



**THE EFFECT OF MOLAR PEROXIDE RATIO ON THE OXIDATION OF 2,4-DINITROANISOLE IN AN ULTRAVIOLET LIGHT EMITTING DIODE
ADVANCED OXIDATION PROCESS**

THESIS

Troy M. Searcy, Captain, USMC
AFIT-ENV-MS-21-M-270

**DEPARTMENT OF THE AIR FORCE
AIR UNIVERSITY**

AIR FORCE INSTITUTE OF TECHNOLOGY

Wright-Patterson Air Force Base, Ohio

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Troy M. Searcy, BS

Captain, USMC

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Troy M. Searcy, BS
Captain, USMC

Committee Membership:

Willie F. Harper, Jr., PhD, PE
Chairman

Lt Col John E. Stubbs, USAF, PhD
Member

Adam C. Burdsall, PhD
Member

Abstract

Insensitive munitions (IMs) are increasingly employed by the U.S. military to prevent unintended detonations associated with conventional munitions. One IM used extensively is 2,4 dinitroanisole (DNAN). Environmental contamination from munitions manufacturing and live-fire exercises requires effective remediation strategies. This research employed an ultraviolet light emitting diode (LED) and hydrogen peroxide advanced oxidation process (AOP) to treat DNAN-contaminated water at the laboratory scale. Five H_2O_2 :DNAN molar peroxide ratios (50:1, 100:1, 250:1, 500:1, 1000:1) were evaluated using the observed pseudo first-order rate constant (k_s) as the performance metric.

The molar peroxide ratio 500:1 possessed the highest average k_s (0.032 min^{-1}), degrading the DNAN relative concentration by 37% over one hour. Statistical analysis showed the optimal ratio to be 250:1 (average $k_s=0.0307 \text{ min}^{-1}$) due to no statistically significant difference existing between the 250 and 500:1 molar ratios. Both peroxide-limiting reactions and hydroxyl radical scavenging were observed over the range of ratios tested, with overall removal of DNAN decreasing above a ratio of 500:1. A regression analysis suggested that molar peroxide ratio is capable of predicting k_s via a quadratic relationship ($R_a^2= 0.707$). Oxidation byproducts (OBP) appeared to persist over the duration of treatment in the AOP, with 1,3-dinitrobenzene and 2,4-dinitrophenol constituting possible DNAN OBPs. This research is among the first to employ LEDs in an AOP for the treatment of DNAN and forms a basis for future studies incorporating co-contaminants and manipulation of additional variables.

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Glossary of Acronyms and Abbreviations

AFIT – Air Force Institute of Technology
ANOVA – Analysis of Variance
AOP – Advanced Oxidation Process
BIP – Blow-in-place
CSTR – Continuously Stirred Tank Reactor
DAD – Diode array detector
DERA – Defense Environmental Restoration Account
DNAN – 2,4 Dinitroanisole
DNP – Dinitrophenol
DoD – United States Department of Defense
HPLC – High performance liquid chromatography
IM – Insensitive Munition
IMX – Insensitive Munitions Explosive
 K_s – kinetic rate constant
LED – Light emitting diode
MS – Mass spectrometry
NQ – Nitroguanidine
NTO – 3-nitro-1,2,4- triazol-5-one
OBP – oxidation byproduct
QSPR – Quantitative structure-property relationship
RDX – hexahydro-1,3, 5-trinitro-1,3,5-triazine
RTA – Range Training Area
SERDP – Strategic Environmental Research and Development Program
TNT – 2, 4, 6-trinitrotoluene
TOC – Total organic carbon
UV – Ultraviolet
UV-LED – ultraviolet light emitting diode
UXO – Unexploded ordnance

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I. Introduction

1.1 Issue and Motivation

The Department of Defense (DoD) requires dependable, flexible, and diverse water treatment processes to sustain mission readiness. Critical military installations reported water scarcity in 2019 with projections for a continued lack of water required for mission accomplishment (GAO, 2019). Energy and water security are intrinsically tied; the stability of homeland resources and projection of combat power relies on sufficient, usable water supplies in domestic and foreign areas of operation (USAF, 2013, 2017).

The DoD actively conducts municipal wastewater treatment and has been involved in remediation of munitions-producing wastewater for decades. In a survey of 167 military installations, Barry (2012) found 53 percent to have at least one wastewater treatment plant (WWTP) on site. Each military service has implemented strategies to reduce energy and water consumption in accordance with federal statutes. Notable progress has been made in water conservation at various installations, with each service implementing net zero initiatives and the entire DoD decreasing potable water consumption by over 25 percent since 2007 (U.S. Department of Defense, 2019, 2020). These water reuse plans require optimization of available treatment technologies. The DoD also maintains interest in water treatment due to prevalent chemical use along with the threat of chemical attack resulting in the need to properly treat wastewater before further disposal (Duckworth et al., 2015). Both on and off installations, toxic chemicals

pose a threat through DoD-affiliated production facilities, transportation, storage practices, and direct use during military live-fire exercises.

Insensitive munitions (IMs) are increasingly implemented as replacements for conventional explosives due to unintentional detonations induced by shock, impact, or overheating (Sikder & Sikder, 2004). Since 1926, 17 major munitions-related incidents have caused more than 600 deaths and four billion dollars in losses (Patel, 2011). Accidents aboard four aircraft carriers resulted in over 200 sailor's deaths and 1.3 billion dollars. Further, 16 in-bore projectile premature detonations aboard U.S. Navy and Coast Guard vessels killed 59 service members between 1965 and 1973 (Beauregard, 2011). The U.S. Navy responded by implementing service-specific munitions with less sensitive characteristics. The Navy's role of transporting sister-service explosives led to a joint IM acquisition process in the late 1980s. By 1995, the Joint Requirements Oversight Council (JROC) established a uniform IM policy across the DoD (Naval Sea Systems Command, 1998).

The DoD uses blends of IMs to replicate explosive properties of widely used conventional compounds such as 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and Composition-B. One example is Insensitive Munitions Explosive (IMX)-101 which is qualified as a TNT replacement. IMX-101 combines the IMs 2,4-dinitroanisole (DNAN) and 3-nitro-1,2,4-triazol-5-one (NTO), along with nitroguanidine (NQ) as a propellant (Felt et al., 2013). DNAN is toxic to mammals (Lent et al., 2012), plants, and microorganisms (Dodard et al., 2013). Increased employment of IMs will inevitably result in future environmental exposure requiring remediation strategies.

Advanced oxidation processes (AOPs) are capable of potable water and industrial wastewater treatment along with remediation of contaminated sites. AOPs generate high concentrations of hydroxyl radicals ($\text{OH}\cdot$) which function as strong oxidants capable of completely mineralizing most organic compounds (Crittenden et al., 2012; Tchobanoglous et al., 2014). There are many types of AOPs, and ultraviolet (UV) light combined with hydrogen peroxide (H_2O_2) has seen full-scale success for decades in water and wastewater applications. UV/ H_2O_2 AOPs typically use low (LP) or medium pressure (MP) mercury lamps as UV light sources (Kommineni et al., 2000; Miklos et al., 2018).

AOPs have been studied by the DoD in the context of explosive-contaminated wastewaters since the 1980s. Andrews (1980) determined UV/ H_2O_2 to be the most direct and economical process for treatment of TNT and RDX when compared to carbon adsorption and UV-ozonation. In 1984, Holston Army Ammunition Plant (HSAAP) was expected to produce 125 million gallons of wastewater per day at full mobilization with no tertiary treatment for removal of explosives surviving secondary treatment. Researchers found the UV/ H_2O_2 AOP effectively degraded mixed-munitions concentrations in the wastewater (Noss & Chyrek, 1984). The conventional explosives under consideration in these studies have been replaced by combinations of IMs in various applications, but primarily high-explosive 155 millimeter artillery rounds (BAE Systems, 2020). This initiated research into treatment methods for IM-producing wastewater, with AOPs constituting a promising option. AOPs have degraded conventional nitroaromatics such as TNT (Ayoub et al., 2010) and appear capable of decolorizing IM-producing wastewater (Felt et al., 2013). Currently, only two studies

have experimentally investigated efficacy of UV/H₂O₂ treatment of DNAN (Su et al., 2019; Yang et al., 2018).

Light emitting diodes (LEDs) have been tested as an alternative to mercury lamps due to the toxicity associated with mercury and increasing efforts to eradicate its use. Currently, 128 countries have signed the Minamata Convention on Mercury which was implemented in 2013 to phase out mercury use in various products and processes (United Nations Environment Programme, 2020). There is a gap in literature concerning UV-LED implementation in AOPs for mineralization of organic chemicals. Advantages of UV-LEDs are potentially significant and various dyes and organics have been effectively degraded in UV-LED/H₂O₂ AOPs (Matafonova & Batoev, 2018). The application of LEDs within the UV/H₂O₂ process for DNAN treatment has not yet been investigated.

1.2 Problem Statement

Increased use of insensitive munitions as replacements for conventional explosives has introduced the nitroaromatic DNAN into the environment. The DoD requires remediation options for DNAN and similar IMs to ensure environmental and public health. The Air Force Institute of Technology (AFIT) is researching advanced oxidation of water pollutants with UV-LEDs. Research is sponsored by the Defense Environmental Restoration Account (DERA). Currently, UV-LED employment in AOPs is limited to laboratory scale; however, previous research at AFIT has shown promise for continued experimentation with various target contaminants (Duckworth, 2014; Mudimbi, 2015; Scott, 2015; Stewart, 2016; Stubbs, 2017).

1.3 Research Objectives and Hypotheses

The overarching goal is to describe the effect of molar peroxide ratio on DNAN degradation. DNAN metabolizes to 2,4-dinitrophenol (Lent, 2019) which can cause human death in concentrations ranging from 1-46 mg/kg-day depending on exposure duration (ATSDR, 1996; National Research Council, 1982). Compared to DNAN's acute oral LD₅₀ of 199 mg/kg-day in rats (Dodd & McDougal, 2002), 2,4-dinitrophenol (2,4-DNP) appears to constitute a more severe risk to humans than DNAN through the ingestion exposure pathway. Studies of DNAN photolysis and AOP treatment have identified 2,4-DNP and other byproducts requiring follow-on treatment (Rao et al., 2013; Shen et al., 2013; Yang et al., 2018). Therefore, two research objectives and respective hypotheses can be formed:

1. Research Objective 1 is to determine the effect of molar peroxide ratio on DNAN degradation. The intent is to describe the relationship between both variables and explain how the manipulation of molar peroxide ratio influences DNAN removal. This effect is quantified through measuring the decrease in relative DNAN concentration (C/C_0) over time and retrieval of pseudo first-order rate constants (k_s) for each molar peroxide ratio. Lower molar peroxide ratios can cause premature reaction termination. Literature comprising AOP treatment of DNAN suggests molar ratios above 250:1 quench the reaction due to the scavenging effect of hydrogen peroxide (Su et al., 2019; Yang et al., 2018). Effectiveness of the UV-LED/H₂O₂ AOP depends on the compound structure, H₂O₂ concentration, and LED output power (Stubbs, 2017). Thus, ideal ratios present in available literature may not be recreated due to variations in reactor design. Hypothesis #1 is that DNAN removal kinetics are expected to be influenced by both

peroxide-limiting reactions and hydroxyl radical scavenging across the range of molar peroxide ratios.

