glycolate returned via DWPF recycle stream through chemical destruction of glycolate.

The approach employed by Savannah River Remediation (SRR) to direct this flowsheet change evaluates mission-level DWPF operations/impacts and potential impacts to the CSTF. SRR and SRNL initiated the glycolic mitigation activity in November 2017. A systems engineering workshop[3] was held to establish potential mitigation options. These possible solutions were intended to address how to and where to destroy glycolate – consistent with DWPF operational capability and process requirements. The workshop identified chemical oxidation of glycolate within the DWPF RCT[†] as the most promising option.

Sodium permanganate and Fenton's reagent (metallic ion catalyzed hydrogen peroxide) were identified as the two most promising oxidants. Feasibility testing was performed by SRNL to verify the ability of these reagents to destroy glycolate in simplified RCT conditions within a timeframe suitable for supporting DWPF operations.[4] These preliminary tests indicated there were conditions in which each oxidant could be sufficiently effective to warrant detailed investigation. Subsequently, SRNL performed this work per the Task Technical and Quality Assurance Plan (TTQAP)[5] and Run Plan.[6] These were written in response to the SRR Task Technical Request[7] (TTR) which requested that SRNL more fully evaluate glycolic mitigation such that a downselection decision between Fenton's reagent and sodium permanganate could be made.

Downselection testing commenced in July 2018. The program targeted widely varying RCT process conditions, oxidant/reactant ratios, and strike conditions. The tests were conducted with discrete liquid sampling events and online offgas analysis for data generation. All tests have been completed and analytical data received. The following sections describe the test conditions selected, the statistical test matrix, test operations, results and data analysis, and provide conclusions/recommendations supporting the downselection.

2.0 Experimental Procedure and Operations

A mitigation effort for the destruction of glycolate was initiated in November 2017 with a systems approach exercise to identify and downselect options[3]. Sodium permanganate and Fenton's reagent (hydrogen peroxide with metallic

[†] The RCT collects offgas condensate from pre-processing, vitrification, and other unit operations performed in DWPF and is the singular return vessel delivering recycle effluent back to CSTF.

catalyst) were selected as the most promising of seven options for oxidation in the RCT. Testing was planned and conducted to support a downselection between using sodium permanganate and Fenton's reagent for the destruction of glycolate in the RCT. Test planning assumed a starting point immediately after transfer of the RCT to the Low Point Pump Pit Recycle Tank, with a 1,400-gallon heel left in the RCT and 5,600 gallons of SMECT or OGCT material. At this time the RCT is high in free hydroxide and nitrite compared to the Slurry Mix Evaporator Condensate Tank (SMECT) and the Offgas Condensate Tank (OGCT) but low compared to the RCT or CSTF assuming it has not been preconditioned with sodium hydroxide and sodium nitrite. The RCT is primarily fed by the SMECT and OGCT, see Figure 2-1. During typical processing, the SMECT and the OGCT condensates are pH 1-3 nitric acid solutions.

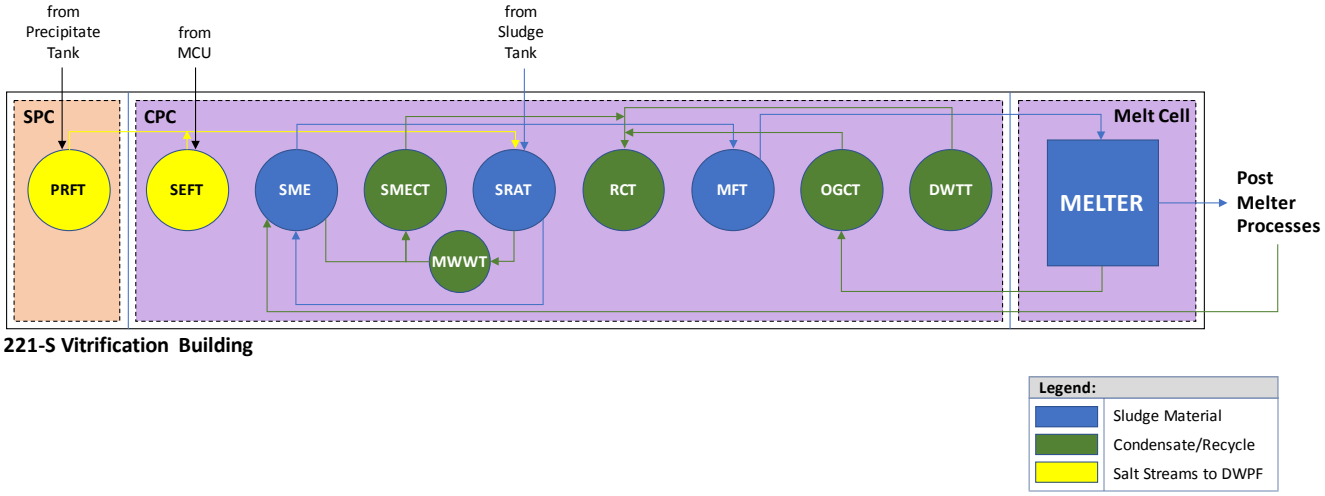


Figure 2-1. DWPF Process Vessels Impacting Generation of Condensate for RCT

2.1.1 *Sodium Permanganate*

Sodium permanganate is a strong oxidizer and ideally oxidizes an organic to CO_2 and water. Sodium permanganate can work over a wide pH range, such as 3 to 13 used in this test matrix. Byproducts of this reaction include sodium hydroxide and insoluble MnO_2. Based on planned stoichiometry equations, for every 1.00 kg of sodium permanganate added, up to 0.61 kg of MnO_2 is produced. Based on current projections,[8] this addition will generate aa few additional DWPF canisters due to the MnO_2 generation. During oxidation at the higher pH conditions, CO_2 is absorbed by the solution, minimizing the generation of offgas.

2.1.2 *Fenton's Reagent*

Fenton's reagent is a strong oxidizer and ideally oxidizes an organic to CO_2 and water. Fenton's reagent works over a narrow pH range, such as 3 to 5 used in this test matrix. Byproducts of this reaction include oxygen and iron oxides and hydroxides. Based on current projections,[8] this addition will generate aa few additional DWPF canisters due to the iron nitrate added to provide the catalyst. The narrow pH range likely means a pH adjustment is needed prior to oxidation. One additional safety concern for the Fenton's reagent process is the generation of oxygen due to decomposition of hydrogen peroxide during processing and in storage.

2.2 Experimental Design

The TTR and TTQAP specified six variables of interest. Ranges for these are included in parentheses.

1. Oxidant (reagent sodium permanganate or hydrogen peroxide)
2. Temperature (15 to 50 °C)
3. Oxidant Addition Rate (10-minute addition (100 gallons per minute equivalent) to 2-hour addition)

4. Amount of oxidant (1 to 1.5 times stoichiometric requirement for oxidation of all organics)
5. Solution pH (pH 3 to 5 for Fenton's reagent, pH 3 to 13 for sodium permanganate)
6. Glycolate concentration (125 to 250 mg/L)

The experimental design is given in Table 2-1. A partial factorial experimental design with controls and blanks was developed using the Design of Experiments platform in JMP® Pro 11.2.1[9] to explore the six variables above. Table 2-1 reflects the series of tests required to develop the data necessary for the downselection decision. The sequence of experiments as performed was not random but, rather, selected to potentially reduce the total number of experiments based on comparative (per oxidant) results. As such, the matrix is further described in 5 blocks of related experiments.

Table 2-1. Experimental Design for Variables of Interest

Test # / Block #	Oxidation Pathway	Temperature (°C)	Oxidant Addition Time (min)	Amount of Oxidant (% stoich factor)	Solution pH	Glycolate Conc (mg/L)
1 / I	Sodium Permanganate	15	120	100	13	125
3 / I	Sodium Permanganate	32.5	65	125	8	187.5
4 / I	Sodium Permanganate	15	120	150	3	250
5 / I	Sodium Permanganate	15	10	150	13	125
10 / I	Sodium Permanganate	15	10	100	3	250
14 / II	Fenton's Reagent	15	120	100	5	125
16 / II	Fenton's Reagent	32.5	65	125	4	187.5
17 / II	Fenton's Reagent	15	120	150	3	250
18 / II	Fenton's Reagent	15	10	150	5	125
23 / II	Fenton's Reagent	15	10	100	3	250
2 / III	Sodium Permanganate	32.5	65	125	8	187.5
13 / III	No Oxidant	32.5	65	0	3	250
15 / III	Fenton's Reagent	32.5	65	125	4	187.5
6 / IV	Sodium Permanganate	50	120	150	13	250
7 / IV	Sodium Permanganate	50	10	100	13	250
8 / IV	Sodium Permanganate	50	120	100	3	125
9 / IV	Sodium Permanganate	50	10	150	3	125
11 / IV	Sodium Permanganate	32.5	65	125	8	0
12 / V	**Fenton's Reagent**	**32.5**	**65**	**125**	**4**	**0**
19 / V	**Fenton's Reagent**	**50**	**120**	**150**	**5**	**250**
20 / V	**Fenton's Reagent**	**50**	**10**	**100**	**5**	**250**
21 / V	**Fenton's Reagent**	**50**	**120**	**100**	**3**	**125**
22 / V	**Fenton's Reagent**	**50**	**10**	**150**	**3**	**125**

Blocks I-III were performed prior to the down select decision. Blocks I and II comprised tests with sodium permanganate and Fenton's reagent, respectively, performed at temperatures under 50 °C. Block III included Test 13, the control test with no oxidant addition, and two duplicate tests from Blocks I and II (Tests 2 and 15). Block IV included Test 11, a control test for the sodium permanganate flowsheet, along with Tests 6-9 which are performed at 50 °C with sodium permanganate. Block IV was performed to better define rates and solution

chemistry as opposed to tests more consistent with DWPF operations. Block V, the five yellow highlighted tests (the four tests with Fenton's reagent at 50 °C and the blank with Fenton's reagent) were not performed as requested by SRR Engineering after a review of Block I, II, and III results.

2.3 Preliminary Screening Testing in 735-11A

Twenty preliminary tests were performed at room temperature (without offgas analysis) to prepare for the matrix tests. Oxidation experiments were performed with glycolate as the only added organic. The preliminary oxidation screening tests were performed with up to 2,000 mg/L glycolate as the only added organic. Early testing was issued in a report.[10]

Excellent glycolate destruction was achieved at a starting pH of 3 and 11 with a starting glycolate concentration at 250 mg/L – note that time zero measured glycolate was lower than the calculated addition of 250 mg/L – for the sodium permanganate testing (MnO_4 dashed lines in graphs), and 2.5 mols of oxidant per mol of glycolate. There was less complete destruction in Fenton's reagent testing (H_2O_2 solid line in graph). The glycolate results from testing at 250 mg/L are summarized in Figure 2-2. Note the legend shows the oxidant, the % oxidant stoichiometry, the time of oxidant addition, the added glycolate concentration (mg/L) and the starting pH.

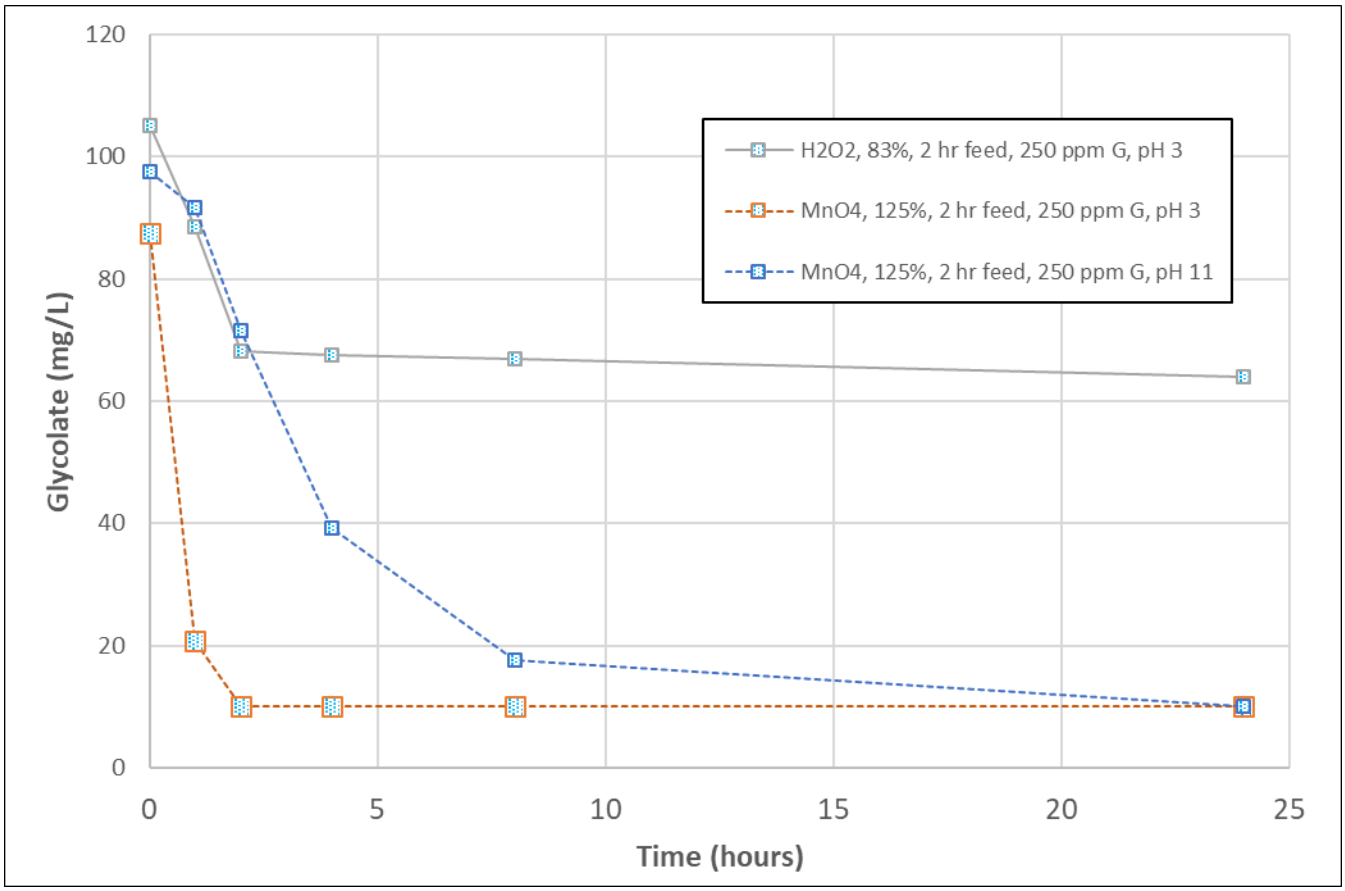


Figure 2-2. Screening Tests for Destruction of Glycolate Starting at 250 mg/L Glycolate

Excellent glycolate destruction was also achieved at a starting pH of 3 to 13 with a starting glycolate concentration of 2,000 mg/L – note that the time zero glycolate was lower than the calculated addition of 2,000 mg/L – and 2-3 mols of oxidant per mol of glycolate. The glycolate results from testing at 2,000 mg/L are summarized in Figure 2-3.

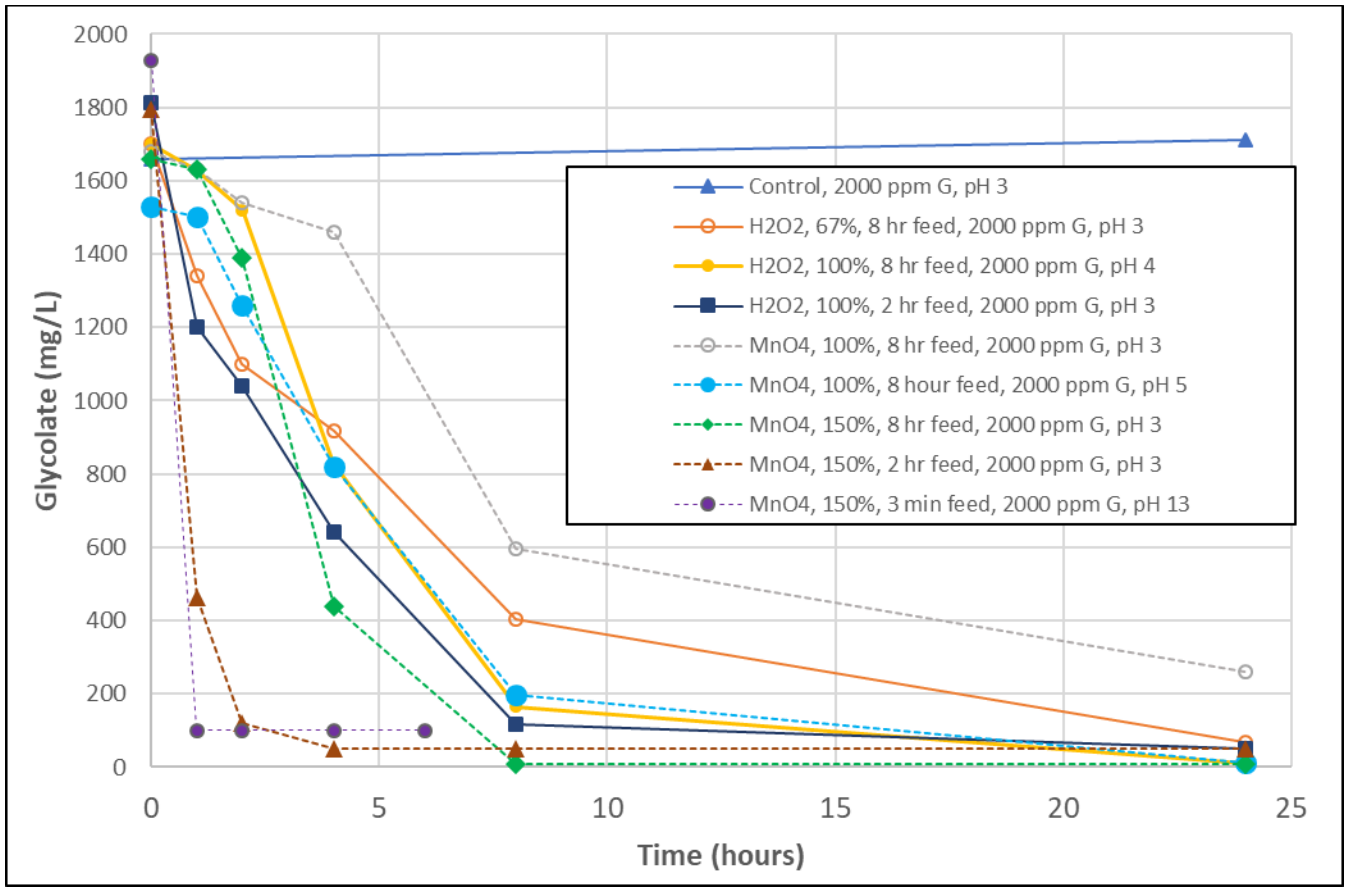


Figure 2-3. Screening Tests for Destruction of Glycolate Starting at 2000 mg/L Glycolate

A three-minute oxidant addition time, in addition to higher glycolate concentrations were evaluated to ensure the matrix parameters are not optimistic or near a process boundary.

2.4 Matrix Study Simulant Composition

The base simulant RCT target composition reflects the RCT without the addition of corrosion control chemicals (i.e., sodium hydroxide and sodium nitrite). For performing an oxidation process, the preferred time was assumed to be prior to addition of the corrosion control chemicals, considering the competing reactions for the oxidant by the organics and by the nitrite. The resulting RCT simulant has a pH of approximately 4; after corrosion control chemicals are added, the resulting pH is >13. The RCT simulant was adjusted, as necessary, with nitric acid or sodium hydroxide to achieve the pH target for each test.

The composition of the typical RCT simulant is summarized in Table 2-2. The composition of the simulant was determined using a 1500-gal RCT heel combined with 3200-gal of SMECT and 3200-gal mixture of OGCT. Note that the OGCT is typically unmixed so the sample is essentially supernate. Iron and manganese were both added to represent a foam-over of sludge, SRAT or SME product in the Chemical Process Cell (CPC), and from entrainment of melter feed in the melter. The simulant composition was based on nominal (not upset) RCT data provided by SRR covering September 2012 to January 2018.[11]

Table 2-2. RCT Simulant Composition (pH ~4)

Species	Conc. (mg/L)	M. W. (g/mol)	Conc. (M)
$NaNO_3$	4150	85	0.0488
$NaNO_2$	7700	69	0.112
$Fe(NO_3)_3 \cdot 9H_2O$	250	404	0.00062
$Mn(NO_3)_2$	50	179	0.00028

The impact of an entrainment event in the CPC or melter could result in a higher or lower pH, higher glycolate and nitrate, and higher metals concentrations. Testing to process the RCT after an entrainment event was not covered by this Run Plan or discussed herein. That work is currently ongoing.

In addition to glycolate, seven other organics were added at concentrations much higher than expected to ensure the decomposition could be tracked analytically. The TTR requested the evaluation of these organics, as shown in Table 2-3. Formate and Oxalate were added because they are decomposition products of glycolate and impurities in glycolic acid.[12] Formaldehyde and glyoxylate were added as they are possible intermediate reaction products. The SMECT and RCT condensates contain trace methylmercury.[13] Propanal and trimethylsilanol were added, as they are decomposition products of Antifoam 747 and both are very soluble in aqueous solutions.[14]

To ensure the process is robust enough to handle these organic species, and that the kinetics for these components could be determined analytically, the organic species were added at the same carbon concentration as glycolate of 0.0067 M C or 250 mg/L (i.e., independent of and nominally quite higher than normal process concentrations). Note that the 250 mg/L glycolate concentration was chosen to be a bounding concentration during nominal operations. Glycolate has a very low vapor pressure so little is expected to be present in the condensate unless there is a foam-over or carryover event. The 125 mg/L glycolate was chosen as the low glycolate concentration as 0 mg/L glycolate was already covered by the glycolate blank test.

Simulant and organics produced at an earlier date were added one at a time just prior to each test. The offgas is collected from the start of simulant preparation to the end the test. Several of the organics such as trimethylsilanol and propanal were volatile; thus, they were monitored with offgas Fourier-Transform InfraRed (FTIR) spectrometer and Mass Spectrometer (MS) during the process. Glycolate and nitrite were the last two chemicals added, due to the concern that they might react prior to oxidant addition.

Table 2-3. Organic Species Requested by TTR

Chemical Species	Chemical Added	Chemical Formula	Molar Mass, g/mol	Concentration, mg/L
Glycolate	Sodium glycolate	$C_2H_3O_3^-$	75.04	250
Formate	Sodium formate	$COOH^-$	45.02	299
Oxalate	Sodium oxalate	$C_2O_4^{2-}$	88.02	293
Glyoxylate	Glyoxylic Acid	$C_2HO_3^-$	73.04	245
Formaldehyde	Formalin*	CH_2O	30.03	201
Methyl Mercury	Monomethyl-mercury hydroxide	$HgCH_3^+$	215.62	1437
Propanal	Propanal	C_3H_6O	58.08	129
Trimethylsilanol	Trimethylsilanol	$C_3H_{10}OSi$	90.20	200

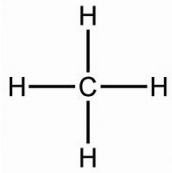
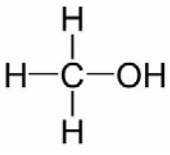
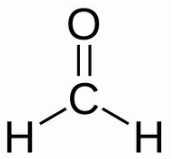
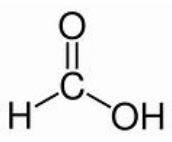
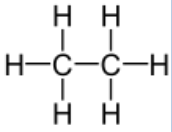
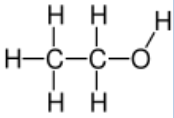
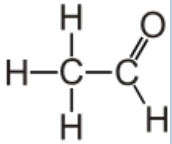
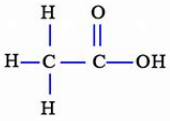
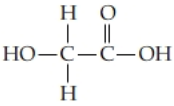
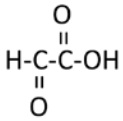
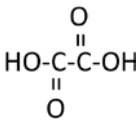
* Formaldehyde is added as a 37 wt% solution and contains 10-15 wt% methanol. Both 15 wt% methanol and 37 wt% formaldehyde are included in calculating the mass of oxidant to be used for each test.

Since kinetics data were requested for the oxidation of these organics, all organics were present in early experiments. Antifoam is only present in appreciable quantities following a carryover event and therefore was not used in these experiments and is not part of this study; it will be studied in future testing by adding SRAT or SME products containing high concentrations of glycolate, residual antifoam 747 and the remaining antifoam fragments). As provided for in the Run Plan, testing was simplified by eliminating the addition of methylmercury hydroxide in later experiments. SRR approved SRNL's request to leave methylmercury hydroxide out of the simulant preparation in later tests as it was not being oxidized (Section 3.4.4) and due to the safety implications of adding or producing dimethylmercury.

2.5 Determination of Oxidant Stoichiometry

The goal of the testing was to determine the extent of oxidation of the various organics added to the simulant. Especially important is the oxidation of glycolate, as glycolate destruction is important to reduce the potential for thermolysis .[15] The oxidation state of some of the one carbon and two carbon organics is given in Table 2-4. For example, methane is the most reduced one carbon species and CO_2 is the most oxidized species. The carbon (or carbons for the two carbon organics) in each compound from left to right is +2 more oxidized than its predecessor, referred to as the stepwise oxidation of species. For example, methanol can be oxidized to formaldehyde, which can be oxidized to formic acid, which can be oxidized to CO_2. The overall reaction is that methanol is oxidized to CO_2. But the extent of the reaction might not be complete, so there can be some formaldehyde or formate present, especially at intermediate points in the experiment.

Table 2-4. Oxidation State of One and Two Carbon Organics

Reduced ←						→ **Oxidized**
C Oxidation State	-4	-2	0	+2	+4	C Oxidation State
Formula	CH_4	CH_3OH	CH_2O	HCOOH	CO_2	Formula
Name	Methane	Methanol	Formaldehyde	Formic acid	Carbon dioxide	Name
Simple Structure					O=C=O	Simple Structure
-3,-3	-3,-1	-3,+1	-3,+3	-1,+3	+1,+3	+3,+3
H_3CCH_3	H_3CCH_2OH	H_3CCCHO	H_3CCOOH	HOH_2CCOOH	OHCCOOH	HOOCCOOH
Ethane	Ethanol	Ethanal	Acetic Acid	Glycolic Acid	Glyoxylic Acid	Oxalic Acid
						

One of the keys to this testing is an understanding of the organic oxidation kinetics. In testing, the stoichiometry of the reactions was used to calculate the moles of oxidant needed for each experiment. The reactions in Table 2-5 summarize the pre-test assumptions for estimating the sodium permanganate or Fenton's reagent requirement for each chemical added. Nitrite is also included in this list as it can also be oxidized to nitrate. Sulfite was included in the list because it was added to each sample to quench permanganate or peroxide prior to analysis. However, no oxidant was added for the oxidation of nitrite. Note that methanol is included, as it is a significant impurity in formaldehyde. For each of the high pH reactions, virtually all the CO_2 is converted to sodium carbonate ($2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$). The equation for calculating the moles of sodium permanganate and peroxide required are shown below:

$$permanganate, mol = 2G + \frac{2}{3}F + \frac{2}{3}O + \frac{8}{3}MHg + \frac{16}{3}P + 8T + \frac{4}{3}Gl + \frac{4}{3}Fo + 2M \quad \textbf{2-1}$$

$$peroxide, mol = 3G + F + O + 4MHg + 8P + 12T + 2Gl + 2Fo + 3M \quad \textbf{2-2}$$

where G is mol glycolate, F is mol formate, O is mol oxalate, MHg is mol methylmercury, P is mol propanal, T is mol trimethylsilanol, Gl is mol glyoxylate, Fo is mol formaldehyde and M is mol methanol.

Table 2-5. Proposed Reactions for Complete Oxidation to CO_2

Chemical Species	Reaction with Hydrogen Peroxide	Low pH Reaction with Sodium Permanganate	High pH Reaction with Sodium Permanganate
Glycolate	$C_2H_4O_3 + 3H_2O_2 \rightarrow 2CO_2 + 5H_2O$	$C_2H_4O_3 + 2NaMnO_4 \rightarrow 2NaOH + 2CO_2 + H_2O + 2MnO_2$	$NaC_2H_3O_3 + 2NaMnO_4 \rightarrow 3NaOH + 2CO_2 + 2MnO_2$
Formate	$HCOOH + H_2O_2 \rightarrow CO_2 + 2H_2O$	$3H_2CO_2 + 2NaMnO_4 \rightarrow 2NaOH + 3CO_2 + 2H_2O + 2MnO_2$	$3NaHCO_2 + 2NaMnO_4 + H_2O \rightarrow 5NaOH + 3CO_2 + 2MnO_2$
Oxalate	$C_2H_2O_4 + H_2O_2 \rightarrow 2CO_2 + 2H_2O$	$3H_2C_2O_4 + 2NaMnO_4 \rightarrow 2NaOH + 6CO_2 + 2H_2O + 2MnO_2$	$3Na_2C_2O_4 + 2NaMnO_4 + 4H_2O \rightarrow 6CO_2 + 8NaOH + 2MnO_2$
Methyl Mercury	$HgCH_3OH + 4H_2O_2 \rightarrow$ $6H_2O + CO_2 + HgO$	$3HgCH_3OH + 8NaMnO_4 \rightarrow$ $2H_2O + 3CO_2 + 3HgO + 8NaOH + 8MnO_2$	$3HgCH_3OH + 8NaMnO_4 \rightarrow$ $2H_2O + 3CO_2 + 3HgO + 8NaOH + 8MnO_2$
Propanal	$C_3H_6O + 8H_2O_2 \rightarrow 3CO_2 + 11H_2O$	$3C_3H_6O + 16NaMnO_4 \rightarrow 9CO_2 + H_2O + 16MnO_2 + 16NaOH$	$3NaC_3H_5O + 16NaMnO_4 + 2H_2O \rightarrow 9CO_2 + 16MnO_2 + 19NaOH$
Trimethylsilanol	$C_3H_{10}OSi + 12H_2O_2 \rightarrow$ $17H_2O + 3CO_2 + SiO_2$	$C_3H_{10}OSi + 8NaMnO_4 \rightarrow$ $H_2O + 3CO_2 + SiO_2 + 8NaOH + 8MnO_2$	$NaC_3H_9OSi + 8NaMnO_4 \rightarrow$ $3CO_2 + 9NaOH + 8MnO_2 + SiO_2$
Glyoxylate	$H_2C_2O_3 + 2H_2O_2 \rightarrow 2CO_2 + 3H_2O$	$3H_2C_2O_3 + 4NaMnO_4 \rightarrow 6CO_2 + H_2O + 4MnO_2 + 4NaOH$	$3NaHC_2O_3 + 4NaMnO_4 + 2H_2O \rightarrow 6CO_2 + 4MnO_2 + 7NaOH$
Formaldehyde	$CH_2O + 2H_2O_2 \rightarrow CO_2 + 3H_2O$	$3CH_2O + 4NaMnO_4 \rightarrow 3CO_2 + H_2O + 4MnO_2 + 4NaOH$	$3CH_2O + 4NaMnO_4 \rightarrow 3CO_2 + H_2O + 4MnO_2 + 4NaOH$
Methanol	$CH_3OH + 3H_2O_2 \rightarrow CO_2 + 5H_2O$	$CH_3OH + 2NaMnO_4 \rightarrow CO_2 + H_2O + 2NaOH + 2MnO_2$	$NaCH_3O + 2NaMnO_4 \rightarrow CO_2 + 3NaOH + 2MnO_2$
Nitrite	$HNO_2 + H_2O_2 \rightarrow H_2O + HNO_3$	$3HNO_2 + 2NaMnO_4 + H_2O \rightarrow 3HNO_3 + 2MnO_2 + 2NaOH$	$3NaNO_2 + 2NaMnO_4 + H_2O \rightarrow 3NaNO_3 + 2MnO_2 + 2NaOH$
Sulfite	$2Na_2SO_3 + 3H_2O_2 \rightarrow$ $2NaSO_4 + 2H_2O + 2NaOH$	$Na_2SO_3 + NaMnO_4 + H_2O \rightarrow NaSO_4 + NaOH + MnO_2$	$NaSO_3 + NaMnO_4 + H_2O \rightarrow NaSO_4 + NaOH + MnO_2$

2.6 Experimental Apparatus and Parameters

Testing was performed using a 2.0-liter borosilicate glass jacketed reactor. The reactor design provided for temperature-controlled operations of approximately 1.8 liters of RCT simulant. Either nitric acid or sodium hydroxide was added to reach the initial pH target. The oxidants were added to the vessel via a syringe pump. An agitator was used throughout testing to ensure the solution was well mixed.

A sampler allowed on-line removal of contents as needed. An in situ pH probe was utilized in all experiments to monitor reaction progress. An air purge of 81 sccm was selected to provide enough turnover in the gas to enable measurement with FTIR and MS. However, this increased purge rate (10 times higher than the scaled DWPF airflow) dilutes the off-gas more than would be seen during processing. As a result, absolute concentrations would need to be scaled to the actual purge rate. A reflux condenser was present to prevent dewatering and to cool the offgas prior to analysis. Offgas analysis was performed with a MS and a FTIR. A gas chromatograph (GC) was used when the MS was not available.

A more detailed list of test parameters and conditions follows.

- Vessel Construction: Borosilicate glass
- Total Available Volume in Vessel: approximately 2.0 L
- Liquid Volume: approximately 1.8 L
- Headspace Volume: approximately 0.25 L including condenser
- Target purge rate: 81 sccm (21.11 °C, 1 atm) or greater with ~1 vol % inert He tracer
- Purge gas composition: Air
- Test duration: 6 hours
- Reaction temperature: 15 to 50 ± 2 °C[a]
- Condenser cooling water setpoint: 10 ± 2 °C
- Condenser gas outlet temperature target: ≤25 °C
- Mixer rate: 100 to 300 rpm

[a]A water bath was used at the minimum temperature required to achieve the desired reaction temperature.

A sketch of the equipment is shown in Figure 2-4. A photo of the equipment is shown in Figure 2-5.

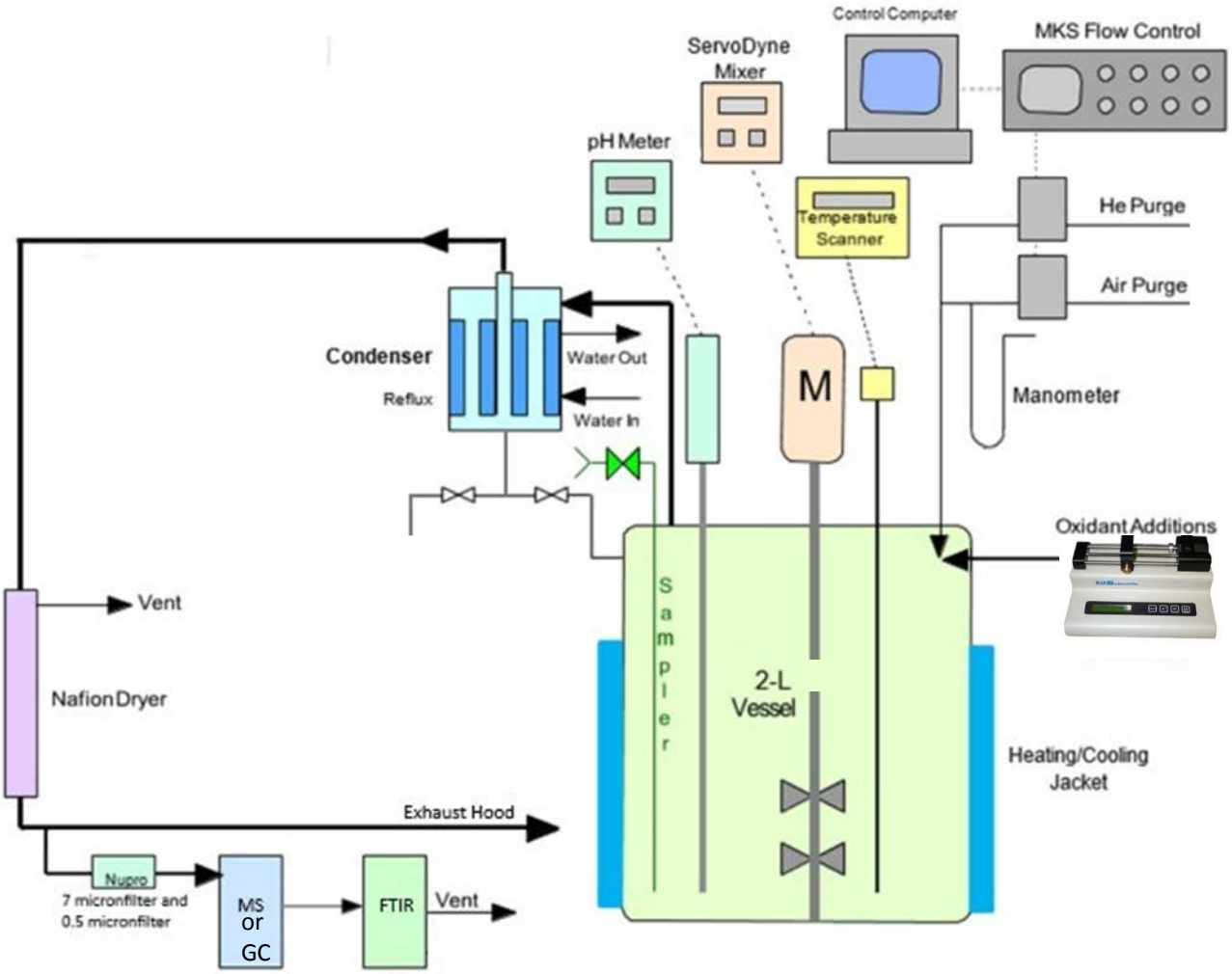


Figure 2-4. Equipment Apparatus Sketch

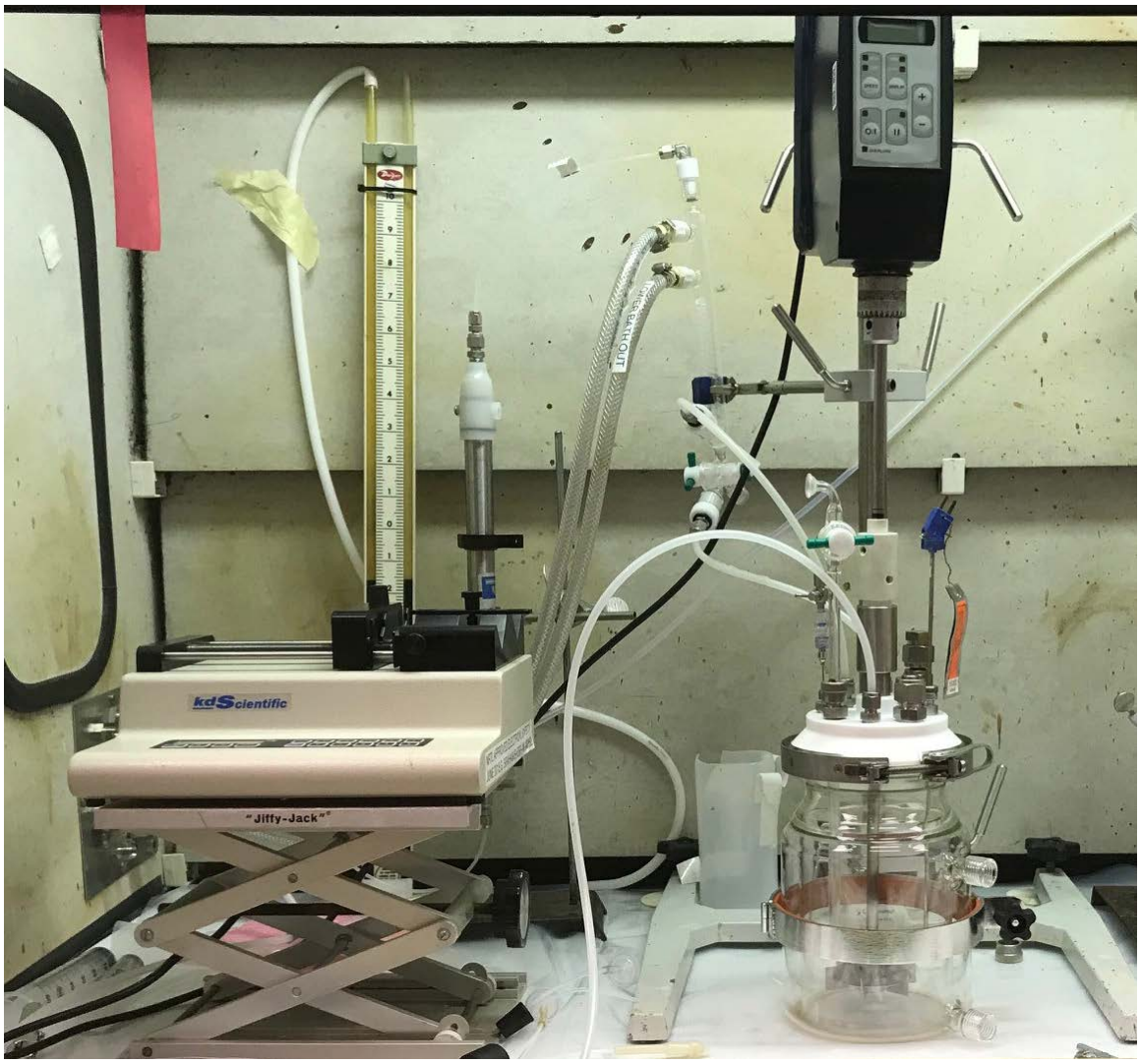


Figure 2-5. Photo of Apparatus

2.7 Scaling

The experimental reactor was 2 L in volume. The RCT is 12,000 gallons and has a working volume of 8,000 gallons. Instead of geometrically scaling the RCT, the working volume of the experimental reactor was set at 1.8 L, to minimize the offgas volume and turnover the offgas more frequently.

The RCT has an air purge of 4.8 standard cubic feet per minute (scfm).[16] The purge in the experiments was set at 81 standard cubic centimeters per minute (sccm). The purge was increased 10x in these experiments compared to geometric scaling to increase the turnover in the vapor space during the experiments. The purge was increased temporarily when needed during chemical additions.

2.8 Offgas Analysis

Offgas samples were analyzed using an FTIR and the MS or GC. The TTR requested analysis for toxic and flammable gases along with H_2, CO_2, and NO_x. The analysis frequency for the FTIR and MS is <10 seconds, so a large data set was generated during each test. The MS was out of service

for about half of the tests and a GC was used in place of the MS in tests 3a, 5a, 6, 7, 8, 9, 10 and 11 to measure the N_2, O_2, N_2O, CO_2, H_2 and He.

An Extrel CMS MAX300-LG MS was used to measure H_2, He, N_2, O_2, NO, NO_2, CO_2, and Ar. The MS is calibrated by a series of gas mixtures that are used to measure background intensity, ion fragmentation, and sensitivity. All gases used were National Institute of Standards and Technology (NIST) traceable. The certificates of analysis are documented in the SRNL Electronic Lab Notebook (ELN)[17]. In addition, qualitative intensity measurements of specific ion masses that might be expected from antifoam degradation products were also measured. Hexamethyldisiloxane was monitored at masses 148, 147, 131, and 73 and trimethylsilanol was monitored at mass 75. Hexamethyldisiloxane and trimethylsilanol are potentially flammable volatile products from decomposed antifoam. Measurements of H_2 by MS were somewhat inaccurate due to the extremely low values that were subject to error due to drift in the MS background signal. For some tests, the He calibration drifted and was corrected by a linear interpolation between the calibration value and the post-calibration check value.