2. Research Objective 2 is to propose oxidation byproducts for DNAN and provide insight on how DNAN is transformed in the AOP. An investigation of DNAN byproduct formation will be based on a review of comparable studies in literature, instrumental analysis, and visual inspection. Hypothesis #2 is that multiple oxidation byproducts will be formed as DNAN is degraded in the AOP.

1.4 Methodology

Two control experiments were conducted to ensure validity of results. The first involved zero application of hydrogen peroxide or UV light while the DNAN-contaminated solution flowed through the reactor. The second consisted of applying UV light to the solution without hydrogen peroxide present (0:1 molar ratio).

Experiments consisted of the following molar ratios (H_2O_2 :DNAN): 50, 100, 250, 500, and 1000:1. Three iterations (trials) were conducted for each molar ratio. For every trial, a control experiment was performed at the specified molar ratio without application of UV light over one hour. This allowed for determination of a representative starting concentration (C_0) of DNAN present in the reactor before the trial began. Trials were conducted over a 60-minute interval where samples were taken during the following time increments: 5, 10, 15, 20, 25, 35, 45, and 60 minutes.

High-performance liquid chromatography (HPLC) was used to determine DNAN concentrations and degradation over time intervals for each molar ratio. HPLC-mass spectrometry (MS) was employed for byproduct examination over multiple molar ratios.

Effluent DNAN concentrations were quantified after HPLC analysis and used to determine the pseudo first-order kinetic rate constant (k_s). A mass balance on the reactor yields the differential equation needed to determine k_s . This was solved using MATLAB (ver. R2020a) and pseudo first-order rate constants were generated for all trials.

An outlier analysis was conducted by subjecting the three rate constants for each molar ratio to the Q-test. These three rate constants (for each molar ratio) were then averaged to determine mean degradation rates. An analysis of variance (ANOVA) was performed to determine whether a statistically significant difference existed between any of the mean rate constants. Tukey's method was used for pairwise comparisons to determine which, if any, individual molar ratios possessed statistically distinct rate constants. A regression analysis was used to determine the predictive power of molar peroxide ratio with respect DNAN degradation in the AOP.

1.5 Assumptions and Limitations

Assumptions:

1. Sampling was conducted in a representative manner through methodical, timed periods of effluent collection during experiments. The reactor functioned as a continuously stirred tank reactor (CSTR) during the collection intervals.
2. The hydrogen peroxide employed was 30 percent concentration by weight and remained constant throughout testing. This was confirmed by safety data sheets, but not through analytical chemistry, and has meaningful implications for molar ratio calculations.

3. LED power output was consistent throughout experiments and diodes functioned properly for the duration of each trial.

Limitations:

1. All kinetics pertain to bench-scale experiments under specific reactor conditions. While proof of concept was the objective, such results will not directly translate to pilot or full-scale implementations.

2. No standard for DNAN was available. The DNAN sourced was 98 percent pure, thus, quantification of starting concentrations and subsequent degradation depended on accurately measuring DNAN samples with a laboratory micro balance scale.

3. The HPLC methodology catered to expedited run times and instrument longevity rather than byproduct analyses due to compressed research timelines.

1.6 Implications

This study builds upon more than six years of research at AFIT focused on UV-LED AOPs and is a collaborative effort with Dr. Adam Burdsall and Major Jeffrey Hart, USMC. The results form a baseline and allow comparison with DNAN degradation involving co-contaminants and cyclical (recycled) treatment methods. Together, this research represents the first known treatment of IM's, and DNAN specifically, with a UV-LED/H₂O₂ AOP.

II. Literature Review

This section begins with a brief history of IMs and explains how and why DNAN has become extensively used. The potential for environmental contamination from IMs is introduced, resultant from IMX-101 manufacturing processes along with live-fire exercises. An overview of DNAN's physical and chemical properties is provided, followed by a discussion of DNAN toxicity and methods of detection in aqueous solutions. Biotic and abiotic degradation methods for DNAN are presented as well as current IM wastewater remediation techniques employed in munitions manufacturing plants. Lastly, AOP theory, relevance to insensitive munitions, LED incorporation, and potential for effective degradation of DNAN is discussed.

2.1 Background on Insensitive Munitions

IMs can be defined as munitions “that reliably fulfill their performance, readiness, and operational requirements on demand, but are designed to minimize the violence of a reaction and subsequent collateral damage when subjected to unplanned heat, shock, fragment or bullet impact, electromagnetic pulse (EMP), or other unplanned stimuli” (Beauregard, 2011). The U.S. Secretary of Defense is required by law to “ensure, to the extent practicable, that insensitive munitions under development or procurement are safe throughout development and fielding when subject to unplanned stimuli” (10 U.S. Code § 2389, 2001).

DNAN has been used since World War II. German warheads employed an explosive mixture termed “Amatol 40” used in V-1 rockets which caused significant destruction to England during bombing campaigns. This mixture of DNAN (50%),

ammonium nitrate (35%), and RDX (15%) was used as a substitute for conventional munitions due to shortages (Fedoroff et al., 1958). DNAN has also seen historical use as an insecticide and in industrial dyes (Davies & Provatas, 2006). Compared to TNT, DNAN has approximately 10 percent less explosive power while maintaining less sensitivity to impact (Fedoroff et al., 1960). Most studies which characterize DNAN properties as an explosive ingredient were conducted before 1950 until Davies & Provatas (2006) investigated its potential for use in melt cast formulas. DNAN is oxygen deficient and possesses low crystal density resulting in minimal effectiveness as a sole explosive ingredient (unlike TNT). Such chemical properties are why DNAN is used in blends of explosives (Davies & Provatas, 2006).

Following the JROC-established IM policy across the DoD (Naval Sea Systems Command, 1998), the U.S. Army began testing IMs in 1999 for replacement of the conventional explosive Composition B (Comp B) present in 60-millimeter mortars. The IM was termed PAX-21 and contained DNAN and ammonium perchlorate (AP). Toxicity testing was conducted at the Air Force Research Laboratory in 1999, noting that DNAN had extremely limited toxicology data and exposure hazards pertained to manufacturing operations rather than soldiers (Dodd & McDougal, 2002). PAX-21 was fielded for several years before incomplete detonation issues and environmental concerns ended production (Fung, Ervin, et al., 2010; Lent, 2019). Insensitive Munitions Explosive (IMX)-104 is currently being evaluated for use in 60, 81, and 120-millimeter mortars as an alternative to the legacy explosive Comp B. IMX-104 is a mixture of NTO, DNAN, and RDX (BAE Systems, 2020; Fung, Ervin, et al., 2010).

IMX-101 was certified as a TNT replacement in 2010 and combines DNAN, NTO and NQ (propellant) (Lee et al., 2010). The new blend incorporates only IMs and replaces TNT in 155-milimeter M795 heavy artillery munitions used in the M777 howitzer. It is suitable for use in any large-caliber munitions requiring comparable performance of TNT (BAE Systems, 2020; Felt et al., 2013). IMX-101 ingredients are manufactured and processed at HSAAP where the IMs are melted, mixed, cast, and processed for packing parameters (Fung et al., 2009). The manufacturing process of IMX-101 relies on melt-casting, where NTO (20%) and NQ (37%) crystals are added to molten DNAN (43%) followed by a cooling period. IMX-104 follows a similar melt-cast procedure where NTO (53%) and RDX (15%) are added to molten DNAN (32%) (Taylor et al., 2015).

Historically, DNAN used in the United States has been solely sourced from China. In 2004, BAE developed a cost-competitive synthesis process where DNAN is produced through direct nitration at HSAAP. This process allowed DNAN to become a standard production item at HSAAP, with more than 200,000 pounds manufactured in 2010 (Fung, Morris, et al., 2010).

2.1.1 Environmental Contamination from Insensitive Munitions

Concerns surrounding widespread use of IMX-101 pertain to both the IM-producing wastewater generated from munitions production as well as energetic residues associated with live-fire training. Historical military activities and improper disposal practices of conventional munitions have resulted in worldwide contamination of environmental media to the point of threatening human, livestock, wildlife, and ecosystem health (Pichtel, 2012).

The load and pack (LAP) process for the manufacture of IMX-101 yields high quantities of IM-producing wastewater. In 2014, approximately 100,000 gallons containing trace amounts of explosives and production intermediates were generated each month from a combination of heating, cooling, and cleaning equipment during the LAP process. The wastewater was stored and treated off-site with no regulations existing for the IM's present in IMX-101 (Fugate et al., 2014). IM waste streams are limited, but generally exist as part of a closed-loop wastewater system which remains confined to a munitions plant until treatment is accomplished. Felt et al. (2013) reported DNAN concentrations to be 140 mg/L in wastewater. Samples taken from raw wastewater produced from the Hubei Dongfang Chemical Company in China range in DNAN concentration from 119 to 127 mg/L (Shen et al., 2013). Published concentrations of IMs in wastewater discharges, soils (in training areas), and natural waters are either nonexistent or sparse. Photo-induced ecotoxicity of IMX-101 elements do not appear to have been investigated with respect to any National Pollutant Discharge Elimination System (NPDES) permit-relevant species. This is a crucial revelation and shows a general lack of understanding surrounding the fate of IMs, and associated toxicity to the environment (Kennedy et al., 2017).

Conducting realistic, live-fire evolutions is vital to DoD readiness. This can result in training ranges becoming saturated with explosive residue leading to contamination of surface and groundwater. The environmental transport and fate of munitions on ranges has been rarely studied over the past two decades and increased use of IMs requires further characterization to ensure environmental conservation (Pennington et al., 2005; M. Walsh et al., 2017). Walsh et al. (2014) studied detonation residues from mortar

rounds containing IMX-104, finding high-order and blow-in-place (BIP) detonation residues to be higher than those of conventional explosives. BIP deposition approached 95% of the original load, highlighting significant environmental contamination potential for training exercises. High solubility and unknown toxicological knowledge of certain IMs, particularly NTO, raised concern over environmental contamination.

Comprehensive testing by the DoD Strategic Environmental Research and Development Program (SERDP) of IMX-101 and IMX-104 in mortar and artillery applications concluded the following: “Insensitive munitions were constructed to resist external stimuli such as bullet impact or fire, and because of that, they resist unintentional detonation. This insensitivity has resulted in a less-efficient detonation, differential performance among the formulation components, and increased residues caused by disposal of UXO by a BIP procedure. We have found through this research that the more insensitive the munitions are, the less efficient they become and the more they deposit residues. In the case where IM constituents are toxic, the live firing of IM rounds into our RTAs will represent an environmental risk and, upon reaching potential receptors, a human health risk” (M. Walsh et al., 2017).

2.2 Characteristics of 2,4-Dinitroanisole (DNAN)

2.2.1 Physical and Chemical Properties of DNAN

Nitroaromatic compounds are heavily used in industrial dyes, polymers, pesticides, and explosives. A nitroaromatic is an organic molecule consisting of at least one nitro group ($-\text{NO}_2$) (Ju & Parales, 2010). DNAN is a nitroaromatic and shares

properties associated with other nitroaromatics such as biodegradability and toxicity to mammals (Lent, 2019). Figure 1 illustrates the molecular structure.