An MKS MultiGas™ 2030 FTIR spectrometer was connected to the offgas system for the duration of the test. The FTIR measures CO, CO_2, NO, NO_2, N_2O, H_2O, and Antifoam degradation products concentrations. Although the GC detects water, the FTIR gives a quantitative concentration for moisture in the chilled offgas leaving the Nafion® drier. The FTIR obtained data roughly every 15 seconds.

An Agilent 3000A dual column micro GC was used when the MS was not available. Column-A can collect data related to He, H_2, O_2, and N_2, while column-B can collect data related to CO_2 and N_2O. The GCs were calibrated with a standard calibration gas containing He, H_2, O_2, N_2, CO_2 and N_2O. The calibration was verified prior to starting the test and after completing the test. Room air was used to give a two-point calibration for N_2. Raw chromatographic data were acquired by the GC approximately every four minutes. The GC data were additionally post-processed to adjust for inaccuracies in the measured N_2 and O_2 concentrations. The concentrations of N_2 and O_2 measured in air at the beginning and end of each test were used to perform linear interpolation corrections of the N_2 and O_2 data. The GC has a lower quantification limit for measuring hydrogen than the MS as discussed in Appendix C.

A summary listing offgas species and analyzer is seen in Table 2-6.

Table 2-6. Analyzer Used in Quantifying Offgas Species

Offgas Species	GC	MS	FTIR
H_2	X	X	
CO_2	X	X	X
NO		X	X
NO_2		X	X
N_2	X	X	
N_2O	X		X
O_2	X	X	
He	X	X	
Ar		X	
NH_3		X	
Hexamethyldisiloxane			X
Trimethylsilanol			X

2.9 Liquid Analyses

pH (logarithm of the reciprocal of hydrogen ion concentration in mols per liter) was used during testing along with liquid sampling and analysis by SRNL's Process Science Analytical Laboratory (PSAL) and SRNL's Analytical Development (AD) laboratories.

2.9.1 *pH*

A pH probe was used throughout testing. In testing with sodium permanganate, NaOH is generated so the pH continually rises until the reductant is consumed. The pH meter was calibrated prior to each test and a check was performed after each test by measuring the pH of 4, 7 and 10 buffer solutions.[18]

2.9.2 *Sampling and Analysis*

Liquid samples were pulled throughout testing and analyzed to track the decomposition of the added organics. For the pH 3 and pH 8 tests, the samples were quenched with sodium hydroxide to stop the destruction of nitrite. In all tests, the samples were quenched with sodium sulfite to stop the oxidation of the organics (i.e., to complete reduction of either permanganate or peroxide). The samples were then analyzed by PSAL and SRNL AD as requested. Note the PSAL used a new anion method using an OnGaurd II cartridge (cation exchange cartridge containing a sulfonic acid functional group) for each sample to minimize matrix effects, remove high levels of alkaline earth and transition metals and improve peak shape.

For mass balance calculations, the sample results were corrected for addition of the quench agents in time zero samples and added quench and oxidant in the post test samples. SRNL AD analyzed samples pulled prior to nitrite addition, so a correction was made to account for the dilution resulting from the nitrite addition/water as if a time zero sample had been analyzed. The corrections will be discussed in the carbon balance, section 3.5.

During each experiment, samples were drawn at selected reaction times from the apparatus and subsequently submitted to PSAL and SRNL AD for Ion Chromatography (IC), Semivolatile Organic Analysis (SVOA), Volatile Organic Analysis (VOA), Total Inorganic Carbon (TIC), Total Organic Carbon (TOC), and Inductively Coupled Plasma Emission Spectroscopy (ICP-ES). These samples included slurry or supernatant samples. The sampling frequency and analysis of each sample is summarized in Table 2-7. To minimize analytical costs after the first several tests, only samples pulled at the start of oxidant addition and post-test were submitted to SRNL AD for analysis. However, all samples shown in Table 2-7 were collected and would have been analyzed by AD if anomalous results were found in the samples measured. Samples with nitrite were quenched with sodium hydroxide to quench the nitrite reactions. Samples with excess oxidant were quenched with sodium sulfite to quench the oxidation reactions.

Table 2-7. Sample Frequency, Quench Method, and Analytical Plan

Sample Time	Sample Matrix	Sample Quench	Analytical Method
Pre-pH Adjustment	Slurry	Caustic	IC-anions,
Pre-pH Adjustment	Slurry	None	VOA/SVOA, TIC/TOC
Post pH Adjustment (time zero)	Slurry	None	ICP-ES
Post pH Adjustment (time zero)	Slurry	Caustic if pH <12	None
30 minutes post start oxidant	Slurry	Caustic, sodium sulfite	IC-Anions, ICP-ES
30 minutes post start oxidant	Slurry	sodium sulfite	None
60 minutes post start oxidant	Slurry	Caustic, sodium sulfite	IC-Anions, ICP-ES
60 minutes post start oxidant	Slurry	sodium sulfite	None
90 minutes post start oxidant	Slurry	Caustic, sodium sulfite	IC-Anions, ICP-ES
90 minutes post start oxidant	Slurry	sodium sulfite	None
120 minutes post start oxidant	Slurry	Caustic, sodium sulfite	IC-Anions, ICP-ES
120 minutes post start oxidant	Slurry	sodium sulfite	None
240 minutes post start oxidant	Slurry	Caustic, sodium sulfite	IC-Anions, ICP-ES
240 minutes post start oxidant	Slurry	sodium sulfite	None
360 minutes post start oxidant addition or posttest	Slurry	Caustic, sodium sulfite	IC-Anions, ICP-ES
360 minutes post start oxidant addition or post test	Slurry	sodium sulfite	VOA/SVOA, TIC/TOC

2.10 Test Chronology

As described Table 2-7 above, the tests were not performed in numerical sequence; instead they were completed in blocks as described in Table 2-1. A list of completed tests and dates reported are summarized in Table 2-8. Note that some of the tests were repeated due to incorrect simulant makeup. For example, Test 1 was repeated and only the results from the third test (1b) are reported.

Table 2-8. Test Chronology

Test	Date
Test 1b	8/19/2018
Test 2a	8/30/2018
Test 3a	8/8/2018
Test 4a	8/14/2018
Test 5a	8/9/2018
Test 6a	10/9/2018
Test 7	10/16/2018
Test 8	10/18/2018
Test 9	10/23/2018
Test 10	8/10/2018
Test 11	10/25/2018
Test 13	9/4/2018
Test 14	8/22/2018
Test 15a	8/29/2018
Test 16	8/23/2018
Test 17	8/24/2018
Test 18	8/27/2018
Test 23	8/28/2018

2.11 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60[19]. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist[20] contained in WSRC-IM-2002-00011, Rev. 2. Data from the experiments was posted in electronic notebooks.[17a, 21]

The TTR for this work specified the testing has a functional class of Safety Class. The hydrogen generation and final glycolate concentration in this testing was used in choosing between two processing options and likely will not be used in safety calculations as it is preliminary data. If glycolate destruction data is used for determining stoichiometry, the whole of the data will be evaluated with any additional data at that time. The TTR Safety Class tasks will be covered by other run plans as the process for glycolate destruction matures.

3.0 Results and Discussion

Comparisons are shown between the two oxidants using side by side figures and tables. These graphics reflect the response shown by Sodium Permanganate and Fenton's reagent when the following process variables were flexed:

- Impact of Oxidant (Section 3.3.1)
- Oxidant stoichiometry (Section 3.3.2
- RCT solution temperature (Section 3.3.3)
- Oxidant strike time or rate of delivery (Section 3.3.4)
- RCT solution pH (Section 3.3.5).

Analysis is based on solution and offgas samples. The key response for solution samples was the destruction efficiency for glycolate; the fate of other organic components was also determined. Tables summarizing the data used in calculating the % glycolate destruction shown in the figures and tables are included in Section 3.3. Other organics included in testing are discussed in Section 3.3.6. Offgas analyses were performed to determine the presence/absence of hydrogen or other flammable gases, reaction kinetics, and to assist in nitrogen and carbon balances. Pertinent results will be shown in tables and figures in this report to allow comparisons and explanations. The sample complete results from all tests and a graph showing glycolate, formate, nitrite, nitrate and pH trends from each test are included in Appendix B.

3.1 Duplicate Test Comparison

Two duplicate experiments were completed for both sodium permanganate (Tests 2A and 3A) and Fenton's reagent (Tests 15A and 16). Two comparisons are presented that include glycolate, formate, and pH (Figure 3-1) along with nitrate and nitrite (Figure 3-2). As can be seen from this data, the agreement within each set of replicate tests is excellent.

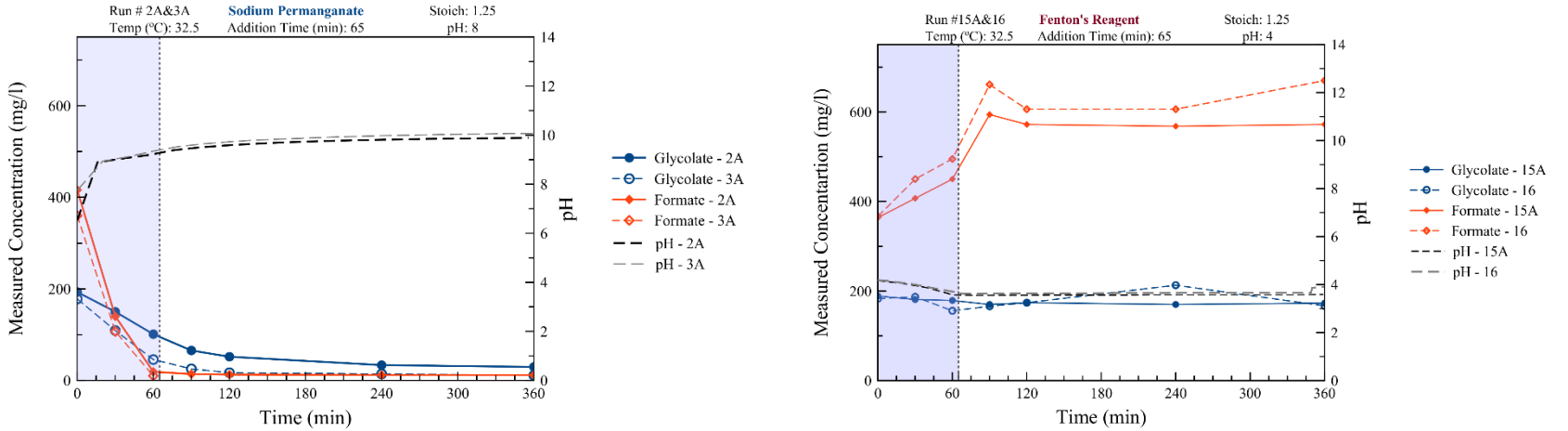


Figure 3-1 Comparison of Duplicate Tests for Glycolate, Formate, and pH

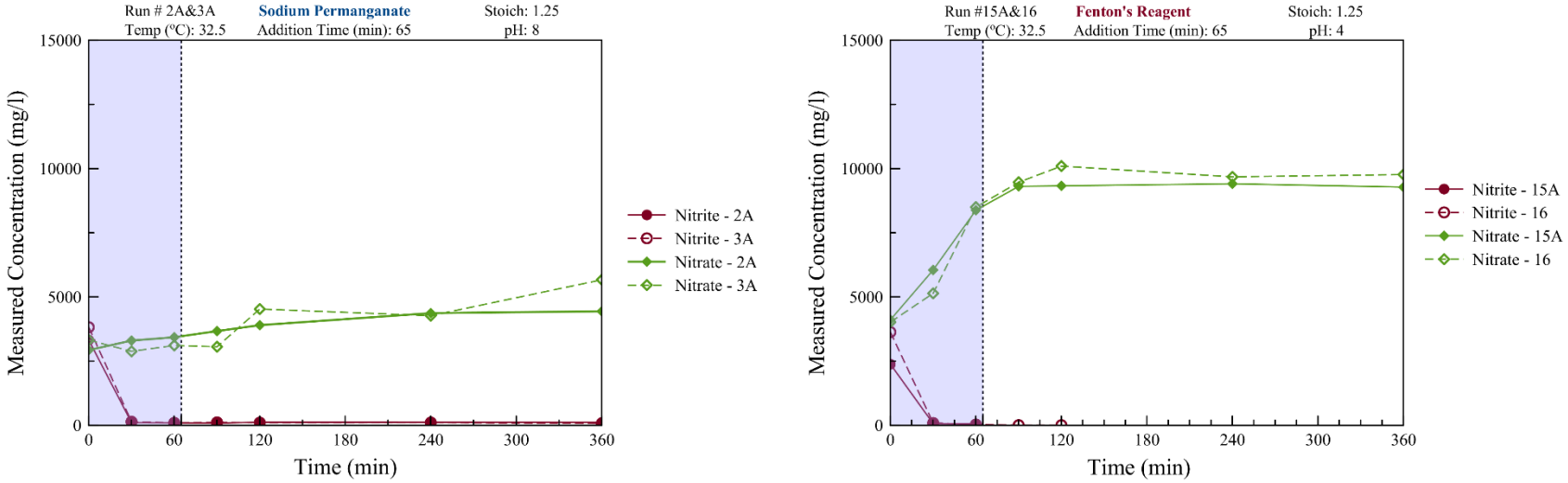


Figure 3-2 Comparison of Duplicate Tests for Nitrite and Nitrate

3.2 Offgas Analyses

The offgas from each test was analyzed using the FTIR and either a MS or GC. The MS was used for Tests 1b, 2a, 4a, 13, 14, 15a, 16, 17, 18 and 23. After the MS equipment failure, GC was used for Tests 3a, 5a, 6a, 7, 8 9, 10, and 11. The offgas profile from a pH 3 experiment, Test 9 (Figure 3-3) and from a pH 13 experiment, Test 6a (Figure 3-4) are shown as representative of the sodium permanganate experiments. Note that the purge used in these experiments was 10 times the scaled DWPF air purge, so the reported gas concentrations would need to be multiplied by 10, although the calculated millimoles (mmol) would be the same.

The primary purpose for the MS and GC was the measurement of hydrogen and helium. The quantification limit for hydrogen is approximately 40 ppm_v (6.48E-04 lb/hr DWPF 8,000-gallon RCT scale) for the GC and 100 ppm_v (1.62E-03 lb/hr DWPF 8,000-gallon RCT scale) for the MS. No hydrogen was detected during oxidant addition in any of the tests with GC. Most of the tests with a MS detected hydrogen during simulant makeup and during oxidant addition. Any perceived accumulation of hydrogen observed in other testing was a result of cumulative positive values in a noisy MS signal. Prior to the MS equipment failure, a negative drift of the hydrogen signal was often observed and resulted in the application of a corrective calculation to registered values. Some of the noisy signal issues were exacerbated by the correction factor producing the apparent hydrogen accumulations. Additional discussion and offgas graphs from each test are included in Appendix C. Note that the simulant was heated or cooled during simulant makeup to prepare the solution for the test conditions. Hydrogen generation during simulant preparation was likely due to thermolysis of the aldehydes or glycolate.

During simulant preparation, the offgas analysis via the FTIR was useful in monitoring the concentration of known flammable species such as propanal and hexamethyldisiloxane. Specifically, when propanal was present in the simulant and trimethylsilanol was added to the vessel, both propanal and hexamethyldisiloxane were observed in the offgas. Monitoring of these species allowed for careful additions of the trimethylsilanol to remain below flammability limits for the offgas species. The offgas analyses were only significant during the first 60 minutes of testing starting from the addition of the oxidant.

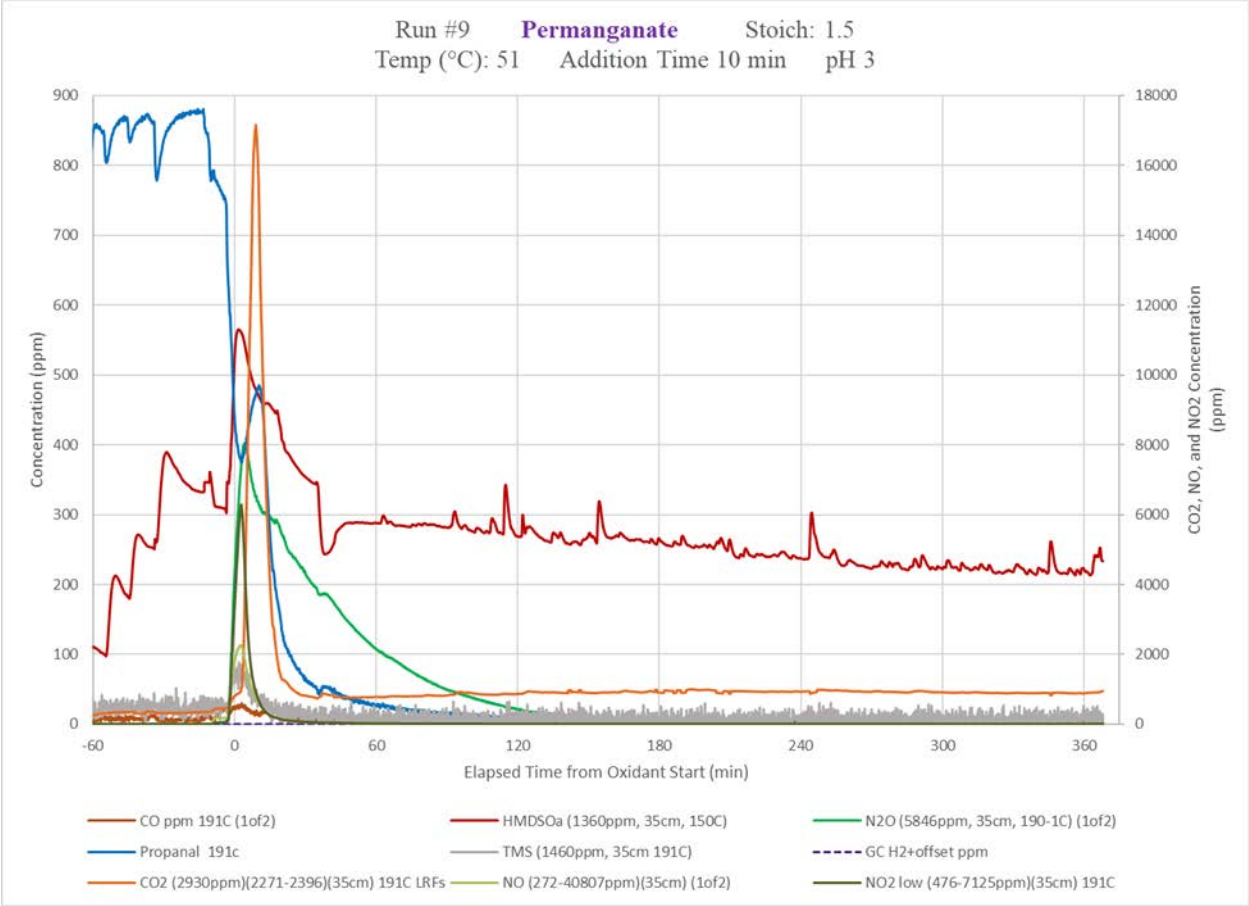


Figure 3-3 Offgas Profile for pH 3 Sodium Permanganate Test 9

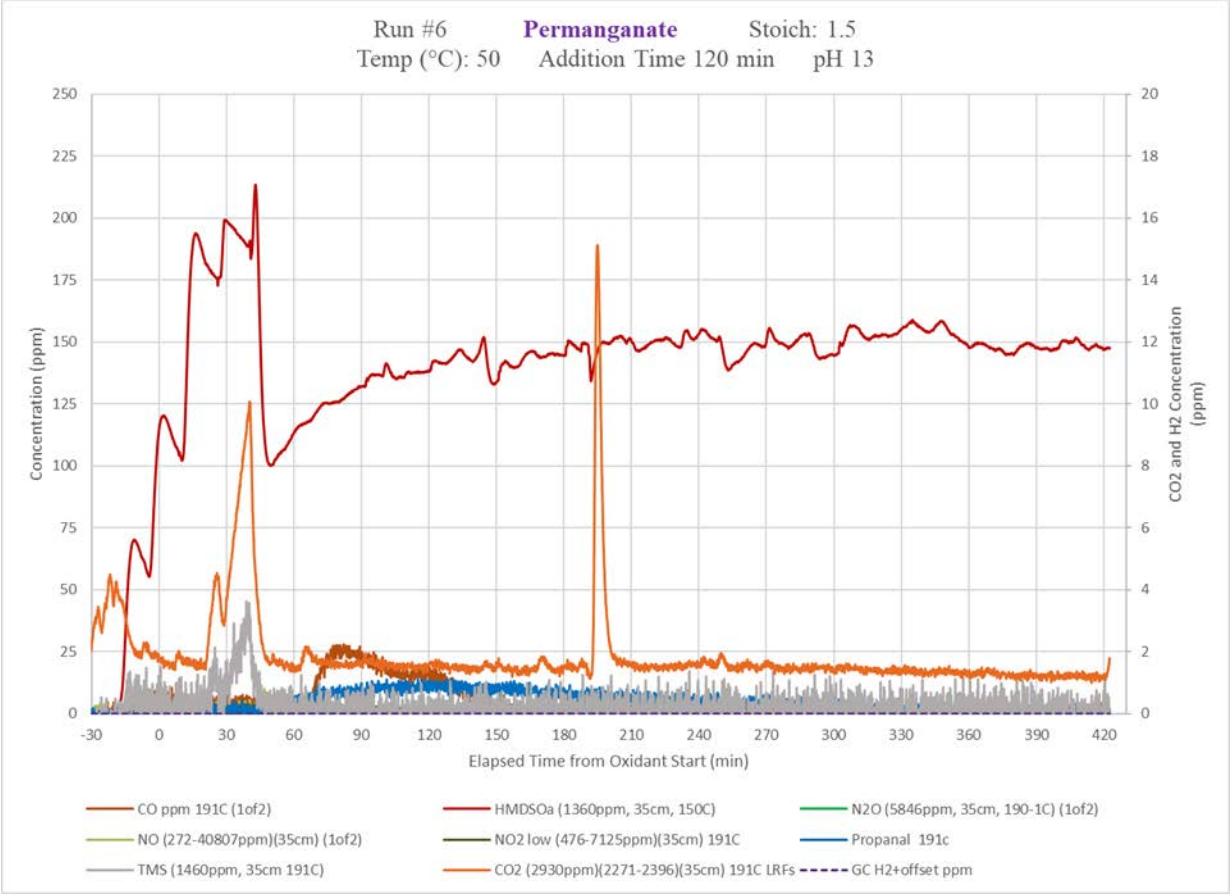


Figure 3-4 Offgas Profile for pH 13 Sodium Permanganate Test 6a

If pH adjustments occurred to target a pH of 3 in the vessel, the FTIR identified the significant production of various NO_x species (supporting the liquid analyses) and one qualitatively identified transient species (i.e., propenyl nitrite) which appears to result from a reaction between propanal and sodium nitrite when the simulant is acidic. Propenyl nitrite was not observed in appreciable quantities and was only observed in the beginning of the testing between pH adjustment and the end of oxidant addition.

With the beginning of oxidant addition and the designated start of testing (time zero in the figures), results were pH-dependent. For pH 3 tests, NO_x formation declined concurrently with the production of CO_2 following oxidant addition in the test. Once pH increases, the solution begins to absorb the CO_2 produced. If the starting pH was already near neutral (pH = 8) or caustic (pH = 13), then the observed CO_2 in the offgas was negligible from the beginning of the test. NO_x and CO_2 observed by the FTIR were typically below any reasonably significant concentration by either the end of oxidant addition or one hour into testing, depending on the oxidant addition rate.

Other species observed in the offgas at significant values, for example hexamethyldisiloxane and propanal, were likely only present as a function of the simulant equilibrating and should not be an issue in actual operations. Pertinent results will be shown in tables and figures to allow comparisons and explanations. Complete results are presented in Appendix C. Graphs show both the offgas profile and totalized gases for CO, CO_2, H_2, NO, NO_2, N_2O, trimethylsilanol, hexamethyldisiloxane, and propanal for each test. Note that the antifoam degradation products (propanal and trimethylsilanol, which were

added, and hexamethyldisiloxane, which was generated) and CO_2 are often plotted on the right-hand y-axis since their concentrations are usually significantly higher than the other gases.

3.3 Destruction of Glycolate

The statistical matrix was designed to determine the impact of five processing parameters on the destruction of organics. This section addresses the results of these five processing parameters on the destruction of glycolate; Section 3.4 will address the destruction of the other organics.

3.3.1 *Impact of Oxidant on Glycolate Destruction Efficiency*

The most important objective in this testing was to determine whether sodium permanganate or Fenton's reagent is preferable for the destruction of glycolate in the RCT. Based on this testing, sodium permanganate was far superior to Fenton's reagent in destroying glycolate based on the data in Table 3-1. The glycolate destruction was excellent, <50 mg/L in all sodium permanganate tests except for Test 10, a low temperature, low oxidant stoichiometry, and slow oxidant addition condition.

Table 3-1. Time Zero and Final Glycolate Concentration for All Tests

Test	Oxidant	Temp, °C	Addition Time, min	Planned Stoich	pH	Time Zero Glycolate, mg/L	Final Glycolate, mg/L	Glycolate Destruction, mol%
1b	Permanganate	15	120	100%	13	148	50	64
2a	Permanganate	32.5	65	125%	8	198	31	83
3a	Permanganate	32.5	65	125%	8	181	<20	>93
4a	Permanganate	15	120	150%	3	276	<20	>93
5a	Permanganate	15	10	150%%	13	122	24	79
6a	Permanganate	50	120	150%%	13	270	20	92
7	Permanganate	50	10	100%	13	273	34	87
8	Permanganate	50	120	100%	3	138	22	>92
9	Permanganate	50	10	150%%	3	140	<20	>88
10	Permanganate	15	10	100%	3	248	158	32
11	Permanganate	32.5	65	125%	8	20	<20	NA
13	No Oxidant	32.5	65	0%	3	219	257	-19
14	Fenton	15	120	100%	5	126	121	2
15a	Fenton	32.5	65	125%	4	191	181	4
16	Fenton	32.5	65	125%	4	186	176	3
17	Fenton	15	120	150%	3	237	229	0
18	Fenton	15	10	150%	5	131	121	5
23	Fenton	15	10	100%	3	225	191	13

Test 11 is a glycolate blank test, with no added glycolate. The sample pulled immediately prior to oxidant addition had a glycolate concentration of 20 mg/L. During the test, the measured glycolate was <10 mg/L in three of the samples and 12 or 13 mg/L in the other three samples. It is possible that a small amount of glycolate was produced during simulant preparation, but it is more likely that the true

quantification limit was closer to 20 mg/L. As a result, sample results less than 20 mg/L are reported as <20 mg/L glycolate.

Test 13 is an oxidant blank test, with no added sodium permanganate. The glycolate concentration was 240-260 mg/L throughout the test (250 mg/L target).

The sample data had to be corrected due to quenching with sodium hydroxide and/or sodium sulfate.

The following equations are used for correcting the data that was reported as mg/L glycolate (Equations 3-1 and 3-2) and mmol (Equations 3-3 and 3-4). These equations were used in correcting other anions using the molecular weight of the anion.

$$Time\ Zero\ Glycolate,\ mg/L = G\frac{mg}{L} * \frac{sample\ with\ quench\ Mass, g}{sample\ Mass, g} \quad \textbf{3-1}$$

$$Final\ Glycolate,\ mg/L = G\frac{mg}{L} * \frac{sample\ with\ quench\ Mass, g}{sample\ Mass, g} \quad \textbf{3-2}$$

where G is the measured glycolate concentration in the quenched sample.

$$Time\ Zero\ Glycolate,\ mmol = 1.8L \times G\frac{mg}{L} * \frac{sample\ with\ quench\ Mass, g}{sample\ Mass, g} \times \frac{mmol}{75.04402\,mg} \quad \textbf{3-3}$$

$$Final\ Glycolate,\ mmol = (1.8+V)L \times G\frac{mg}{L} * \frac{sample\ with\ quench\ Mass, g}{sample\ Mass, g} \times \frac{mmol}{75.04402\,mg} \quad \textbf{3-4}$$

where G=measured glycolate, mg/L, and V= Volume of added oxidant, L.

A calculation was made to determine the glycolate destruction using equation 3-5

$$Glycolate\ Destruction, \% = 100 * \left[1 - \frac{Final\ Glycolate, mmol}{Time\ Zero\ Glycolate, mmol}\right] \quad \textbf{3-5}$$

3.3.2 *Impact of Oxidant Stoichiometry on Glycolate Destruction Efficiency*

A second objective in this testing was to assess the impact of oxidant stoichiometry on glycolate destruction. In this testing, oxidant stoichiometry was varied between 100% and 150% as defined by calculating the total amount of oxidant needed to oxidize each organic to CO_2 but assuming that nitrite was not oxidized by the oxidant. The final oxidant stoichiometry will be recalculated as many of the organics were not oxidized and some of the nitrite was oxidized. The data is summarized in Figure 3-5. An alternative calculation of oxidant stoichiometry is included in Section 3.7.

Note that the oxidant addition did not always match the target. In sodium permanganate tests, the oxidant addition was often 85-90% of target. This means that despite adding less oxidant than planned, high glycolate destruction was still achieved. In Fenton's reagent tests, all runs were near or above target. The oxidant addition target mass, actual mass, and % of target are summarized in Table 3-2.

Table 3-2. Oxidant Addition Compared to Oxidant Target

Test	Oxidant	Planned Stoich, %	Oxidant Target, g	Oxidant Added, g	% of target
1b	Permanganate	100	94.05	80.17	85.2
2a	Permanganate	125	89.94	77.26	85.9
3a	Permanganate	125	120.08	101.30	84.4
4a	Permanganate	150	147.11	129.90	88.3
5a	Permanganate	150	141.08	126.50	89.7
6a	Permanganate	150	110.95	95.80	86.3
7	Permanganate	100	73.97	66.77	90.3
8	Permanganate	100	69.94	62.45	89.3
9	Permanganate	150	104.92	114.85	109.5
10	Permanganate	100	98.07	101.39	103.4
11	Permanganate	125	82.42	72.22	87.6
13	No Oxidant	0	0.00	0.00	
14	Fenton	100	17.85	21.98	123
15a	Fenton	125	22.96	22.68	98.8
16	Fenton	125	22.96	23.19	101
17	Fenton	150	28.32	28.47	101
18	Fenton	150	26.78	26.90	100
23	Fenton	100	18.88	18.97	100

The % glycolate destruction was greater than 78% for all sodium permanganate tests with an oxidant stoichiometry of 125% or higher. The % glycolate destruction was less than 20% for all Fenton's reagent tests. It should be noted that for the 100% oxidant stoichiometry test the % glycolate destruction for the sodium permanganate testing was much higher than any of the Fenton's reagent tests. Note that the Fenton's reagent testing was completed over a pH range of 3-5, typically the optimum range for Fenton's reagent. Despite this, the Fenton's reagent process was ineffective in destroying glycolate in all tests. This may be due to the complexation of the iron catalyst due to the presence of formaldehyde or oxalate.[22]

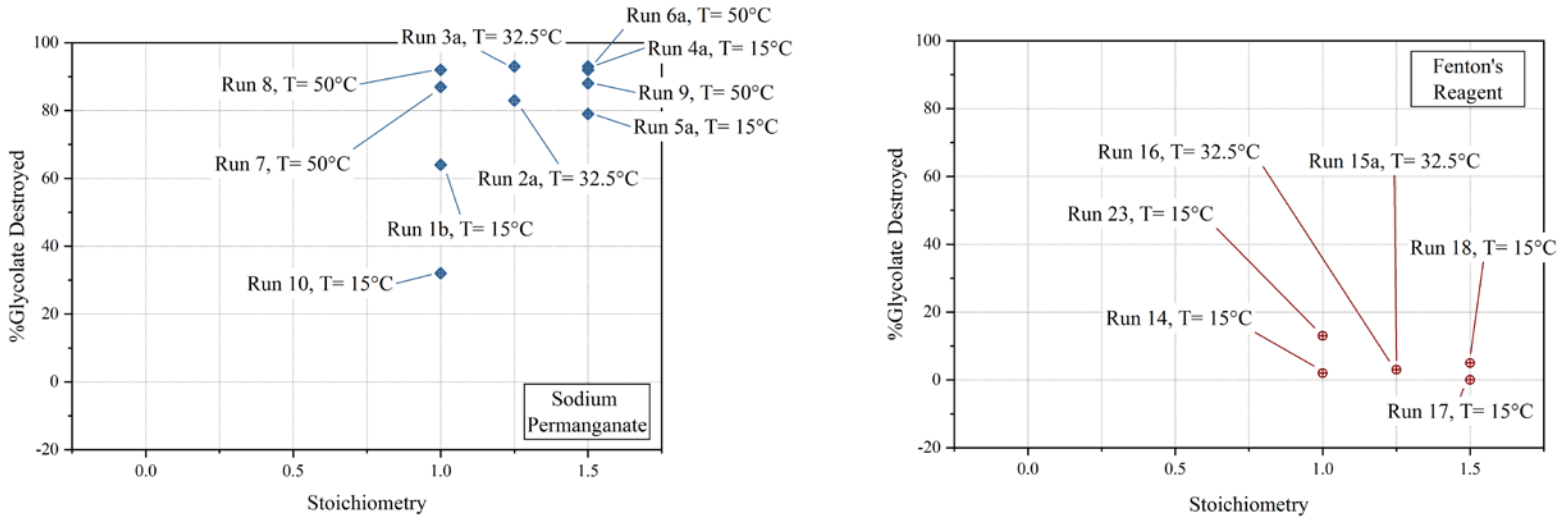


Figure 3-5. Impact of Oxidant Stoichiometry on Overall Glycolate Destruction

3.3.3 *Impact of Temperature on Glycolate Destruction Efficiency*

A third objective in this testing was to determine the optimum temperature for glycolate destruction. The simplest process would not require any temperature control during oxidant addition. The glycolate destruction trended higher in the high temperature tests (even at 100% oxidant stoichiometry) for the sodium permanganate. Three of the tests at 15 °C had the lowest glycolate destruction. Although the glycolate destruction was higher at higher temperatures, the destruction rate was appreciable even at 15 °C for the sodium permanganate process. Higher temperature processing might be desirable to increase the destruction efficiency and kinetics in processing the RCT after a foam-over or carryover event.

The glycolate destruction was less than 20% for all Fenton's reagent tests. Graphs summarizing the data for the sodium permanganate and Fenton's reagent testing are summarized in Figure 3-6.

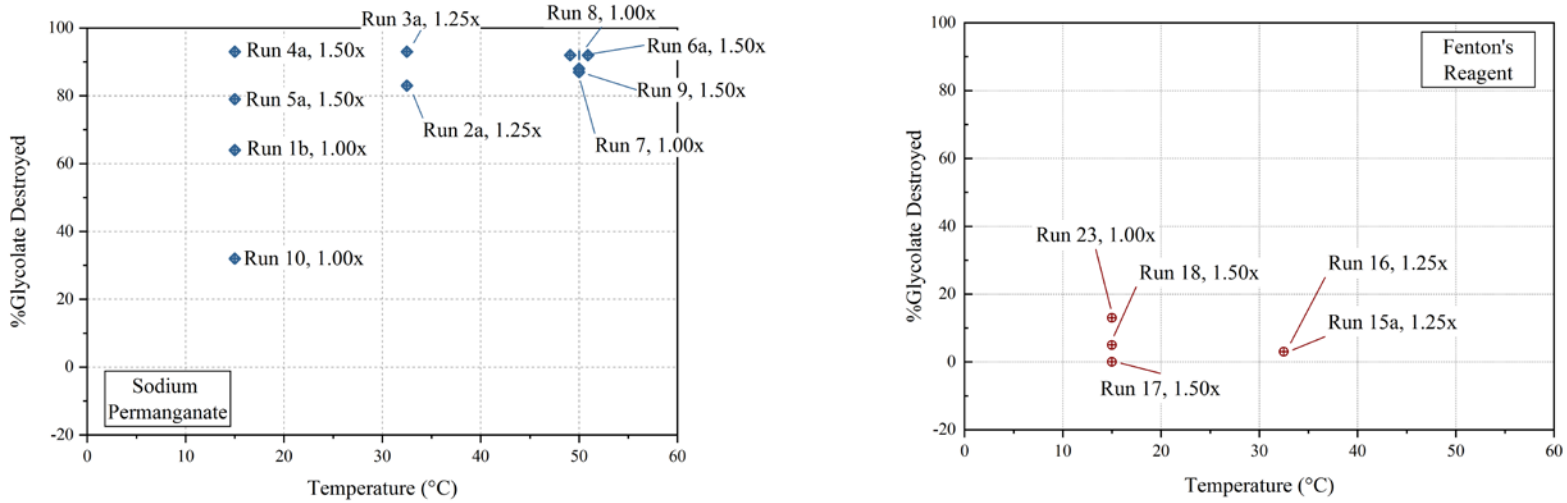


Figure 3-6. Impact of Temperature on Overall Glycolate Destruction

3.3.4 *Impact of Oxidant Feed Rate on Glycolate Destruction Efficiency*

A fourth objective was to identify acceptable oxidant addition rates for glycolate destruction. The simplest process would be a fast oxidant addition, allowing the most time for oxidation and minimizing the total time needed for oxidant addition.

For the sodium permanganate experiments, the slower addition rate had a slightly lower glycolate concentration at the end of six hours. However, both fast and slow addition rates provided for appreciable destruction of glycolate. For the Fenton's reagent experiments, the faster addition rate had a slightly lower glycolate concentration at the end of six hours. For the Fenton's reagent process, the slower addition rate did not yield high extent of glycolate destruction. The feed rate trends for the sodium permanganate and Fenton's reagent testing are summarized in Figure 3-7.

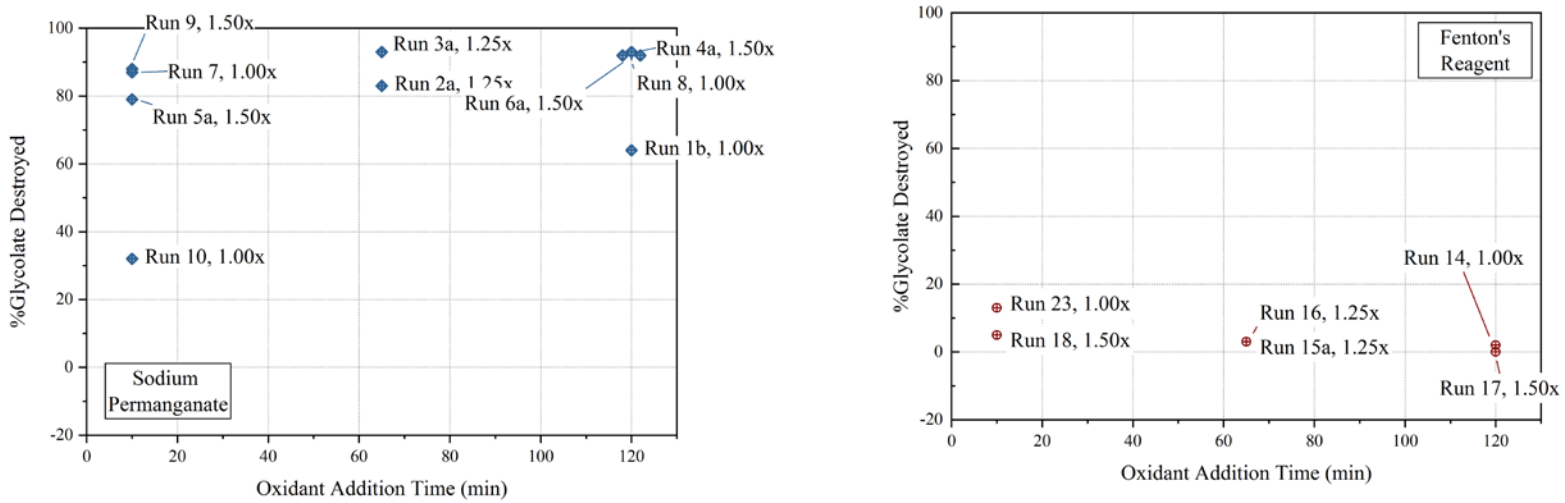


Figure 3-7 Impact of Oxidant Addition Time on Glycolate Destruction

3.3.5 *Impact of Starting pH on Glycolate Destruction Efficiency*

A fifth objective in this testing was to determine the impact of pH on glycolate destruction. No attempt was made to control pH during the testing to reflect desired implementation strategy in parameters of DWPF. The sodium permanganate testing demonstrated excellent glycolate destruction across the pH testing range of 3 to 13. Fenton's reagent was not effective in the pH testing range. The sodium permanganate process has an added benefit of a wide pH range, meaning the sodium permanganate process is far superior in effectiveness and flexibility. The glycolate destruction is appreciable across the pH range of 3 to 13.

Regarding sodium permanganate experiments, a starting condition of pH 3 resulted in a final pH of at least 7, while a starting condition of pH 8 resulted in a final pH of 10. There was no significant pH change measured for the high pH sodium permanganate experiments due to the poor resolution of the pH probe above pH 12.5. The pH increase was due to the production of sodium hydroxide and the magnitude of this change depends on the amount of organic destruction. The pH decreased for Fenton's reagent experiments, as some of the organics were oxidized to organic acids and nitrite was oxidized to nitric acid. The pH trends for the sodium permanganate and Fenton's reagent testing are summarized in Figure 3-8.

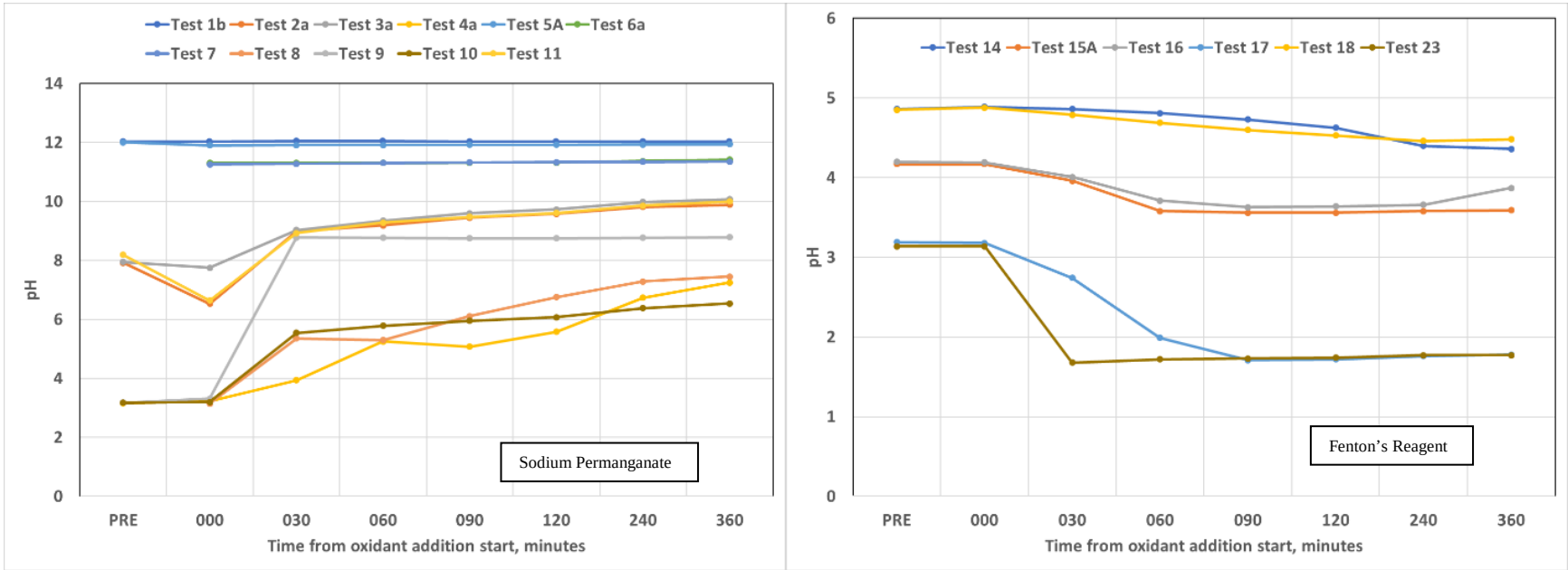


Figure 3-8 pH Trends for Sodium Permanganate and Fenton's Reagent Testing

Glycolate was destroyed throughout the pH range of 3-13 for the sodium permanganate experiments with >78% destruction with 125% stoichiometry or higher. In similar experiments with Fenton's reagent, <20% of the glycolate was destroyed. Graphs summarizing the data for the sodium permanganate and Fenton's reagent testing are summarized in Figure 3-9.