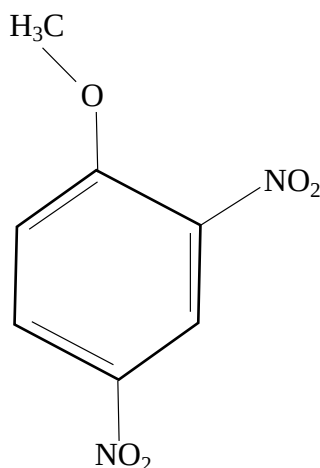


Figure 1: DNAN molecular structure

DNAN is categorized as a Class 4.1 flammable solid and is therefore subject to less stringent international transportation requirements. DNAN can be manufactured from raw materials 2,4-dinitrochlorobenzene (DNCB), methanol, and sodium hydroxide. Wastewater is almost always characterized by a yellow-tint which typically includes traces of DNCB, methanol, and 2,4 DNP (Shen et al., 2013). Taylor et al. (2017) sampled DNAN from HSAAP and found traced amounts of chloronitrobenzenes and 1-ethoxy-2,4-dinitrobenzene.

The fate of DNAN upon entering the environment is dictated by the physicochemical properties of the compound and the dominant environmental conditions at the point of release. Therefore, the aqueous solubility (s_w), octanol-water partition coefficient (k_{ow}), and Henry's law constant (k_H) are important properties of DNAN to quantify. These parameters describe the tendency of DNAN to partition between solid-liquid, liquid-liquid, and water-air media, respectively (Boddu et al., 2008).

Discrepancies exist concerning these values due to differences in experimental methods and inherent variability. Table 1 provides relevant properties of DNAN from two sources commonly used in literature.

		Reference
Molecular Formula	$C_7H_6N_2O_5$	
Molecular Weight (g/mol)	198.13	
Aqueous Solubility (g/L at 25 °C)	0.276 ± 0.025	Boddu et al. (2008)
	0.213 ± 0.012	Hawari et al (2015)
Octanol-water partition coefficient (log K_{ow} at 25 °C)	1.612 ± 0.014	Boddu et al. (2008)
	1.58 ± 0.01	Hawari et al (2015)
Henry's law constant (m^3Pa/mol at 25 °C)	1.366	Boddu et al. (2008)

Table 1: Physiochemical properties of DNAN

Henry's constant is the ratio of the gas-phase concentration to the aqueous-phase concentration for a volatile species when the system is in equilibrium and infinitely dilute (nearly pure water). When defined as this ratio, higher values of a chemical's Henry's constant correspond to higher volatility (or lower solubility) (Benjamin, 2015). The k_H of DNAN indicates insignificant volatility (Richard & Weidhaas, 2014).

All three constituents of IMX-101 are soluble, though DNAN is significantly less soluble than NTO (17.2 g/L) and NQ (3.2 g/L) (M. E. Walsh, 2016). DNAN is more soluble than TNT (0.1015 g/L) in water (Ro et al., 1996), has a lower melting point by 14 degrees, is less dense (1.336 vs. 1.654 g/cm³) and is characterized by needles in a solid state (Davies & Provatas, 2006). The solubility of IM's is particularly important regarding live-fire training areas. Rainwater and environmental conditions will dissolve DNAN and other IMs present in IMX-101 and IMX-104. Migration of DNAN into groundwater or off military installations can result in limiting or closure of training areas. The increased solubility of DNAN (and particularly NTO) compared to TNT and RDX

increases risk associated with groundwater contamination from live-fire training (Taylor et al., 2015). The fate of DNAN in the environment can also be influenced by adjacent chemicals in the IM mixture. Taylor et al. (2015) found dissolution of IMX-101 and IMX-104 components principally depend on solubility rather than the contact area of respective crystals with water molecules. Drip tests showed that these explosives, when combined, dissolve sequentially in order of decreasing solubility.

2.2.2 Toxicity of DNAN

DNAN is toxic to mammals (Lent et al., 2012), plants, and microorganisms (Dodard et al., 2013), though it seems to be equal or less toxic than TNT (Hawari et al., 2015; Kennedy et al., 2017). Currently, DNAN has no long-term carcinogenicity studies, does not appear to be a human mutagen, and is considered “moderately” toxic via the oral route and “slightly” toxic via inhalation (Lent, 2019). DNAN toxicity data is limited, though lethal dose values comprised of in-vivo rat studies suggest a LD₅₀ of 199 mg/kg-day (Dodd & McDougal, 2002) and an approximate lethal dose (ALD) of 300 mg/kg-day (Lent et al., 2012).

Lent (2019) describes DNAN as having limited ecotoxicity and transport to groundwater due to natural attenuation attributable to soil sorption. Manufacturing exposures appear to constitute the highest risk to humans via inhalation and dermal routes. The Workplace Environmental Exposure limit (WEEL) conducted by the Occupational Alliance for Risk Science (OARS) for DNAN is 0.01 mg/m³ (0.01 ppm) as an 8-hour time-weighted average for inhalation exposure (OARS WEEL, 2018).

DNAN is metabolized to 2,4 DNP in the human body and if 2,4 DNP is found in blood or urine, exposure to DNAN should be considered (U.S. Department of Health and

Human Services, 1995). The U.S. EPA has established a reference dose (RfD) of 2 $\mu\text{g/kg-day}$ for 2,4-DNP (US EPA, 2005). Human death has occurred from oral ingestion of 2,4-DNP in concentrations ranging from 14-43 mg/kg (National Research Council, 1982). The Agency for Toxic Substances and Disease Registry (ATSDR) describes deaths occurring from high (3-46 mg/kg-day) or low (1-4 mg/kg-day) dosages of 2,4-DNP for short and long periods of exposure, respectively (ATSDR, 1996). DNAN-producing wastewater is typically characterized by discoloration (yellow-hue) which indicates the presence of dinitrophenol (Felt et al., 2013; Kennedy et al., 2013) produced from hydrolysis of DNAN (Sviatenko et al., 2014; M. Walsh et al., 2017). Numerous treatment methods involving UV light have observed 2,4-DNP present in DNAN wastewater before and after treatment (Shen et al., 2013; Sviatenko et al., 2014; Yang et al., 2018). Rao et al. (2013) found 2,4-DNP was produced during the during photo-transformation of DNAN in concentrations exceeding chronic oral exposure limits (US EPA, 2005).

The ecotoxicity of DNAN before and after exposure to UV light in aqueous solution is particularly important considering the likelihood of explosive residues on range training areas being introduced to sunlight and migrating to surface waters. Compared to the individual components of IMX-101, along with the complete blend of all three constituents, DNAN appears to be the most toxic before application of UV light (Kennedy et al., 2017; Moores, Kennedy, et al., 2020). Using the ecotoxicological model *Ceriodaphnia dubia*, Kennedy et al. (2017) found DNAN to possess a median lethal concentration yielding 50% mortality (LC_{50}) of 43 mg/L prior to irradiation of samples, being classified as “slightly toxic.” Compared to 2,4,6-TNT (classified as “slightly” to

“moderately toxic”), DNAN appears to be less toxic under non-photolyzed conditions. Following application of UV light, the photo-induced toxicity doubled for DNAN. One hypothesis surrounding the increase in toxicity after photo-transformation relates to the product 2,4 DNP, which is two to three times more toxic to *Ceriodaphnia dubia* than DNAN (Kennedy et al., 2017).

Similarly, Moores, Kennedy, et al. (2020) reported DNAN (median LC₅₀ of 25.2 mg/L) to be the most toxic of all IMX-101 components before UV light was applied using the ecotoxicological model *Daphnia Pulex*. Compared to TNT’s LC₅₀ of 4.0 using *Daphnia Magna* as the model (Burton et al., 1993), DNAN appears to be less toxic than TNT to certain freshwater aquatic species prior to UV irradiation. After the application of UV light, photo-induced toxicity of DNAN decreased slightly (LC₅₀=27.6 mg/), disagreeing with previous studies (Kennedy et al., 2017). Moores, Kennedy, et al. (2020) found that UV-degradation of DNAN resulted in the formation of dinitrophenol, aligning with literature comprising the photochemical degradation of DNAN (Halasz et al., 2018; Hawari et al., 2015; Kennedy et al., 2017; Rao et al., 2013).

2.2.3 Detection of DNAN in Water

Numerous methods have successfully detected DNAN in water, with most using HPLC-DAD reverse-phase column variations. Lounds et al. (2014) measured the absorbance of DNAN with a UV-vis spectrophotometer as an alternative to HPLC and gas chromatography (GC). The spectra of all DNAN stock solutions showed dominant peaks at 300 nm. The method appears to be an affordable alternative for ecotoxicology testing in laboratories requiring rapid quantification of DNAN for stock concentration validation and verification of serial dilutions.

The standard EPA Method 8330B (US EPA, 2006) recommends reverse-phase C18 or C8 columns for detection of nitroaromatics. Although DNAN can be detected using reverse-phase HPLC and GC methods, these are not ideal for all IMX-101 constituents (NQ and NTO) due to high polarity (M. E. Walsh, 2016). EPA Method 8330B has been modified by numerous researchers to provide optimal resolution and detection of DNAN (Chow et al., 2009; Felt et al., 2013; Platten III et al., 2010). The majority of literature employs a combination of water and methanol for the mobile phase, though acetonitrile and isopropanol are used as well. Most flow rates are isocratic 1 mL min⁻¹ with absorbance values ranging from 220 to 300 nm. Chow et al. (2009) developed a novel method capable of separating DNAN in a solution of 14 energetic compounds using a mobile phase of water/methanol/acetonitrile (68:28:4) and noted that addition of acetonitrile increased the resolution of DNAN while in the presence of other water matrix constituents. M. E. Walsh (2016) effectively employed an alternative separation method based on hydrophilic-interaction chromatography (HILIC) in which analytes elute in the order of increasing polarity. Table 2 summarizes various methods which have effectively detected DNAN in water.

Mobile Phase	Flow Rate (mL/min)	Monitored Absorbance (nm)	Column variations	Reference
Water:Methanol (57:43)	1	254	Acclaim Explosives E2	Boddu et al., 2008
Water:Methanol (50:50)	1	254	LC-18	Ahn et al., 2011
Water:Methanol:Acetonitrile (68:28:4)	1	220	LC-8	Chow et al., 2009
Water:Methanol (50:50)	1	255	C18	Yang et al., 2018
Water:Methanol (70:30)	1	284	C18	Su et al., 2019
Water:Methanol (60:40)	1	210	C18	Platten III et al., 2010;
Water:Methanol (50:50)	1	298	C18	Saad et al., 2012
Water:Methanol:Acetonitrile (ratios not specified)	0.75	296	C18	Temple et al., 2018
Water:Methanol (50:50)	1	220	Acclaim Explosives E2	Rao et al., 2013
Water:Acetonitrile:Aqueous trifluoroacetic acid (55:45:5): (Note: Apparent error in ratios)	1.1	Not specified	C18	Moore et al., 2020
Water:Isopropanol (85:15)	1.4	295	C8	Walsh et al., 2014
Water:Acetonitrile (25:75)	0.5	315	Hydrophilic-interaction chromatography (HILIC)	M. E. Walsh, 2016
Water:Isopropanol (85:15)	1.4	295	C8	M. E. Walsh, 2016
Water:Methanol (57:43)	1	300	C18	Arthur et al., 2017
Water:Methanol (50:50)	1	Not specified	C18	Salter-Blanc et al., 2013
Water:Methanol (50:50)	1	298	C18	Halasz et al., 2018
Water:Methanol (50:50)	1	298	C18	Hawari et al., 2015;
Water:Isopropanol (85:15)	1.4	295	C8	Taylor et al., 2017
Water:Acetonitrile (1:3)	1.5	295	<i>Hypercarb</i> (100% porous graphite column)	Taylor et al., 2017
Water:Methanol (50:50)	1	298	C18	Perreault et al., 2012

Table 2: Methods of DNAN Detection in Aqueous Solution

2.3 Current DNAN Remediation Strategies

2.3.1 Natural Attenuation in Environmental Media

Although DNAN has been in use for decades, its environmental fate in soil and water media has only recently been studied. Explosive residues present on range training areas will degrade biotically or abiotically via soil microorganisms and plants or through hydrolysis and photolysis (Halasz et al., 2018). The tendency of DNAN to travel from surface soils to groundwater is dictated by its rate of dissolution, photo-transformation as a solid in aqueous solutions, and the interactions of DNAN with soil and water during transport. Similar to TNT, DNAN's presence can often be identified visually due to its

color change (yellow-hue) when exposed to sunlight (Taylor et al., 2017). Monteil-Rivera et al. (2009) provides an insightful review of nitroaromatic (primarily TNT) fates in the environment, neatly summarizing biotic (aerobic and anaerobic biodegradation) and abiotic (hydrolysis, photolysis and ZVI) pathways which may apply to DNAN.