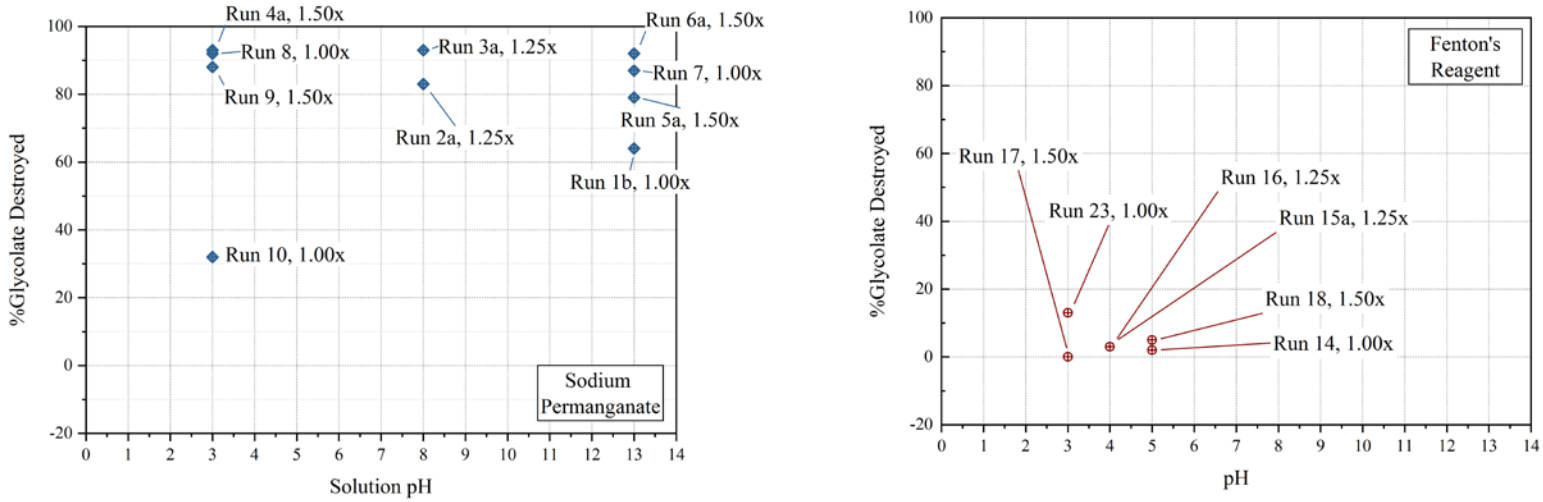


Figure 3-9. Impact of Initial pH on Overall Glycolate Destruction

In all testing with added oxidants, the nitrite was essentially destroyed (pH range 3-13). In the high pH experiments, the sodium sulfite quench might also be responsible for destroying nitrite. This means that nitrite will need to be added to the RCT after oxidation is complete to meet CSTF corrosion control requirements. For the sodium permanganate process, no pH adjustment is needed prior to the oxidant addition. Note that the addition of sodium nitrite for corrosion control may result in the destruction of any excess oxidant, but this was not demonstrated in this testing.

3.3.6 *Statistical Review of Data*

A statistical review of the data was completed by Dr. Tommy Edwards using JMP® Pro 11.2.1.[23] The conclusion from this analysis was that glycolate destruction was statistically correlated only to liquid temperature and oxidant stoichiometry for the sodium permanganate process. Addition time, initial pH, and initial glycolate concentration were not statistically significant in predicting glycolate destruction. It is also obvious from this analysis that sodium permanganate is far superior to Fenton's reagent in destroying glycolate. A graphical summary of the data is shown in Figure 3-10. Use of colors (Red for pH 3-5, Green for pH 8, Blue for pH 13) and symbols (B for 125, C for 187.5, and D for 250 mg/L starting glycolate) were used to help identify trends. Note that the data will be rearranged in various graphs to make the trends more obvious.

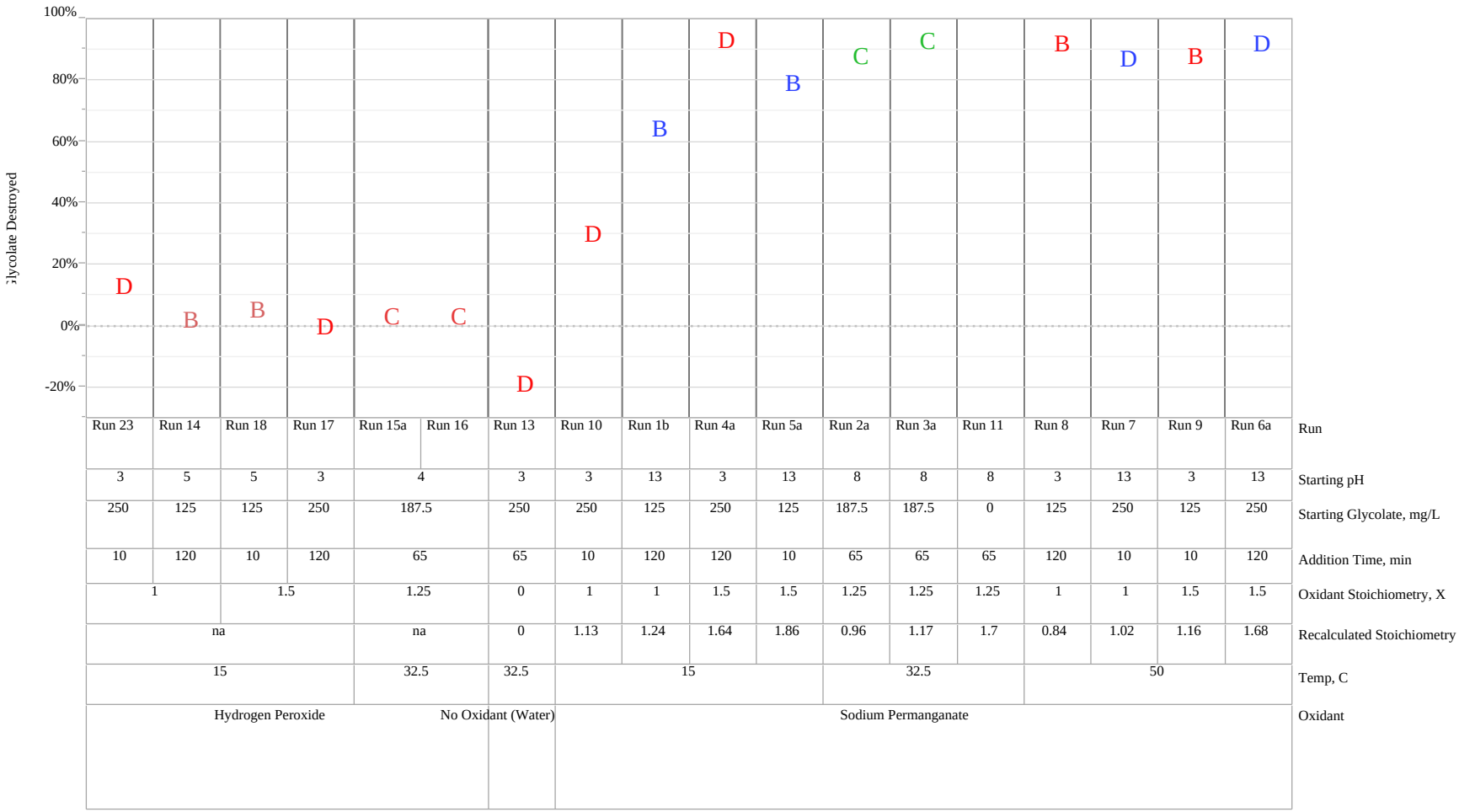


Figure 3-10. Statistical Analysis Variability Chart of Glycolate Destroyed

An equation predicting the percent Glycolate destruction for the sodium permanganate process is:

% glycolate destroyed = 0.0964 + 0.006643T + 0.395S – 0.0220 (S-1.25)*(T-32.5) 3-6

Where T = Temperature, ℃, S=fractional stoichiometry based on all organic oxidation to CO_2.

A chart sorted by oxidant stoichiometry is shown in Figure 3-11 below. For sodium permanganate, the tests at the highest oxidant stoichiometry also had the highest glycolate destruction. It is also apparent that for sodium permanganate, higher temperature is also an important factor in glycolate destruction. Due to the complexity of the testing utilizing nine organics, additional model development from tests with only glycolate present may be more useful than this equation in predicting glycolate destruction.

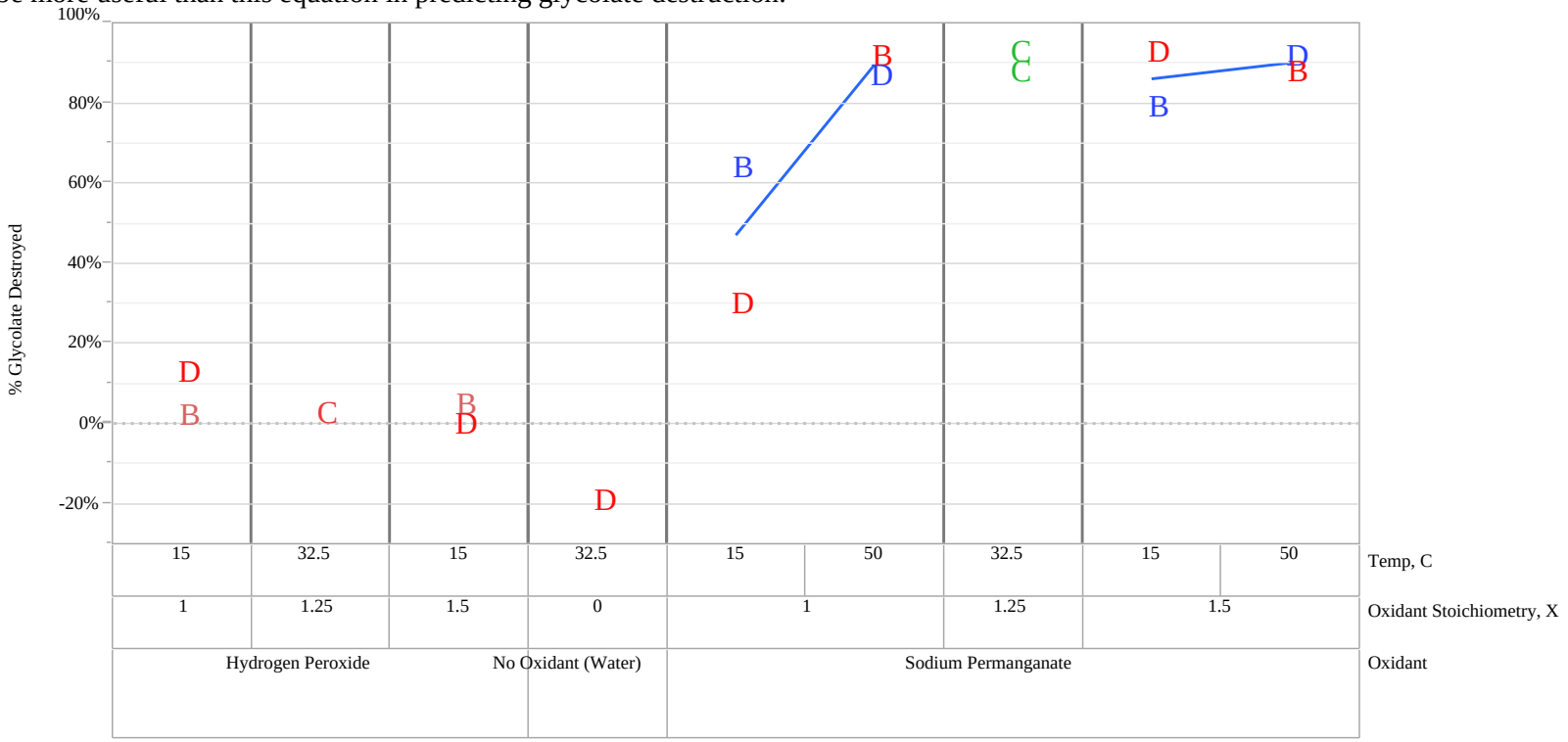


Figure 3-11. Oxidant Stoichiometry Statistical Analysis Variability Chart of Glycolate Destroyed

More details concerning the output from the statistical analysis are included in Appendix D

3.4 Destruction of Other Organics

Eight organics (sodium glycolate, sodium formate, sodium oxalate, methylmercury hydroxide, propanal, trimethylsilanol, glyoxylic acid, and formaldehyde) were added during the testing. The formaldehyde solution also contained 15 wt % methanol to minimize polymerization. The organics were all added at the same carbon concentration as 250 mg/L of glycolate. These organics were all added at concentrations much higher than expected to be seen during processing to improve organic quantification.

3.4.1 *Organic Carbon Destruction*

The simplest measure of the effectiveness of the organic destruction is the increase in the TIC concentration and the decrease in the TOC concentration during each test. For the sodium permanganate process, almost all the CO_2 produced by the destruction of the organics was absorbed by the solution resulting in an increase in TIC. The exception to this was that for the pH 3 experiments, less CO_2 was absorbed in the first few minutes until enough NaOH was produced to raise the pH of the solution high enough for complete absorption. For the Fenton's reagent tests, the pH is so low that very little CO_2 would be absorbed, and the TIC concentration remained unchanged.

Samples from solution after the addition of all reagents except nitrite and its water dilution were submitted to SRNL AD for TIC and TOC. TIC is primarily a measure of the sodium carbonate and bicarbonate present in the samples. TOC includes any other form of carbon from the added organics. Since the time zero sample was not analyzed, the samples were corrected by using the glycolate concentration in the Time Zero sample. The following equation was used for correcting the data that was reported as mg/L C (Equation 3-6)

$$Time\ Zero\ C, mg/L = Post\ Nitrite\ C \times \frac{Time\ Zero\ Glycolate, mg/L}{Post\ Nitrite\ Glycolate, mg/L} \quad \textbf{3-6}$$

where C can be TIC, TOC or Total Carbon (TC).

The added organic carbon concentration, which varied as the glycolate concentration varied, was calculated by summing the contribution from each added organic. The added TOC was calculated to be between 299 and 472 mg C/L (see Table 3-2, Added TOC Calc column) using Equation 3-7)

$$Calculated\ TOC, mg/L = \frac{Mass\ Organic\ Added, mg}{1.8\,L} * \frac{\#C * 12.0107\ g/mol}{MW, g/mol} \quad \textbf{3-7}$$

where #C is the number of carbons in each molecule, MW = molecular weight of organic, g/mol.

The Time Zero TOC, ranging from 300 to 494 mg C/L, agreed well with the Calculated TOC.

The Time Zero TIC concentration was expected to have been zero for all tests since no sodium carbonate was added. However, Time Zero TIC was much higher, ranging from 9 to 144 mg/L. The source for this could have been CO_2 that was produced prior to oxidation and was absorbed by

the liquid or sodium carbonate/sodium bicarbonate present in the reagents. Note. Note that the air purge used during these experiments was very low in CO_2.

Time zero and final samples cannot be compared directly as the solution was diluted by the addition of oxidant. As a result, the mmol of TOC were calculated for both the time zero and final samples. These samples were quenched with sodium sulfite and/or sodium hydroxide, and a correction is needed for this mass change. The equations used to calculate the TOC concentration are below (Equations 3-8 and 3-9):

$$Time\ Zero\ TOC,\ mmol = 1.8L \times C\frac{mg}{L} * \frac{sample\ with\ quench\ Mass, g}{sample\ Mass, g} \times \frac{mmol}{12.0107\ mg} \quad \textbf{3-8}$$

$$Final\ TOC,\ mmol = (1.8 + V)L \times C\frac{mg}{L} * \frac{sample\ with\ quench\ Mass, g}{sample\ Mass, g} \times \frac{mmol}{12.0107\ mg} \quad \textbf{3-9}$$

where C=measured TOC, mg/L, V= Volume of added oxidant, L.

A calculation was used to determine the % TOC Lost using Equation 3-10 below:

$$TOC\ Lost, \% = 100 * \left[1 - \frac{Final\ TOC, mmol}{Time\ Zero\ TOC, mmol}\right] \quad \textbf{3-10}$$

In tests that started at pH 8 or 13, the TIC concentration increased during testing as CO_2 was produced and absorbed by the caustic solutions. In this testing about 30-50% of the TOC was destroyed in sodium permanganate experiments. In testing with Fenton's reagent, little TOC was destroyed. The data is summarized in Table 3-3.

Table 3-3. Carbon Concentration and Destruction

Test	Oxidant	pH	Time Zero TIC, mg/L	Final TIC, mg/L	Delta TIC, mg/L	TOC Calc, mg/L	Time Zero TOC, mg/L	Final TOC, mg/L	Delta TOC, mg/L	TOC Lost, mol%
1b	Permanganate	13	118	275	156	589	413	296	-117	26
2a	Permanganate	8	61	284	224	582	425	245	-180	40
3a	Permanganate	8	90	264	174	628	447	297	-150	31
4a	Permanganate	3	143	121	-23	635	472	261	-211	42
5a	Permanganate	13	117	281	165	674	386	273	-113	25
6a	Permanganate	13	71	295	225	435	474	233	-241	49
7	Permanganate	13	58	289	231	410	494	262	-232	45
8	Permanganate	3	55	62	7	547	453	284	-169	36
9	Permanganate	3	51	309	258	565	435	162	-273	61
10	Permanganate	3	91	42	-49	628	403	458	55	-19
11	Permanganate	8	51	243	191	525	364	210	-154	41
13	No Oxidant	3	66	39	-26	562	436	494	58	-13
14	Fenton	5	62	34	-29	354	398	407	9	-3
15a	Fenton	4	71	39	-32	493	459	407	-52	11
16	Fenton	4	46	21	-26	349	301	402	101	-35
17	Fenton	3	52	21	-31	390	432	452	20	-6
18	Fenton	5	31	21	-10	305	407	386	-21	4
23	Fenton	3	46	20	-25	352	425	466	40	-10

3.4.2 *Formate Destruction*

Formate was added at 300 mg/L during simulant preparation to give the same carbon concentration as the addition of 250 mg/L glycolate. In addition, 200 mg/L of formaldehyde was added to each test and presumably was oxidized to formate prior to oxidant addition. So, for all tests, the time zero formate concentration at the start of oxidation was >300 mg/L, likely due to the oxidation of formaldehyde to formate as described below.

Further, formate can also be a decomposition product of glycolate or oxalate in the stepwise oxidation (Table 2-4). To simplify the analysis, the percent destruction of formate is hence defined by equation 3-11:

$$\textbf{\% Formate Destruction} = 100\% * \left[1 - \frac{Final\ Formate, mmol}{Time\ Zero\ Formate, mmol}\right] \quad \textbf{3-11}$$

For tests with sodium permanganate at pH above 7, the final formate was very low. The formate destruction was low for the pH 3 experiments, with no net destruction of formate, except Test 9. The reason for the formate destruction in Test 9 is not fully understood. However, there could have been formate destruction in other experiments if any formaldehyde, oxalate, or glycolate was oxidized to formate.

For tests with Fenton's reagent, the formate concentration was often greater than 600 mg/L, likely due to oxidation of formaldehyde. The data is summarized in Table 3-4.

Table 3-4. Time Zero and Final Formate Concentration for All Testing

Test	Oxidant	Temp, °C	Addition Time, min	Planned Stoich, %	pH	Time Zero Formate, mg/L	Final Formate, mg/L	Formate Destruction mol%
1b	Permanganate	15	120	100	13	407	12	97
2a	Permanganate	32.5	65	125	8	425	12	97
3a	Permanganate	32.5	65	125	8	364	<10.46	100
4a	Permanganate	15	120	150	3	365	326	4
5a	Permanganate	15	10	150	13	528	6	99
6a	Permanganate	50	120	150	13	452	16	96
7	Permanganate	50	10	100	13	461	22	95
8	Permanganate	50	120	100	3	389	695	-89
9	Permanganate	50	10	150	3	406	38	90
10	Permanganate	15	10	100	3	407	464	-21
11	Permanganate	32.5	65	125	8	403	26	93
13	No Oxidant	32.5	65	0	3	347	418	-22
14	Fenton	15	120	100	5	390	564	-48
15a	Fenton	32.5	65	125	4	368	597	-65
16	Fenton	32.5	65	125	4	372	706	-94
17	Fenton	15	120	150	3	422	717	-75
18	Fenton	15	10	150	5	399	658	-69
23	Fenton	15	10	100	3	352	434	-26

3.4.3 *Oxalate Destruction*

Oxalate was added at 295 mg/L. In the sodium permanganate testing, the oxalate concentration increased to a final oxalate as high as 703 mg/L in high pH testing. In some of the sodium permanganate testing at pH 3, the oxalate was effectively destroyed. In the Fenton's reagent testing, the final oxalate concentration was equal, within analytical uncertainty, to the Time Zero oxalate concentration, showing no net creation or destruction. Glyoxylate, equivalent to 295 mg/L oxalate, was likely oxidized to oxalate (Section 3.4.7). The data is summarized in Table 3-5. The oxalate destruction is calculated using Equation 3-12.

$$\textbf{\% Oxalate Destruction} = 100\% * \left[1 - \frac{Final\ Oxalate, mmol}{Time\ Zero\ Oxalate, mmol} \right] \quad \textbf{3-12}$$

Table 3-5. Time Zero and Final Oxalate Concentration for All Testing

Test	Oxidant	Temp, °C	Addition Time, min	Planned Stoich, %	pH	Time Zero Oxalate, mg/L	Final Oxalate, mg/L	Oxalate Destruction, mol %
1b	Permanganate	15	120	100	13	338	606	-89
2a	Permanganate	32.5	65	125	8	242	375	-64
3a	Permanganate	32.5	65	125	8	280	481	-82
4a	Permanganate	15	120	150	3	330	<10	100
5a	Permanganate	15	10	150	13	378	575	-63
6a	Permanganate	50	120	150	13	294	542	-97
7	Permanganate	50	10	100	13	265	703	-176
8	Permanganate	50	120	100	3	229	<10	95
9	Permanganate	50	10	150	3	253	118	50
10	Permanganate	15	10	100	3	337	255	20
11	Permanganate	32.5	65	125	8	310	328	-11
13	No Oxidant	32.5	65	0	3	250	288	-17
14	Fenton	15	120	100	5	267	280	-7
15a	Fenton	32.5	65	125	4	280	302	-10
16	Fenton	32.5	65	125	4	311	309	-1
17	Fenton	15	120	150	3	310	280	7
18	Fenton	15	10	150	5	266	280	-8
23	Fenton	15	10	100	3	291	311	-9

3.4.4 *Methylmercury Destruction (Methylmercury Added to Tests 1b, 3a, 4a, 5a, and 10 Only)*

Methylmercury hydroxide was added at 1,440 mg/L to five sodium permanganate tests (1b, 3a, 4a, 5a, and 10). It was not used in any of the Fenton's reagent testing. In these early tests, the average methylmercury analysis at the completion of tests was 1,410 mg/L. Methylmercury is very resistant to oxidation and was not oxidized in these experiments. In addition, dimethylmercury was detected in some samples, although its presence has not been validated. Since the methylmercury was not oxidized, it was left out of the simulant in later tests. Results of methylmercury analyses are provided in Appendix B.

Tests 2a and 3a were duplicates for the sodium permanganate process. Since the decision had been made to leave methylmercury out of the simulant prior to running the second of the duplicates, Test 3a included methylmercury and Test 2a did not. As can be seen in Figure 3-1 and Figure 3-2, the glycolate destruction profile and final glycolate concentration was very similar. For this data it is concluded that leaving out the methylmercury did not impact the results of the testing.

3.4.5 *Antifoam Degradation Products (Propanal, Trimethylsilanol and Hexamethyldisiloxane)*

Two of the antifoam degradation products, propanal and trimethylsilanol, were added to all the tests. Both are slightly soluble, but due to their volatility, neither was detected in the liquid samples pulled just prior to oxidant addition. Propanal at 3.5 mmols was added to each test. Very little

propanal was detected in the post test products (0.46 mmol was the maximum). Very little propanal was detected in the offgas (0.49 mmol was the maximum). It is likely that the propanal was lost due to its volatility and was not oxidized.

Trimethylsilanol can react with itself through a condensation reaction to produce hexamethyldisiloxane (see reaction below). Hexamethyldisiloxane, insoluble in aqueous solutions, was detected in the offgas as soon as trimethylsilanol was added (prior to oxidant addition) and forced the trimethylsilanol additions to be performed as small aliquots to prevent exceeding 25% of the lower explosive limit in the vapor space. Significant trimethylsilanol was detected in the post test product because little of it was oxidized. However, little hexamethyldisiloxane was detected in the final products, except in Tests 5a, 8, 9 and 11. The concentration of the antifoam degradation products in the post test sample is summarized in Table 3-6. Note that additional liquid analysis data, including the initial propanal, trimethylsilanol and hexamethyldisiloxane are included in Appendix C.

$$2\left(CH_3\right)_3 SiOH \rightarrow \left(CH_3\right)_3 SiOSi\left(CH_3\right)_3 + H_2O$$

Table 3-6. Final Antifoam Degradation Products (Propanal, Trimethylsilanol and Hexamethyldisiloxane)

Test	Oxidant	Temp, °C	Addition Time, min	Planned Stoich, %	pH	Final Propanal, mg/L	Final Trimethyl-silanol, mg/L	Final Hexamethyldi-siloxane, mg/L
1b	Permanganate	15	120	100	13	<0.1	38	<0.1
2a	Permanganate	32.5	65	125	8	<0.1	39	<0.1
3a	Permanganate	32.5	65	125	8	<0.1	52	0.2
4a	Permanganate	15	120	150	3	5.1	37	<0.1
5a	Permanganate	15	10	150	13	<0.1	143	0.2
6a	Permanganate	50	120	150	13	<0.1	29	<0.1
7	Permanganate	50	10	100	13	<0.1	29	<0.1
8	Permanganate	50	120	100	3	16.3	235	5.0
9	Permanganate	50	10	150	3	0.2	245	6.1
10	Permanganate	15	10	100	3	3.7	47	<0.1
11	Permanganate	32.5	65	125	8	0.2	266	11.3
13	No Oxidant	32.5	65	0	3	1.7	33	<0.1
14	Fenton	15	120	100	5	5.0	40	<0.1
15a	Fenton	32.5	65	125	4	3.7	99	<0.1
16	Fenton	32.5	65	125	4	1.6	38	<0.1
17	Fenton	15	120	150	3	<0.1	28	<0.1
18	Fenton	15	10	150	5	7.7	38	<0.1
23	Fenton	15	10	100	3	<0.1	22	<0.1

3.4.6 *Formaldehyde Destruction*

Formaldehyde was added at a concentration of 200 mg/L. No formaldehyde was detected in any of the offgas samples. The introduction of formaldehyde also introduces methanol, which is not

expected as an intermediate in processing. Formaldehyde was likely oxidized to formate (Section 3.4.2).

Formaldehyde should be omitted from future RCT simulants. for this test program. The expected concentration is significantly below test conditions and no impact is clearly discernible. The introduction of formaldehyde also introduces methanol, which is not expected as an intermediate in processing.

3.4.7 *Glyoxylate Destruction*

Glyoxylate was added at a concentration of 245 mg/L. No glyoxylate was detected in any of the aqueous or offgas samples. Glyoxylate was likely oxidized to oxalate (Section 3.4.3).

Glyoxylate should be omitted from future RCT simulants for this test program. The expected concentration is significantly below test conditions and no impact was noted in the testing except it increased the oxalate concentration.

3.4.8 *Organic Summary*

Some of the organics were oxidized during the sodium permanganate testing (primarily glycolate, oxalate, and formate). Other organics were removed due to their vapor pressure to the offgas or through reactions to other gases and were detected in the offgas (i.e., propanal, trimethylsilanol and hexamethyldisiloxane). Other organics were not oxidized at all or were oxidized to other anions (monomethylmercury, fomaldehyde, and glyoxylate).

Omit trimethylsilanol, propanal, formaldehyde, glyoxylate, and methylmercury hydroxide in future experiments in this test program; organics that are added should be quantifiable when present at or near expected RCT concentrations. However, testing may require the addition of a SRAT product containing antifoam fragments (trimethylsilanol, propanal, hexamethyldisiloxane, etc.), which would simulate entrainment in the CPC or melter.

3.5 Carbon Balance

The carbon balance herein is more complete than the TIC/TOC destruction analysis in Section 3.4.1 because it includes all organic species except TOC (to not double count the organic carbon) and all carbon containing species in the offgas data. A carbon balance was completed using the data collected in these experiments. For each experiment, the carbon balance was completed at four points in time: added organics, organics at time zero based on sample analyses, organics at six hours based on sample analyses, and organics totalized from offgas measurements from oxidant addition to 6-hour point. Note that methylmercury was left out of all balances, as it was not oxidized (Section 3.4.4) and was not present in all tests. The data is summarized in Table 3-7.

The sum of the carbon from each organic was calculated (75.8 to 89.3 g) at the start of each experiment (Table 3-7) column labeled C Pre-Test, mmol). Samples were analyzed at time zero for anions and after nitrite addition for the TIC/TOC, VOA and SVOA (Table 3-7), column labeled Carbon Time Zero, mmol). The organics in the offgas were analyzed by the FTIR and the carbon was totalized from oxidant addition to 6-hour point (Table 3-7), column labeled Offgas Carbon, mmol). At the completion of the test, the measured carbon combined with the totalized carbon in the offgas should equal the calculated total carbon added in preparing the simulant. The percent closure of the carbon balance was also calculated. The carbon balanced averaged 88% for the tests

with sodium permanganate and 75% for the Fenton's reagent tests. It should be noted that the carbon balances were lower in the tests where the starting pH was lower.

Table 3-7. Carbon Balance without Methylmercury

Test	Oxidant	Temp, °C	Addition Time, min	Planned Stoich, %	pH	Carbon Pre-Test, mmol	Carbon Time Zero, mmol	Offgas Carbon, mmol	Carbon End, mmol	C closure, , mol%
1b	Permanganate	15	120	100	13	80.7	72.7	0.1	73.6	91
2a	Permanganate	32.5	65	125	8	81.6	87.2	1.2	64.44	80
3a	Permanganate	32.5	65	125	8	74.5	75.3	0.8	65.7	89
4a	Permanganate	15	120	150	3	86.1	84.5	35.1	36.5	83
5a	Permanganate	15	10	150	13	84.1	88.7	0.4	79.9	95
6a	Permanganate	50	120	150	13	83.7	65.1	1.3	72.8	88
7	Permanganate	50	10	100	13	89.3	61.5	2.0	78.7	90
8	Permanganate	50	120	100	3	80.1	82.0	16.2	55.3	89
9	Permanganate	50	10	150	3	79.7	84.7	4.3	72.0	96
10	Permanganate	15	10	100	3	86.4	88.0	11.5	48.0	69
11	Permanganate	32.5	65	125	8	75.8	78.6	1.1	70.2	94
13	No Oxidant	32.5	65	0	3	86.0	84.2	3.0	48.9	60
14	Fenton	15	120	100	5	77.1	53.1	10.5	48.1	76
15a	Fenton	32.5	65	125	4	83.6	73.9	13.4	57.7	85
16	Fenton	32.5	65	125	4	84.7	52.4	14.2	55.3	82
17	Fenton	15	120	150	3	87.7	58.5	8.7	56.5	74
18	Fenton	15	10	150	5	81.5	45.7	11.3	50.2	75
23	Fenton	15	10	100	3	86.8	52.8	4.9	44.0	56

3.6 Nitrogen Balance

Both nitrite and nitrate are present in the RCT and the simulant. Nitrate in the condensate is added as nitric acid and is scrubbed from the NO_2 produced during SRAT and SME processing. Nitrate can also be added to the condensate through foam-overs in the SRAT and SME and from carryover in the melter. Sodium nitrite and sodium hydroxide are added as corrosion control chemicals in the RCT. Sodium nitrite or nitrous acid can be both an oxidant or a reductant. Much of the oxidant was likely consumed by the oxidation of nitrite but nitrite also can be destroyed by a variety of reactions including acid hydrolysis. Some nitrite destruction reactions follow.

$$2HNO_2 \rightarrow HNO_3 + 2NO + H_2O$$

$$2HNO_2 \rightarrow NO + NO_2 + H_2O$$

$$C_2H_4O_3 + 3HNO_2 \rightarrow \frac{3}{2}N_2O + 2CO_2 + \frac{7}{2}H_2O$$

$$C_2H_4O_3 + HNO_2 \rightarrow \frac{1}{2}N_2O + 2HCO_2H + \frac{1}{2}H_2O$$

$$C_2H_4O_3 + 2HNO_2 \rightarrow N_2O + (COOH)_2 + 2H_2O$$

NO_2 (which is in equilibrium with N_2O_4) can react with water to produce nitrous and nitric acid. This means that not all the NO_2 will survive to the offgas, some will produce nitric acid:

$$N_2O_4 + H_2O \rightarrow HNO_2 + HNO_3$$

NO can be oxidized to NO_2 as follows:

$$NO + \frac{1}{2}O_2 \rightarrow NO_2$$

The result is that it is difficult to determine the extent of the nitrite destruction reactions with the offgas results because of the conversion of NO_2 to nitric acid and the oxidation of NO to NO_2.

3.6.1 *Offgas Production of Oxides of Nitrogen*

Nitrite (about 200 mmol) was added late in the simulant preparation as it readily degraded even prior to oxidant addition. At most, 1% of the nitrite was measured in the offgas as N_yO_x for the permanganate tests and 3% of the nitrite was measured in the offgas for the Fenton's reagent tests. The experiment with the highest nitrite conversion was Test 13, the blank without glycolate, with 4.2% conversion. Another way of saying this is that only 1% of the nitrite is converted to offgas based on the permanganate experiments, meaning little offgas will be created during processing from nitrite destruction. The mmol of each oxide of nitrogen in the offgas is summarized in Table 3-8.

An interesting ratio to understand the chemical reaction route that produced NO, N_2O or NO_2 traversed is the % N as N_2O in the offgas. The maximum % N from N_2O in the offgas for the permanganate tests was 26.2%, while the maximum was 47.8% in the Fenton's reagent tests. The N_2O was highest in tests with low pH and high oxidant addition rate. In this testing, the N_2O, an oxidant, was produced at very slow rates throughout processing.

Table 3-8. Oxides of Nitrogen in the Offgas

Test	Oxidant	Temp, °C	Addition Time, min	Planned Stoich, %	pH	NO, mmol	NO_2, mmol	N_2O, mmol	Nitrite to N_yO_x, mol %	Offgas N as N_2O, mol%
1b	Permanganate	15	120	100	13	0.0004	0.0005	0.0003	0.00	20.8
2a	Permanganate	32.5	65	125	8	0.0030	0.0181	0.0028	0.01	10.5
3a	Permanganate	32.5	65	125	8	0.0009	0.0273	0.0031	0.02	9.1
4a	Permanganate	15	120	150	3	0.1538	0.1644	0.0268	0.19	7.2
5a	Permanganate	15	10	150	13	0.0003	0.0008	0.0006	0.00	26.2
6a	Permanganate	50	120	150	13	0.0009	0.0031	0.0007	0.00	12.7
7	Permanganate	50	10	100	13	0.0001	0.0025	0.0012	0.00	23.6
8	Permanganate	50	120	100	3	0.2882	0.6187	0.3241	0.77	20.8
9	Permanganate	50	10	150	3	0.0867	0.1605	0.0710	0.19	18.2
10	Permanganate	15	10	100	3	0.0609	0.0463	0.0111	0.06	8.6
11	Permanganate	32.5	65	125	8	0.0014	0.0194	0.0016	0.01	6.7
13	No Oxidant	32.5	65	0	3	2.2420	4.8762	0.6627	4.20	7.8
14	Fenton	15	120	100	5	0.0168	0.0596	0.0071	0.05	7.9
15a	Fenton	32.5	65	125	4	0.1104	0.0494	0.5765	0.65	43.9
16	Fenton	32.5	65	125	4	0.1147	0.0503	0.4826	0.56	42.7
17	Fenton	15	120	150	3	0.3686	0.4009	2.8243	3.19	44.0
18	Fenton	15	10	150	5	0.0068	0.0382	0.0035	0.03	6.8
23	Fenton	15	10	100	3	0.1508	0.1173	2.9304	3.05	47.8

3.6.2 *Destruction of Nitrite/Production of Nitrate*

Nitrate addition varied from 92.3 mmol at pH 8 or 13 to 216 mmol at pH 3 because of the nitric acid added for the pH adjustment. As discussed previously, 200 mmol of nitrite was added late in simulant preparation to minimize nitrite degradation prior to start of oxidant addition. The pH adjustment was completed just prior to the start of oxidant addition and samples were pulled (Time Zero) and submitted to PSAL for anion analysis. Data is summarized in Table 3-9. The closure of the nitrogen balance was poor in many of the tests using nitrite and nitrate concentrations from sample analysis and offgas results. However, many of the balances were improved by using the added nitrite and nitrate by mass (Total N Added pre-test, mmol) instead of the time sample results, especially the Fenton's reagent tests. The addition of sodium sulfite to quench the oxidant and prevent further oxidation of organics likely also led to destruction of nitrite[24] post sampling. Use of the sodium sulfite quench should be evaluated to ensure that it is working as intended.

Table 3-9. Nitrogen Balance

Test	Oxidant	Temp, °C	Planned Stoich, %	pH	Total N Added Pre-Test, mmol	Total N Time Zero, mmol	Total N Offgas, mmol	Total N End, mmol	N Closure Time Zero Sample Results, mol %	N Closure from Calc of Added Nitrite and Nitrate, mol%
1b	Permanganate	15	100	13	293.2	221.4	0.002	95.4	43	33
2a	Permanganate	32.5	125	8	293.2	246.5	0.027	144.3	66	49
3a	Permanganate	32.5	125	8	293.2	248.9	0.034	183.1	74	62
4a	Permanganate	15	150	3	417.3	323.1	0.372	385.1	119	92
5a	Permanganate	15	150	13	293.2	211.7	0.002	138.0	65	47
6a	Permanganate	50	150	13	293.2	184.1	0.005	103.3	56	35
7	Permanganate	50	100	13	293.2	207.0	0.005	119.1	58	41
8	Permanganate	50	100	3	355.2	276.4	1.555	274.9	100	78
9	Permanganate	50	150	3	348.5	297.4	0.389	306.1	101	86
10	Permanganate	15	100	3	397.0	321.0	0.129	419.1	127	103
11	Permanganate	32.5	125	8	293.2	176.8	0.024	168.8	96	58
13	No Oxidant	32.5	0	3	373.3	273.0	8.444	201.2	77	56
14	Fenton	15	100	5	293.2	226.8	0.091	275.4	121	94
15a	Fenton	32.5	125	4	303.3	214.8	1.313	284.8	133	94
16	Fenton	32.5	125	4	306.1	261.8	1.130	301.7	116	99
17	Fenton	15	150	3	412.8	339.0	6.418	375.2	113	92
18	Fenton	15	150	5	293.2	204.7	0.052	268.3	131	92
23	Fenton	15	100	3	409.4	228.5	6.129	389.7	173	97

3.7 Recalculated Oxidant Stoichiometry

The oxidant stoichiometry was recalculated before each test based on the oxidant stoichiometry factor, the moles of each organic added and the moles of oxidant needed to convert each mole of organic to carbon dioxide. The assumption was that no oxidant was needed for destroying nitrite. However, some organics either did not react or evaporated prior to addition of oxidant, so oxidant was not utilized for these organics. Since other organics do not appear to react strongly to the presence of the oxidant, more oxidant was added than needed to destroy glycolate. Also, nitrite can be destroyed by reaction with acid or by oxidation. Since the molarity of the nitrite is higher than the organics, much of the oxidant was used to destroy nitrite. The oxidant stoichiometry for each test was recalculated using Equation 3-14 and the recalculated oxidant stoichiometry is summarized in Table 3-10. In the planned stoichiometry column, the oxidant addition was calculated using the equations for the nine organics in Table 2-5. For the recalculated stoichiometry, the oxidant addition was calculated using the equations in Table 2-5 for nitrite, glycolate, oxalate, formate, formaldehyde, glyoxylate and methanol. The stoichiometry was only calculated for the sodium permanganate tests. Note that this calculation could be further refined in future testing by determining the split of oxidant and acid needed to destroy nitrite and to add a factor of 0 or 1 for oxalate and formate, depending on the starting pH.

$$Recalcuated\ permanganate, mol = 2G + \frac{2}{3}F + \frac{2}{3}O + \frac{4}{3}Gl + \frac{4}{3}Fo + 2M + \frac{2}{3}NO_2 \quad \textbf{3-7}$$

where G is mol glycolate, F is mol formate, O is mol oxalate, Gl is mol glyoxylate, Fo is mol formaldehyde, M is mol methanol, and NO_2 is mol nitrite.

Table 3-10. Recalculated Oxidant Stoichiometry

Test # / Block #	Test ID	Starting pH	Planned Stoichiometry	Recalculated Stoichiometry
1 / I	1b	13	110%	124%
2 / III	2a	8	125%	96%
3 / I	3a	8	125%	117%
4 / I	4a	3	150%	164%
5 / I	5	13	150%	186%
6 / IV	6	13	150%	168%
7 / IV	7	13	100%	102%
8 / IV	8	3	100%	84%
9 / IV	9	3	150%	116%
10 / I	10	3	100%	113%
11 / IV	11	8	125%	170%

3.8 Solids Generation

The MnO_2 produced through decomposition of sodium permanganate is a fine solid that remained suspended in testing at 15 and 32.5 °C. In testing at 50 °C, the solids were larger and settled quickly. Since the RCT temperature has been below 33 °C for the past decade, it is expected that this process will produce fine MnO_2 solids that will be easily transferred to CSTF. This testing was not designed to look for long term changes in these solids such as agglomeration of the fine solids.

3.9 Process Implications

The ideal process for glycolate destruction would include all the process goals listed in Table 3-11. For the sodium permanganate process, all the process goals listed can be met, except that MnO_2 will be produced as a byproduct of the oxidation of organics. So, based on this testing, the sodium permanganate can meet the processing goals proposed. In contrast, Fenton's reagent failed to achieve most of the process goals.