Numerous studies have investigated reduction pathways of DNAN in soils. Hawari et al. (2015) identified 2-amino-4-nitroanisole (2-ANAN) and 2,4-diaminoanisole (DAAN) as major DNAN products. The successive replacement of $-\text{NO}_2$ by $-\text{NH}_2$ enhanced irreversible sorption and reduced bioavailability under oxic conditions. The study concluded that “although DNAN is more soluble than TNT, its lower hydrophobicity and its tendency to form amino derivatives that sorb irreversibly to soil contribute to make it less toxic than the traditional explosive TNT.” Arthur et al. (2017) studied DNAN adsorption in soils and determined environmental fate is largely dictated by organic matter and clay, noting DNAN adsorbs to non-sandy soils in a manner that significantly decreases concentration during transport, thus reducing groundwater contamination risk. Temple et al. (2018) tested all IMX-101 compounds in soil column experiments. Results showed DNAN began degradation within 24 hours in soils with high organic content and was completely degraded after sixty days with the major degradation product being 2-ANAN.

Microbial reduction strategies for DNAN have been studied to better understand potential remediation options. Richard & Weidhaas (2014) examined aerobic biodegradation of IMX-101 components in enrichment cultures to determine environmental fate on training ranges and inform the design of engineered treatment systems. Results pointed to DNAN being used as a nitrogen source during exponential

microbial growth and the first step of DNAN degradation caused by oxidative removal of the O-methyl group and transient formation of 2,4 DNP. Olivares et al. (2016) found DNAN was mainly reduced in soils under anaerobic conditions, producing a plethora of transformation products which impact DNAN's environmental fate and transport in soil and water media. In sludge, DNAN biotransformation appears to be most rapid under anaerobic conditions with 2-methoxy-5-nitroaniline (MENA) and DAAN constituting major metabolites produced (Olivares et al., 2013). Platten III et al. (2010, 2013) used an anaerobic fluidized-bed bioreactor (AFBB) due to success in other industrial and munitions wastewater applications, finding DNAN was effectively reduced by the process while transforming to DAAN.

Apart from microorganism degradation, the fate of nitroaromatic compounds in groundwater is largely influenced by reduction via alkaline hydrolysis (Salter-Blanc et al., 2013). Water molecules split apart in aqueous solutions through a process termed hydrolysis, resulting in H^+ and OH^- ions. When the chemical activity of OH^- is greater than that of H^+ , the solution is alkaline (or basic). Hydrolysis is the transfer of a hydrogen ion from one water molecule to another (Benjamin, 2015). Salter-Blanc et al. (2013) studied the alkaline hydrolysis of TNT and DNAN. Results suggest a Meisenheimer complex was an intermediate in the formation of 2,4 dinitrophenolate. This reaction may take place via hydroxide addition. Hill et al. (2012) found DNAN to undergo much slower hydrolysis compared to TNT, though under natural environmental conditions, DNAN does not appear to hydrolyze (Hawari et al., 2015).

Photolysis of nitroaromatics has been studied due to its potential as a major degradation pathway for explosives in the environment. Photolysis describes the process

of a chemical absorbing photons supplied by ultraviolet light, leading to an unstable molecule and subsequent reactions or degradation of the compound (Tchobanoglous et al., 2014). Moores et al. (2020) determined molar absorption coefficient spectra for all constituents of IMX-101 over a range of 200 to 440 nm, providing insight on how DNAN molecules are affected by UV light in the environment and during various water treatment processes. Molar absorption coefficient values appear to be approximately $8500 \text{ M}^{-1}\text{cm}^{-1}$ at a wavelength of 250 nm. Similarly, Yang et al. (2018) found the molar absorption coefficient of DNAN to be $8635 \text{ M}^{-1}\text{cm}^{-1}$ at 254 nm through UV-vis spectrophotometer analysis.

Taylor et al. (2017) studied photo-transformation of DNAN as a solid (analyzed aqueously), intending to simulate degradation of DNAN under field conditions after incomplete detonation. The solubility of NTO and NQ result in high dissolution rates, leaving DNAN exposed to irradiation. Further, any photo-transformation intermediates more polar than DNAN enter the subsurface more quickly than DNAN. The study showed that masses of transformation products were small (less than 1% of dissolved DNAN mass). Methoxy nitrophenols and methoxy nitro-anilines were the most common DNAN transformation products. MENA, a known toxin, was found similar to other studies (Olivares et al., 2013, 2016). Small quantities of 2,4 DNP were identified but did not appear to persist. The researchers concluded that DNAN itself, rather than transformation products, was the most prevalent compound entering soil and continuing potential migration to groundwater.

Rao et al. (2013) studied the photochemical transformation of DNAN under solar-simulated UV wavelengths in water. The rate of photolysis depended on wavelength and

light source, with shorter (UV-B) wavelengths yielding higher rates. The reaction intermediates were nitrite, nitrate, and 2,4 DNP. Environmental factors such as temperature, pH, and organic matter present in the media had little impact. Degradation rates were primarily first order with an average value of 0.98 day^{-1} . Notably, when DNAN concentrations of 10 mg/L were photolyzed, the resulting 2,4 DNP exceeded the EPA's chronic oral exposure limit (US EPA, 2005). Such conclusions raise awareness into the potential for DNAN toxicity in water media when exposed to sunlight in the environment. Similarly, Hawari et al. (2015) photolyzed a DNAN aqueous solution and reported a first-order rate constant of 0.22 day^{-1} . Byproducts included 2-hydroxy-4-nitroanisole (2- HONAN) and 2,4 DNP. Halasz et al. (2018) investigated photolysis of IMX-101 (all compounds concurrently) and reported 2,4 DNP and 2-methoxy-5-nitrophenol as major products which aligns with both aforementioned DNAN photolysis studies (Hawari et al., 2015; Rao et al., 2013) in solar simulators. When DNAN was photolyzed individually rather than as an IMX-101 mixture, it possessed a degradation rate constant significantly lower (0.137 vs. 0.262 day^{-1}). This study provided new insight into how the three IMX-101 components (DNAN, NTO, and NQ) can be photodegraded in surface water along with how degradation products are individually and complexly influenced by other components.

Moores et al. (2020) determined experimental rate constant, half-life, and quantum yield values for DNAN in eleven different water samples ranging from brackish ocean water to DI water at different pH levels. The kinetics for all rate constants were pseudo first-order with DNAN possessing a half-life of 0.83 days. Kennedy et al. (2017) photodegraded an aqueous solution of DNAN in a reactor simulating 48 hours of sunlight

with the goal of quantifying aquatic toxicity. The initial DNAN concentration was reduced by 13%, noting the percent reduction was dependent on starting concentration. The researchers emphasized risk management practices must take into account site-specific IM-concentration levels when considering potential adverse effects of UV irradiation to DNAN-contaminated surface waters, training areas, and wastewaters. Overall, photolysis of nitroaromatic compounds in water appears to be a slow, inefficient process requiring catalysts for economical employment in wastewater treatment settings (Einschlag et al., 2002).

2.3.2 Munitions Manufacturing Practices

Currently, GAC columns appear to be extensively used in IM munitions plants (effluent is reused within the plant) and have been the industry standard for traditional explosives-contaminated water treatment (Felt et al., 2013; Fugate et al., 2014). Boddu et al. (2009) found activated carbon capable of removing 99% of DNAN in water. In 2013, the U.S. Army Engineer Research and Development Center (ERDC) evaluated ten IM wastewater treatment technologies due to the inability of GAC treatment to completely remove all IM constituents and decolorize IM-wastewater (Felt et al., 2013). Additionally, the GAC columns employed required replacement after 750 gallons of effluent treatment at a cost of 2,700 U.S. dollars per column (Fugate et al., 2014). Felt et al., (2013) compared biological, filtration, and advanced chemical treatment processes to GAC efficacy. Issues with GAC column disposal, compliance with the Resource Conservation and Recovery Act (RCRA), poor removal rates of intermediates and end products, and economic viability create uncertainty surrounding the sustainable

production of IMs using adsorption techniques as the primary treatment method (Felt et al., 2013).

2.4 Advanced Oxidation of Nitroaromatics and Insensitive Munitions

DNAN is a nitroaromatic compound and AOPs have shown promise for removing similar contaminants such as TNT (Ayoub et al., 2010; Rodgers & Bunce, 2001). Felt et al. (2013) summarizes ten IM-producing wastewater treatment technologies based on destructive or filtration systems, noting that AOPs appear promising but are not extensively used for remediation of explosive-contaminated water due to widespread use granular activated carbon (GAC).

As early as 1980, UV/H₂O₂ AOPs have been successfully implemented, and even preferred over other AOPs and treatment options (including GAC) for the removal of nitroaromatics as seen in Andrews (1980). Noss & Chyrek (1984) effectively treated mixed-munitions wastewater via UV/H₂O₂ and noted higher concentrations of hydrogen peroxide may be required when TNT constitutes the majority of the wastewater. Goi and Trapido (2001) demonstrated multiple AOPs, including UV/H₂O₂, were capable of mineralizing 2,4-DNP and Einschlag et al. (2002) used UV/H₂O₂ to oxidize four nitroaromatic compounds (including 2,4-DNP). Hwang et al. (2004) conducted effective decolorization and further mineralization of alkaline hydrolysis-treated TNT wastewater through a UV/H₂O₂ AOP.

Non-destructive light absorbance and optimal hydrogen peroxide concentrations are challenges for UV/H₂O₂ treatment of nitroaromatics. TNT has a high molar absorption coefficient (10,715 M⁻¹cm⁻¹ at 254 nm) which interferes with radical

production in UV-based AOPs due to the UV light being absorbed by TNT vice hydrogen peroxide, thus reducing photochemical degradation. Doubling TNT concentrations has resulted in degradation rate constants reduced by 50%. Similarly, hydrogen peroxide concentrations greater than 0.1% of the aqueous solution have proven detrimental to degradation of TNT via UV/H₂O₂ AOPs (Noss & Chyrek, 1984). These studies point to the potential need for pretreatment (i.e., GAC) of IM-producing wastewater prior to AOP employment.

NTO, an IM present in IMX-101, has been effectively mineralized through Fenton oxidation and titanium dioxide (TiO₂-) catalyzed photolysis. NTO was minimally degraded when UV/H₂O₂ was used exclusively, though addition of H₂O₂ in the presence of TiO₂- showed positive results (Le Campion et al., 1999). Terracciano et al. (2018) focused on NTO due to its high solubility and examined both industrial wastewater and synthetic NTO samples. Complete mineralization of NTO was achieved using the UV/H₂O₂ method.