Fenton reagent process were similar in operation (i.e. both pump in a liquid and wait for the reaction to go to completion), leading to the "Yes" for "Simple to implement and operate.". The Fenton reagent process was judged "No" for "Does not impact cycle time" since the required destruction efficiency in the required timeframe was not achievable with the conditions evaluated in this study. Higher concentrations and longer processing times could improve the effectiveness of this process, but it would most likely impact the RCT cycle time. For sodium permanganate, the destruction was acceptable under the conditions evaluated so it was deemed not to impact the RCT cycle time. Sodium permanganate was found to meet the process goal of "Provide minimum impact to DWPF facility" since existing equipment could be repurposed for this process; whereas the Fenton's

reagent process would require new equipment designed specifically for handling the peroxide. This added equipment could pose a significant impact relative to meeting this goal.

Table 3-11. Comparison of Processes

Process Goal	Sodium Permanganate	Fenton's Reagent
Work at any pH	**Yes**	No
Allow very fast oxidant additions	**Yes**	**Yes**
Work at any RCT temperature	**Yes**	No
Quickly destroy glycolate	**Yes**	No
No flammable or toxic generation within existing RCT purge	**Yes**	**Yes**
Simple to implement and operate	**Yes**	**Yes**
Does not impact RCT cycle time (No sample and hold)	**Yes**	No
Provide minimum impact to DWPF facility	**Yes**	No
No new downstream operating challenges	MnO_2 manageable	$Fe(OH)_3$ manageable

4.0 Conclusions

SRNL performed testing to support a downselection between two processing options for oxidizing glycolate in the DWPF RCT, sodium permanganate and Fenton's reagent. Eighteen tests were completed to determine the decomposition rate of glycolate and 7 additional organics. The organics were added at concentrations much higher than DWPF process projections to allow quantification of the destruction. The sodium permanganate oxidation process was significantly more effective in destroying glycolate. For the permanganate process, effective glycolate destruction was achieved over the full range of conditions that were tested:

- Oxidant stoichiometry ≥ 125% (as defined in this study),
- Temperature range from 15-50 °C,
- Oxidant addition time from 10 minutes to 2 hours,
- pH range from 3-13, and
- Glycolate concentration from 125-250 mg/L in this study and ≤2,000 mg/L in related studies.

A downselection meeting was held between SRR and SRNL[25] on September 20, 2018. A recommendation was made by SRNL to select the sodium permanganate oxidation process for continued glycolate destruction evaluation. Additional work is underway to advance the sodium permanganate oxidation process for DWPF implementation.[26] This testing will include processing with prototypic RCT simulant, worst case testing (i.e., a foam-over in the CPC or an entrainment event in the melter), and radioactive waste (or large scale) testing.

5.0 Recommendations

The sodium permanganate oxidation process for the destruction of glycolate is recommended. The process should be demonstrated under nominal and off-normal conditions as planned with SRR.

The following process recommendations are made.

- Rapid addition of sodium permanganate will shorten processing time and simplify processing. Subsequent testing should utilize a rapid addition.

- Oxidant stoichiometry (here as ≥125%) for optimum glycolate destruction without excess MnO_2 and NaOH generation is key. It is recommended future work focus on stoichiometric reactions and reaction sequences.

- No pH adjustment is recommended prior to the oxidant addition. Sodium nitrite needed for corrosion control should be added after the oxidation is complete. Note that addition of sodium nitrite for corrosion control should result in the destruction of any excess oxidant but this was not demonstrated in this testing.

- No temperature control is needed or recommended.

The following testing recommendations are made.

- Since many of the organics did not participate in aqueous phase reactions with permanganate, it is recommended that trimethylsilanol, propanal, formaldehyde, glyoxylate, and methylmercury hydroxide be removed from future experiments.

- Samples specific for nitrite and nitrate analysis should not be quenched with sodium sulfite.

- Corrosion coupons are recommended for subsequent laboratory testing in permanganate solutions to determine if localized corrosion is an issue.

6.0 References

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Appendixes

Appendix A – Corrosion Paper Study A-2
Appendix B – Sample Analyses B-1
Appendix C – Offgas Analyses C-1
Appendix D – Statistical Review of Data D-1

Appendix A: Corrosion Paper Study

A corrosion evaluation was completed by John Mickalonis.[27] The concern is that the oxidation process could increase the corrosion rate in the RCT significantly and could impact corrosion in downstream vessels. The primary recommendation was the inclusion of corrosion coupons in future testing. The text of his evaluation follows.

SRNL is currently investigating for SRR the destruction of glycolate added during processing waste in DWPF. This process is proposed to help ensure the RCT material will meet the potential new waste compliance plan requirements for glycolate to send the recycle material to the CSTF. Glycolate can be carried over in condensate systems within DWPF to the RCT, which is transferred back to the CSTF. SRR asked for a proposed process of destroying the glycolate in the RCT prior to transfer. Currently, the condensate waste streams, which are acidic, are added to the heel remaining in the RCT that has been adjusted with hydroxide and nitrite for corrosion protection of the waste tanks, and then transferred to the CSTF. SRNL is investigating the use of both sodium permanganate or the Fenton reaction for glycolate destruction.

During recent experiments at SRNL for permanganate destruction of a resin, the test cell and agitator, fabricated of 304 stainless steel, and the heater rods, fabricated of Inconel 800, were heavily pitted, especially along the liquid/air interface and for the heater rod along a seam, possibly a weld.[28] For the test cell, the liquid/air interface was near a weld between the flange top and side wall. The heater rod perforated over the course of 35 hours from exposure to simulated waste containing the resin and added permanganate and hydroxide. On the test cell two lines of pitting were seen which may be associated with the initial liquid level (15-hour exposure) and after the hydroxide addition (20-hour exposure).The localization of the corrosion in this case to primarily the air/liquid interface reinforces the oxidizing condition that the materials were exposed to, especially at a solution temperature of 80 °C.

This corrosion also raises the concern for the glycolate destruction process that is currently being investigated for the RCT in DWPF, which is fabricated from C276. The test conditions include RCT simulants (low nitrate/nitrite concentrations (0.05/0.112M NO_3/NO_2)) containing organics, including glycolate (concentration ~0.0067M),), treated with stochiometric ratios of 1-1.5 of the oxidizers at temperatures between 15 and 50 °C. The pH will vary with test conditions ranging from 3-13. Some of these conditions may also result in aggressive corrosion potential.

From a cursory literature survey, permanganate solutions are used as cleaning, decontamination, and descaling solutions for both stainless steel and Inconel alloys (4-6% permanganate and 1-2% hydroxide) due to the oxidizing nature of such solutions. In a SRNL study performed in both a caustic and acidic permanganate cleaning solution, Type 304L stainless steel samples were tested in immersion exposures for four weeks and accelerated electrochemical tests (SRNL-STI-2016-00465).[29] The four-week immersion tests performed at 25 and 50 °C did not exhibit any localized corrosion, with general corrosion rates less than 0.1 mil per year (mil is 0.001 inches). In electrochemical tests, localized corrosion susceptibility was observed at 75 °C, although not at lower temperatures. The oxidizing nature of these solutions shifted corrosion potentials to noble values; with the shift depending on temperature and specific solution chemistry.

Recommendation: Since a large amount of corrosion data is not available, corrosion coupons are recommended for a portion of the subsequent testing performed during laboratory testing in permanganate solutions to determine if localized corrosion is an issue.

Appendix B: Liquid Sample Results

The tables and figures included in this appendix are in addition to what was included in the body of the report. For each test, a table with liquid sample results, a figure of the formate, glycolate, and pH, along with a figure of the nitrate and nitrite concentration are included.

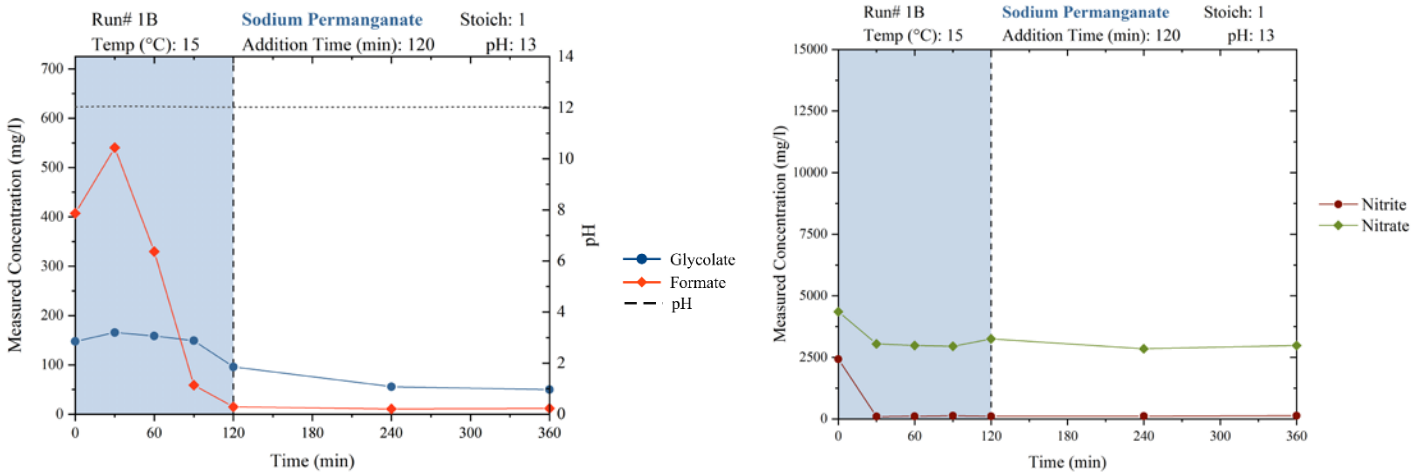


Figure B-1 Test 1b Formate, Glycolate, Nitrate and Nitrite, mg/L, pH Plot

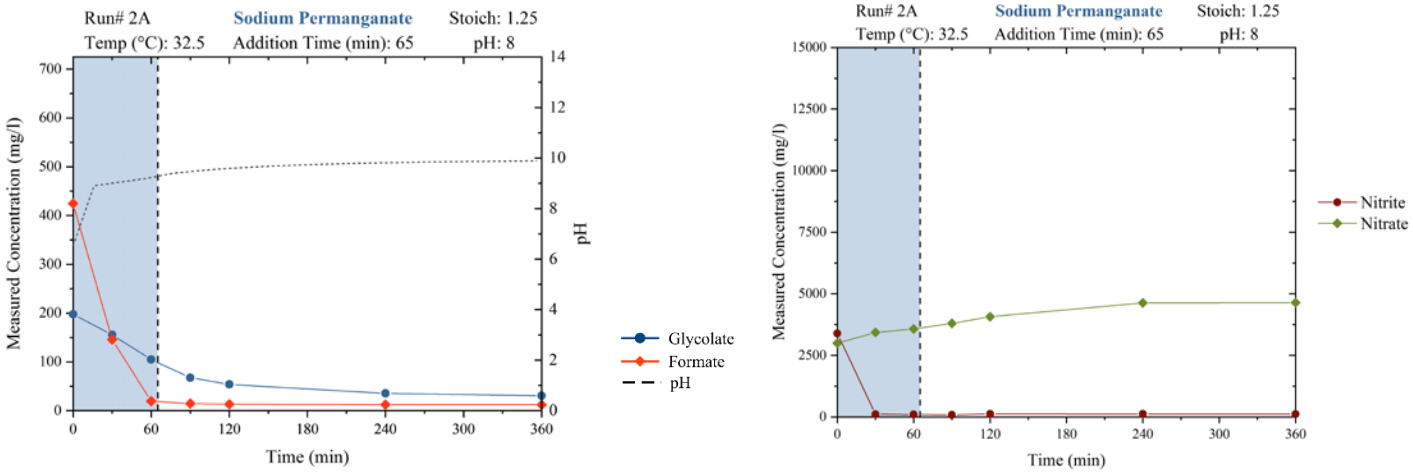


Figure B-2. Test 2A Formate, Glycolate, Nitrate and Nitrite, mg/L, pH Plot

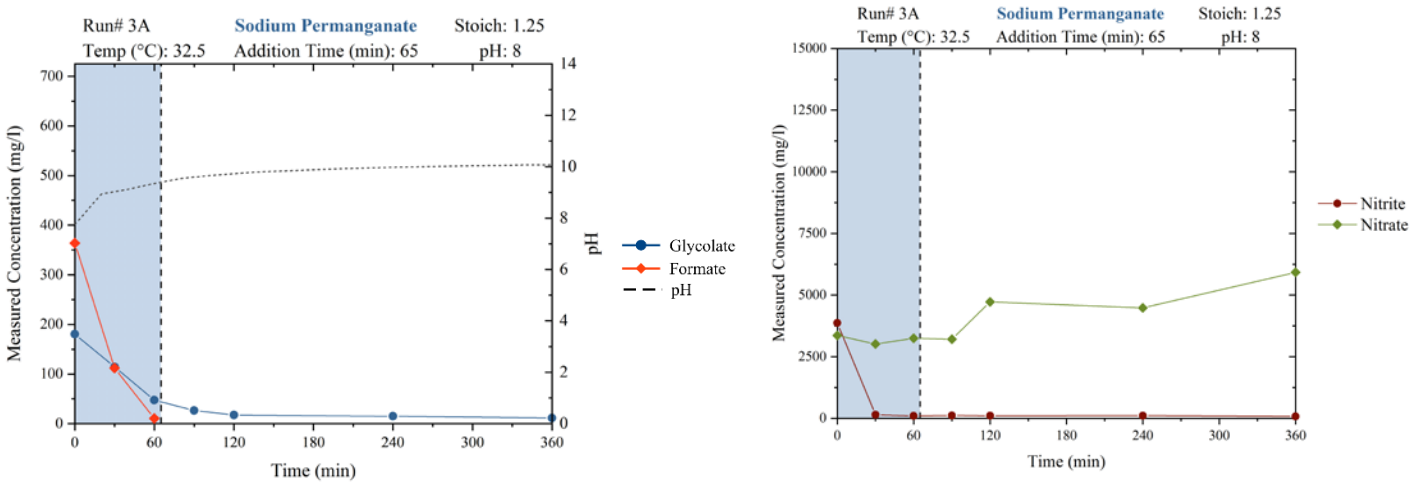


Figure B-3. Test 3A Formate, Glycolate, Nitrate and Nitrite, mg/L, pH Plot

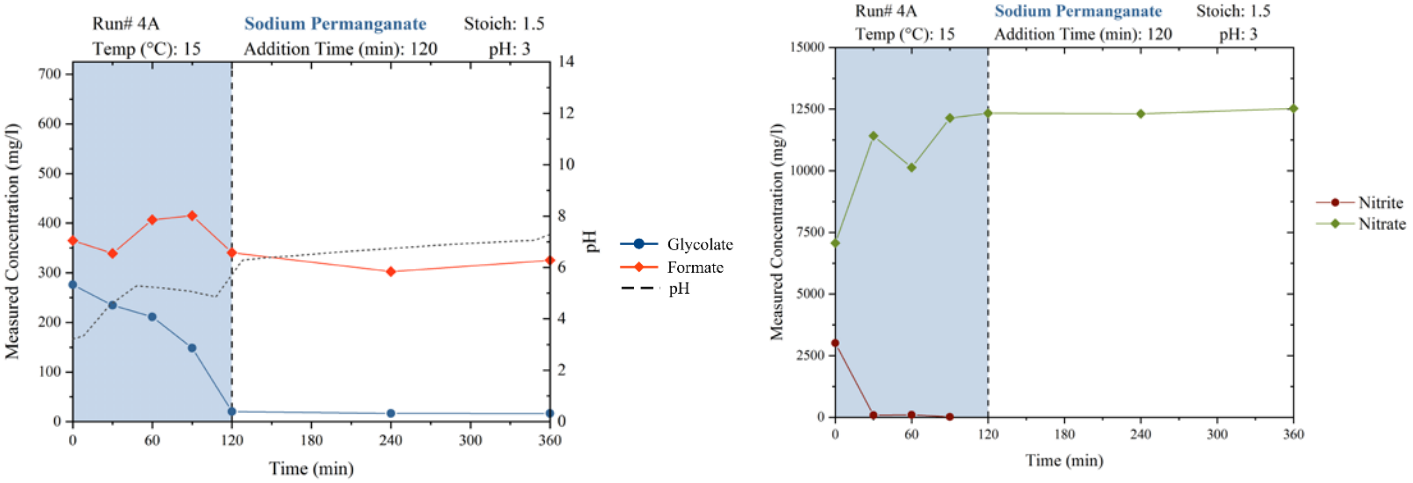


Figure B-4. Test 4A Formate, Glycolate, Nitrate and Nitrite, mg/L, pH Plot

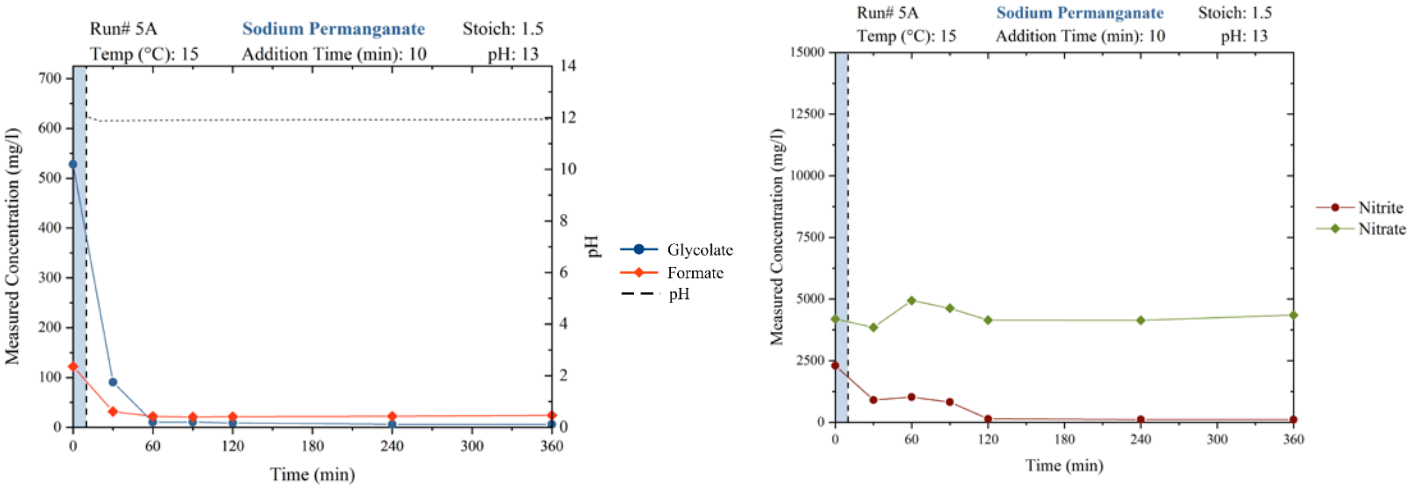


Figure B-5. Test 5A Formate, Glycolate, Nitrate and Nitrite, mg/L, pH Plot

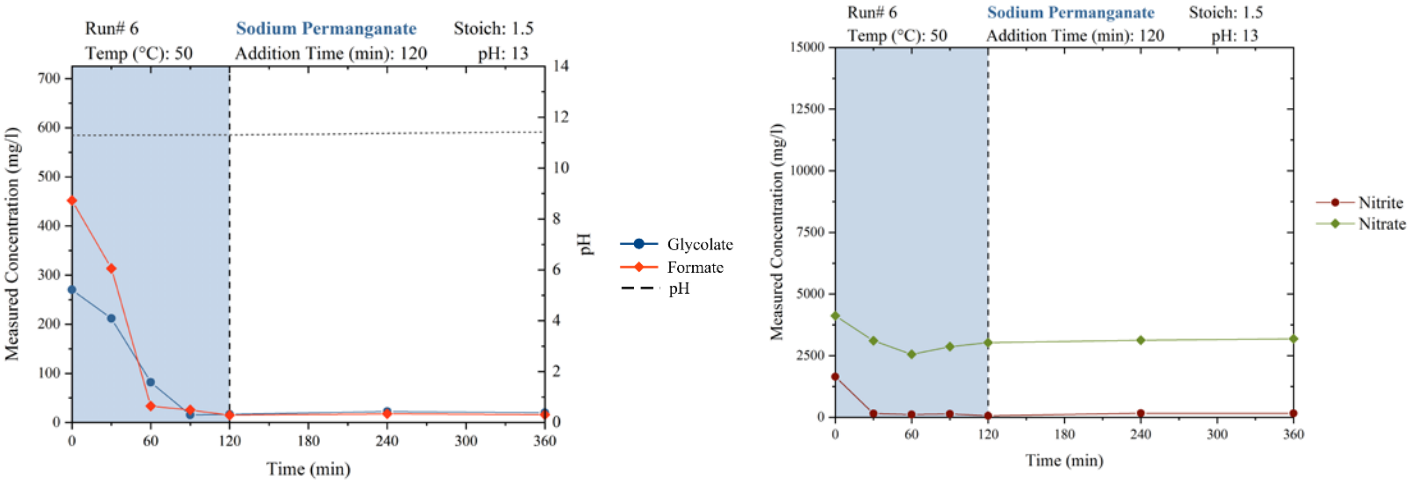


Figure B-6. Test 6A Formate, Glycolate, Nitrate and Nitrite, mg/L, pH Plot

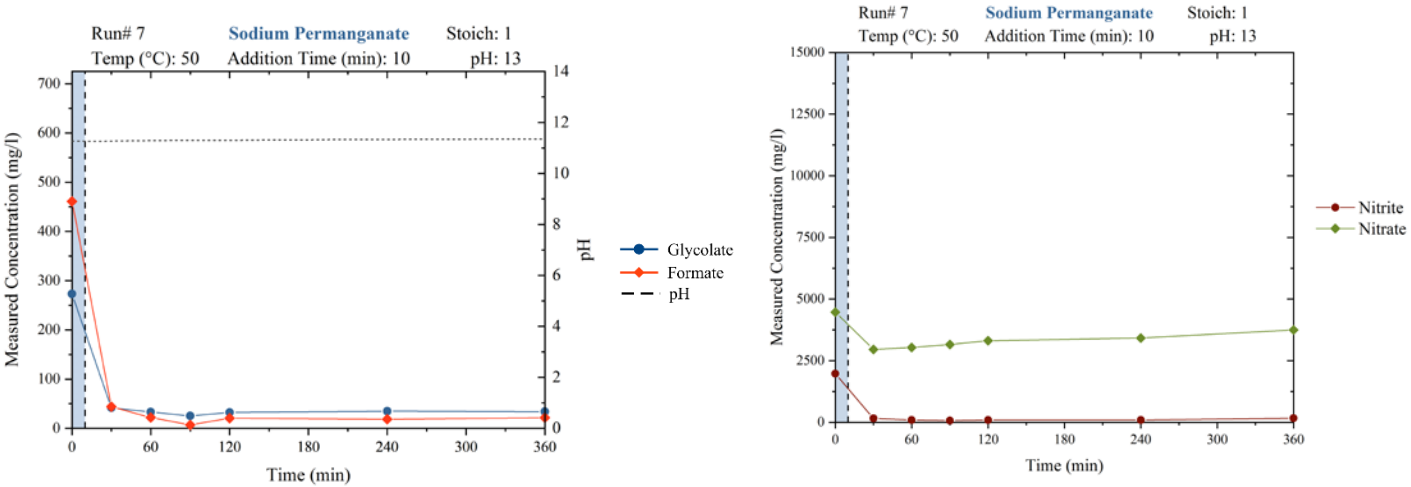


Figure B-7 Test 7 Formate, Glycolate, Nitrate and Nitrite, mg/L, pH Plot

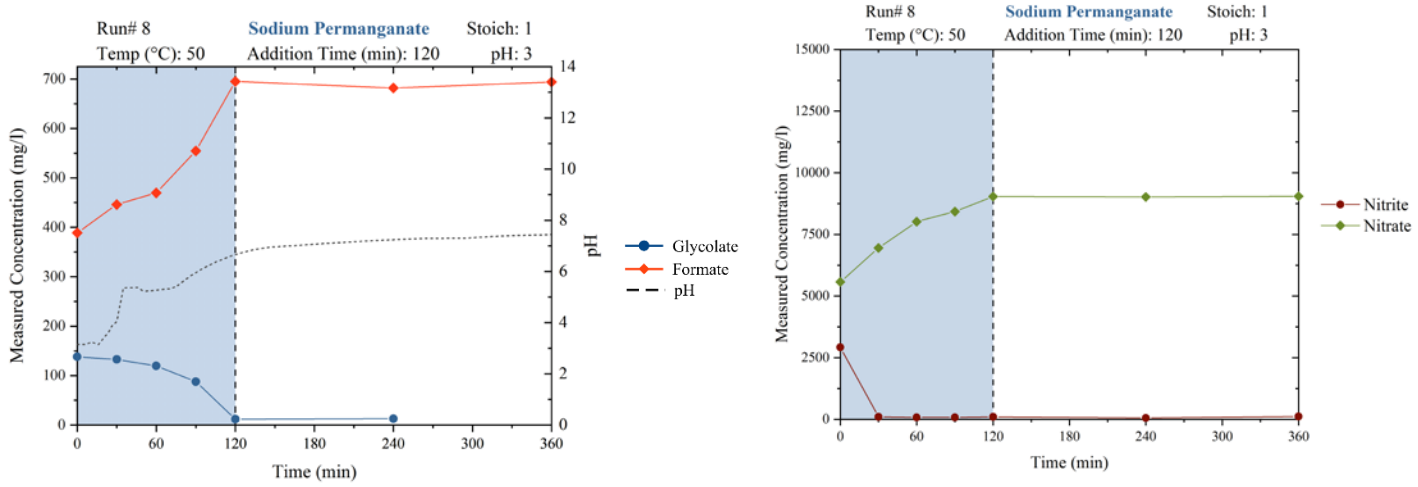


Figure B-8. Test 8 Formate, Glycolate, Nitrate and Nitrite, mg/L, pH Plot

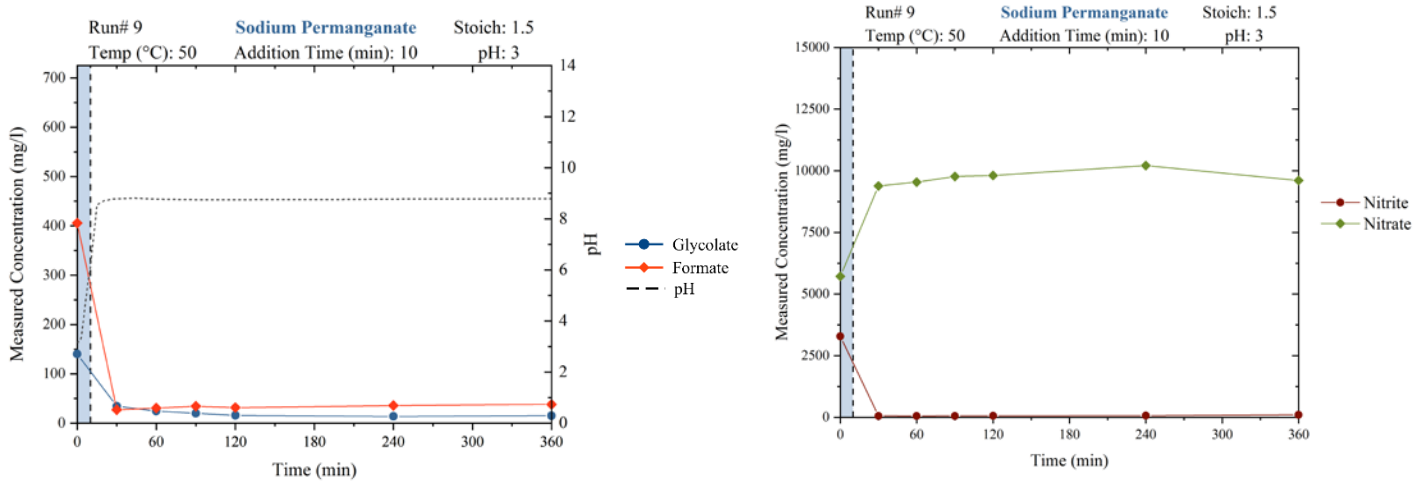


Figure B-9. Test 9 Formate, Glycolate, Nitrate and Nitrite, mg/L, pH Plot

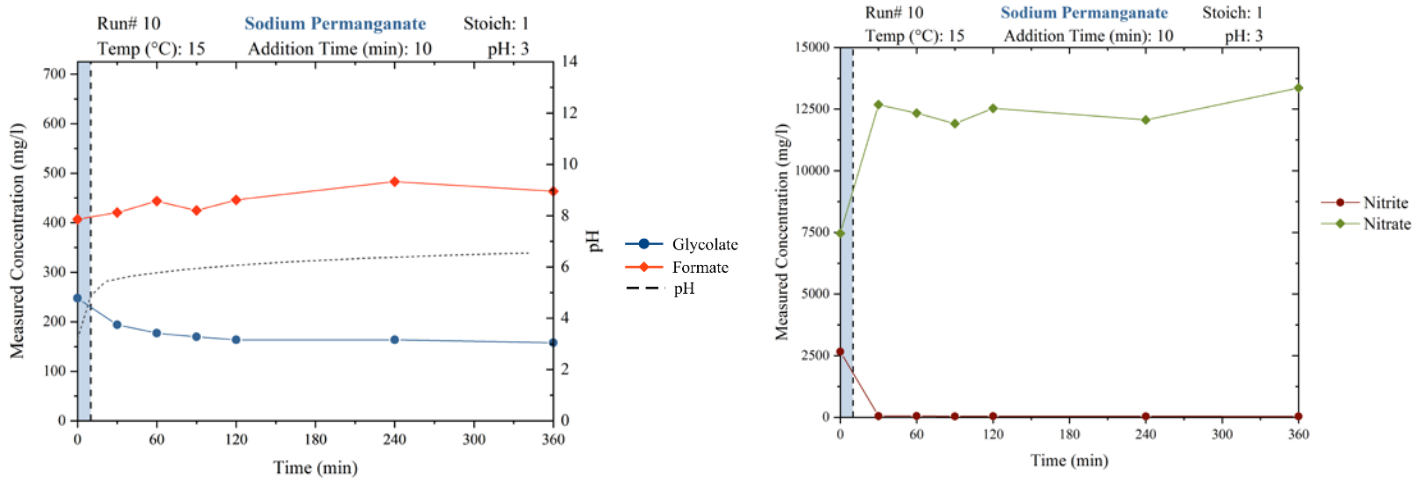


Figure B-10. Test 10 Formate, Glycolate, Nitrate and Nitrite, mg/L, pH Plot

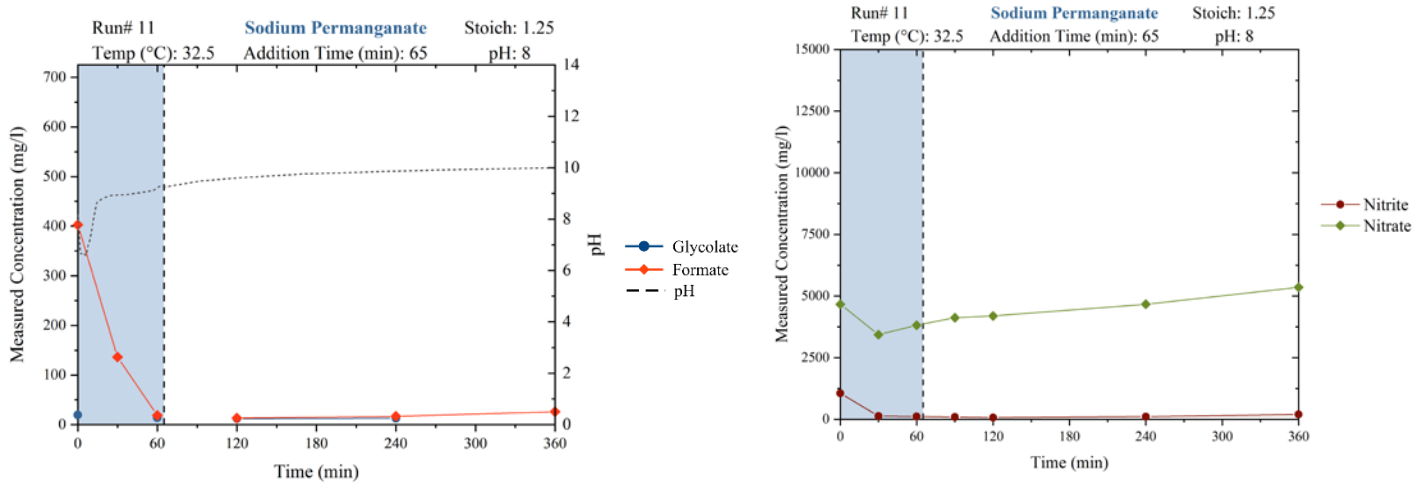


Figure B-11. Test 11 Formate, Glycolate, Nitrate and Nitrite, mg/L, pH Plot

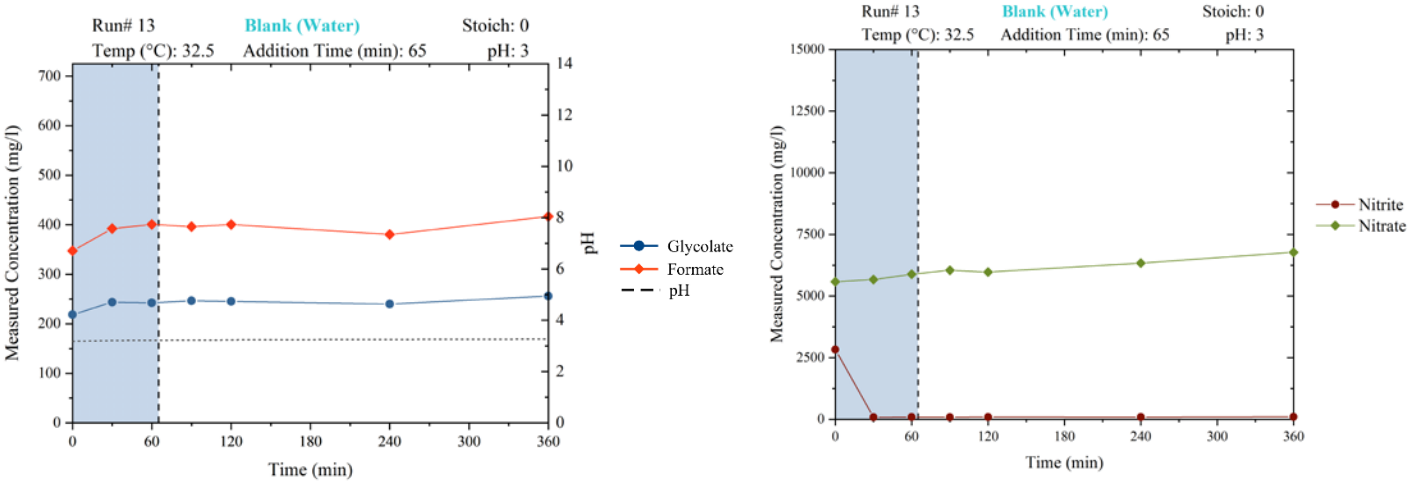


Figure B-12. Test 13 Formate, Glycolate, Nitrate and Nitrite, mg/L, pH Plot

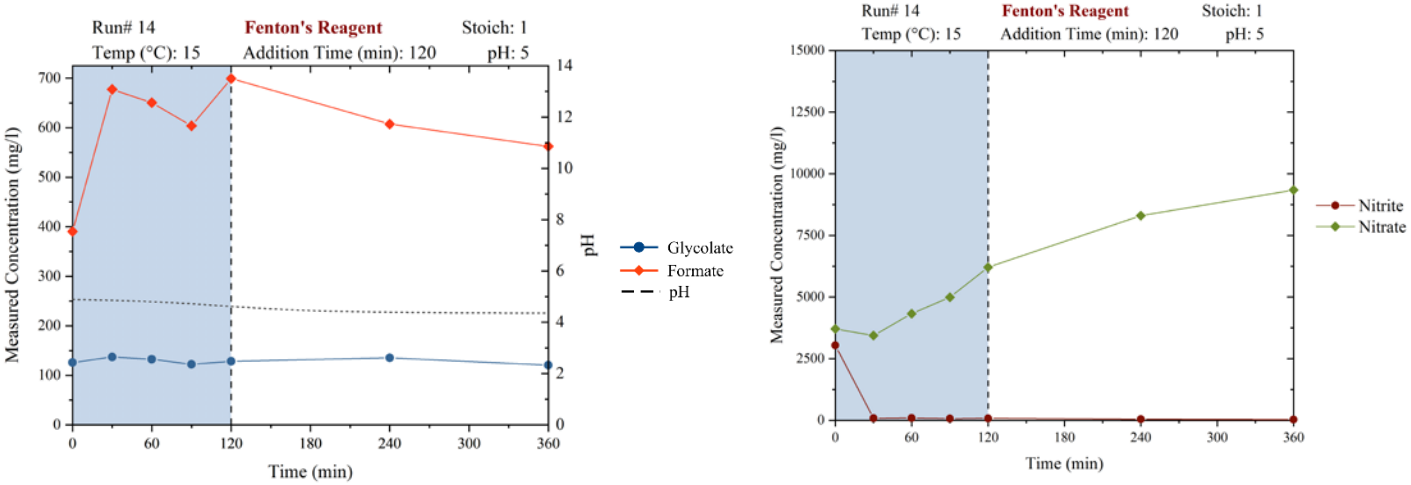


Figure B-13. Test 14 Formate, Glycolate, Nitrate and Nitrite, mg/L, pH Plot

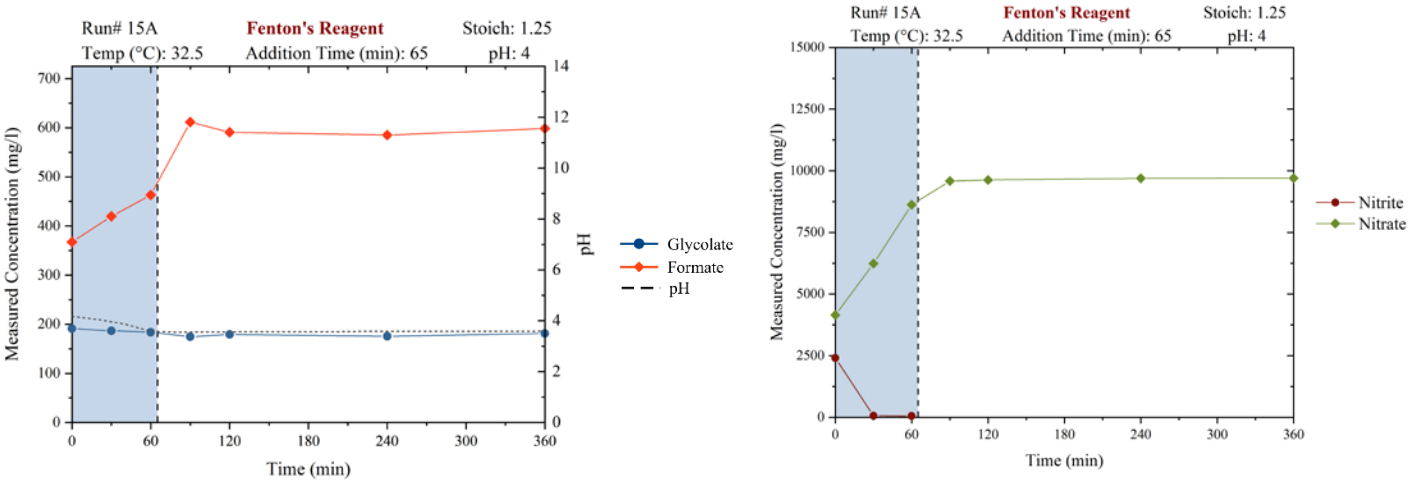


Figure B-14. Test 15A Formate, Glycolate, Nitrate and Nitrite, mg/L, pH Plot

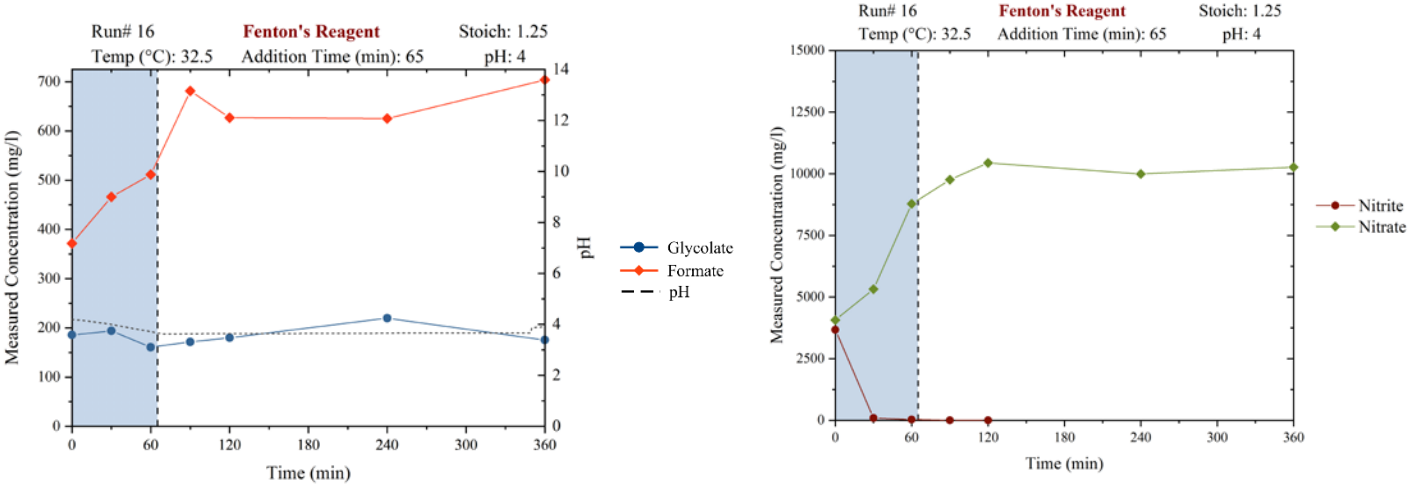


Figure B-15. Test 16 Formate, Glycolate, Nitrate and Nitrite, mg/L, pH Plot

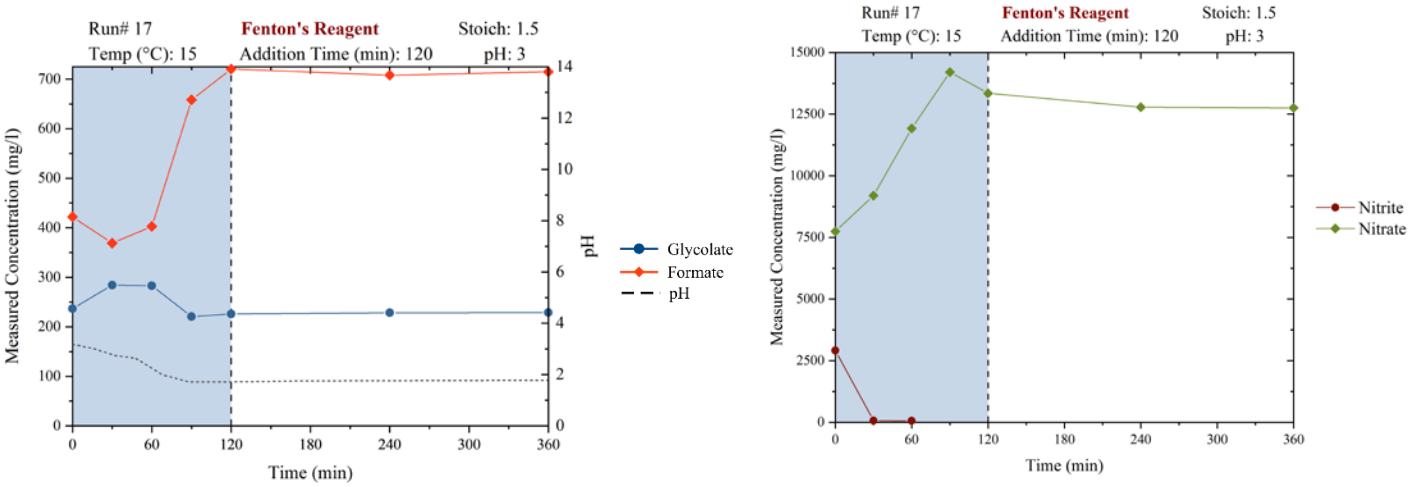


Figure B-16. Test 17 Formate, Glycolate, Nitrate and Nitrite, mg/L, pH Plot

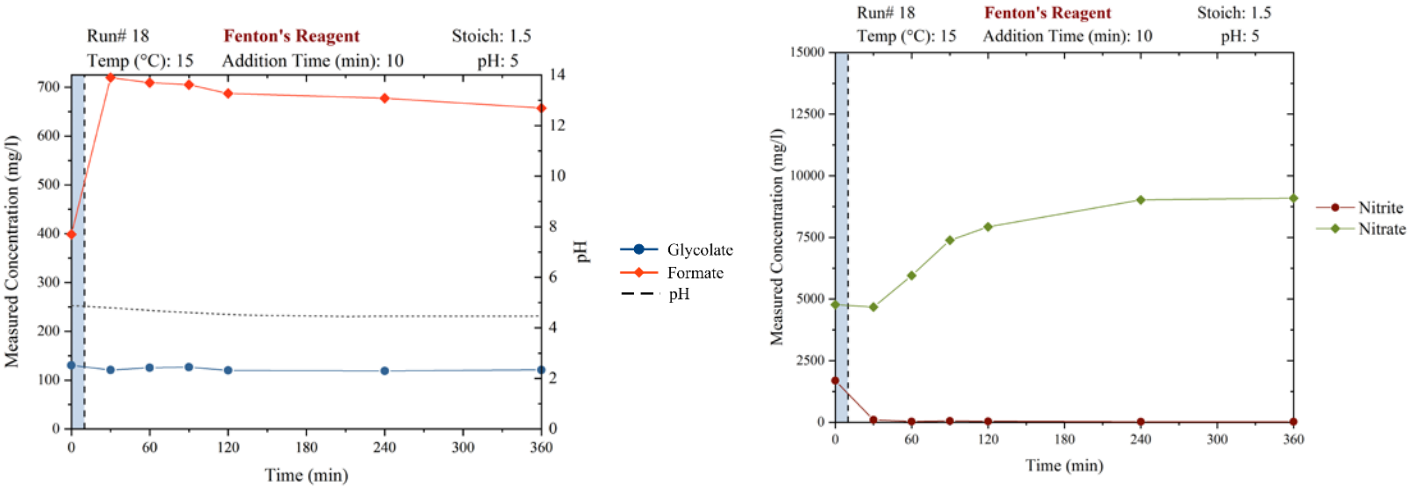


Figure B-17. Test 18 Formate, Glycolate, Nitrate and Nitrite, mg/L, pH Plot

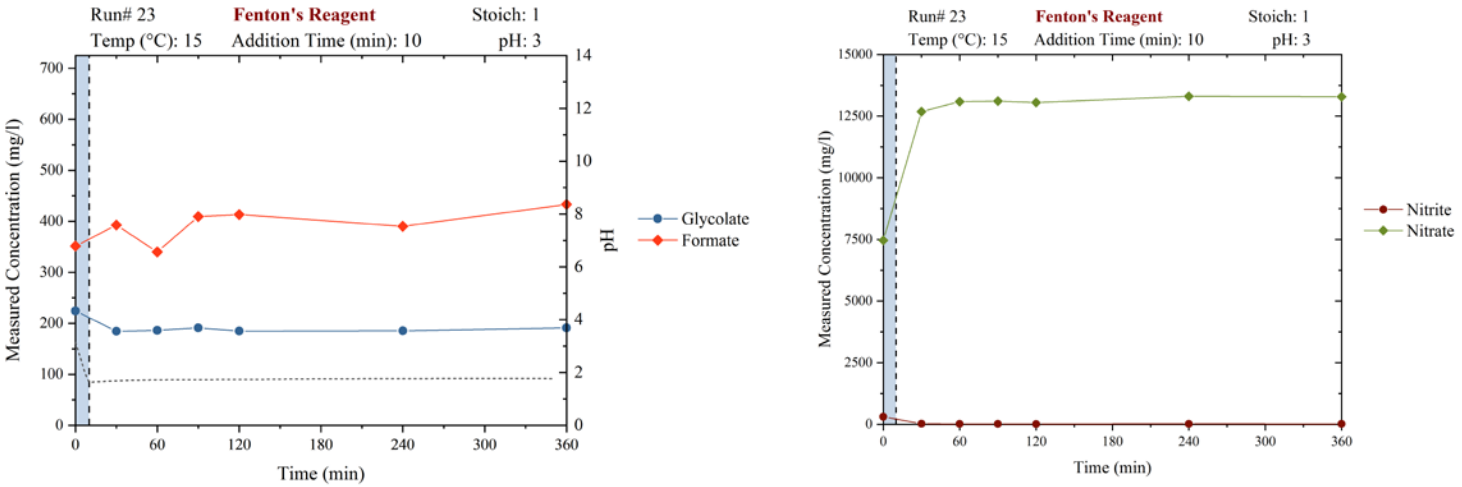


Figure B-18. Test 23 Formate, Glycolate, Nitrate and Nitrite, mg/L, pH Plot

Table B-1 PSAL Liquid Sample Results

			Lab and sample information		Anion Sample Dilution Correction Mass				IC ANIONS, mg/L supernate					
	Test #		Sample # PSAL	Time (min)	Sample Mass, g	Sample Mass plus quench, g	Mass Oxidant Added, g	pH (In-situ)	Glycolate Target	Glycolate	Formate	Nitrite	Nitrate	Oxalate
BLOCK 1	1B	LW--AD-PROJ-180813-2	S-8052	PRE	12.76	13.03	0.00	12.03	0	202	530	<10.21	3,818	434
			S-8053	000	13.05	13.31	16.62	12.03	0	148	407	2,427	4,355	338
			S-8054	030	15.24	15.89	36.66	12.05	0	166	541	99	3,055	378
			S-8055	060	14.68	15.28	56.70	12.05	0	159	330	109	2,986	402
			S-8056	090	14.31	14.88	76.75	12.03	0	149	59	132	2,953	423
			S-8057	120	13.58	14.13	96.79	12.02	0	96	15	112	3,257	539
			S-8058	240	13.95	14.65	96.79	12.02	0	56	11	115	2,857	542
			S-8059	360	99.41	105.905	96.79	12.03	0	50	12	133	2,994	606
	3A	LW-AD-PROJ-180808-1	S-8019	PRE	9.89	10.10	0.00	7.95	0	218	333	<10.21	3,206	326
			S-8017	000	16.68	16.88	0.30	7.75	188	181	364	3,867	3,361	280
			S-8021	030	10.58	11.10	47.05	9.03	0	115	113	144	3,021	396
			S-8022	060	11.36	11.88	93.81	9.35	0	48	11	98	3,252	388
			S-8023	090	10.71	11.25	101.60	9.60	0	26	<10.51	118	3,215	430
			S-8024	120	11.94	12.48	101.60	9.73	0	<20	<10.45	106	4,733	413
			S-8025	240	11.81	12.41	101.60	9.98	0	<20	<10.51	112	4,487	469
			S-8026	360	127.56	133.47	101.60	10.07	0	<20	<10.46	79	5,933	481
	4A	LW-AD-PROJ-180813-1	S-8044	PRE	9.15	9.36	0.00	3.16	0	331	504	<10.23	3,795	401
			S-8045	000	11.44	11.65	11.00	3.22	250	276	365	3,012	7,072	330
			S-8046	030	12.97	13.48	43.48	3.94	0	235	340	84	11,435	285
			S-8047	060	13.35	13.88	75.95	5.25	0	211	407	100	10,150	293
			S-8048	090	13.75	14.29	108.43	5.08	0	149	416	20	12,160	153
			S-8049	120	13.74	14.26	140.90	5.58	0	21	341	<10.38	12,356	14
			S-8050	240	14.53	15.06	140.90	6.74	0	<20	303	<10.36	12,327	<10.36
			S-8051	360	103.83	108.59	140.90	7.25	0	<20	326	<10.46	12,550	<10.46

Table B 1 PSAL Liquid Sample Results

Lab and sample information				Anion Sample Dilution Correction Mass				IC ANIONS, mg/L supernate					
Test #	AD #	Sample # PSAL	Time (min)	Sample Mass, g	Sample Mass plus quench, g	Mass Oxidant Added, g	pH (In-situ)	Glycolate Target	Glycolate	Formate	Nitrite	Nitrate	Oxalate
5A	LW-AD-PROJ-180806-6	S-8009	PRE	13.44	13.62	0.00	12.00	0	155	584	<10.14	3,458	580
		S-8010	000	13.56	13.76	17.37	11.90	125	122	528	2,303	4,190	378
		S-8011	030	14.55	15.04	143.87	11.91	0	32	90	902	3,855	520
		S-8012	060	14.28	14.78	143.87	11.91	0	22	11	1,023	4,947	588
		S-8013	090	14.46	14.95	143.87	11.92	0	21	10	818	4,632	545
		S-8014	120	13.01	13.53	143.87	11.92	0	21	9	139	4,149	568
		S-8015	240	13.67	14.18	143.87	11.93	0	22	6	115	4,147	654
		S-8016	360	125.80	130.80	143.87	11.94	0	24	6	110	4,356	575
10	LW-AD-PROJ-180809-2	S-8035	PRE	12.47	12.67	0.00	3.17	0	378	541	<10.16	4,001	492
		S-8036	000	12.98	13.16	9.20	3.20	250	248	407	2,666	7,462	337
		S-8037	030	11.83	12.32	110.58	5.54	0	194	421	53	12,703	258
		S-8038	060	12.44	12.92	110.58	5.78	0	177	444	51	12,359	248
		S-8039	090	13.10	13.59	110.58	5.95	0	170	425	43	11,930	230
		S-8040	120	13.15	13.64	110.58	6.07	0	164	447	46	12,554	227
		S-8041	240	13.08	13.63	110.58	6.38	0	164	484	44	12,083	216
		S-8042	360	128.61	133.38	110.58	6.54	0	158	464	37	13,378	255
BLOCK 2 14	LW-AD-PROJ-180821-2	8063	PRE	12.97	13.13	0.00	4.86	0	179	500	<10.12	3,987	354
		8064	000	13.96	14.16	0.09	4.89	127	126	390	3,042	3,711	267
		8065	030	13.69	14.16	5.58	4.86	0	137	678	82	3,443	266
		8066	060	11.41	11.92	11.08	4.81	0	133	652	95	4,336	289
		8067	090	15.06	15.58	16.57	4.73	0	122	605	67	4,999	267
		8068	120	13.84	14.38	22.07	4.63	0	129	700	78	6,217	260
		8069	240	13.28	13.82	22.07	4.4	0	136	608	45	8,311	251
		8070	360	101.74	107.05	22.07	4.36	0	121	564	31	9,364	280

Table B 1 PSAL Liquid Sample Results

Lab and sample information				Anion Sample Dilution Correction Mass				IC ANIONS, mg/L supernate					
Test #	AD #	Sample # PSAL	Time (min)	Sample Mass, g	Sample Mass plus quench, g	Mass Oxidant Added, g	pH (In-situ)	Glycolate Target	Glycolate	Formate	Nitrite	Nitrate	Oxalate
16	LW-AD-PROJ-180822-1	8071	PRE	13.02	13.12	0.00	4.2	0	274	523	<10.08	3,710	341
		8072	000	12.95	13.11	1.15	4.19	190	186	372	3,673	4,068	311
		8073	030	13.75	14.26	11.85	4.01	0	194	467	91	5,331	293
		8074	060	15.00	15.51	22.56	3.71	0	161	512	29	8,791	275
		8075	090	16.30	16.82	24.34	3.63	0	172	682	3	9,768	293
		8076	120	15.06	15.59	24.34	3.64	0	180	628	3	10,455	310
		8077	240	15.10	15.61	24.34	3.66	0	220	626	<10.34	10,008	293
		8078	360	100.03	105.43	24.34	3.87	0	176	706	<10.54	10,298	309
17	LW-AD-PROJ-180223-2	8079	PRE	14.45	14.65	0.00	3.19	0	317	526	<10.14	3,994	364
		8080	000	15.00	15.30	10.60	3.18	255	237	422	2,916	7,749	310
		8081	030	16.38	16.97	17.72	2.74	0	284	369	67	9,205	284
		8082	060	15.93	16.39	24.83	1.99	0	283	403	61	11,936	284
		8083	090	16.67	17.18	31.95	1.71	0	221	659	<10.3	14,220	324
		8084	120	14.66	15.18	39.07	1.72	0	226	721	<10.36	13,365	292
		8085	240	15.94	16.45	39.07	1.76	0	229	709	<10.32	12,798	287
		8086	360	96.68	101.30	39.07	1.78	0	229	717	<10.48	12,784	280
18	LW-AD-PROJ-180827-1	8087	PRE	13.87	14.03	0.00	4.85	0	146	472	<10.12	3,682	361
		8088	000	15.09	15.26	1.33	4.88	126	131	399	1,689	4,775	266
		8089	030	16.59	17.06	28.23	4.79	0	121	720	99	4,679	279
		8090	060	17.58	18.05	28.23	4.69	0	125	710	31	5,956	275
		8091	090	16.16	16.64	28.23	4.6	0	127	706	51	7,391	273
		8092	120	17.71	18.10	28.23	4.53	0	120	687	42	7,931	273
		8093	240	17.34	17.82	28.23	4.46	0	119	678	24	9,032	282
		8094	360	95.91	100.12	28.23	4.48	0	121	658	24	9,113	280
23	LW-AD-PROJ-180827-2	8095	PRE	17.10	17.29	0.00	3.14	0	239	394	<10.11	3,196	283
		8096	000	14.85	15.04	10.30	3.14	253	225	352	302	7,472	291
		8097	030	15.38	15.88	29.27	1.68	0	185	393	21	12,696	289
		8098	060	15.26	15.75	29.27	1.72	0	186	341	14	13,106	304
		8099	090	14.73	15.22	29.27	1.73	0	191	410	14	13,126	293
		8100	120	17.03	17.52	29.27	1.74	0	185	413	12	13,067	294
		8101	240	12.49	13.00	29.27	1.77	0	186	391	18	13,331	285
		8102	360	118.12	122.81	29.27	1.77	0	191	434	14	13,308	311

Table B 1 PSAL Liquid Sample Results

Lab and sample information					Anion Sample Dilution Correction Mass				IC ANIONS, mg/L supernate						
Block #	Test #	AD #	Sample # PSAL	Time (min)	Sample Mass, g	Sample Mass plus quench, g	Mass Oxidant Added, g	pH (In-situ)	Glycolate Target	Glycolate	Formate	Nitrite	Nitrate	Oxalate
BLOCK 3	2A	LW-AD-PROJ-180829-1	S-8117	PRE	13.96	14.26	0.00	7.92	0.00	266	508	<10.21	3,912	330
			S-8121	000	13.46	13.76	0.27	6.53	187.50	198	425	3,394	2,995	242
			S-8122	030	13.47	14.02	35.93	8.98	0.00	156	146	108	3,435	287
			S-8123	060	13.08	13.64	71.59	9.19	0.00	105	20	101	3,576	311
			S-8124	090	15.18	15.74	77.53	9.45	0.00	68	15	87	3,805	335
			S-8125	120	12.67	13.24	77.53	9.58	0.00	54	13	124	4,075	351
			S-8126	240	8.75	9.31	77.53	9.81	0.00	36	13	123	4,650	380
			S-8127	360	109.64	114.84	77.53	9.89	0.00	31	12	117	4,650	375
	15A	LW-AD-PROJ-180828-2	S-8128	PRE	15.45	15.62	0.00	4.17	0.00	236	466	<10.11	3,853	364
			S-8129	000	16.90	17.07	0.90	4.17	187.50	191	368	2,404	4,151	280
			S-8130	030	15.81	16.31	6.57	3.96	0.00	187	420	65	6,242	283
			S-8131	060	15.82	16.29	12.24	3.58	0.00	184	463	53	8,632	294
			S-8132	090	16.00	16.49	17.91	3.56	0.00	175	612	<10.3	9,592	284
			S-8133	120	14.05	14.52	23.58	3.56	0.00	179	591	<10.33	9,642	279
			S-8134	240	15.41	15.89	23.58	3.58	0.00	176	586	<10.31	9,706	286
			S-8135	360	107.63	112.30	23.58	3.59	0.00	181	597	<10.43	9,683	302
	13	LW-AD-PROJ-180830-7	S-8103	PRE	13.73	13.90	0.00	3.17	0.00	270	454	<10.13	3,230	306
			S-8104	000	14.22	14.44	7.10	3.18	250.00	219	347	2,833	5,585	250
			S-8105	030	14.15	14.67	35.88	3.21	0.00	244	393	82	5,681	284
			S-8106	060	12.82	13.33	64.66	3.22	0.00	243	401	90	5,895	281
			S-8107	090	14.30	14.83	69.45	3.23	0.00	247	397	87	6,057	289
			S-8108	120	14.14	14.68	69.45	3.24	0.00	246	401	94	5,979	285
			S-8109	240	14.61	15.14	69.45	3.25	0.00	240	381	90	6,343	278
			S-8110	360	108.53	114.29	69.45	3.27	0.00	257	418	102	6,792	288
BLOC	6A	LW-AD-PROJ-181001-1	S-8267	PRE	15.08	15.34	0.00	13.16	0	315	536	<10.17	4,201	354
			S-8268	000	14.10	14.50	18.54	13.34	250	270	452	1,645	4,124	294
			S-8269	030	15.41	16.03	42.49	13.35	0	212	314	152	3,110	327
			S-8270	060	15.51	16.14	66.44	13.35	0	82	34	117	2,560	361
			S-8271	090	14.62	15.21	90.39	13.36	0	16	26	138	2,871	521
			S-8272	120	16.33	16.91	114.34	13.35	0	<20	15	60	3,034	537
			S-8273	240	14.22	14.74	114.34	13.35	0	22	18	166	3,130	555
			S-8274	360	99.98	105.14	114.34	13.44	0	20	16	162	3,197	542

Table B 1 PSAL Liquid Sample Results

Lab and sample information				Anion Sample Dilution Correction Mass				IC ANIONS, mg/L supernate					
Test #	AD #	Sample # PSAL	Time (min)	Sample Mass, g	Sample Mass plus quench, g	Mass Oxidant Added, g	pH (In-situ)	Glycolate Target	Glycolate	Formate	Nitrite	Nitrate	Oxalate
7	LW-AD-PROJ-181010-3	S-8275	PRE	14.73	14.92	0.00	13.20	0	340	540	<10.13	3,860	334
		S-8276	000	16.46	16.65	18.27	13.17	250	273	461	1,973	4,472	265
		S-8277	030	13.63	14.12	34.96	13.20	0	42	44	161	2,963	576
		S-8278	060	15.46	15.96	51.65	13.18	0	33	22	90	3,035	656
		S-8279	090	16.97	17.46	68.35	13.17	0	25	7	72	3,159	659
		S-8280	120	15.05	15.55	85.04	13.20	0	32	21	96	3,315	679
		S-8281	240	15.68	16.17	85.04	13.17	0	35	19	96	3,424	691
		S-8282	360	112.88	118.07	85.04	13.33	0	34	22	172	3,755	703
8	LW--AD-PROJ-181017-1	S-8309	PRE	16.25	16.47	0.00	12.97	0	164	516	<10.13	3,860	306
		S-8310	000	15.50	15.96	5.50	13.19	125	138	389	2,924	5,580	229
		S-8311	030	16.21	16.76	67.95	13.02	0	133	447	101	6,958	253
		S-8312	060	15.62	16.12	67.95	12.98	0	120	470	81	8,027	218
		S-8313	090	15.35	15.92	67.95	13.11	0	88	555	79	8,440	40
		S-8314	120	14.34	14.98	67.95	13.16	0	<20	697	99	9,052	<10.45
		S-8315	240	25.08	25.60	67.95	12.89	0	<20	682	57	9,025	<10.21
		S-8316	360	114.80	120.00	67.95	13.27	0	<20	695	115	9,063	<10.45
9	LW--AD-PROJ-181022-1	S-8317	PRE	16.69	16.88	0.00	12.90	0	167	509	<10.12	3,774	302
		S-8318	000	16.78	17.00	4.90	12.85	125	140	406	3,282	5,724	253
		S-8319	030	22.03	22.53	119.75	12.74	0	34	27	56	9,387	134
		S-8320	060	23.53	24.03	119.75	12.71	0	24	31	52	9,548	125
		S-8321	090	21.43	21.94	119.75	12.70	0	20	34	56	9,775	133
		S-8322	120	22.49	23.00	119.75	12.75	0	<20	32	60	9,816	123
		S-8323	240	19.87	20.38	119.75	12.82	0	<20	36	68	10,216	129
		S-8324	360	113.59	119.14	119.75	13.19	0	<20	38	101	9,628	118
11	LW--AD-PROJ-181022-2	S-8325	PRE	15.95	16.21	0.00	12.94	0	24	561	<10.16	3,516	352
		S-8326	000	15.13	15.33	0.09	12.91	0	20	403	1,053	4,670	310
		S-8327	030	20.68	21.15	33.43	12.79	0	<20	136	129	3,435	288
		S-8328	060	17.23	17.95	66.76	13.11	0	<20	19	116	3,824	282
		S-8329	090	15.59	16.08	72.31	12.82	0	<20	<10.31	95	4,125	287
		S-8330	120	18.40	18.88	72.31	12.85	0	<20	13	74	4,196	265
		S-8331	240	19.35	19.87	72.31	12.89	0	<20	17	109	4,672	269
		S-8332	360	108.00	113.22	72.31	13.15	0	<20	26	200	5,367	328

Table B 2 AD Liquid Sample Results

Lab and sample information					Sample Masses		ADLIMS, mg/L supernate								
							TIC/TOC			VOA(1)			VOA(2)	SVOA	MeHg
Block #	Test #	LW-AD-PROJ-	Sample # ADLIMS	Time (min)	Sample, g	Sample + Quench, g	TC	TIC	TOC	Propanal	Trimethylsilanol	HMDSO	All Other	All Other	MeHg
1	1B	180813-2	LW11372	PRE	12.11	12.46	725	162	564	0.1	45	0.17	<0.26	NR	1533
			LW11379	360	100.47	102.98	571	275	296	0.1	38	0.10	<0.26	<1	1671
	3A	180808-1	LW11316	PRE	14.61	14.80	647	108	539	<0.1	182	0.30	<0.25	NR	1631
			LW11323	360	111.67	114.18	560	264	297	<0.1	52	<0.1	<0.26	<1	1190
	4A	180813-1	LW11364	PRE	12.55	12.79	739	172	567	0.1	49	0.17	<0.25	NR	923
			LW11371	360	113.46	116.02	381	121	261	5.1	37	<0.1	<0.26	<1	1391
	5A	180806-6	LW11281	PRE	12.58	12.79	635	147	488	<0.1	173	0.36	<0.25	NR	1118
			LW11288	360	109.98	112.47	554	281	273	<0.1	143	0.15	<0.26	<1	1176
	10	180809-2	LW11343	PRE	14.31	14.49	755	139	616	<0.1	304	1.62	<0.25	NR	666
			LW11350	360	114.24	116.75	500	42	458	3.7	47	<0.1	<0.26	<1	1727

Table B 2 AD Liquid Sample Results

Lab and sample information					Sample Masses		ADLIMS, mg/L supernate								
							TIC/TOC			VOA(1)			VOA(2)	SVOA	MeHg
Block #	Test #	LW-AD-PROJ-	Sample # ADLIMS	Time (min)	Sample, g	Sample + Quench, g	TC	TIC	TOC	Propanal	Trimethylsilanol	HMDSO	All Other	All Other	MeHg
2	14	180821-2	LW11455	PRE	14.83	15.02	656	89	567	0.1	49	0.21	<0.25	NR	NR
			LW11462	360	105.94	108.46	441	34	407	5.0	40	<0.1	<0.26	NR	NR
	16	180822-1	LW11471	PRE	15.36	15.51	513	69	444	0.1	45	0.19	<0.25	NR	NR
			LW11478	360	96.15	98.65	402	<20.5	402	1.6	38	<0.1	<0.26	NR	NR
	17	180223-2	LW11480	PRE	13.39	13.61	647	69	578	0.1	45	0.27	<0.25	NR	NR
			LW11487	360	91.51	94.02	452	<20.5	452	<0.1	28	<0.1	<0.26	<1	NR
	18	180827-1	LW11496	PRE	13.99	14.19	489	34	454	0.1	45	0.26	<0.25	NR	NR
			LW11503	360	94.02	96.53	386	<20.5	386	7.7	38	<0.1	<0.26	<1	NR
	23	180827-2	LW11504	PRE	18.93	19.12	501	48	453	0.1	36	0.12	<0.25	NR	NR
			LW11511	360	116.73	119.23	466	<20.4	466	<0.1	22	<0.1	<0.26	<1	NR

Table B 2 AD Liquid Sample Results

Lab and sample information					Sample Masses		ADLIMS, mg/L supernate								
							TIC/TOC			VOA(1)			VOA(2)	SVOA	MeHg
Block #	Test #	LW-AD-PROJ-	Sample # ADLIMS	Time (min)	Sample, g	Sample + Quench, g	TC	TIC	TOC	Propanal	Trimethylsilanol	HMDSO	All Other	All Other	MeHg
3	2A	180829-1	LW11528	PRE	14.71	15.02	653	82	572	<0.1	429	0.31	<0.26	NR	NR
			LW11535	360	109.83	112.35	530	284	245	<0.01	39	<0.1	<0.26	<1	NR
	15A	180828-2	LW11517	PRE	15.21	15.38	654	87	566	<0.1	222	0.12	<0.25	NR	NR
			LW11527	360	113.07	115.58	446	39	407	3.7	99	<0.1	<0.26	<1	NR
	13	180830-7	LW11569	PRE	12.98	13.17	621	81	540	<0.1	365	0.20	<0.25	NR	NR
			LW11576	360	86.27	88.78	533	39	494	1.7	33	<0.1	<0.26	<1	NR

Table B 2 AD Liquid Sample Results

Lab and sample information					Sample Masses		ADLIMS, mg/L supernate								
							TIC/TOC			VOA(1)			VOA(2)	SVOA	MeHg
Block #	Test #	LW-AD-PROJ-	Sample # ADLIMS	Time (min)	Sample, g	Sample + Quench, g	TC	TIC	TOC	Propanal	Trimethylsilanol	HMDSO	All Other	All Other	MeHg
4	6A	181001-1	LW11837	PRE	13.99	14.21	635	82	553	<0.1	31	0.17	<0.25	NR	NR
			LW11844	360	110.82	113.27	528	295	233	<0.1	29	0.10	<0.26	<1	NR
	7	181010-3	LW11913	PRE	16.88	17.08	688	72	615	<0.1	38	0.54	<0.25	NR	NR
			LW11917	360	113.11	115.61	551	289	262	<0.1	29	0.11	<0.26	0	NR
	8	181017-1	LW11964	PRE	16.42	16.70	602	65	537	0.2	315	68	<0.1	NR	NR
			LW11971	360	117.49	120.00	346	62	284	16.3	235	5.0	<0.1	<1	NR
	9	181022-1	LW11990	PRE	15.92	16.13	579	61	519	0.2	334	74	<0.1	NR	NR
			LW11997	360	111.12	113.64	470	309	162	0.2	245	6.1	<0.1	<1	NR
	11	181022-2	LW11998	PRE	16.92	17.22	507	63	444	0.2	316	72	<0.1	NR	NR
			LW11705	360	109.02	111.58	452	243	210	0.2	266	11	<0.1	<1	NR

Appendix C: Offgas Data

The offgas from each test was analyzed using the FTIR and either MS or GC. The MS had an equipment failure between tests, so a GC was used for the remainder of the experiments. The primary purpose for MS and GC was the measurement of hydrogen. Of the GC data, no hydrogen was detected during tests. No appreciable hydrogen was detected by the MS after simulant preparation during any of the tests. Note that much of the hydrogen was generated during simulant preparation and was likely due to thermolysis of one or more of the added organics. Any perceived accumulation of hydrogen observed in other testing was a result of cumulative positive values in a noisy MS signal. Realistically, no hydrogen was produced, and the values shown in the cumulative plots are artificial due to interferences by all species at the hydrogen signal in the MS at these low concentrations. Also, prior to the MS equipment failure, a negative drift of the hydrogen signal was often observed and resulted in the application of a corrective calculation to registered values. Some of the noisy signal issues were exacerbated by the correction factor producing the apparent hydrogen accumulations. In some plots, the hydrogen is not even displayed for clarity of the other species due to the lack of any appreciable hydrogen signal resulting in a noisy graph; cumulative noise in the signal is also responsible for the apparent presence of hydrogen observed in the cumulative mmol plots. Trimethylsilanol, CO, and methanol are not plotted on the figures if they were not detected during the test.

For each test, two graphs are included. First, a graph showing the offgas profile in ppm_v over time typically for CO, CO_2, H_2, NO, NO_2, N_2O, trimethylsilanol (referred to as TMS in captions for appendix), hexamethyldisiloxane (referred to as HMDSO in captions for appendix), propanal along with other intermittently detected species. Second, a graph showing the totalized offgas in cumulative mmol for each species in the test, typically displaying CO, CO_2, H_2, NO, NO_2, N_2O, trimethylsilanol, and hexamethyldisiloxane, among other intermittently detected species. Note that the antifoam degradation products (propanal and trimethylsilanol, which were added, and hexamethyldisiloxane, which was generated) and/or CO_2 are often plotted on the righthand y-axis since their concentrations are usually significantly higher than the other gases. Note that the purge used in these experiments was 10 times the scaled DWPF air purge, so the concentrations of all gases would have been 10 times that measured in ppm_v. The totalized mmol adjusted for the volumetric scale factor would be the same between the experiments and DWPF.

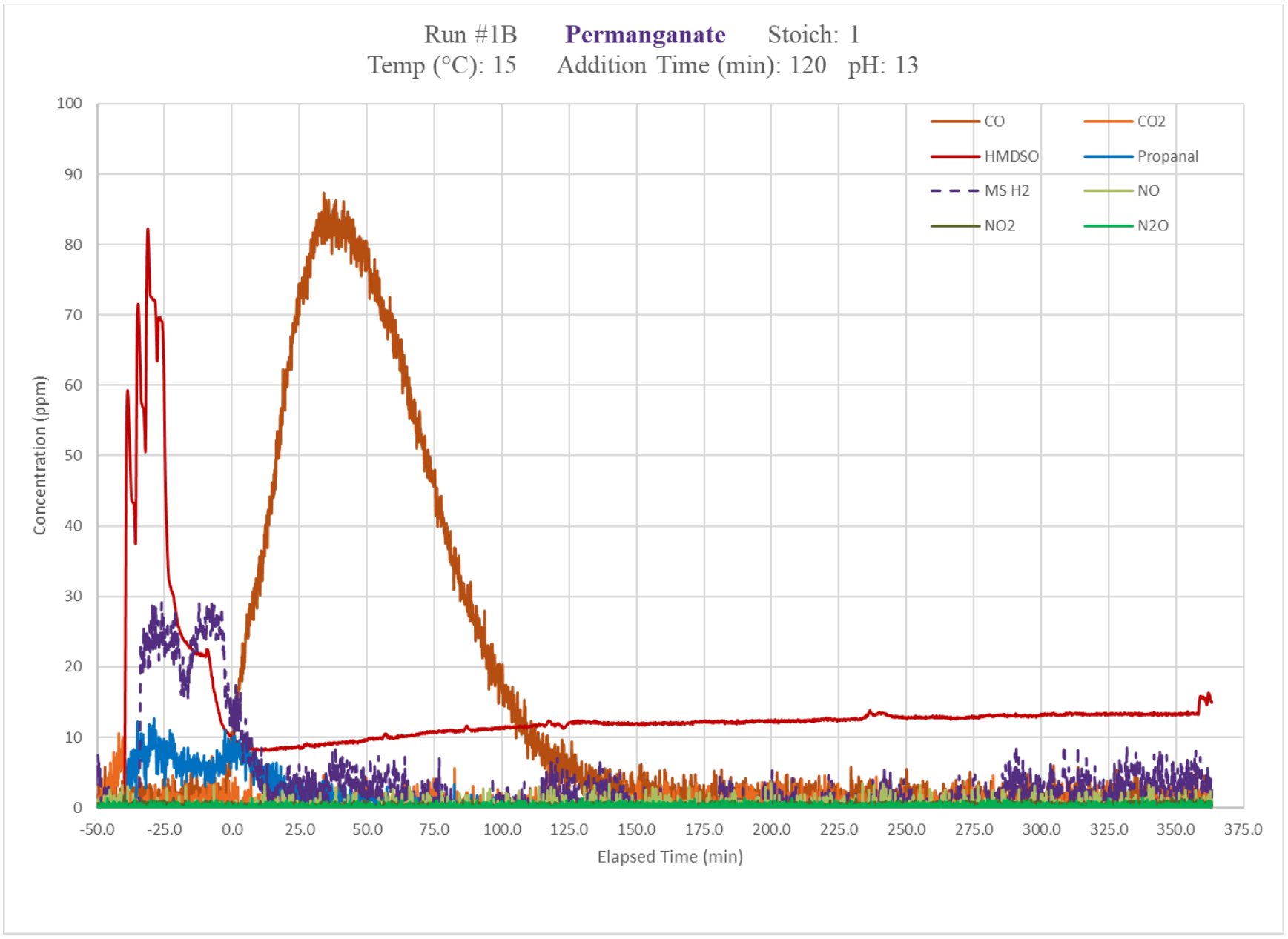


Figure B-19. Test 1b Offgas Profile CO, CO_2, H_2, NO, NO_2, N_2O, HMDSO, and Propanal

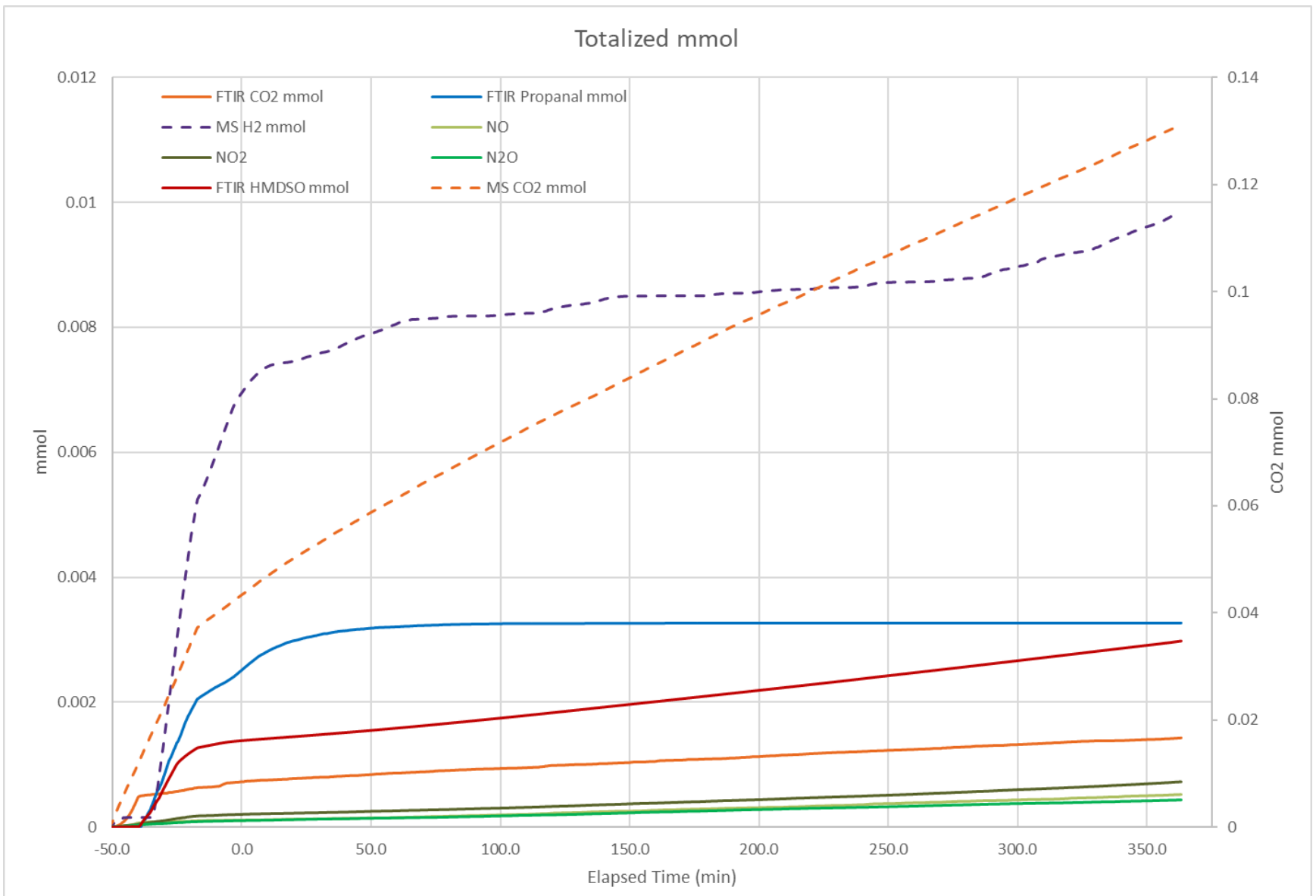


Figure B-20. Test 1b Totalized Offgas CO_2, H_2, NO, NO_2, N_2O, HMDSO, and Propanal

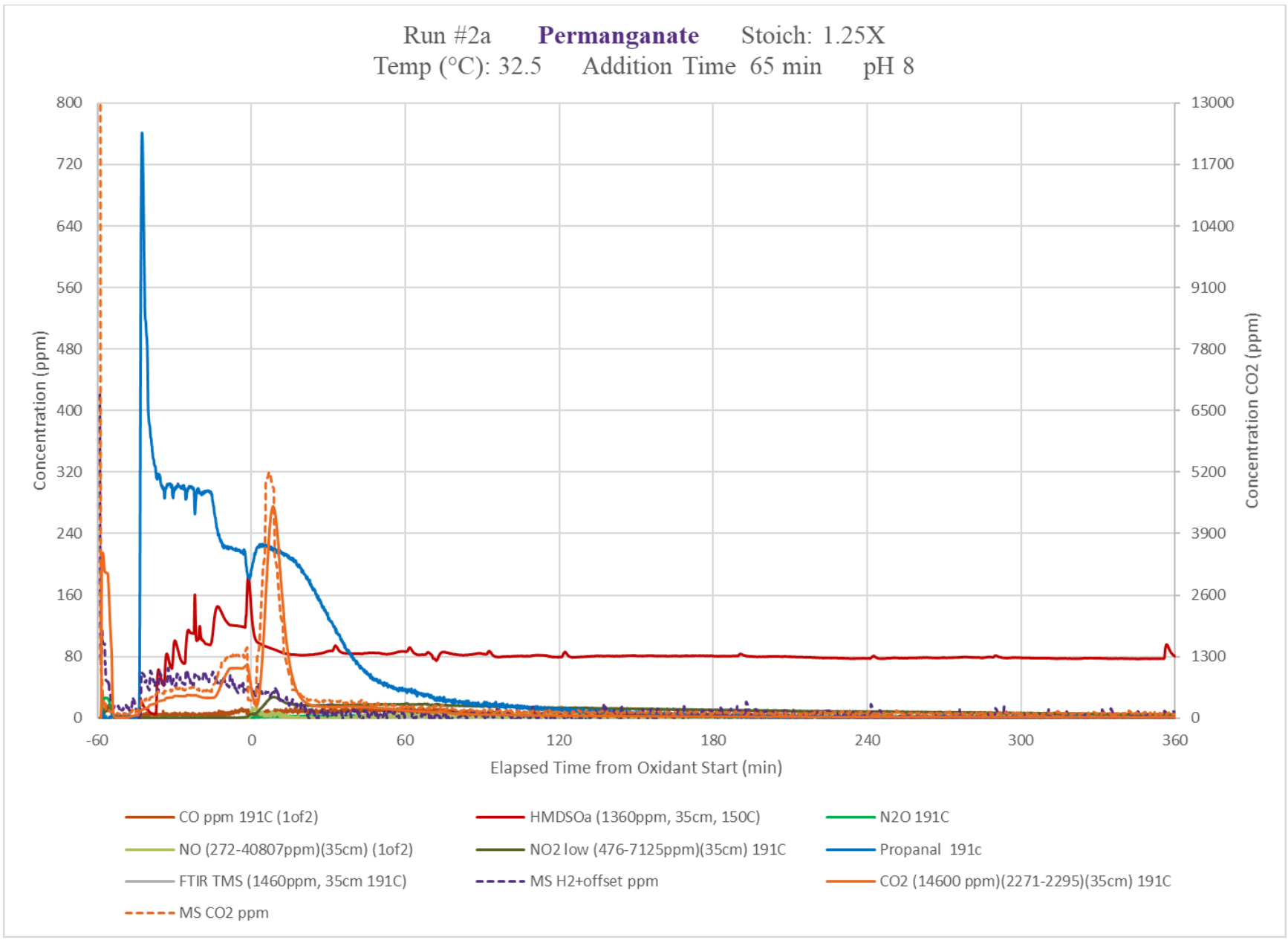


Figure B-21. Test 2a Offgas Profile CO, CO_2, H_2, NO, NO_2, N_2O, TMS, HMDSO, and Propanal