Only three studies were found to have conducted AOP treatment of DNAN. These include a combined zero-valent iron (ZVI) with Fenton oxidation process (Shen et al., 2013), UV/H₂O₂ (Su et al., 2019; Yang et al., 2018), and UV/persulfate (UV/PS) (Yang et al., 2018). Thus far, no UV-LEDs have been used as irradiation sources in published literature.

2.4.1 AOP History, Theory, and Reaction Mechanisms

Historically, water treatment has included physical, biological, and chemical treatment methods to screen solids, degrade contaminants, and disinfect effluent before release to the environment or distribution to the local population. The emergence and

detection of micropollutants complicates these treatment processes since many are not designed to completely eliminate such small contaminants. These micropollutants are diverse and include pharmaceuticals, personal care products, steroid hormones, industrial chemicals, pesticides, and other trace organic chemicals ranging in concentrations from a few nanograms to several micrograms per liter. Many of these organic chemicals are not effectively removed in wastewater treatment plants (Luo et al., 2014; Ribeiro et al., 2015).

The term “oxidation” is defined as “the transfer of one or more electrons from an electron donor (reductant) to an electron acceptor (oxidant) which has a higher affinity for electrons, resulting in the chemical transformation of both the oxidant and the reductant” (Kommineni et al., 2000). This can result in highly unstable chemical species possessing an odd number of valence electrons known as radicals. These radicals act as a powerful oxidant capable of destroying a wide range of organic compounds (Crittenden et al., 2012).

AOPs can be defined as the *in situ* generation of strong oxidants (radicals) for the oxidation of organic compounds. These radicals react in a nonselective manner with both organic and inorganic contaminants at ambient temperature and pressure, thus minimizing treatment costs (Crittenden et al., 2012). AOPs possess the advantage of complete mineralization of contaminants via hydroxyl radicals ($\text{OH}\bullet$), where organic compounds are “destroyed” yielding carbon dioxide, water, and mineral acids. This is preferable to other advanced treatment technologies (i.e., GAC) which require follow on disposal. The “dot” after the radical indicates the unpaired electron which is responsible for the radical’s extreme affinity for electron-rich compounds. Reactions with $\text{OH}\bullet$ are

second order and depend on concentrations of both $\text{OH}\cdot$ and the compound being oxidized (Tchobanoglous et al., 2014).

AOPs have been employed for four decades, initially being implemented for drinking water treatment in the 1980s and later wastewater (sewage) treatment due to success removing both organic and inorganic pollutants (Deng & Zhao, 2015). AOPs are often used for “advanced” or tertiary treatment, but have also been effectively employed for pretreatment of wastewater resulting in effluent which is more easily treated (i.e. biologically) in later stages, thus reducing residence time and cost (Ribeiro et al., 2015).

Glaze et al (1987) concluded that all advanced oxidation systems appeared to generate hydroxyl radicals and are differentiated from other conventional oxidants such as chlorine via the “very high reactivity of this radical.” The majority of AOPs utilize $\text{OH}\cdot$ as the oxidant of choice; however, both sulfate and chlorine radicals are implemented, though greater uncertainty appears to exist concerning site and process-specific byproduct formation (Deng & Zhao, 2015; Miklos et al., 2018).

After Fluorine, hydroxyl radicals are the strongest oxidant known (Pera-Titus et al., 2004; Tchobanoglous et al., 2014) and are capable of being generated through numerous methods (various AOPs) allowing municipalities and industries to choose the most appropriate option based on wastewater characteristics (Ribeiro et al., 2015). Second-order rate constants for $\text{OH}\cdot$ are on the order of 10^8 to 10^9 L/moles for many reactions with organic compounds (Buxton et al., 1988). Hydroxyl radicals are capable of attacking molecules in aqueous solutions through four methods: (1) electron transfer (resulting in the formation of ions of a higher valence), (2) hydrogen abstraction (where the radical removes a hydrogen atom from the organic compound forming a free radical

and water molecule), (3) radical addition (the radical adds to an unsaturated compound to form a free radical product), and (4) radical interaction (or combination) where two radicals combine to form a stable product (Dorfman & Adams, 1973). As $\text{OH}\cdot$ production propagates, oxidation continues in an unselective fashion between both the radicals and other oxidants (i.e. UV photolysis, hydrogen peroxide) present within a system until thermodynamically stable products are formed (Deng & Zhao, 2015; Kommineni et al., 2000).

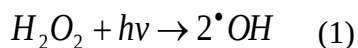
One challenge for AOPs in the destruction of toxins is hydroxyl radical scavengers. As the name implies, these compounds consume $\text{OH}\cdot$ and prevent radicals from oxidizing target pollutants. Concentrations of bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) are known to react with radicals, reducing the rate of organics destruction and overall AOP efficiency. Wastewaters often have high concentrations of these scavengers and those with high pH levels and alkalinity further contribute to the issue. The pH has the potential to directly affect AOP performance due to its impact on the distribution of HCO_3^- and CO_3^{2-} species. For AOPs incorporating H_2O_2 , the pH controls the concentration of HO_2^- , (H_2O_2 has a pK_a value of 11.6), therefore, a UV/ H_2O_2 AOP may increase efficacy at higher pH levels. Solution pH levels also affect the charge on the organic chemical of interest (Crittenden et al., 2012; Tchobanoglous et al., 2014). Other properties such as natural organic matter (NOM) and reduced metal ions (iron and manganese) act as $\text{OH}\cdot$ scavengers. Light transmission, or turbidity, is another factor of particular importance to AOPs incorporating ultraviolet light (Crittenden et al., 2012; Pera-Titus et al., 2004; Ribeiro et al., 2015).

The efficiency of AOPs driven by electricity is described by the term “electrical energy per order” (E_{EO}), which is defined as the kilowatt-hours required to degrade one unit mass of a contaminant in water (Bolton et al., 2001). Most published values pertain to the electricity used to initiate and complete the process (i.e. mercury lamp electricity consumption for UV-based AOPs). Miklos et al. (2018) conducted a rigorous comparison of more than four hundred studies, proposing AOPs with median values less than 1 kWh/m³ are realistic for full range applications, while those surpassing this threshold are not likely mature enough to be implemented industrially.

During the oxidation process, OH• react quickly with target chemicals along with other organic and inorganic species comprising the water matrix. Ideally, pollutants are completely mineralized and transformed into harmless substances such as carbon dioxide and water. This is not always the case, and often compounds known as oxidation byproducts (OBPs) are formed as a result of incomplete mineralization (Kommineni et al., 2000; Luo et al., 2014). AOP byproducts vary greatly and depend on factors such as radical type, scavengers present, and other oxidants used in the AOP. Minimizing OBP formation is crucial to prevent the potential of treated water becoming more toxic (or toxic in a different manner) than the original composition (Miklos et al., 2018).

There are many AOPs, with some combining stand-alone oxidants and technologies. The use of UV light to generate OH• from H₂O₂ has successfully treated drinking water at full-scale for decades (Crittenden et al., 2012; Miklos et al., 2018) with Glaze et al. (1987) stating, “In principle, the most direct method for the generation of hydroxyl radicals is through cleavage of hydrogen peroxide, a relatively inexpensive and readily available chemical intermediate.” UV light photolyzes H₂O₂ in a range of

wavelengths spanning from 200-280 nm (Tchobanoglous et al., 2014) via the following reaction in Equation 1:



Oxidation of contaminants is accomplished through direct photolysis from UV irradiation or through reactions with OH•, where the ability of H₂O₂ to absorb UV light and generate radicals depends on UV wavelength, hydrogen peroxide concentration, control systems (pH and temperature), and background water matrix constituents acting as scavengers (Crittenden et al., 2012). Hydrogen peroxide is very soluble and can be added to water at high concentrations leading to greater radical formation compared to other processes. The dosage applied is particularly important. Rather high concentrations are used in UV/H₂O₂ systems due to the molar absorption coefficient of peroxide being fairly low, leading to high concentrations required for radical production and follow-on removal of residual H₂O₂ before distribution or consumption (Crittenden et al., 2012; Kommineni et al., 2000; Miklos et al., 2018). Molar peroxide ratios between 100 and 3000 moles of H₂O₂/moles of contaminant (C) have been used, with some studies suggesting an optimal concentration of 500 moles H₂O₂/mole C for various dyes tested in bench-scale studies. Organic chemicals with high molar absorptivity ratios appear to require greater concentrations of H₂O₂, while those with low molar absorptivity (i.e. achromatic chemicals) possess optimal molar ratios as low as 100:1 (Stubbs, 2017).

In all UV-based AOPs, an understanding of water matrix properties is significantly important. Light transmission in the UV region must unobstructed or light will be absorbed by various species other than target pollutants, resulting in wasted energy (Crittenden et al., 2012). Some studies have found that mutagenic organic by-

product formation is possible during UV-based AOPs with water containing nitrate. Nitrated aromatic compounds may be the most toxic by-products formed during the process (Hofman-Caris et al., 2015; Martijn et al., 2016). Most UV applications utilize low (LP) or medium-pressure (MP) mercury lamps in combination with hydrogen peroxide (Miklos et al., 2018); however, LEDs have been tested in lab-scale scenarios for oxidation of various organic compounds (Duckworth et al., 2015; R. Scott et al., 2017; Stewart et al., 2018; Stubbs, 2017).

A final note pertains to the issue of wastewaters generally possessing many different chemicals in the water matrix requiring removal. Developing tools capable of predicting degradation during UV-based AOP treatment, particularly UV-LED processes, is a current need and gap in the literature. Quantitative structure-property relationships (QSPRs) are one tool capable of accomplishing this through the prediction of removal efficacy based on molecular structure. Numerous QSPRs have been developed relating chemical structures to degradation in AOPs (Borhani et al., 2016; Stubbs, 2017; Sudhakaran et al., 2012; Sudhakaran & Amy, 2013).

2.4.2 Ultraviolet Light Emitting Diode AOPs

A LED uses semi-conducting materials to create a “p-n junction (hole and electron)” which emits radiation, with wavelength depending on semiconductor material composition (Song et al., 2016). UV-induced AOPs have been studied extensively over the past three decades; however, LP and MP mercury lamps are overwhelmingly the radiation sources applied (Chevremont et al., 2013). LEDs offer an attractive alternative to mercury lamps due to the toxicity associated with mercury and increasing efforts to eradicate its use. Currently, 128 countries have signed the Minamata Convention on

Mercury which was implemented in 2013 to eventually phase out mercury use in various products and processes (Matafonova & Batoev, 2018; United Nations Environment Programme, 2020).

Numerous studies have investigated UV-LED efficacy on microorganism inactivation for water disinfection (Jarvis et al., 2019). Song et al. (2016) summarizes the effect of UV wavelength on microorganism inactivation based on three categories: (1) 315-400 nm (UVA), (2) 280-315 nm (UVB), and (3) less than 280 nm (UVC). The power output of LEDs is significantly lower than mercury lamps, requiring UV-LEDs to be placed close to water samples. Apart from containing no mercury, UV-LEDs provide more flexibility than mercury lamps through instant startup/shutdown, durability, longer lifetime, compact size, and wavelength tailoring (Chen et al., 2017; Close et al., 2006; Würtele et al., 2011). Since wavelength impacts disinfection efficiency, the capability of various wavelengths from LEDs leads to potential benefits (Vilhunen & Sillanpää, 2009). Of particular interest to the DoD could be the lower voltage requirements of LEDs, allowing battery or photovoltaic solar cell powering (Chen et al., 2017; Matafonova & Batoev, 2018).