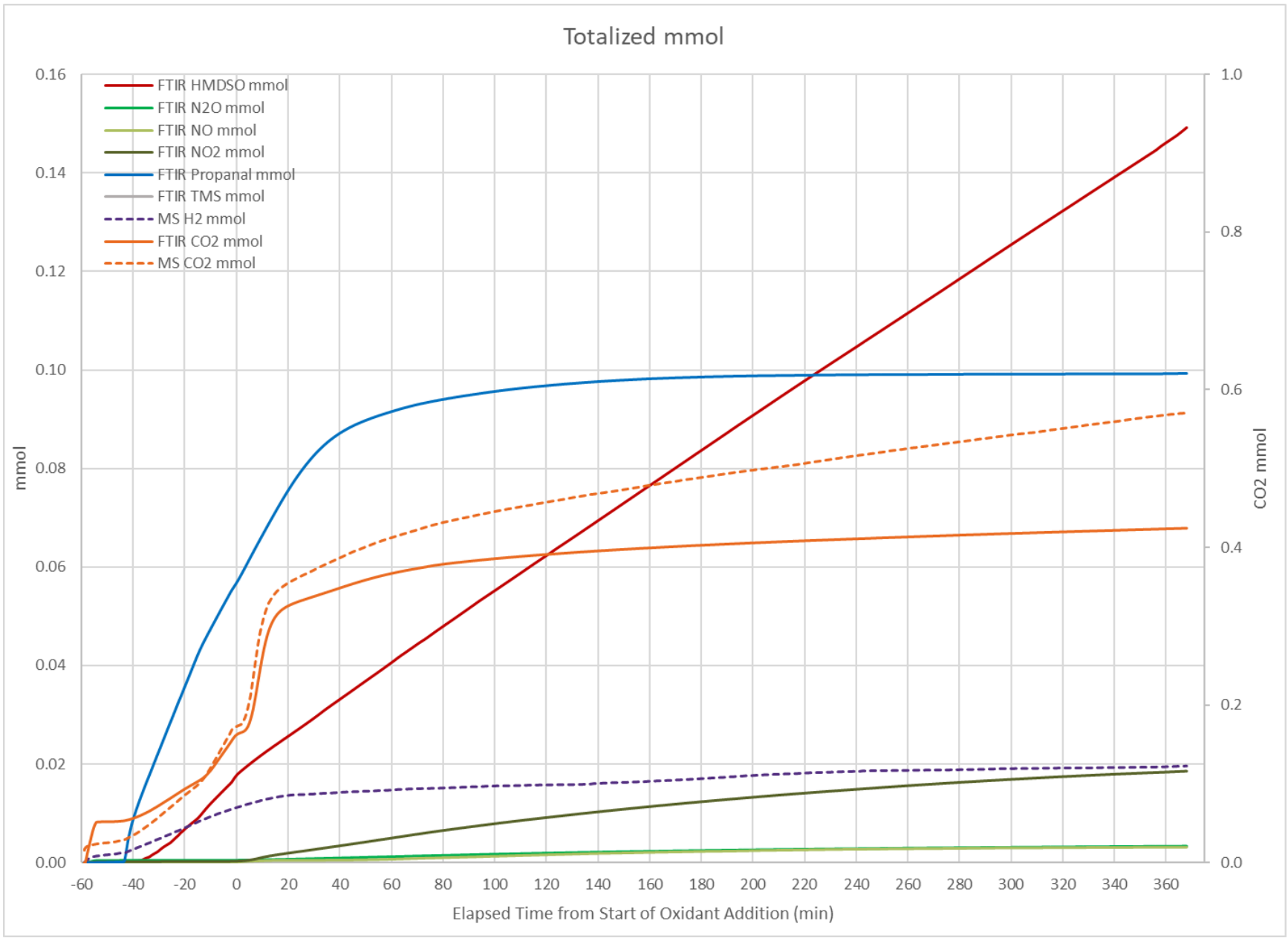


Figure B-22. Test 2a Totalized Offgas CO_2, H_2, NO, NO_2, N_2O, TMS, HMDSO, and Propanal

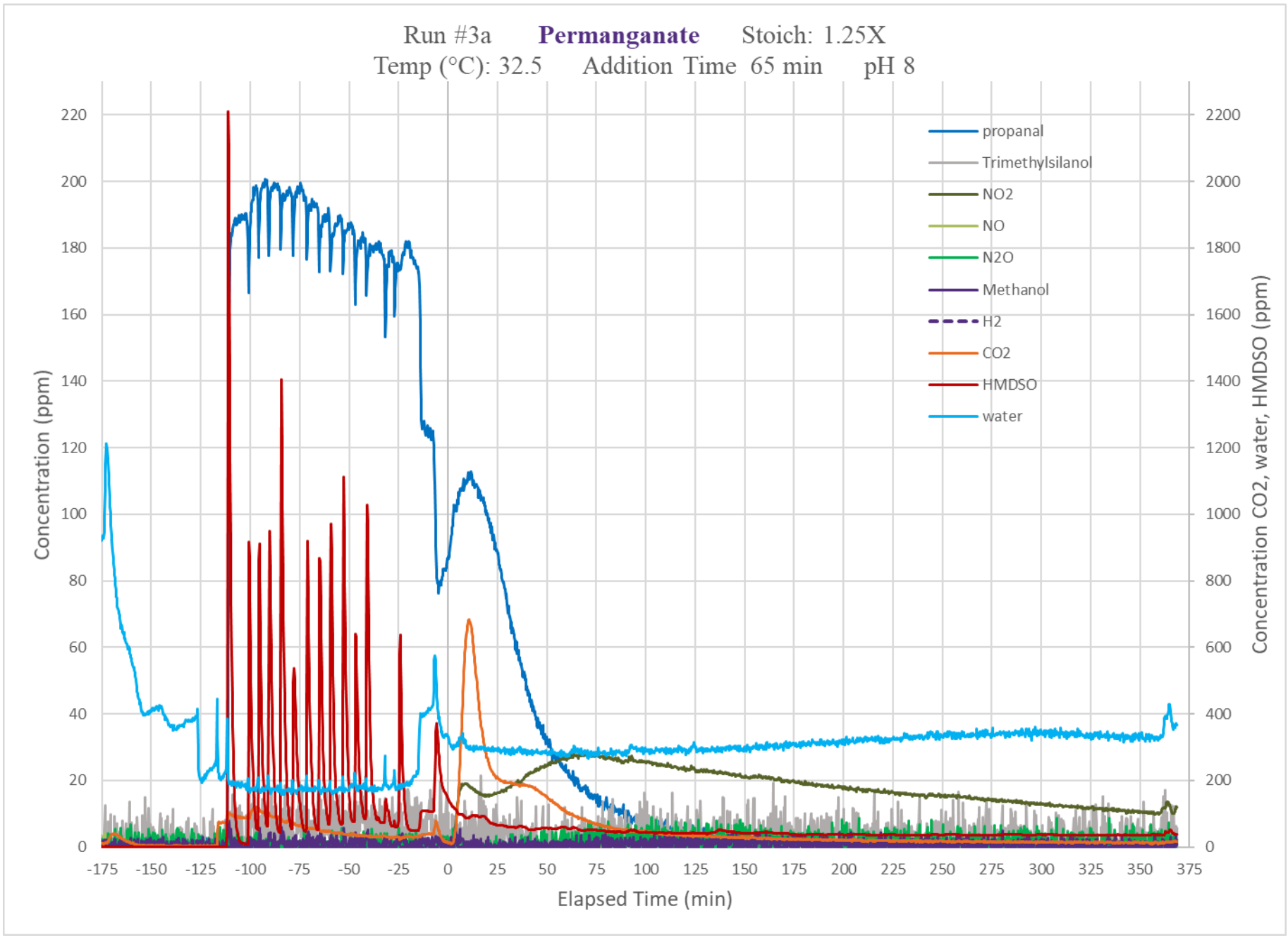


Figure B-23. Test 3a Offgas Profile CO_2, H_2, NO, NO_2, N_2O, Methanol, TMS, HMDSO, and Propanal

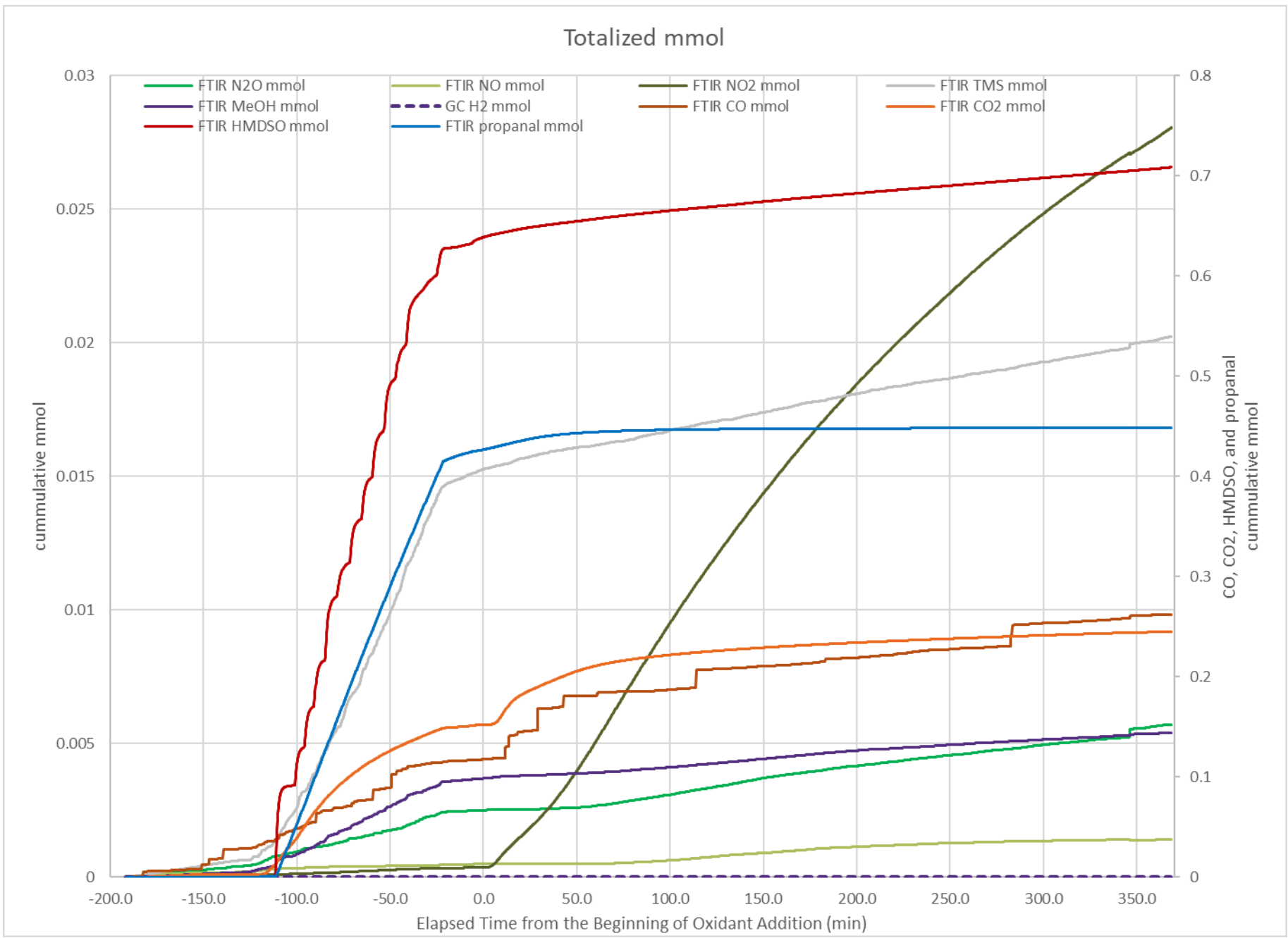


Figure B-24. Test 3a Totalized Offgas CO, CO_2, H_2, NO, NO_2, N_2O, Methanol, TMS, HMDSO, and Propanal

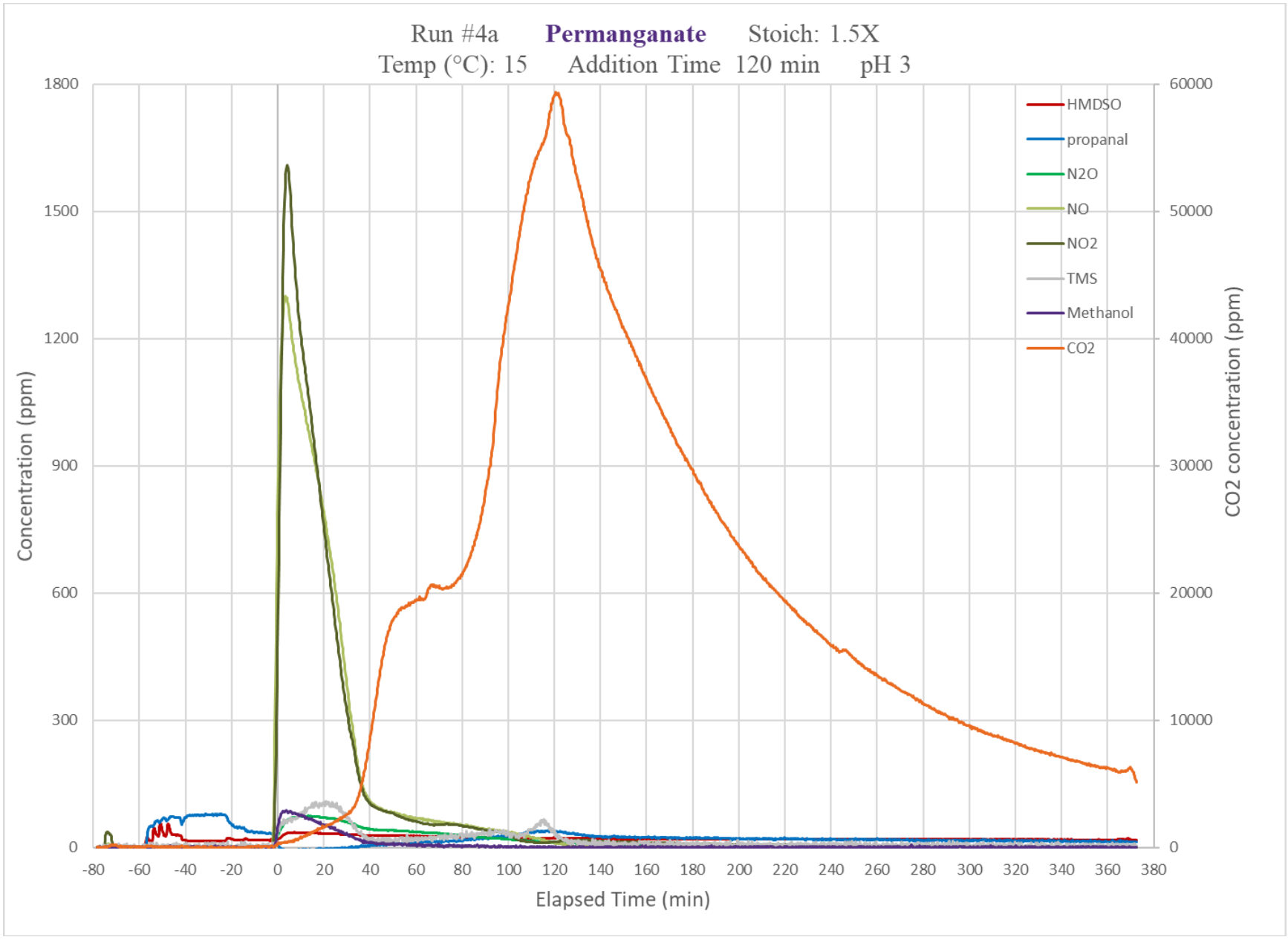


Figure B-25. Test 4a Offgas Profile CO, CO_2, NO, NO_2, N_2O, TMS, HMDSO, and Propanal

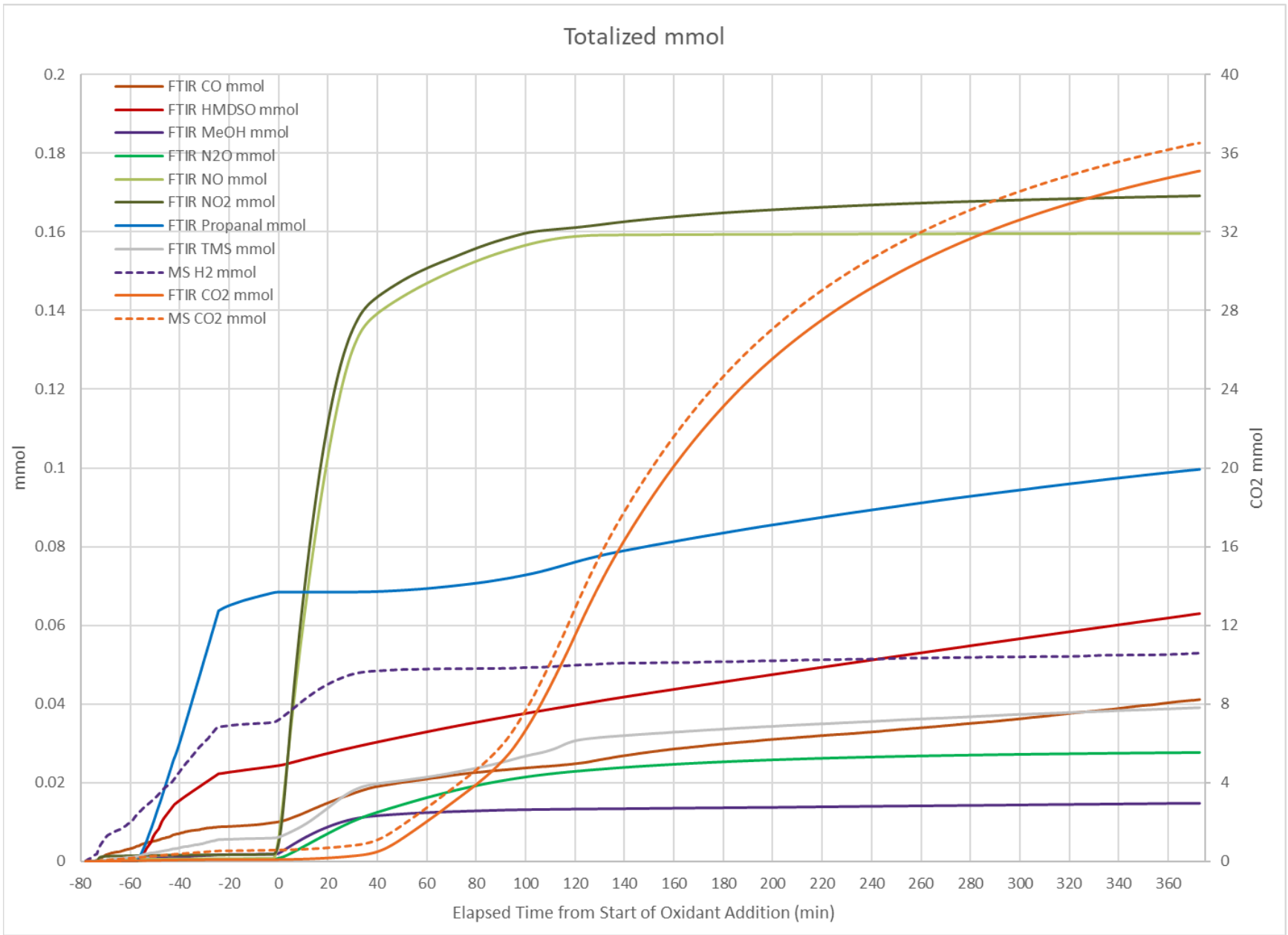


Figure B-26. Test 4a Totalized Offgas CO, CO_2, H_2, NO, NO_2, N_2O, Methanol, TMS, HMDSO, and Propanal

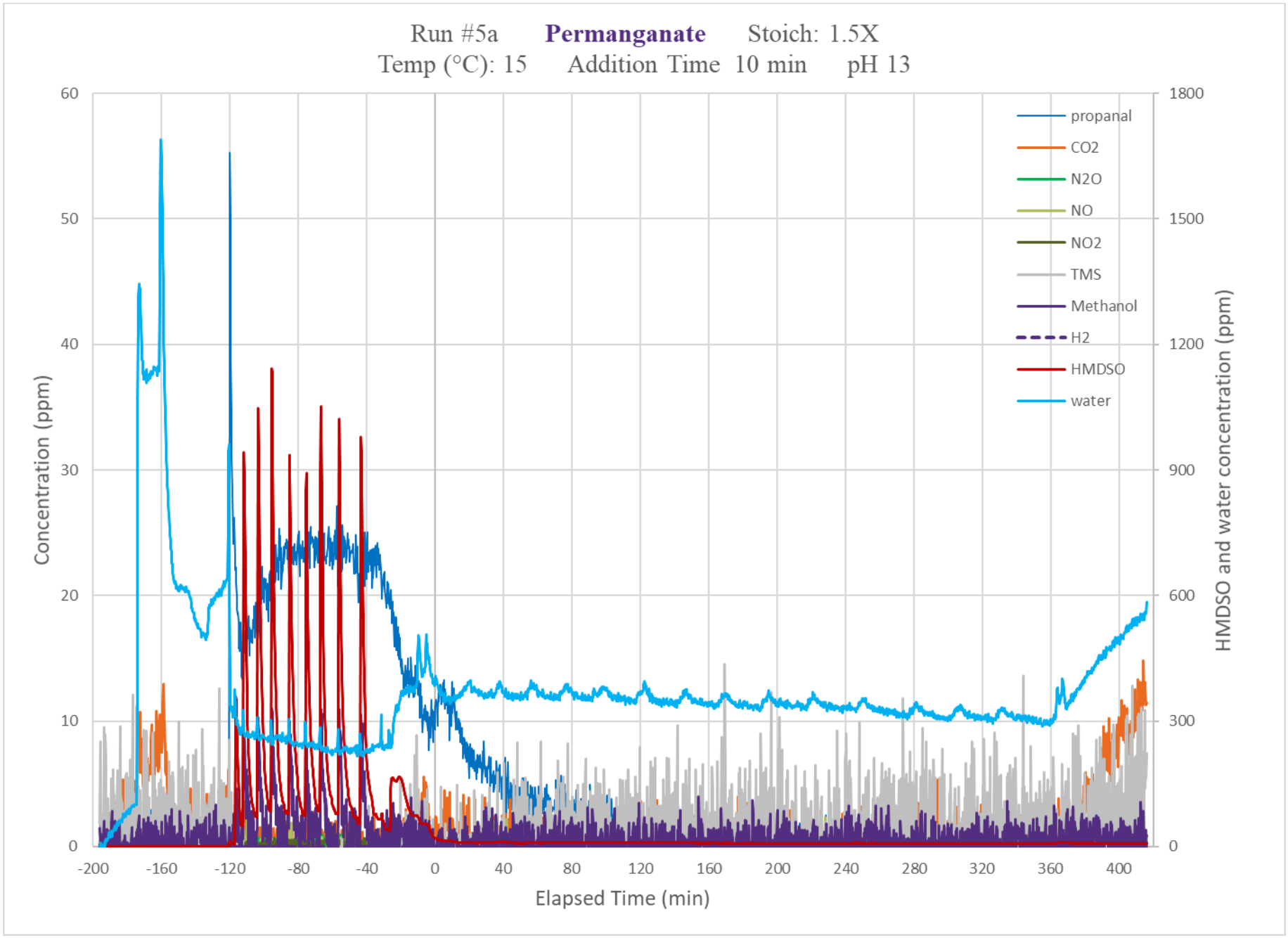


Figure B-27. Test 5a Offgas Profile CO_2, H_2, NO, NO_2, N_2O, Methanol, TMS, HMDSO, and Propanal

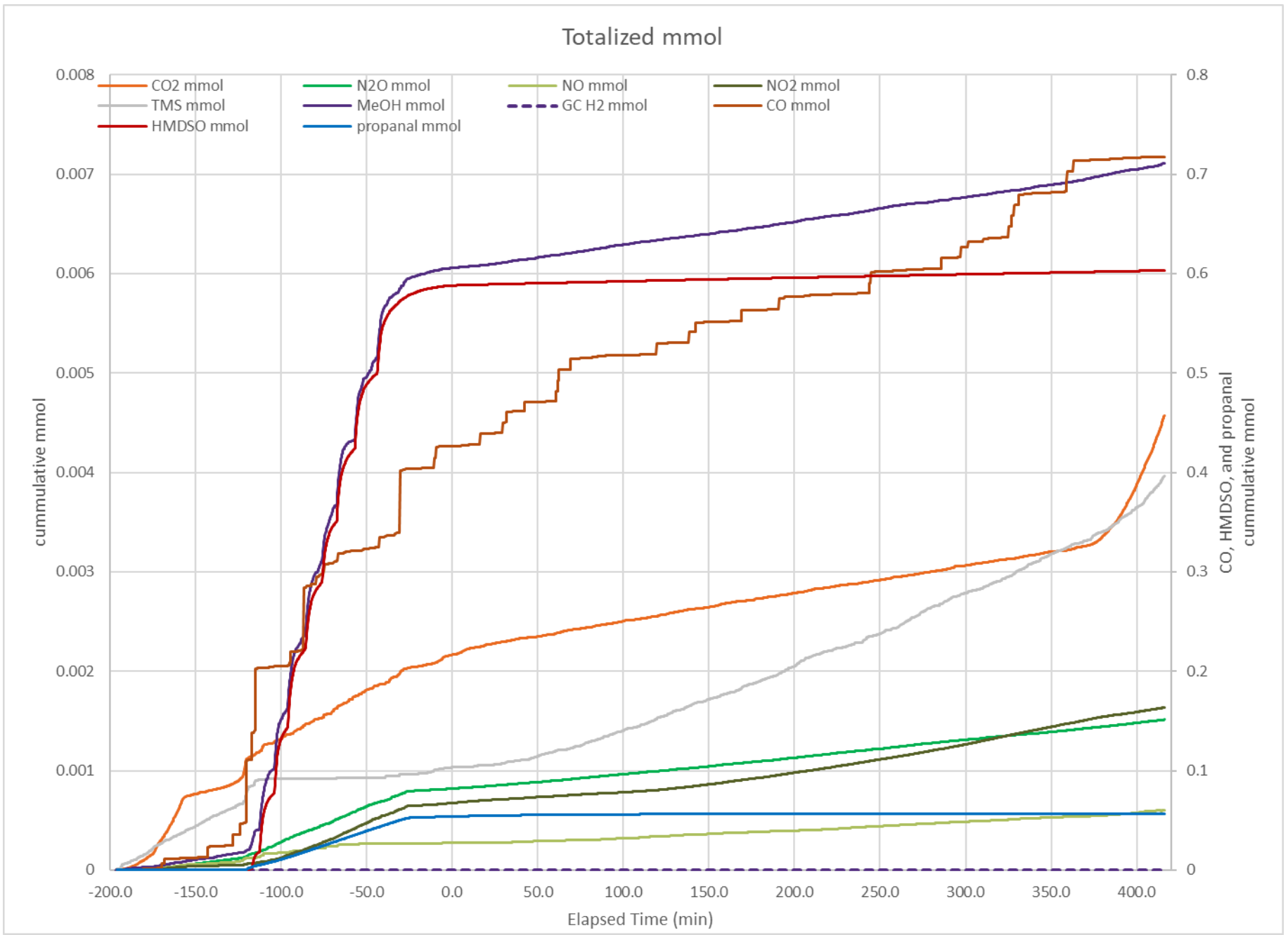


Figure B-28. Test 5a Totalized Offgas CO, CO_2, H_2, NO, NO_2, N_2O, Methanol, TMS, HMDSO, and Propanal

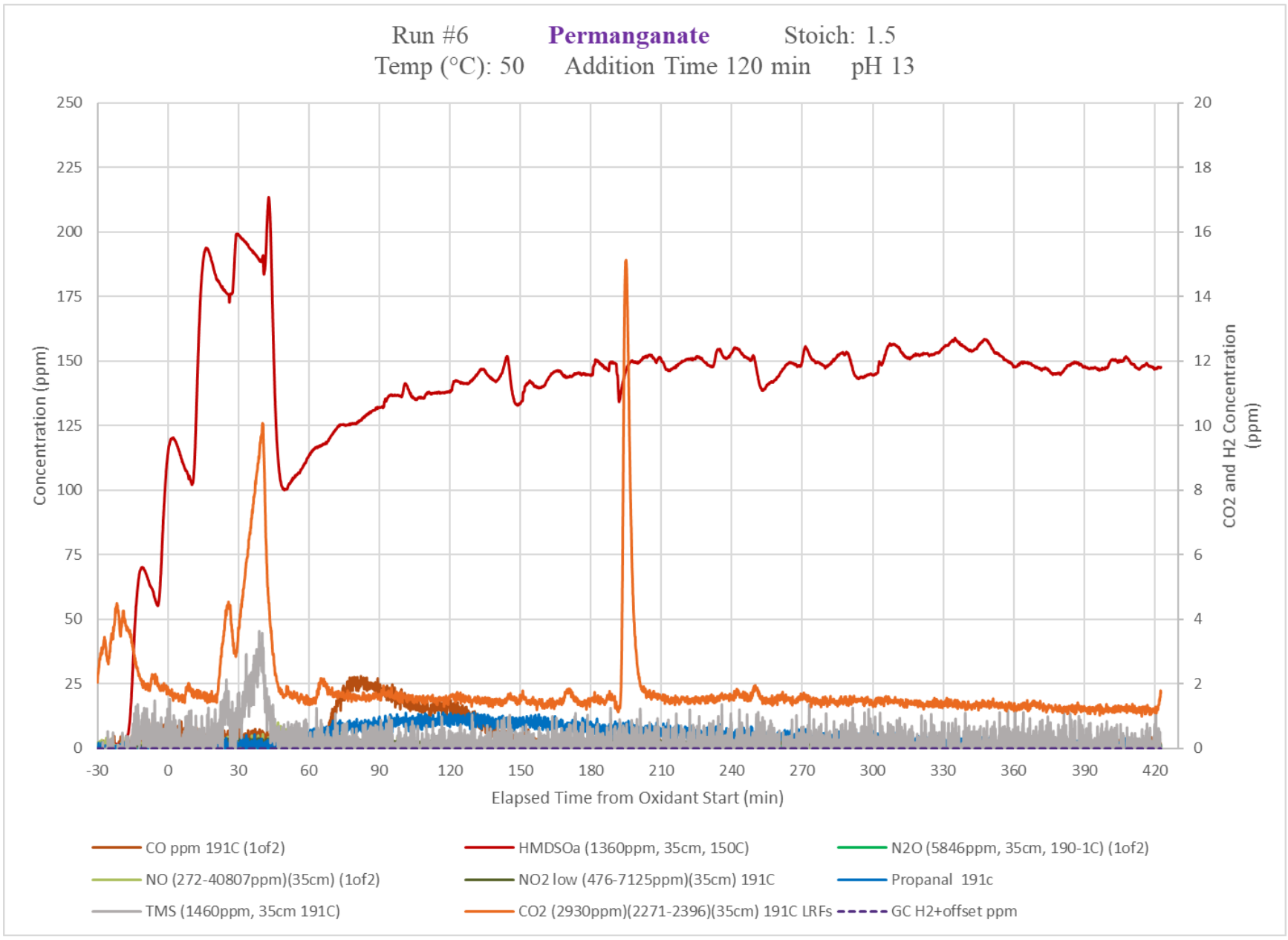


Figure B-29. Test 6a Offgas Profile CO, CO_2, H_2, NO, NO_2, N_2O, TMS, HMDSO, and Propanal

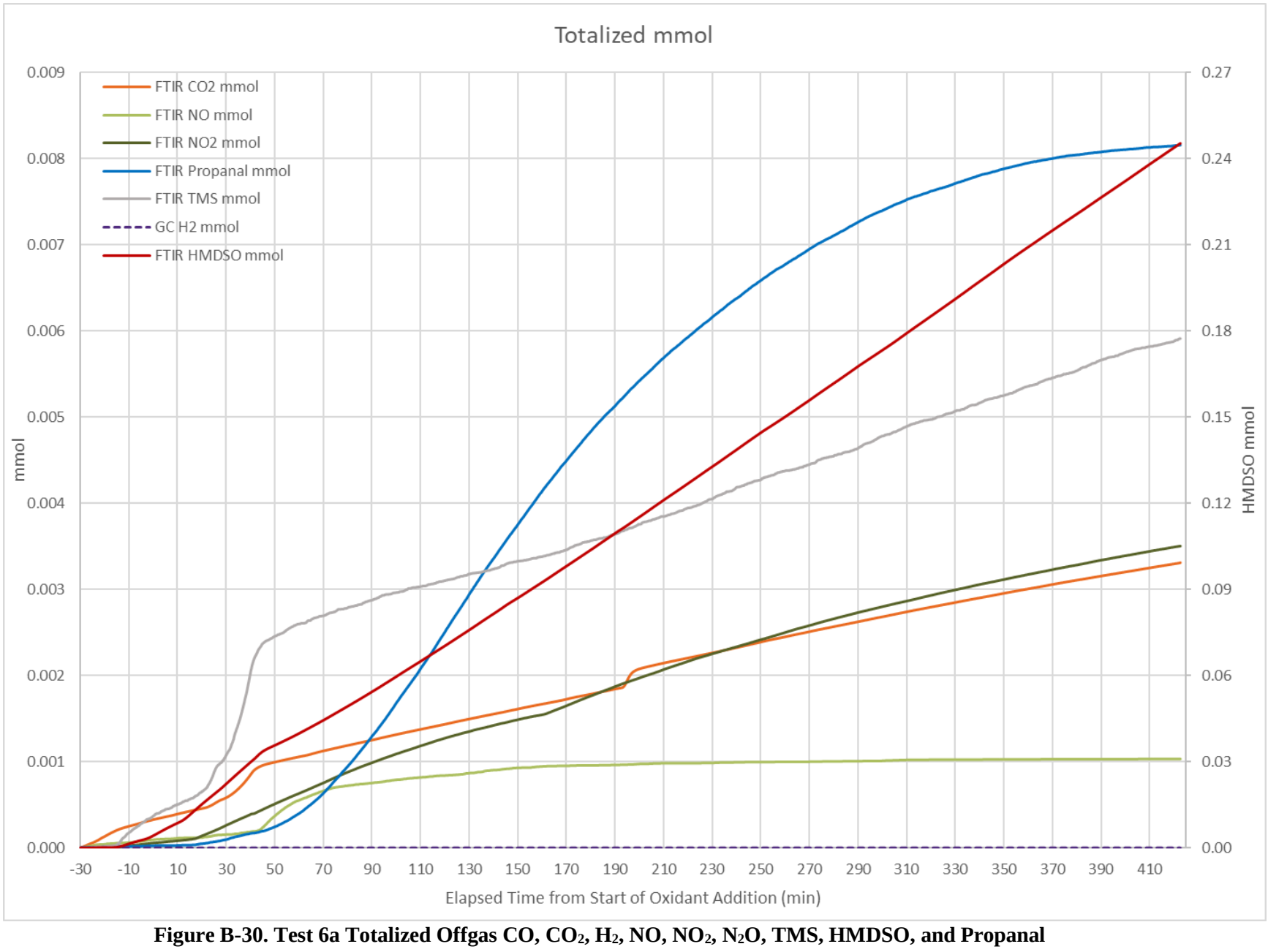


Figure B-30. Test 6a Totalized Offgas CO, CO_2, H_2, NO, NO_2, N_2O, TMS, HMDSO, and Propanal

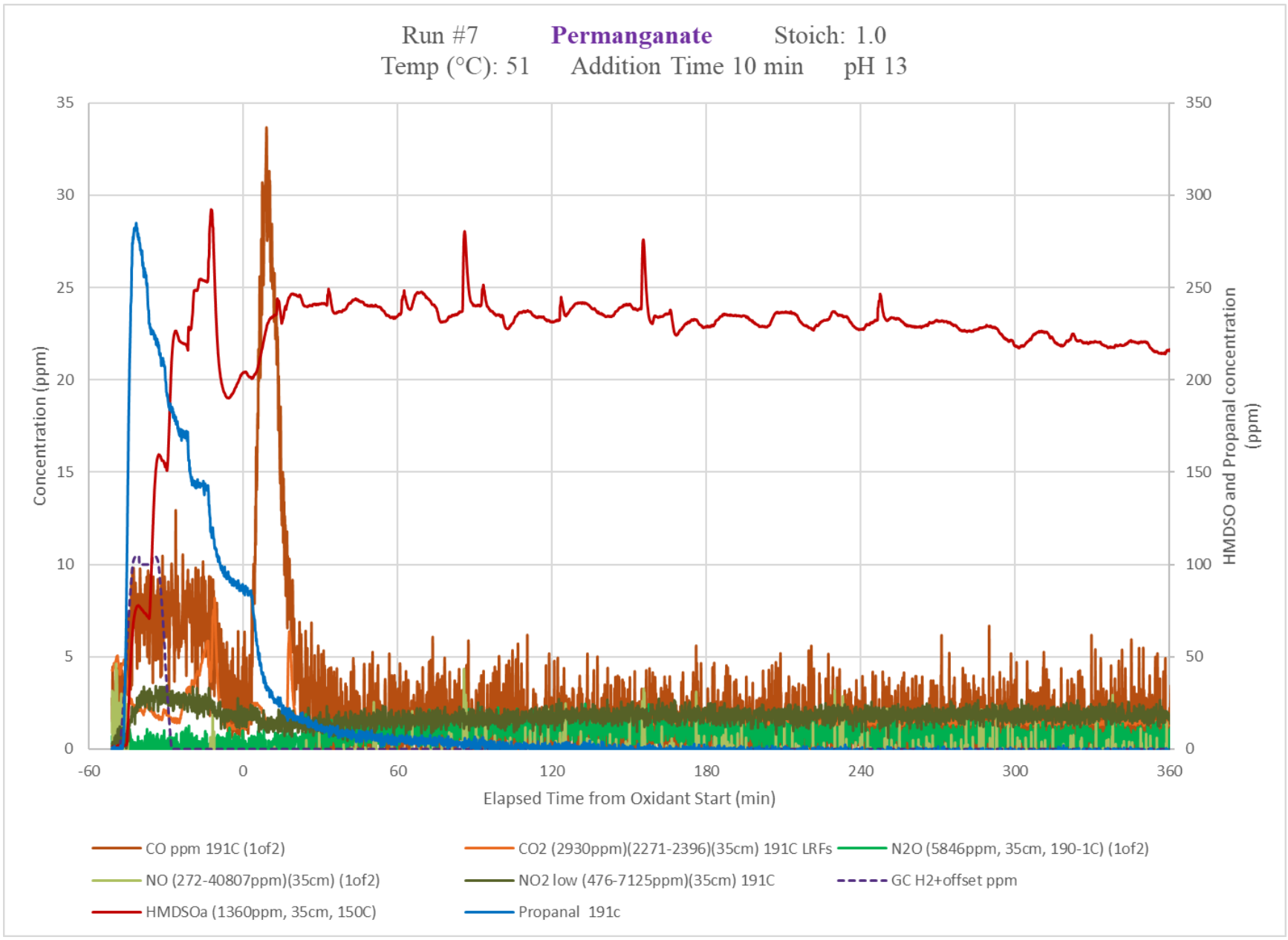


Figure B-31. Test 7 Offgas Profile CO, CO_2, H_2, NO, NO_2, N_2O, TMS, HMDSO, and Propanal

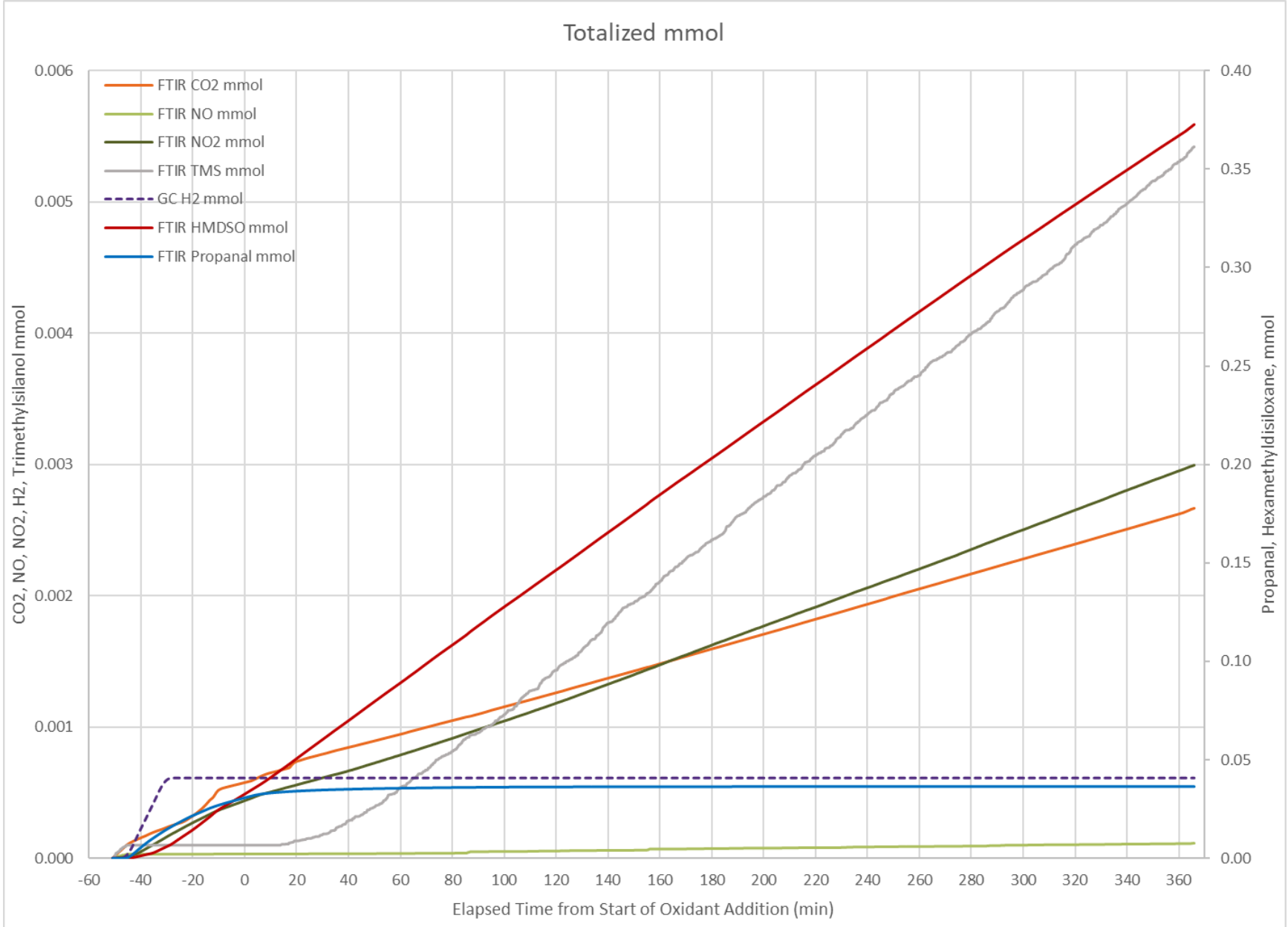


Figure B-32. Test 7 Totalized Offgas CO_2, H_2, NO, NO_2, N_2O, TMS, HMDSO, and Propanal

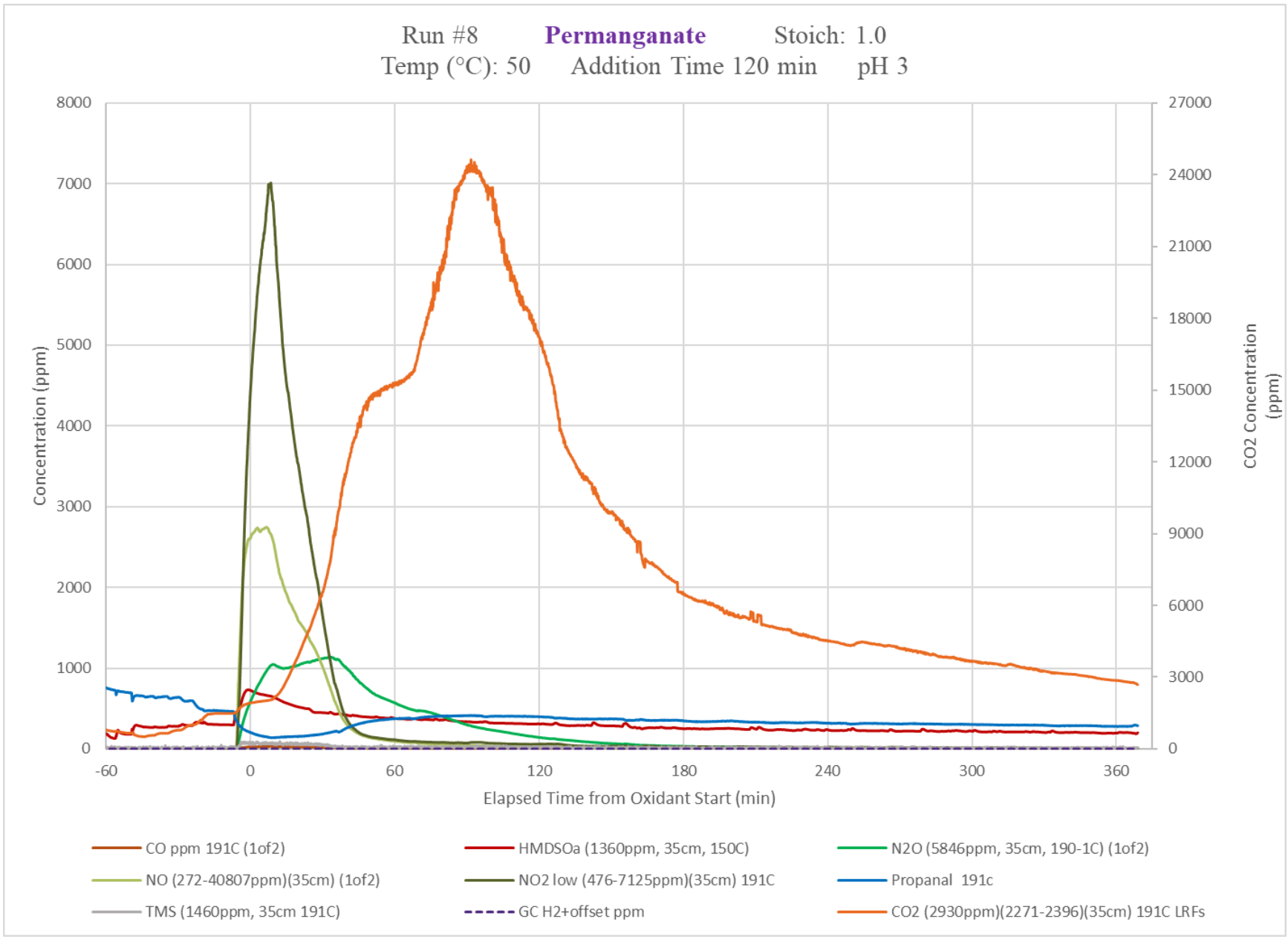


Figure B-33. Test 8 Offgas Profile CO, CO_2, H_2, NO, NO_2, N_2O, TMS, HMDSO, and Propanal

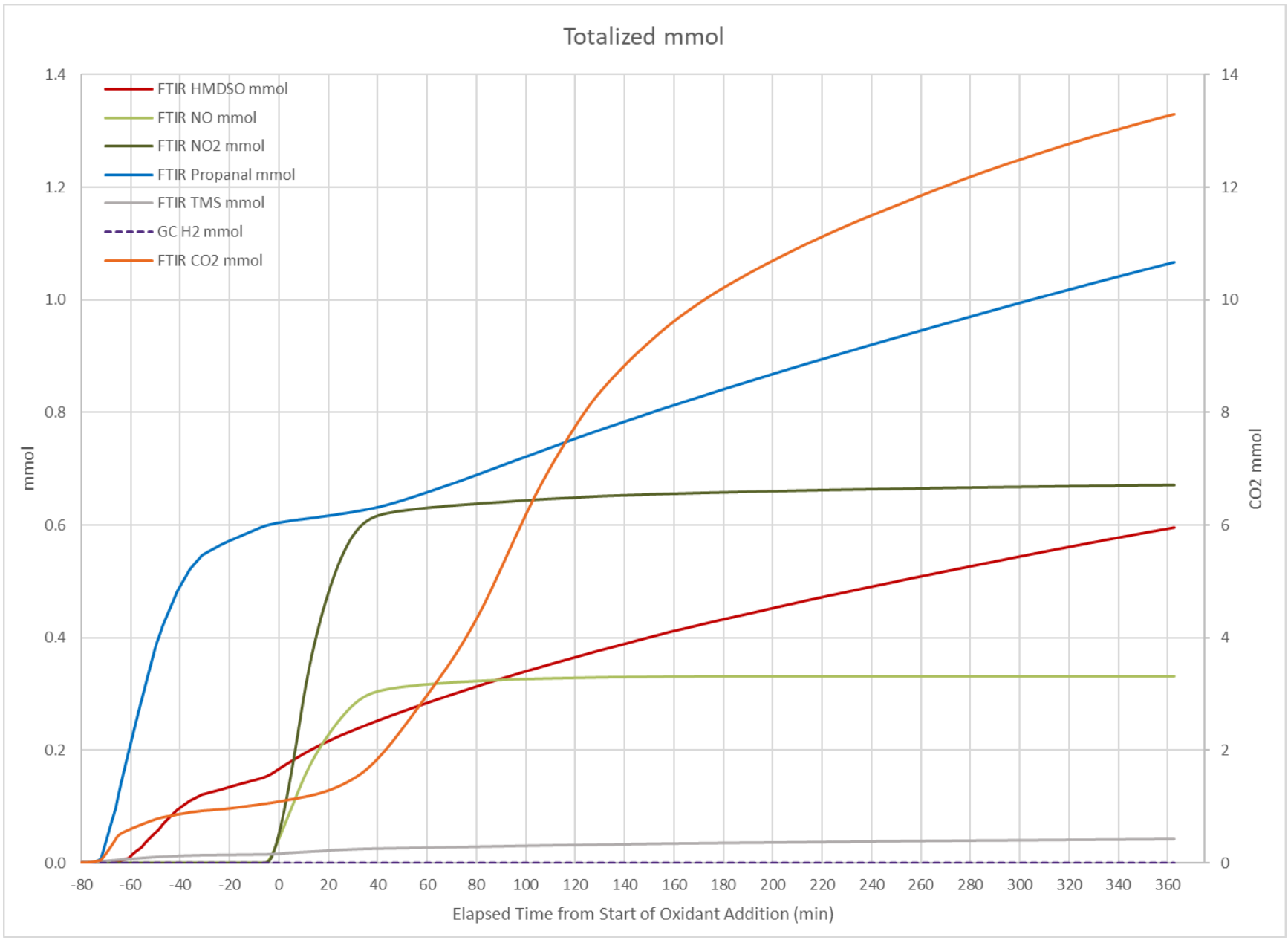


Figure B-34. Test 8 Totalized Offgas CO_2, H_2, NO, NO_2, N_2O, TMS, HMDSO, and Propanal

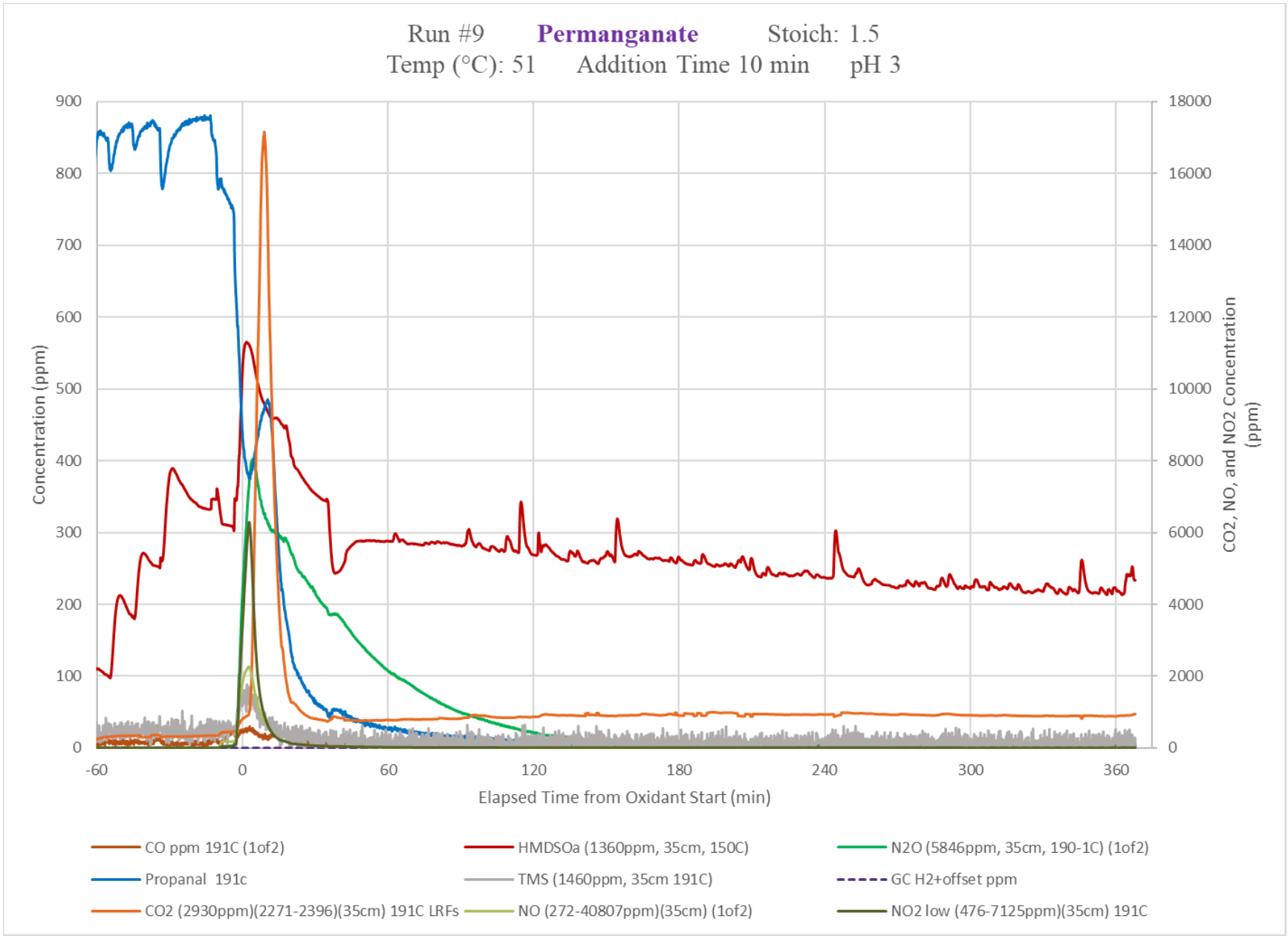


Figure B-35. Test 9 Offgas Profile CO, CO_2, H_2, NO, NO_2, N_2O, TMS, HMDSO, and Propanal

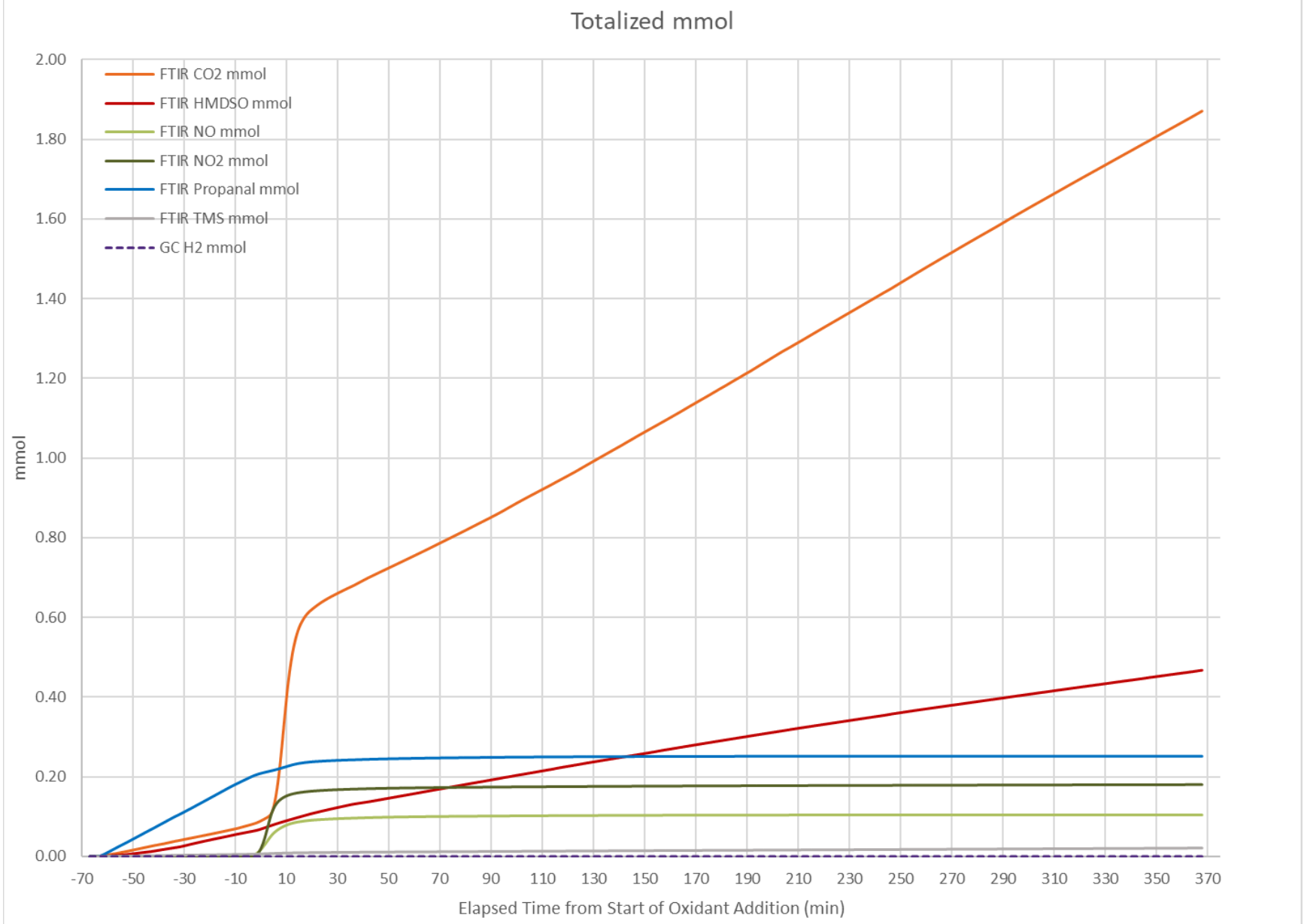


Figure B-36. Test 9 Totalized Offgas CO_2, H_2, NO, NO_2, N_2O, TMS, HMDSO, and Propanal

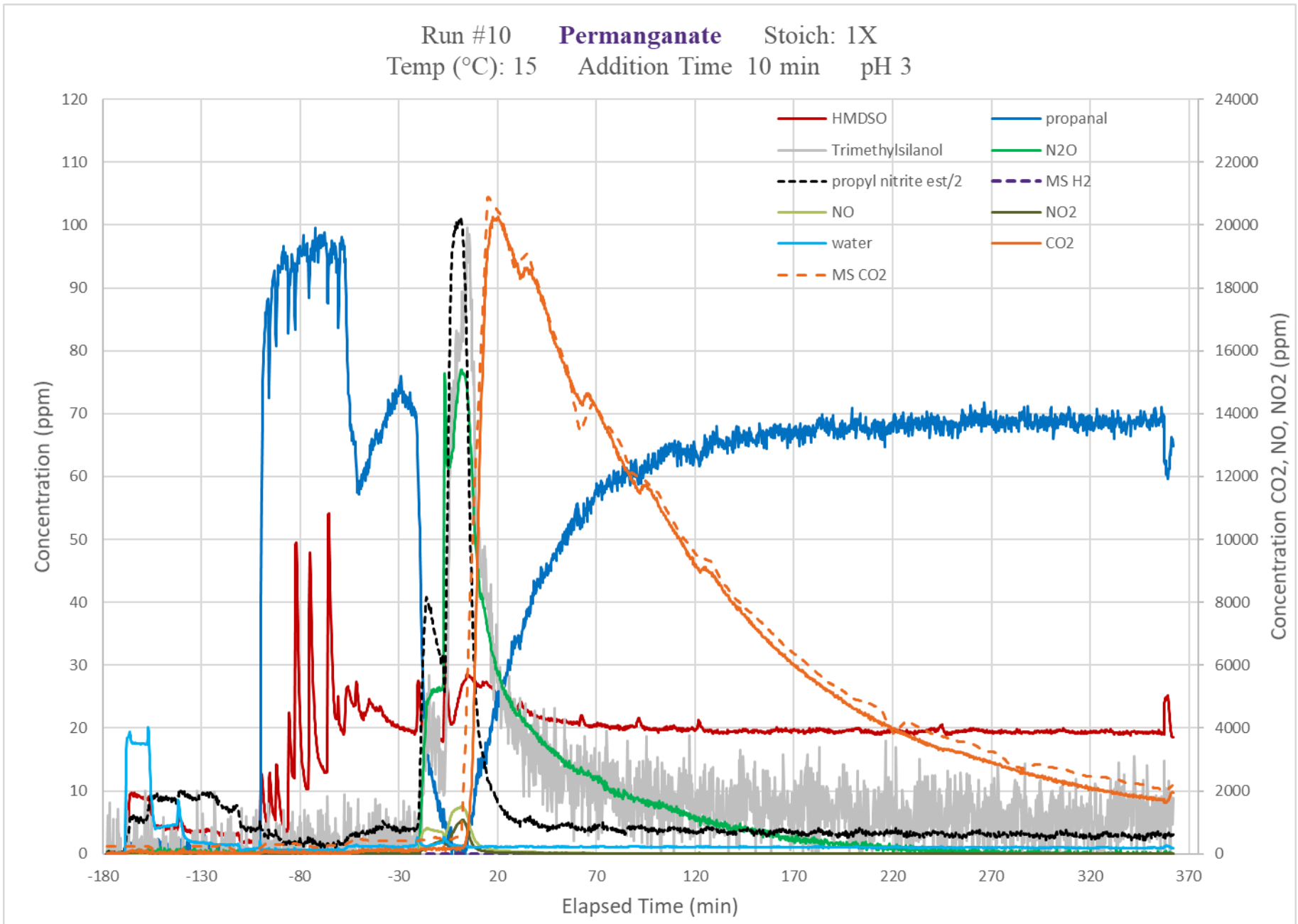


Figure B-37. Test 10 Offgas Profile CO_2, H_2, NO, NO_2, N_2O, Methanol, TMS, HMDSO, and Propanal

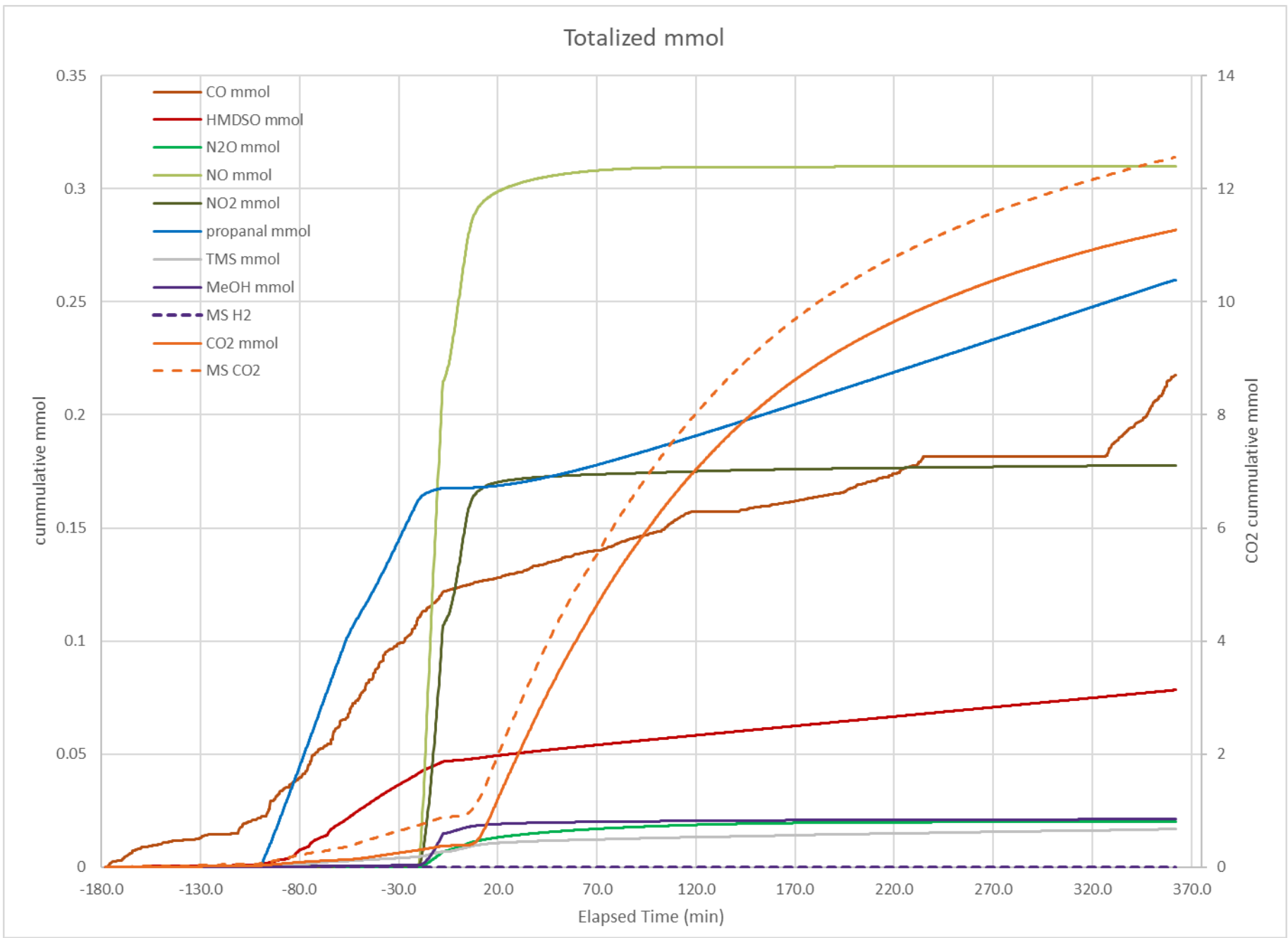


Figure B-38. Test 10 Totalized Offgas CO, CO_2, H_2, NO, NO_2, N_2O, TMS, HMDSO, and Propanal

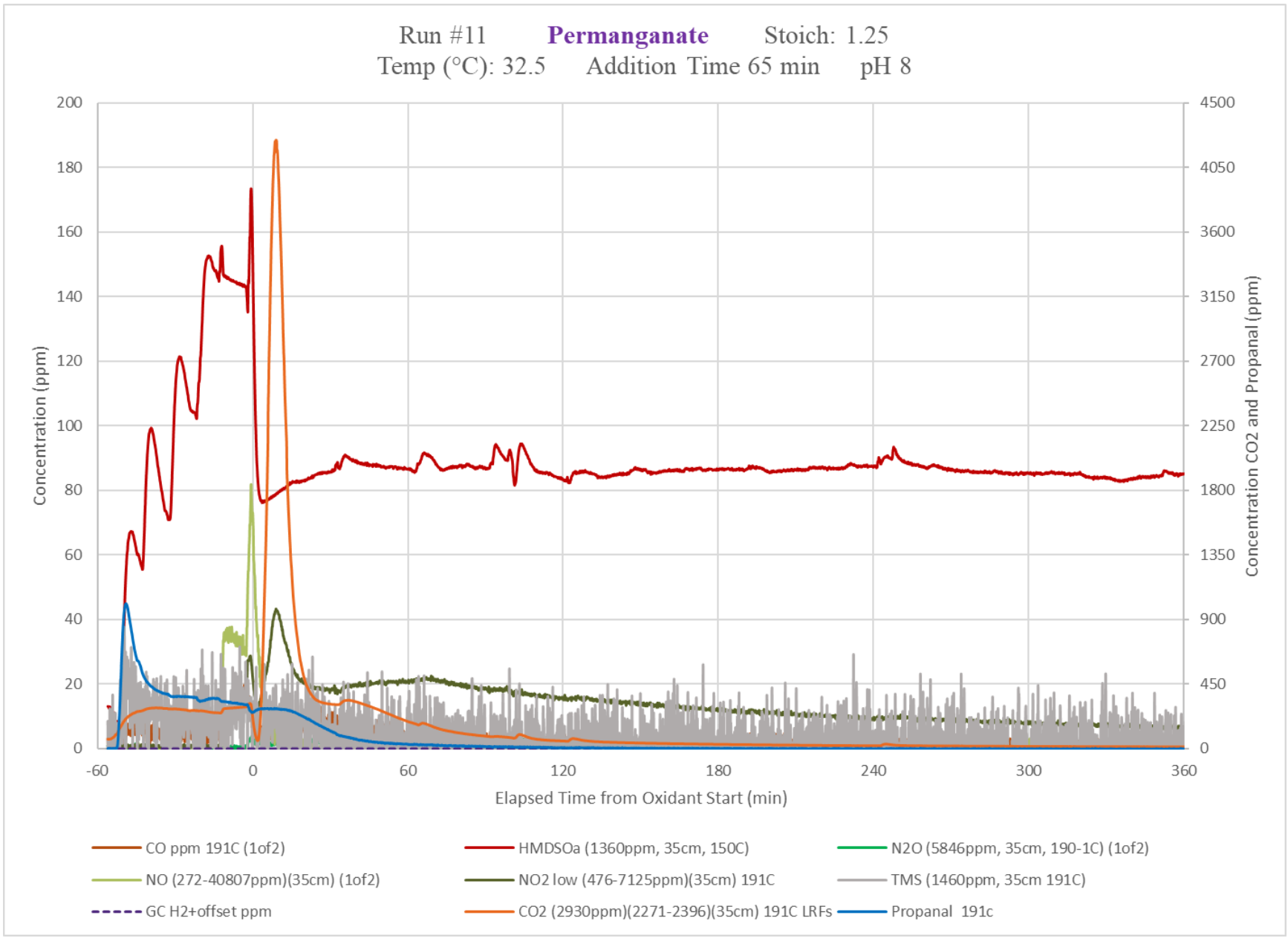


Figure B-39. Test 11 Offgas Profile CO, CO_2, H_2, NO, NO_2, N_2O, TMS, HMDSO, and Propanal

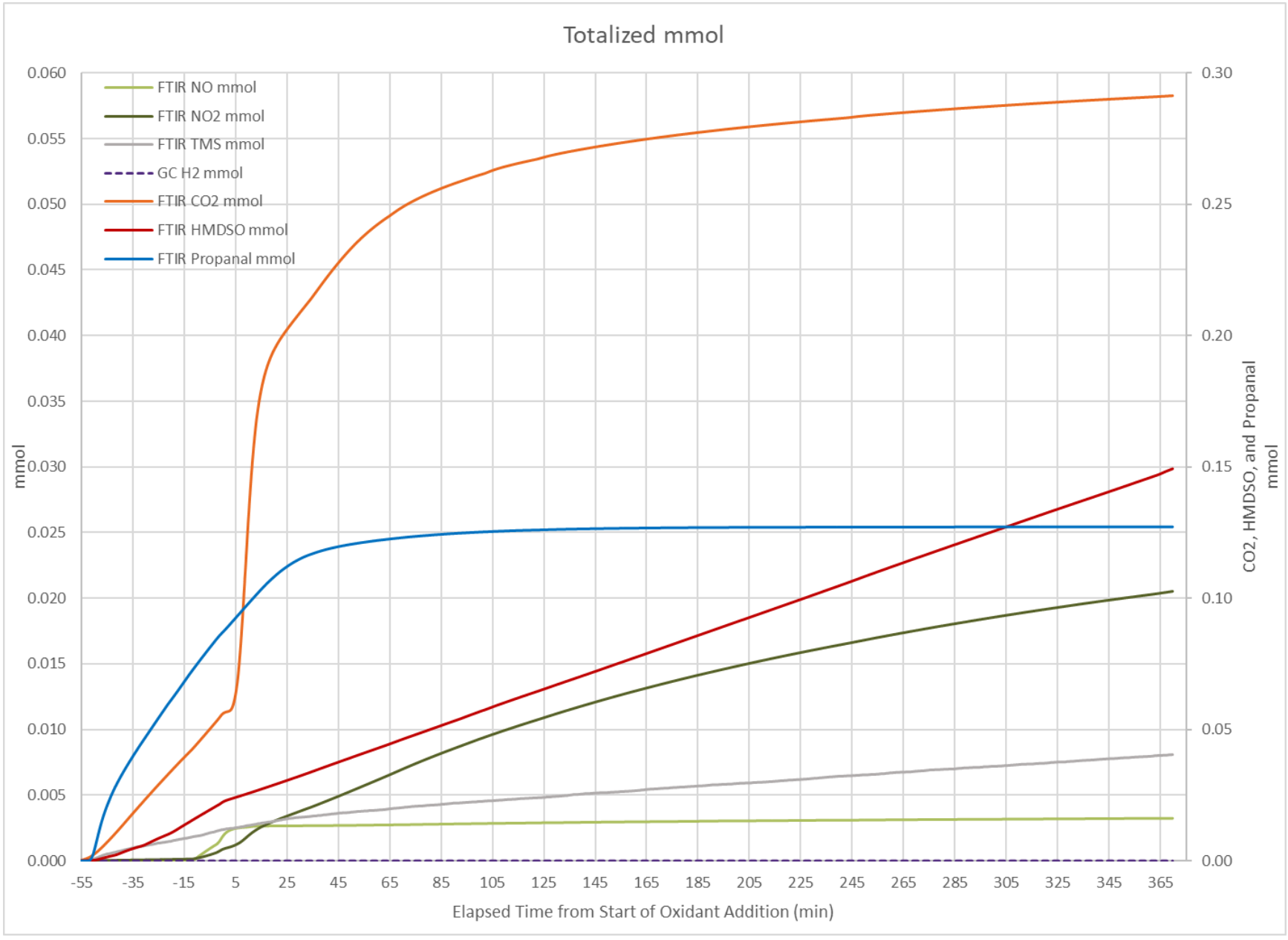


Figure B-40. Test 11 Totalized Offgas CO_2, H_2, NO, NO_2, N_2O, TMS, HMDSO, and Propanal

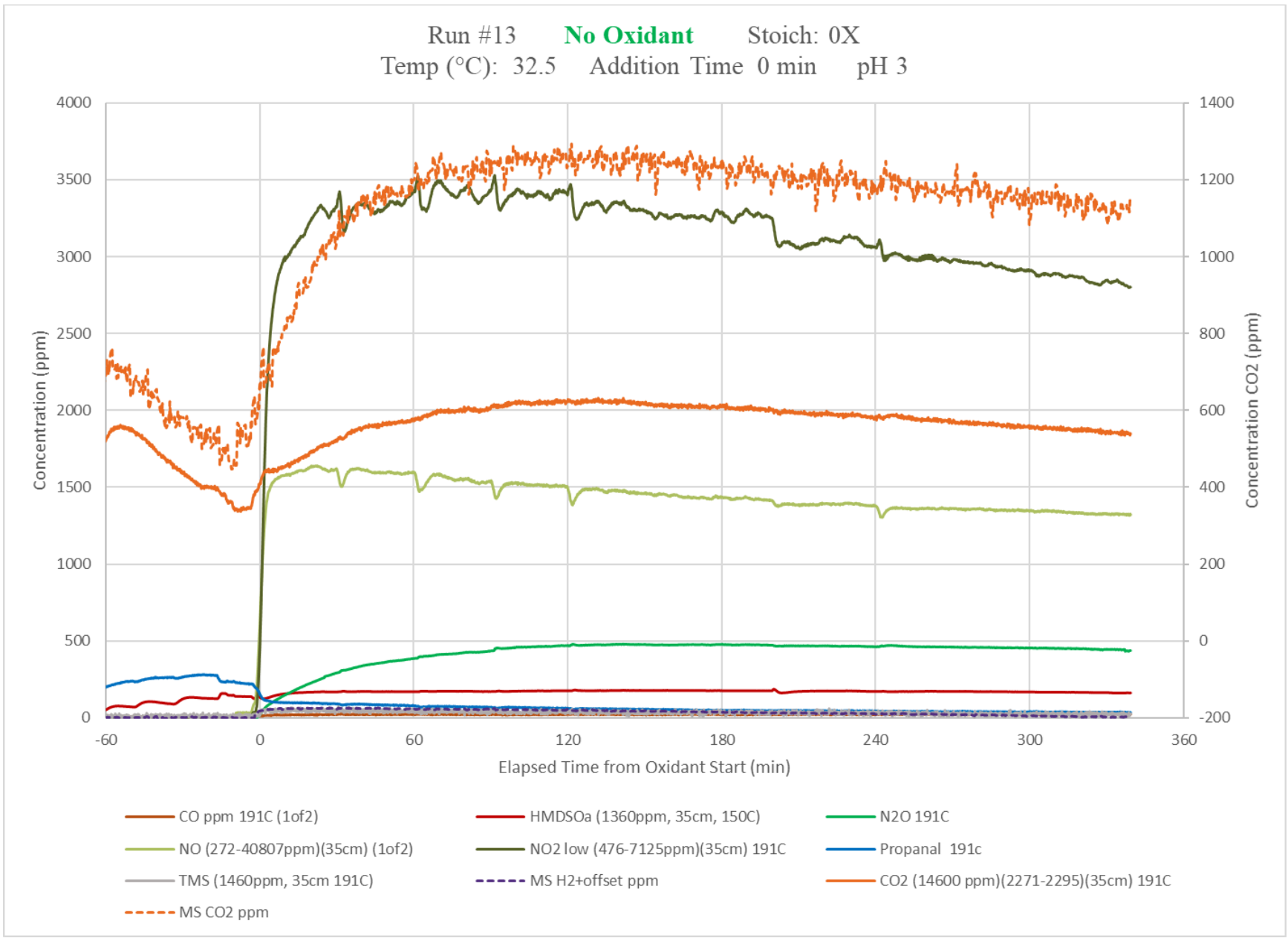


Figure B-41. Test 13 Offgas Profile CO, CO_2, H_2, NO, NO_2, N_2O, TMS, HMDSO, and Propanal

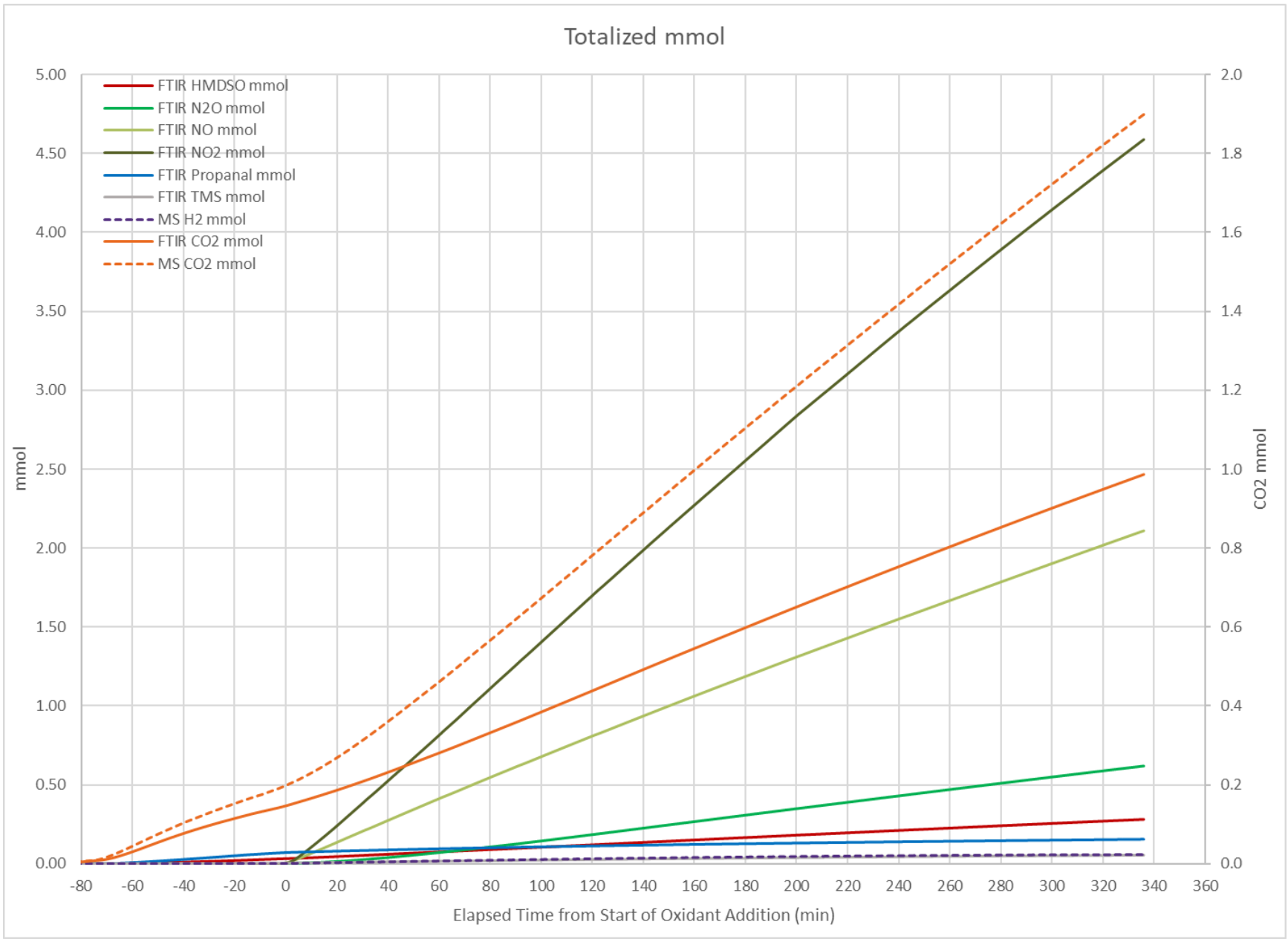


Figure B-42. Test 13 Totalized Offgas CO_2, H_2, NO, NO_2, N_2O, TMS, HMDSO, and Propanal

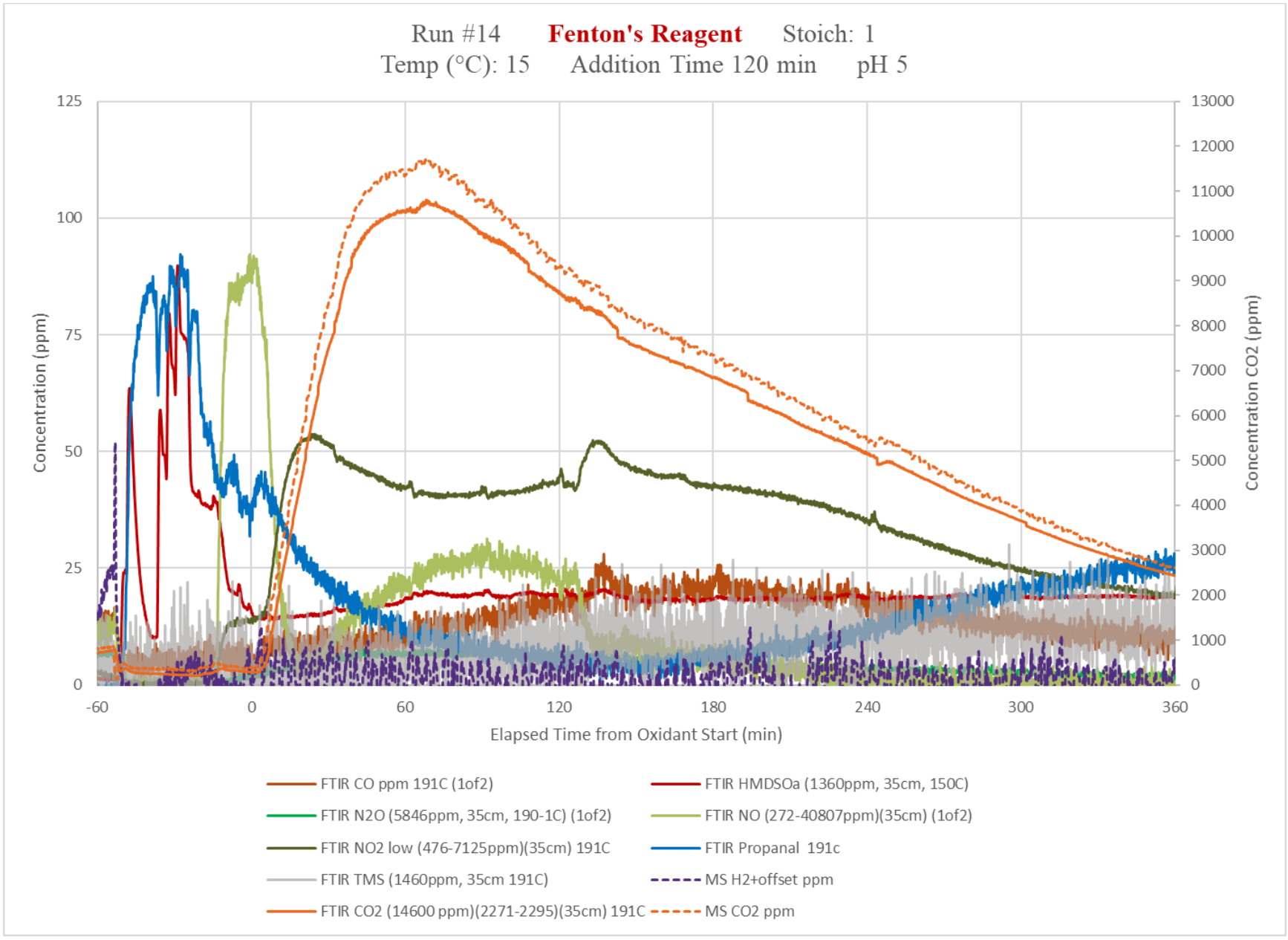


Figure B-43. Test 14 Offgas Profile CO, CO_2, H_2, NO, NO_2, N_2O, TMS, HMDSO, and Propanal

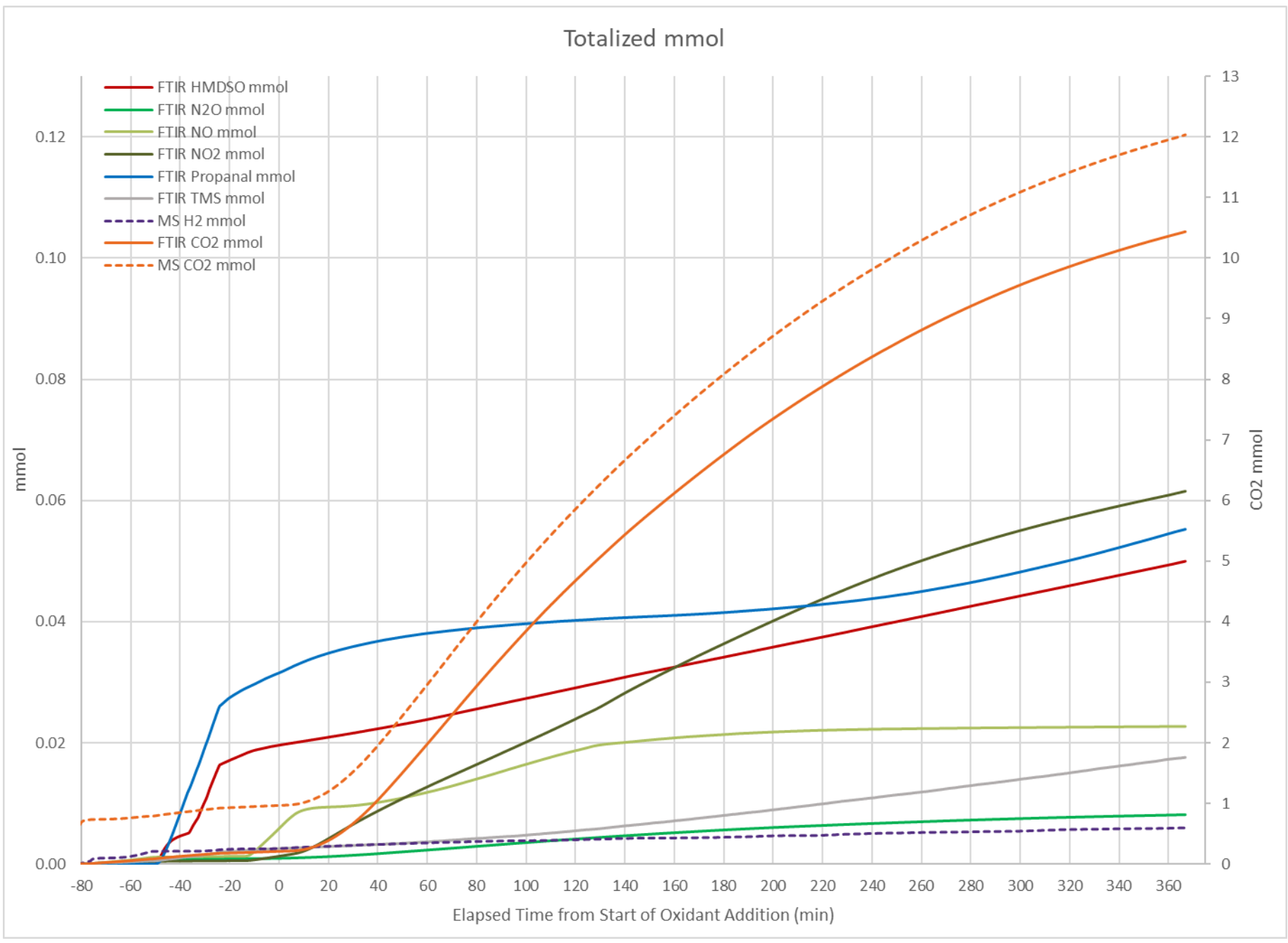


Figure B-44. Test 14 Totalized Offgas CO_2, H_2, NO, NO_2, N_2O, TMS, HMDSO, and Propanal