Most research concerning UV-LED AOPs to date has been conducted in pure water, batch-scale applications. Disadvantages of UV-LEDs include low wall-plug efficiency and requirements for forced cooling, leading to higher costs. Water samples with high turbidity and dissolved organic carbon (DOC) decreases contaminant oxidation, and full-scale water treatment is currently difficult to implement economically (Matafonova & Batoev, 2018). Autin et al. (2013) demonstrated that LEDs meet irradiation requirements for AOPs and speculated economically viable replacement

options for traditional mercury lamps were feasible by the year 2020. More recent studies show this does not appear to be the case. UV-LED AOPs were excluded from an exhaustive review conducted by Miklos et al. (2018) due to a perceived lack of efficiency in AOPs compared to conventional mercury lamps (Wang et al., 2017).

Key factors influencing degradation in a UV-LED/H₂O₂ AOP include the molecular structure of the chemical, hydrogen peroxide dosage present in the aqueous solution, and the LED power output (Stubbs, 2017). Matafonova and Batoev (2018) conducted a review of literature (primarily after 2014) focused on UV-LED implementation for degradation of organic pollutants including dyes, phenols, pharmaceuticals, insecticides, estrogens, and cyanotoxins in water. Specifically, sources were examined on the application of UV-LED/H₂O₂ where nine studies were compared, ranging from deionized water with organic dyes as contaminants, to municipal wastewater effluent in reverse osmosis concentrate. Most studies utilized UVC LEDs due to its strong peroxide absorption and higher OH• generation. The researchers concluded that UV-LED AOP applications appear to be environmentally safe and preferable in certain cases.

Wang et al. (2017) employed a UV-LED/chlorine and UV-LED/H₂O₂ AOP to successfully degrade carbamazepine (CBZ), a common refractory micropollutant detected in wastewater and water reclamation treatment processes. Rate constant values were higher for UV-LED/chlorine due to the molar absorbance of chlorine being much higher than that of hydrogen peroxide at wavelengths utilized (280 and 310 nm). Fujioka et al. (2020) used a 2.0 watt (W), 265 nm UV-LED to degrade N-nitroamines and 1,4 dioxane. Direct photolysis and addition of hydrogen peroxide to the solution was

conducted alongside a conventional LP mercury lamp induced AOP. Results showed that N-nitroamines and 1,4 dioxane degradation increased for the mercury lamp AOP, but negligible changes were observed for the UV-LED AOP. The researchers concluded that development of shorter wavelength emitting LEDs is required for UV-LED technology before effective application in water reuse.

Performance of UV-LED AOPs can be significantly affected by surface fouling, as demonstrated by Duckworth et al. (2015). During UV-LED/H₂O₂ treatment of a solution with methylene blue (MB) as the target contaminant, the LED quartz windows adsorbed MB, reducing the average optical power output by nearly half over the duration of the experiment. As with mercury lamps, LED AOPs appear to require self-cleaning systems to maximize efficiency. Scott et al. (2017) continued experiments with the same reactor but used brilliant blue (BB) and tartrazine (TAR). Results showed surface fouling was greatly reduced due to the tendency of anionic dyes to not adsorb to negatively charged surfaces such as the quartz lenses.

Numerous studies (Duckworth, 2014; Mudimbi, 2015; R. W. Scott, 2015; Stewart, 2016) at AFIT used a vertically oriented (up-flow) stainless steel reactor for UV-LED/H₂O₂ AOP experiments. Gallucci (2016) compared efficacy of both low and high-power LEDs in a Teflon® reactor with three different wall thicknesses, using TAR as a witness dye. The high-power UV-LEDs produced rate constants ten times higher than those of low-power UV-LEDs, but no benefits were attributable to reactor thickness variations.

Stubbs (2017) explored UV-LED/H₂O₂ degradation of various soluble organic chemicals, proving a linear relationship exists between input drive current, optical output

power, and first-order rate constants. Manipulating molar peroxide ratios altered degradation kinetics, revealing peroxide-limited reactions and hydroxyl radical scavenging. Variations in chemical removal rates were linked to molar absorptivity and a novel QSPR was proposed based on degradation profiles for eleven chemicals. Zero-point energy (ZPE) and molar absorptivity were shown to be capable of predicting chemical degradation for UV-LED AOPs at the LED output wavelength of 265 nm. Notably, the nitroaromatic 2,4-dinitrotoluene (DNT) was tested due to its representativeness of explosive byproducts found in munitions manufacturing and range training areas. The study showed DNT to be one of the most resistant compounds to UV-LED/H₂O₂ AOP degradation, ultimately achieving 74.5% removal at 200 mA.

Stewart et al. (2018) expounded upon previous UV-LED/H₂O₂ AOP research conducted at AFIT (Duckworth et al., 2015; Mudimbi, 2015; R. Scott et al., 2017) by manipulating duty cycle (percentage of time irradiation is applied) and pH for the oxidation of TAR. First-order reaction rate constants were positively correlated with duty cycle (DC) and negatively correlated with pH, with optimality at 100% DC and pH of 6.

2.4.3 Advanced Oxidation of DNAN

Felt et al. (2013) conducted a review of IM-wastewater treatment technologies and determined AOPs, including Fenton oxidation and UV/H₂O₂, were favorable for future employment although proof of efficacy could only be hypothesized. At that time, AOPs had successfully treated multiple nitroaromatics, but no studies of DNAN degradation kinetics or AOP performance parameters had been published.

The first research to investigate DNAN degradation by AOP appears to be through the use of a combined zero-valent iron (ZVI)-Fenton process to pretreat DNAN-

producing wastewater prior to biological treatment. The study combined ZVI (reduction agent) in order to make DNAN more susceptible to oxidation through Fenton's reaction (AOP). The study sourced DNAN-producing industrial effluent from the Hubei Dongfang Chemical Co. Ltd. in Hubei Province, China. The effluent contained DNAN (123.1 ± 3.8 mg/L), DNCB (249.3 ± 6.9 mg/L), and DNP (110.4 ± 4.2 mg/L). Nearly complete reduction of nitroaromatic compounds was achieved and ideal parameters were identified for pH, H₂O₂ dosage, retention time, and H₂O₂:Fe²⁺ molar ratios. The study found AOP pre-treatment of DNAN-producing wastewater to be prospective considering the effluent could be readily polished through bioprocesses (Shen et al., 2013).

Yang et al. (2018) achieved DNAN oxidation by both UV/H₂O₂ and UV/persulfate (UV/PS) experiments, finding the latter to be more efficient. A low-pressure mercury lamp was used in a 15W merry-go-round photoreactor emitting monochromatic light at a wavelength of 254 nm with incident photon irradiance determined to be 6.67×10^{-8} Einstein L⁻¹ s⁻¹. Temperature was maintained at approximately 20° C and DNAN solutions were prepared in batches of 50 mL by volume and 40 µM (7.925 ppm) in DNAN concentration. A UV-vis spectrophotometer was used to measure the adsorption coefficient of DNAN ($8635 \text{ M}^{-1} \text{ cm}^{-1}$) and 2,4 DNP ($44,389 \text{ M}^{-1} \text{ cm}^{-1}$) at 254 nm. Concentrations of all analytes was quantified by a Hitachi L-2000 HPLC equipped with a diode array detector (DAD). Separation of mobile and stationary phases was achieved by an Agilent ZORBAX Eclipse Plus C18 column, with the mobile phase being composed of 50% water and 50% methanol (MeOH). The mobile phase was acidified with 0.1% formic acid at a flow rate of 1.0 mL min⁻¹ and detection wavelengths were based on the maximum absorbance in the UV-vis spectrum of each individual

compound. At a detection wavelength of 255 nm, retention times for DNAN and DNP were 9.70 and 8.50 minutes, respectively.

Yang et al. (2018) found no DNAN degradation was observed by photolysis alone over one-hour trials which agrees with aforementioned studies of nitroaromatic photo-transformation being a slow process (Einschlag et al., 2002). For the UV/H₂O₂ experiments, molar ratios of 50, 125, and 250: 1 (H₂O₂:DNAN) were evaluated at a constant pH of 7.0 and demonstrated increasing rate constants as H₂O₂:DNAN molar ratios were increased from 50 to 125:1. Higher molar ratios of 250:1 appeared to quench the reaction and the researchers attributed the poor performance to the scavenging effect of hydrogen peroxide and re-combination of hydroxyl radicals at higher molar ratios. The molar ratio 125:1 appeared most effective, achieving a degradation of approximately 25% of the initial concentration over 60 minutes. The UV/PS system resembled pseudo-first-order kinetics under mirrored conditions, with a maximum rate constant of 0.0189 min⁻¹. The rate constant increased from 0.0014 to 0.0189 min⁻¹ as PS dosage was increased from 2 to 10 mM, achieving 100% degradation over 120 min for the 10 mM PS concentration. In contrast to the UV/H₂O₂ experiments, the UV/PS AOP did not quench reactions at high PS concentrations which was attributed to the lower rate of sulfate radical re-combination.

An important conclusion of the study (Yang et al., 2018) pertained to the significant formation of byproducts (primarily 2,4 DNP) which were not incorporated into the kinetic modeling and therefore resulted in a discrepancy between experimental results and model prediction values. Separate experiments using 2,4 DNP as a substrate were conducted to better understand overarching transformation pathways of DNAN. The

transformation of 2,4-DNP produced 2,4,6-trinitrophenol (2,4,6-TNP) as a major intermediate and time-dependent evolution of 2,4-DNP was capable of being described by a sequential kinetic model. During UV/PS experiments, the yield of 2,4-DNP increased up to 32.7% for a PS dosage of 2 mM. The molar coefficient of 2,4-DNP is significantly higher than DNAN and the reaction between sulfate radicals and 2,4-DNP resulted in a rate constant one order magnitude higher than that of DNAN. This points to 2,4-DNP inhibiting DNAN degradation due to light obstruction along with premature radical quenching. It is also possible for DNAN transformation to proceed through denitration/hydroxylation which generates 2-methoxy-5-nitrophenol (2-MeO-5-NP) or 4-methoxy-3-nitrophenol (4-MeO-3-NP) as intermediates (Taylor et al., 2017), though Yang et al. (2018) did not find such intermediates during HPLC analysis. The presence of other light-screening and radical scavenging compounds in the water matrix was tested via addition of Suwannee River fulvic acid (SRFA) and nitrate (NO_3^-), with both impeding DNAN degradation. For the UV/PS AOP, various pH levels (3.03, 7.10, and 10.08) were employed with no statistically significant differences in DNAN degradation.