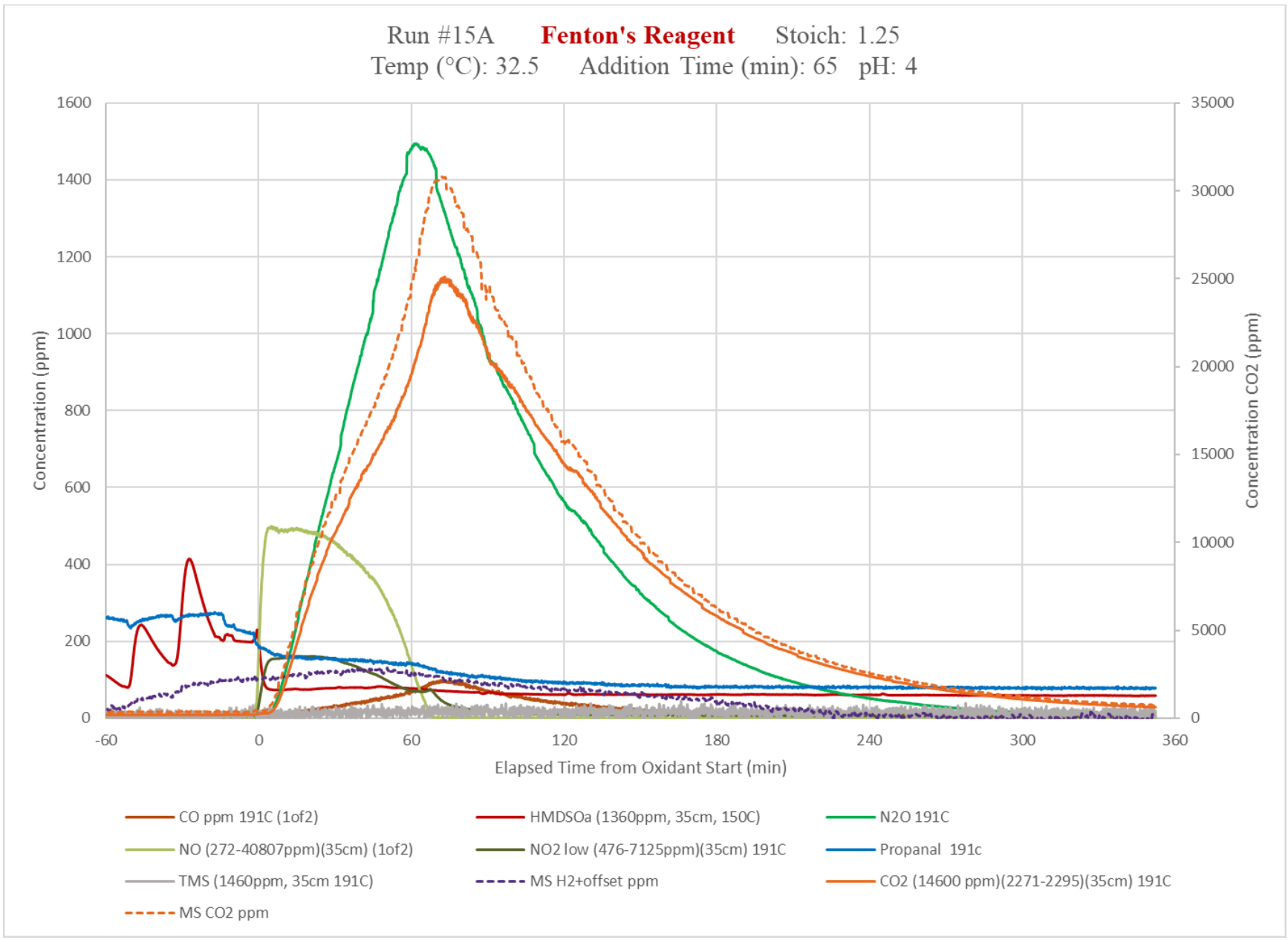


Figure B-45. Test 15a Offgas Profile CO, CO_2, H_2, NO, NO_2, N_2O, TMS, HMDSO, and Propanal

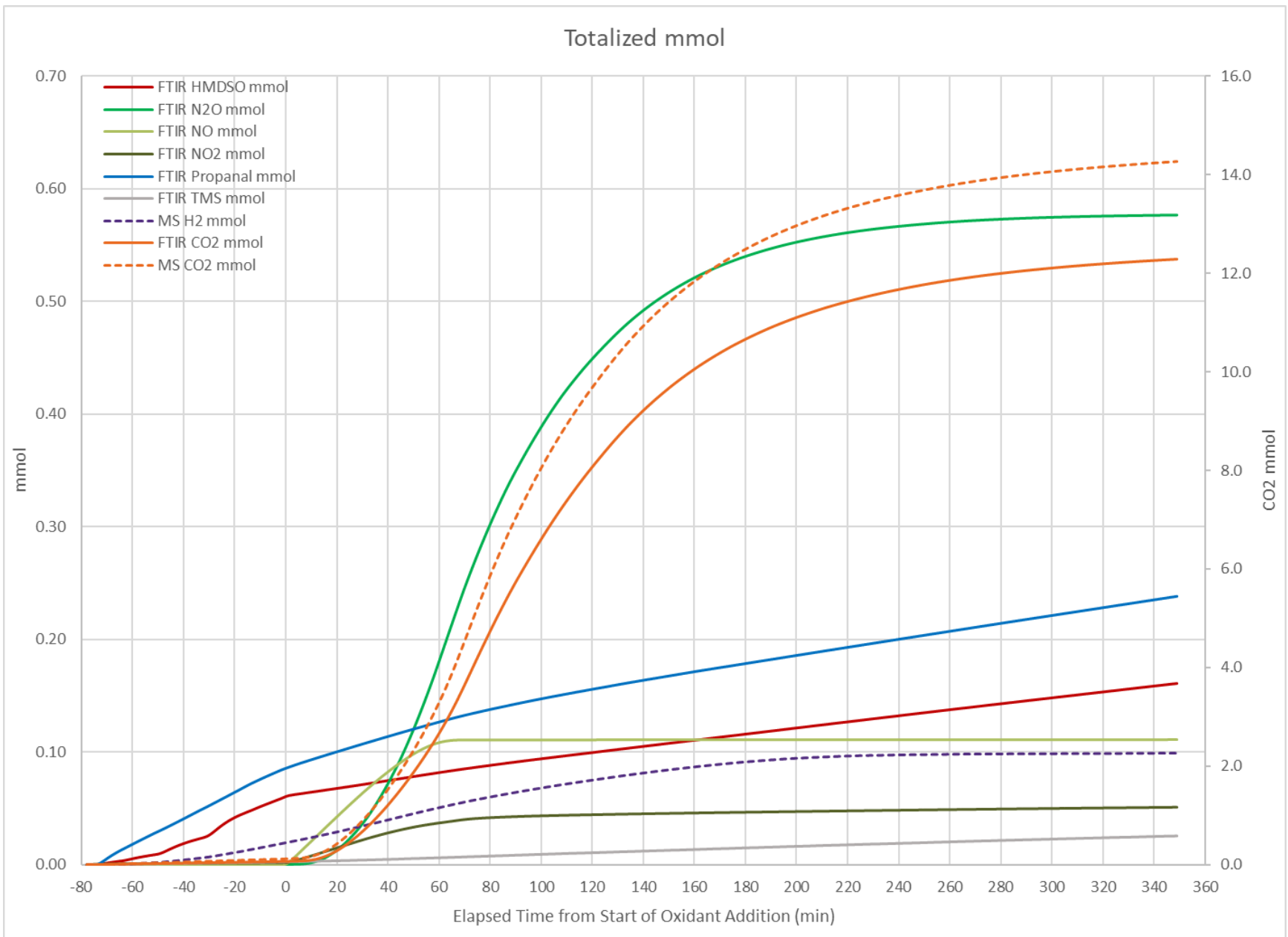


Figure B-46. Test 15a Totalized Offgas CO_2, H_2, NO, NO_2, N_2O, TMS, HMDSO, and Propanal

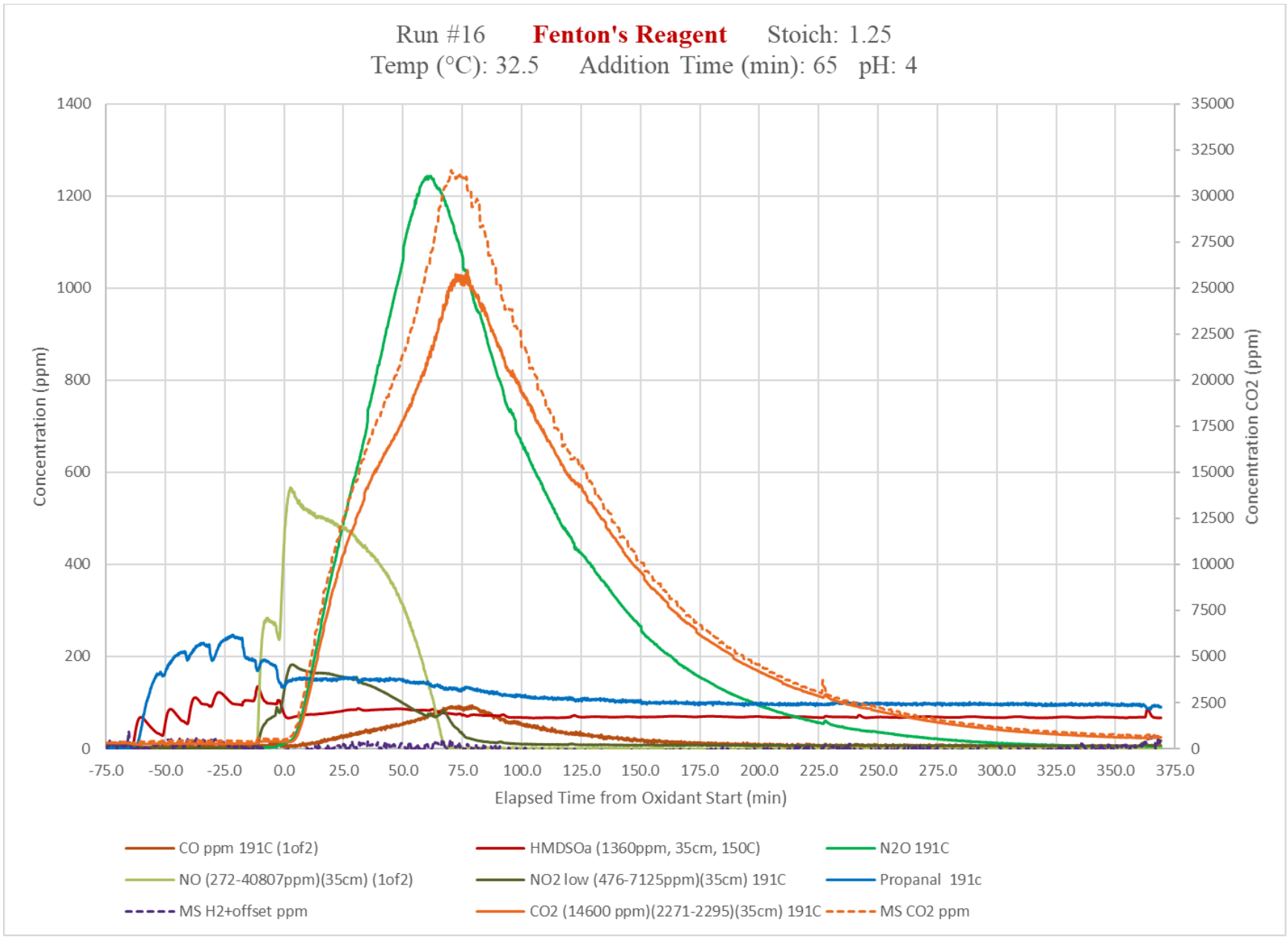


Figure B-47. Test 16 Offgas Profile CO, CO_2, H_2, NO, NO_2, N_2O, TMS, HMDSO, and Propanal

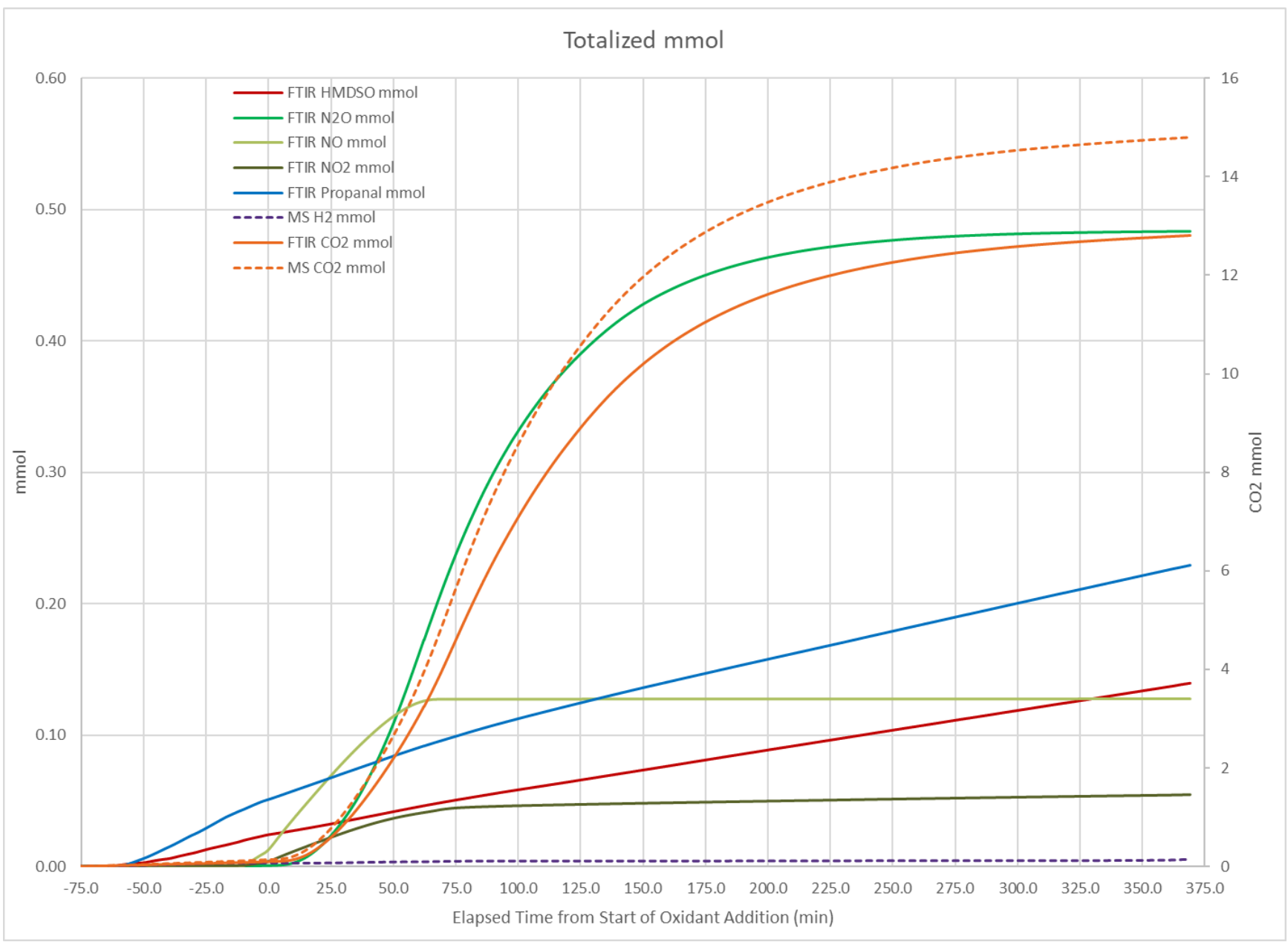


Figure B-48. Test 16 Totalized Offgas CO_2, H_2, NO, NO_2, N_2O, HMDSO, and Propanal

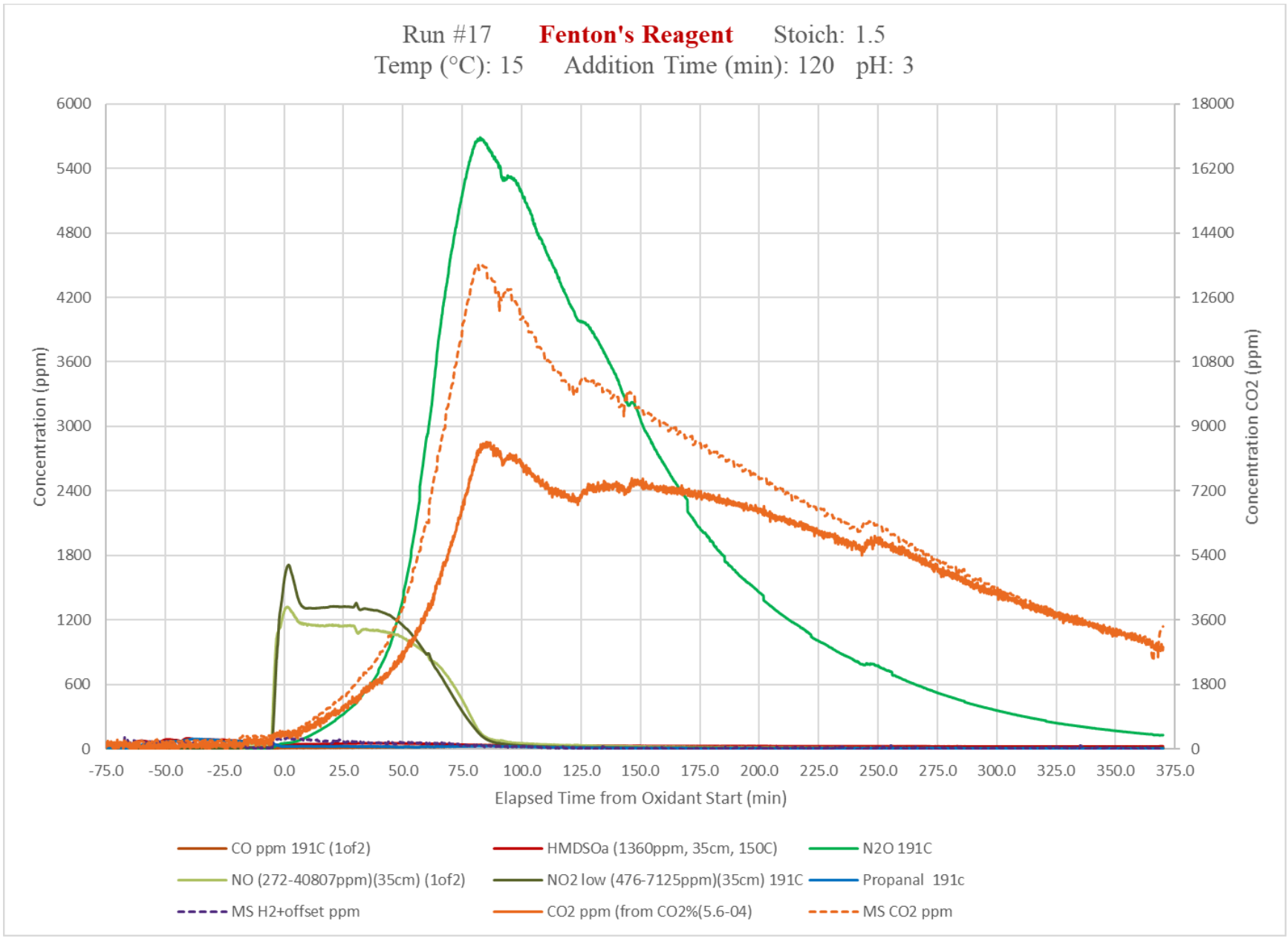


Figure B-49. Test 17 Offgas Profile CO, CO_2, H_2, NO, NO_2, N_2O, TMS, HMDSO, and Propanal

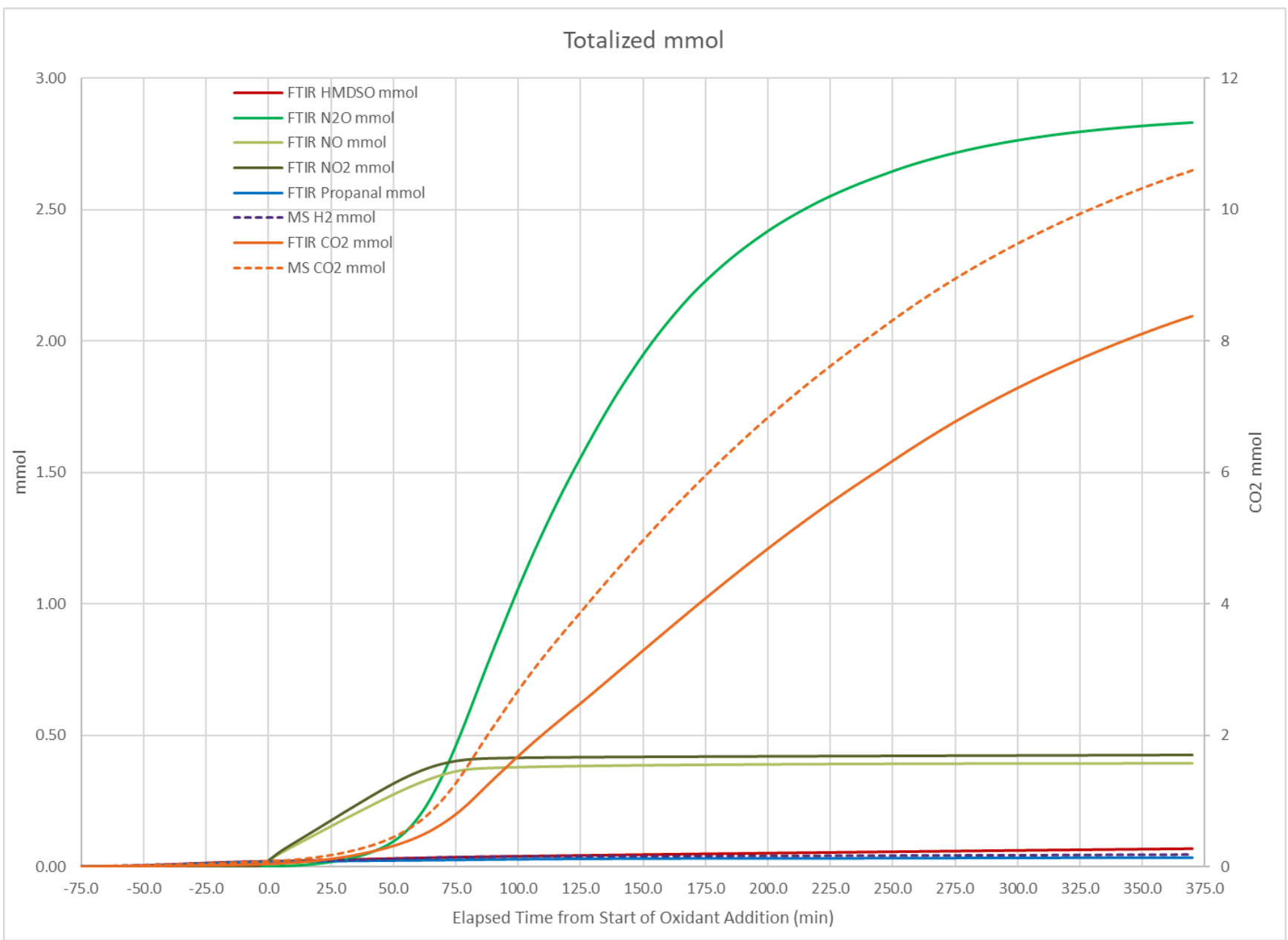


Figure B-50. Test 17 Totalized Offgas CO_2, H_2, NO, NO_2, N_2O, HMDSO, and Propanal

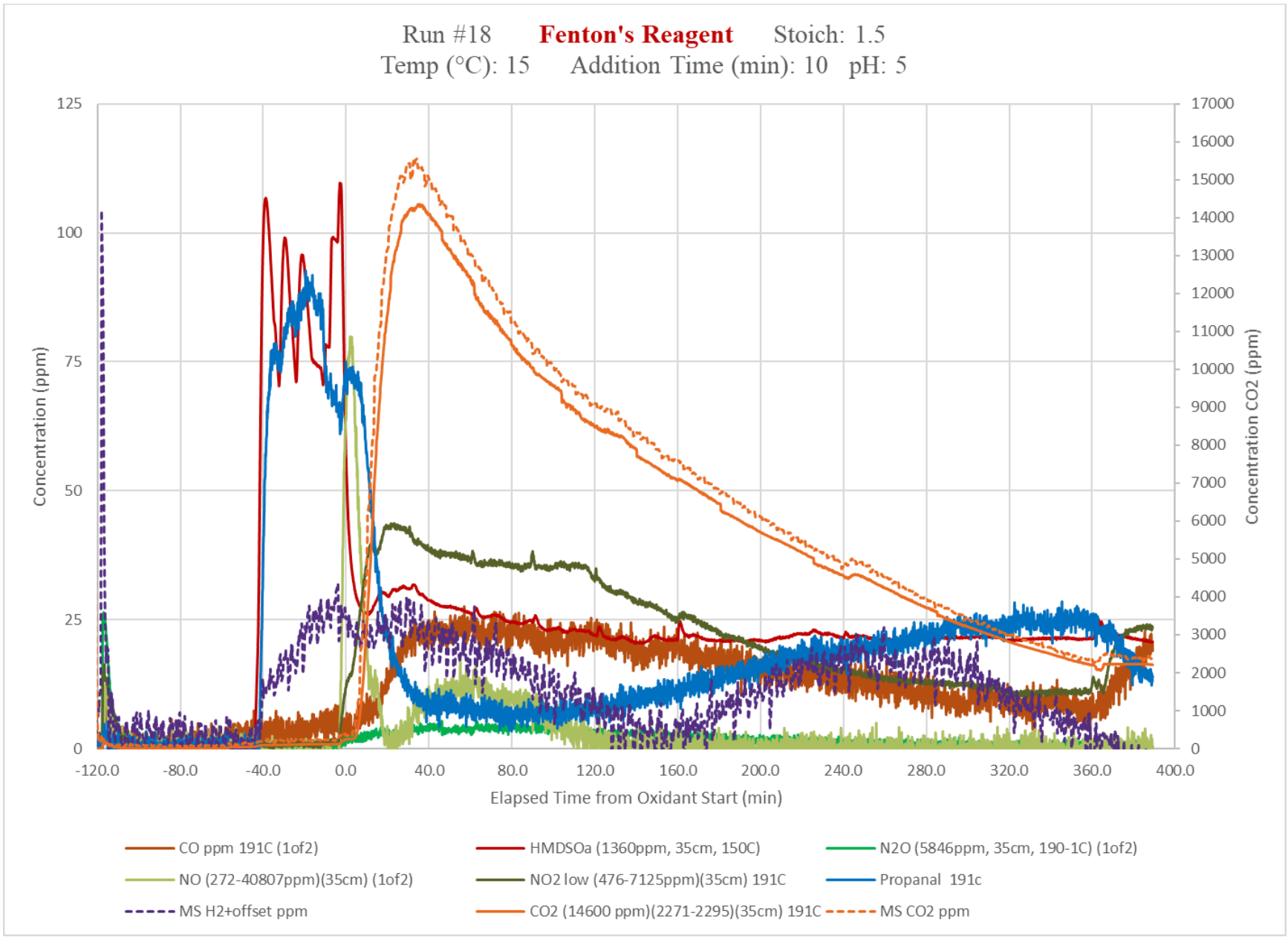


Figure B-51. Test 18 Offgas Profile CO, CO_2, H_2, NO, NO_2, N_2O, TMS, HMDSO, and Propanal

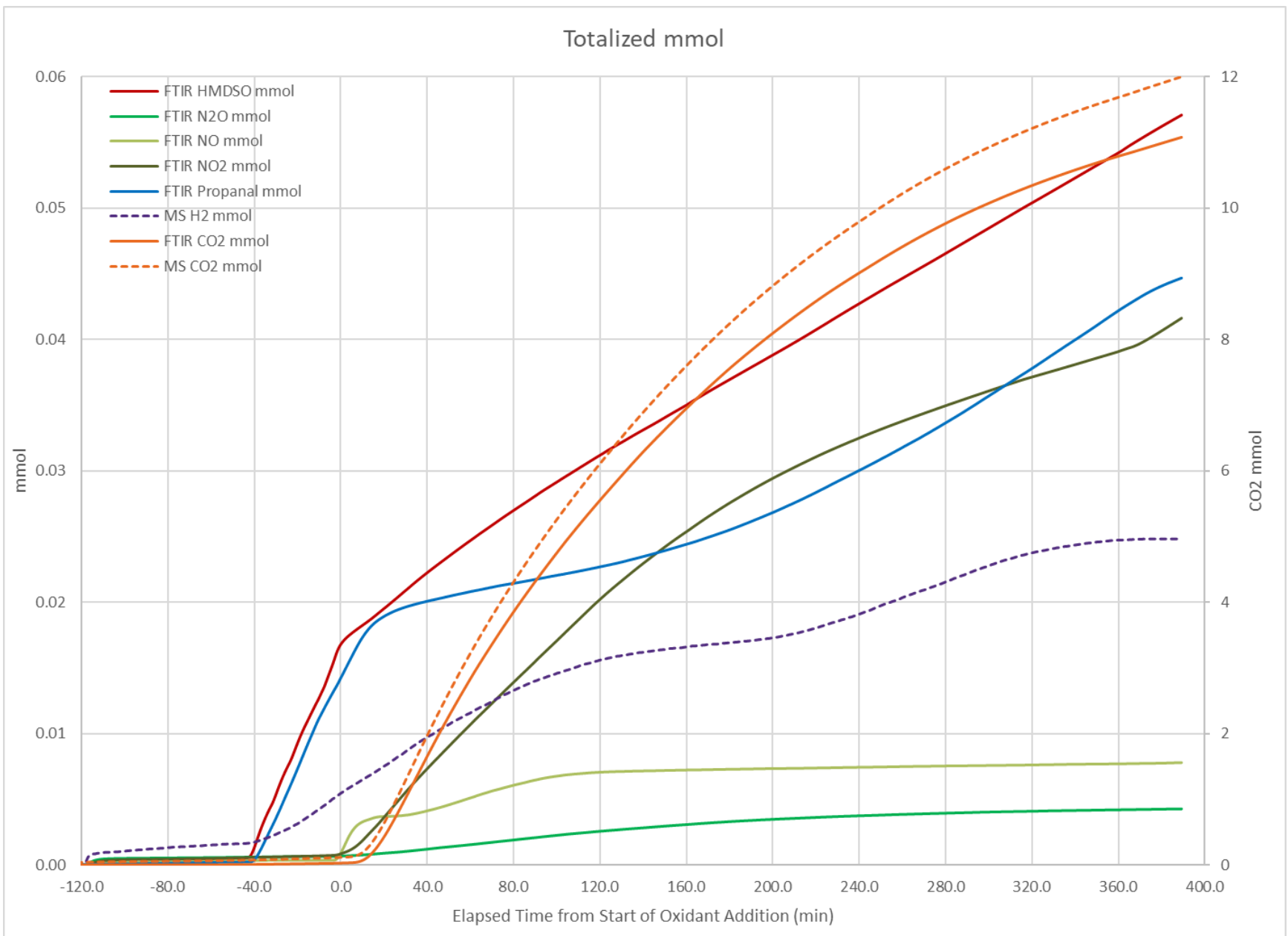


Figure B-52. Test 18 Totalized Offgas CO_2, H_2, NO, NO_2, N_2O, HMDSO, and Propanal

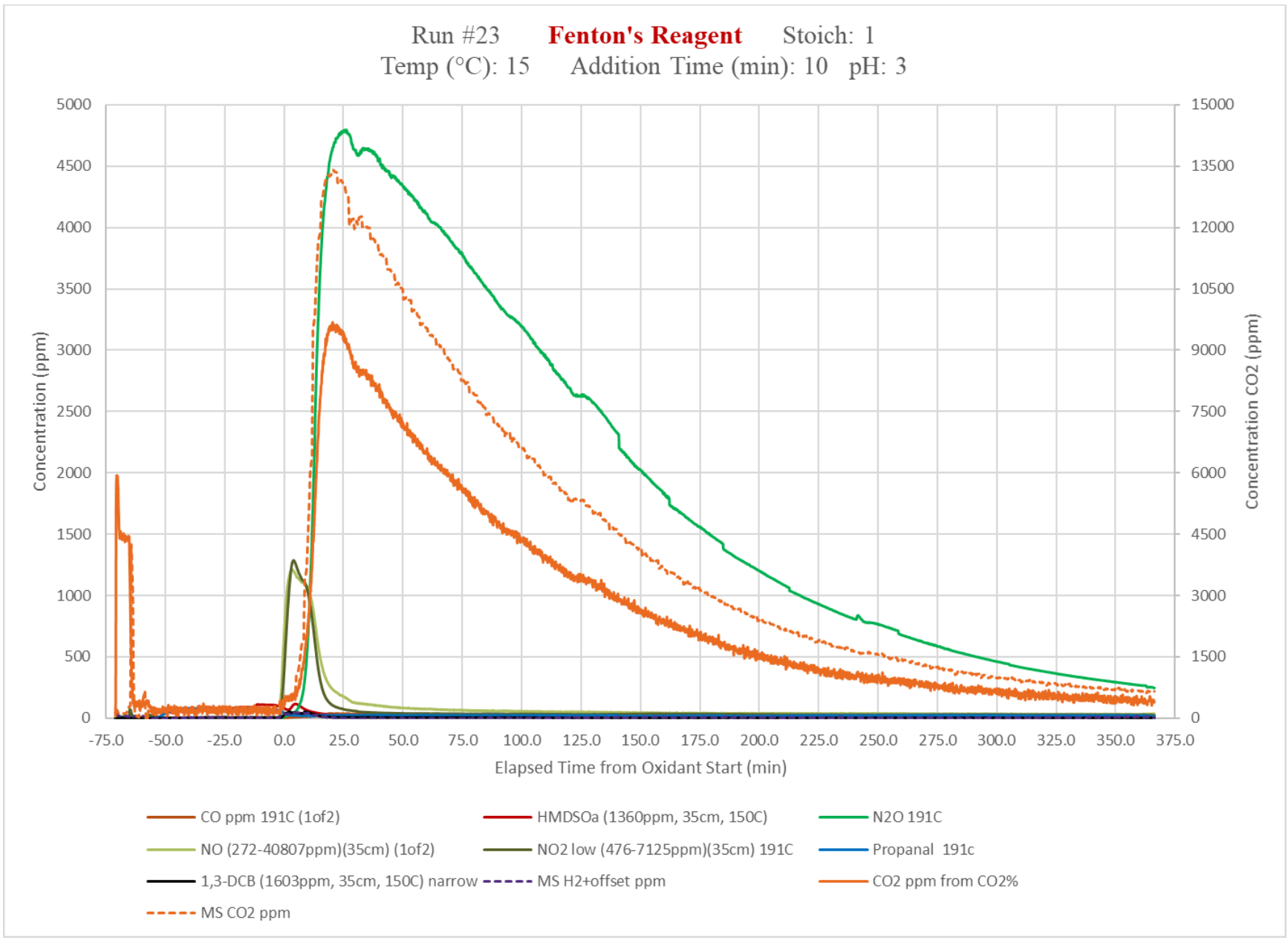


Figure B-53. Test 23 Offgas Profile CO, CO_2, H_2, NO, NO_2, N_2O, TMS, HMDSO, and Propanal

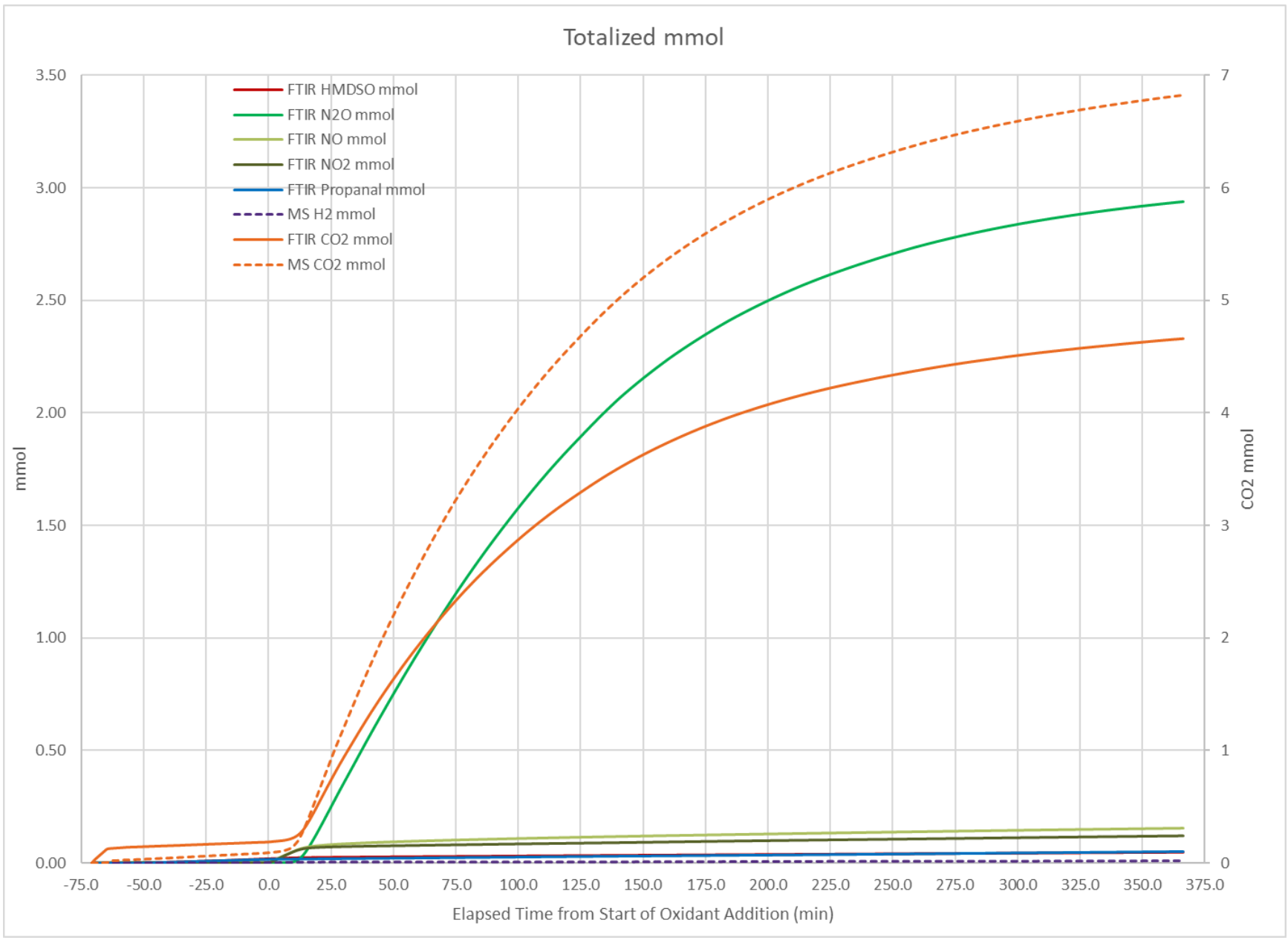
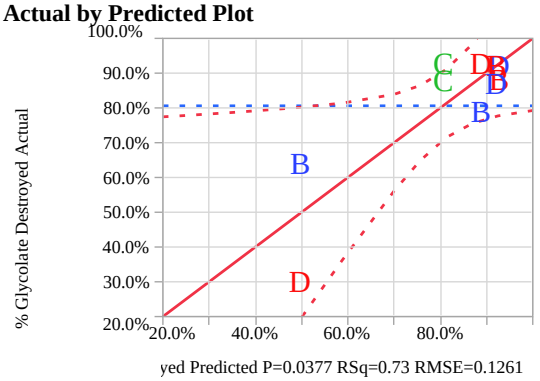


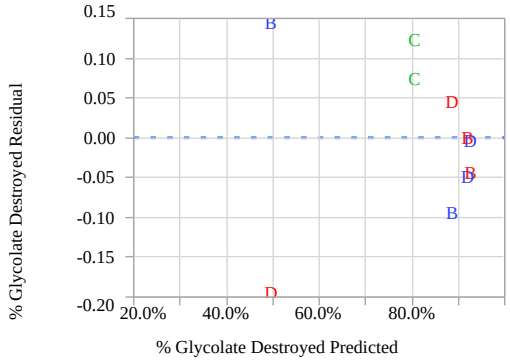
Figure B-54. Test 23 Totalized Offgas CO_2, H_2, NO, NO_2, N_2O, HMDSO, and Propanal

Appendix D: Statistical Analysis of Data

Response % Glycolate Destroyed Oxidant=Sodium Permanganate
Whole Model
Actual by Predicted Plot



Residual by Predicted Plot



Summary of Fit

RSquare	0.731744
RSquare Adj	0.597616
Root Mean Square Error	0.126097
Mean of Response	0.806
Observations (or Sum Wgts)	10

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	3	0.26023750	0.086746	5.4556
Error	6	0.09540250	0.015900	**Prob > F**
C. Total	9	0.35564000		0.0377*

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	1	0.02450250	0.024502	1.7280
Pure Error	5	0.07090000	0.014180	**Prob > F**
Total Error	6	0.09540250		0.2457
				Max RSq

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	0.0963571	0.24111	0.40	0.7033
Temp, C	0.0066429	0.002548	2.61	0.0403*
Oxidant Stoichiometry, X	0.395	0.178328	2.22	0.0687
(Oxidant Stoichiometry, X-1.25)*(Temp, C-32.5)	-0.022	0.01019	-2.16	0.0742

Distribution:

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bruce.wiersma@srnl.doe.gov
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connie.herman@srnl.doe.gov
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