A more recent study demonstrated DNAN is effectively oxidized via the UV/ H_2O_2 AOP (Su et al., 2019). A continuously mixed batch solution of 98% pure DNAN dissolved in tap water was used in experiments implementing a 13W LSE Lighting UV Bulb (UV 4500 lx) at 254 nm. A volume of 800 mL of DNAN solution was treated over 9 hours at an initial DNAN concentration of 250 ppm. Unlike Yang et al. (2018), the reactor consisted of a 1000 mL beaker with the UV lamp fixed in the center of the beaker, submerged into the aqueous DNAN solution. Both pH (4, 5, 6, and 7) and H_2O_2 dosages (1500, 2250, 3000, and 4500 ppm) were manipulated during the

experiment. The molar ratios used during experiments correspond to 34.95, 52.43, 69.90, and 104.85:1 (H_2O_2 :DNAN). DNAN concentrations were quantified by HPLC-DAD. An analytical wavelength of 284 nm was used in a 70:30 methanol-water mobile phase flowing at 1 mL min^{-1} , resulting in a retention time of 4.9 min for DNAN. Initially, an optimal ratio of 3000 ppm H_2O_2 to 250 ppm DNAN (molar ratio of approximately 70:1) was reported over a range of 1500-4500 ppm H_2O_2 . Linear regression analysis resulted in zero-order kinetics and a maximum rate constant of 73.72 hour^{-1} (1.129 min^{-1}) at a molar ratio of 70:1. The highest molar ratio tested ($\sim 105:1$) resulted in less degradation than 70:1, indicating excess hydrogen peroxide competed with DNAN for reaction with hydroxyl radicals at such a high concentration. Additional experiments were conducted at lower concentrations of 750 ppm H_2O_2 (17.48:1 molar ratio) with pseudo first-order kinetics observed corresponding to less DNAN degradation over time. The conclusion was drawn that the oxidation rate of DNAN was not affected by decreasing DNAN concentration over the duration of treatment.

A separate round of experiments was conducted by Su et al. (2019) to investigate whether the initial pH affected DNAN degradation. Higher pH levels generated faster degradation up to a pH of 7. The researchers proposed that pH effects are modest compared to the effects of hydrogen peroxide dosage and that a pH of 7 is ideal. This conclusion, along with all zero-order rate constants reported, may warrant further investigation due to identical experiments (35:1 molar ratio at pH 7) yielding significantly different rate constants. For experiments manipulating molar ratio, rate constants increased from 56.76 h^{-1} to 73.72 h^{-1} over a molar ratio range of 35 to 70:1. At a constant molar ratio of 35:1, increasing pH from 4 to 7 resulted in an increased rate

constant from 53.74 h⁻¹ to 75.84 h⁻¹, respectively. The effects of pH on the AOP appear to play more of a role than what is insinuated. The authors provided a final conclusion that the optimal combination is a molar ratio of 35:1 (1500 ppm H₂O₂) at a pH of 7.

Su et al. (2019) measured total nitrogen species to better understand OBP formation during the AOP. No volatile nitrogen was formed, and nitrite concentrations were very low, disappearing after complete degradation of DNAN. Nitrite was oxidized quickly to nitrate after being generated from DNAN degradation and continued to increase until residual levels were comparable to that of initial DNAN-N concentrations. The researchers suggested this indicates nearly all DNAN nitrogen species were transformed to nitrite in a similar manner to other nitroaromatics treated with UV/H₂O₂ as seen in Einschlag et al. (2002) and Goi & Trapido (2001). Nitrate concentrations increased more rapidly during DNAN degradation than after completion of treatment, indicating cleavage of nitro groups occurred early. Upon conclusion of treatment, approximately 77% of total nitrogen was transformed to nitrate while only 65% of TOC remained, indicating that nitrification is faster than mineralization during treatment of DNAN in the AOP. Total organic carbon (TOC) and total carbon (TC) were measured over the course of experiments, with both decreasing during degradation of DNAN indicating that gaseous carbon (primarily CO₂) was generated and no carbonate or bicarbonate was present in treated effluent. The aforementioned pH decrease over the course of treatment further explains the lack of carbonate species and generation of acids from DNAN oxidation.

Modeling efforts point to AOP technology degrading DNAN in a similar manner to other nitroaromatics (i.e., TNT). A lack of experimental data makes such

computational efforts challenging to compare for accuracy; however, relating DNAN degradation models to those of similar explosives have provided further support for experimental research. Zhou et al. (2018) used density functional theory (DFT) methods to explore the reaction mechanism of DNAN with hydroxyl radicals in AOPs. Previous studies on the kinetics of alkaline hydrolysis of DNAN (Hill et al., 2012; Salter-Blanc et al., 2013; Sviatenko et al., 2014) were used to design complete hydrogen abstraction reaction pathways for DNAN. The initial step during oxidation of DNAN by $\text{OH}^\bullet$ appears to be abstraction of one H atom from the CH_3 group of DNAN, producing radical intermediates and a water molecule. The study concluded that similar to TNT and DNT, hydrogen abstraction constitutes an important and primary reaction method for DNAN in AOPs, with direct substitution of the nitro-group playing a key role. The intermediate OBPs 2,6-dinitrobenzaldehyde and 2,4-dinitrobenzoic acid were proposed after a series of hydrogen abstraction and dehydration reactions. A final radical intermediate, 1,3-dinitrobenzene, was determined to be relatively stable. The researchers concluded that degradation mechanisms for DNAN in AOPs are very similar to those for TNT and DNT (including generation of OBPs).

III. Methodology

3.1 Materials, Equipment, and Methods

This section is organized in a manner which resembles the sequential order of actions required for bench-scale AOP experiments and analysis of degradation rate constants. The reactor used in this research was first constructed and tested by Gallucci (2016). The methodology is largely based on procedures developed by Stubbs (2017) and Dr. Adam Burdsall. A schedule of experiments is located in Appendix A.

3.1.1 Solution Preparation

Aqueous stock DNAN solutions were prepared in 250 mL glass volumetric flasks by dissolving reagent-grade DNAN (98% purity, CAS: 119-27-7, Alfa Aesar, Thermo Fisher Scientific Chemicals Inc., Ward Hill, MA) in reverse osmosis (RO), purified, deionized water (DI Water, AFIT ENV Lab) between four and five days prior to each experiment. The stock DNAN consisted of pale-yellow crystals with a density of 1.34 g/cm³ at 20°C per the manufacturer. The target DNAN concentration for each solution was 10 mg/L in 250 mL of water. This corresponds to 2.5 mg of DNAN crystals requiring dissolution. The mass of DNAN was measured in square (41x41x8mm), polystyrene weighing dishes (WB) (Fisherbrand, Fisher Scientific, China) with a micro balance (1.0 ± 0.1 ug) scale (Model XP26, Mettler Toledo, Columbus, OH). Triplicate WB measurements were conducted to compute an average value, with multiple repetitions necessary due to fluctuations in laboratory humidity and scale sensitivity. The target DNAN mass (0.0025g) was then added to the average WB mass for an overall target weight (DNAN+WB). DNAN crystals were then transported from the stock DNAN

container via a metal spatula and placed on the WB, subsequently weighed, and repeated until three measurements were within ± 0.5 mg of the target mass. The three measurements were then averaged followed by subtraction of the WB mass, yielding the approximate DNAN mass. The resulting DNAN mass was then divided by the volume of water in the solution (0.250L). Using this process, the DNAN concentrations ranged from 9.997 to 10.059 mg/L with a mean and standard deviation of 10.009 and 0.0143 mg/L, respectively. Appendix B lists all stock DNAN solution concentrations by date prepared.

Following mass measurements, a small amount of DI water was added to the WB to ensure adequate transfer of DNAN from the WB to the 250 mL volumetric flask. The crystals were carefully poured from the WB into the flask and multiple rinses of the WB were conducted. The flask was then filled with 250 mL of DI water and a one-inch magnetic polytetrafluoroethylene (PTFE)-coated stir bar was placed inside for mixing the solution. The flask was closed with a stopper, sealed with paraffin tape, wrapped in aluminum foil, rotated end-over-end for 5 minutes, and then placed on a stir plate at 850 rotations per minute (rpm) until the day of the experiment.

3.1.2 UV-LED Reactor and System

The reactor was constructed from McMaster-Carr brand PTFE in a cylindrical shape with heat dissipating fins at each longitudinal axis where LEDs are mounted. The center tube containing DNAN solution undergoing treatment was constructed of 6 mm thick PTFE which fit into end caps securing influent and effluent tubing. The central cylinder has an internal diameter of 22.1 mm with a length of 80.52 mm, yielding a volume of 36.54 mL using capsule-shape volumetric calculations when the internal diameter of each end cap is 22.1 mm (Stubbs, 2017). Heat sinks were fabricated via

copper fins attached to each end cap and in contact with the adjacent LED inside the assembly. A digital MasterFlex peristaltic pump (Model 77200-50, Cole Parmer, USA) operating at 2 mL/min (7 rpm) was used to pump stock DNAN solution through MasterFlex 14 PharMed® BPT tubing (Cole Parmer, Vernon Hills, IL) into the reactor where it was treated and subsequently pumped out the opposite end of the reactor and into a waste container. The reactor was oriented horizontally with a 0.5-inch magnetic stir bar placed inside, enabling CSTR modeling. Figure 2 shows the reactor in a horizontal orientation along with imagery of tubing and wiring connections. Stubbs (2017) approximated the usable volume inside the reactor to be 35 mL when taking into account the volume displaced by the stir bar, yielding a residence time of 17.5 minutes as calculated in Equation 2. The LEDs were procured from Sensor Electronic Technology Incorporated (Model UV-CLEAN, SETi, Columbia, SC) and provided a peak output wavelength of 265 nm. The UV-CLEAN model has nine diodes, and all experiments employed a drive current of 100 mA. Prior to the first experiment, the LED optical power output at 100 mA was evaluated with a Labsphere (model CDS 1100) integrating sphere calibrated with a Deuterium lamp to measure the optical power of the LEDs at the drive current. The integrating sphere data was processed in Illumia® Pro Software (Labsphere Inc., North Sutton, NH). The combined photon production from all nine diodes was measured approximately two years prior to the start of this research, with a value of 2.02×10^{16} photons/L when normalized to the volume of the reactor. The combined photon production at the end of all experiments was 1.59×10^{16} photons/L when normalized to the volume of the reactor. Between the two measurements, the LEDs are estimated to have operated for no less than 31 hours. Considering this, the rate of decay for the LEDs was

approximately 1.39×10^{14} photons/L-hour. Appendix P outlines procedures for operating the Lapshere equipment along with details for calculating LED photon output. The circuit board employed 20mA resistors (LUXdrive 4006-020, LEDdynamics, Randolph, VT) and was powered by a digital power supply (Model E3620A, Keysight Technologies, Santa Rosa, CA). Figure 3 provides an interior view of the reactor along with LED placement.

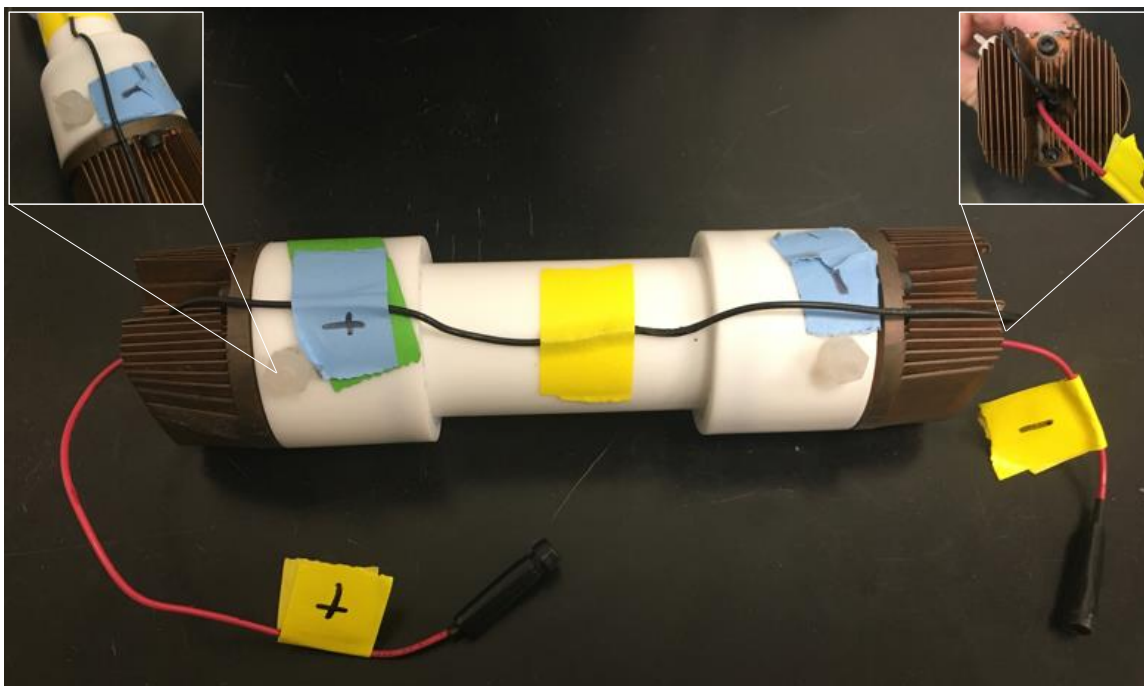


Figure 2: Assembled UV-LED reactor

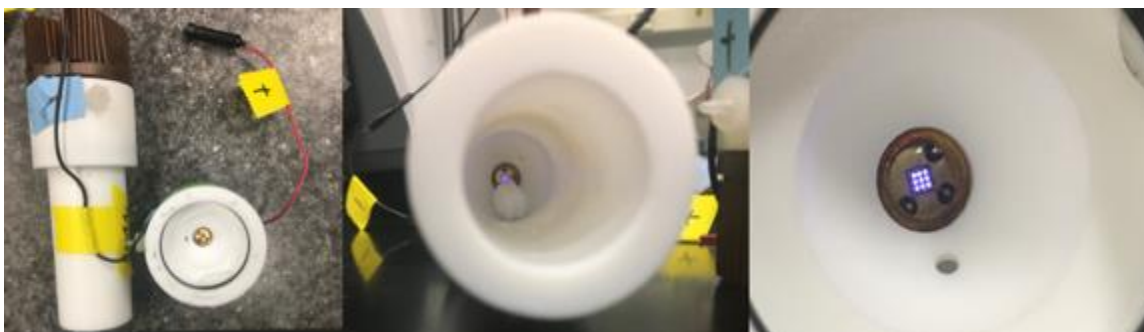


Figure 3: Interior view of UV-LED reactor

3.2 Experimental Procedure

To accomplish research objective 1, five molar ratios of hydrogen peroxide to DNAN concentrations were tested (50, 100, 250, 500, and 1000:1). Each molar ratio underwent three separate trials following the same procedure, resulting in a total of 15 experiments. One experiment (1000:1 molar ratio) was repeated following an outlier analysis indicating a pipette error occurred. The goal of incremental testing of molar ratios was to identify the optimal ratio for maximum degradation corresponding to high levels of hydroxyl radical production. Additionally, threshold values for high and low ratios provided indication of H_2O_2 radical scavenging (too much H_2O_2) for rate limited radical production (too little H_2O_2) (Stubbs, 2017).

After approximately four days and complete dissolution of DNAN in the aqueous solution, hydrogen peroxide (30%, by weight in water, Fisher Scientific, Fair Lawn, NJ) was pipetted from the stock H_2O_2 directly into the 250 mL volumetric flask containing the DNAN solution and hand-shaken for 5 minutes followed by no less than 20 minutes on a stir plate at 850 rpm. The method of calculating H_2O_2 volume addition for each molar ratio is provided in Appendix C and incorporates the density of H_2O_2 at 4°C as described by Schumb et al., (1953). For example, the molar ratio of 100:1 corresponds to 128 μL of H_2O_2 in the 10 ppm DNAN solution. The pH was measured with a SevenMulti pH Meter (Mettler-Toledo, Columbus, OH) following the addition of hydrogen peroxide as described in Appendix D. Kimtech Kimwipes® (Kimberly-Clark, Roswell, GA) were used to clean the pH meter diode throughout the calibration process. All DI water was sourced from the same AFIT laboratory RO system; however, the pH varied from 4.853 to 7.154 over the course of experiments. Stewart (2016) experienced similar variations in

the AFIT laboratory DI water supply, attributing inconsistencies to potential malfunction in the storage and production of the DI water.

Samples for calibration curve development were prepared in zero (blank), 10, 20, 40, 60, 80, and 100% DNAN solution with DI water. All samples were drawn out of the 250 mL volumetric flask with a 10 mL syringe (Luer-Lok Tip, Becton, Dickinson and Co., Franklin Lakes, NJ) and filtered with 13mm, 0.2 μ m pore diameter PTFE membrane filters (Millex® Hydrophobic Fluoropore™, Merck Millipore Ltd., Ireland) into 2 mL amber or clear vials (Part Number: 5182-0716, Agilent Technologies, USA) and capped with PTFE silicone caps (Part Number: 5182-0718, Agilent Technologies, USA). The proper ratios were pipetted by sourcing filtered DNAN solution from an adjacent amber vial. All mixtures were then hand-held on a vortex mixing unit (3000 RPM Vortex mixer, Model No. SBV1000, Southwest Science, Taiwan) for approximately 30 seconds. These 7 calibration curve mixtures were set aside for future HPLC analysis within 24 hours (along with all other samples). Microsoft® Excel (ver. 16.42) was used to plot all calibration curves and verify a linear fit.

The 250 mL DNAN solution was placed on a stir plate operating at 850 rpm for the duration of the experiment. The reactor was also placed directly above a magnetic stir plate (115 V Magnetic Stirrer Cat. No. 14-511-2, Fisher Scientific, USA) to mimic CSTR conditions. Sections of the aforementioned tubing approximately two feet in length served as the influent pathway from the DNAN solution to the reactor, as well as the effluent pathway from the reactor to the waste container. The influent tubing was placed completely inside the 250 mL volumetric flask containing the DNAN solution, with cognizance of proximity to the rotating stir bar. Before starting the peristaltic pump, the

tubing and reactor were first primed with approximately 45 mL of DNAN solution via a 50 mL syringe (Luer-Slip Plastic, Part Number: S7510-50, Thermo Scientific, Rockwood, TN). Air was purged from the tubing network and reactor with the flow of solution. Approximately 10 mL of solution was run through the system and disposed into the waste container to ensure any residual constituents present in the tubing or reactor were removed before testing commenced. The pump was then turned on to ensure proper flow before initiating timed experiments. Figure 4 illustrates the system flow and organization of laboratory equipment.

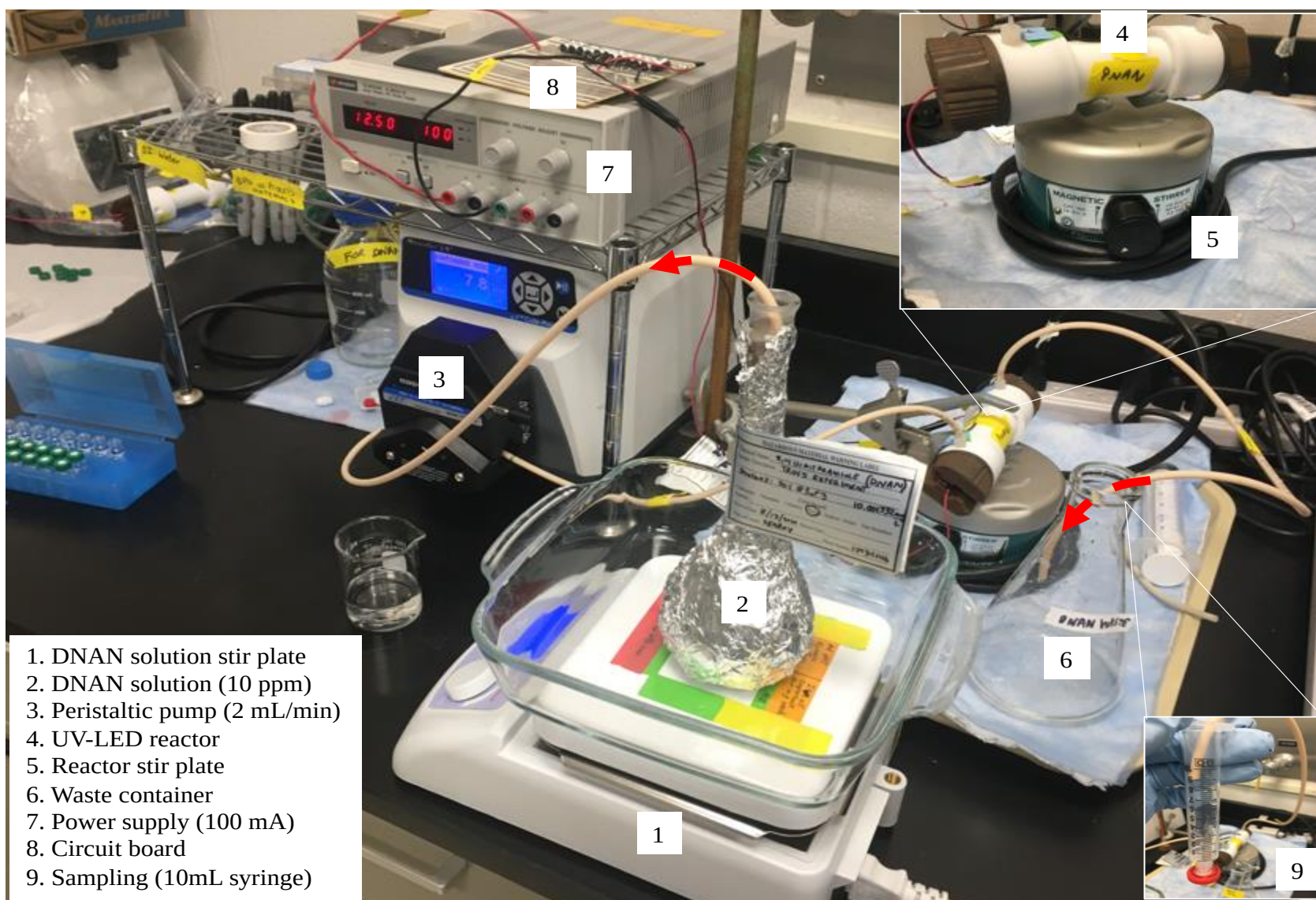


Figure 4: Laboratory experimental setup

3.2.1 Control Experiments

Two controls were conducted before molar ratio manipulation. The first involved application of zero hydrogen peroxide in the presence of zero irradiation while the DNAN solution flowed through the reactor. The second applied UV light to the solution without hydrogen peroxide present (0:1 molar ratio). Both were expected to demonstrate degradation rate constants of approximately zero. Degradation present in either control would point to potential photolysis reactions or significant losses in the system due to equipment or material error (i.e., DNAN adsorption to PTFE or tubing).

Prior to the conduct of DNAN solution treatment in the AOP, localized controls were run for each individual trial (and every molar ratio) where the DNAN solution was pumped through the reactor without any UV-LED irradiation applied. This provided insight into potential DNAN loss occurring due to adsorption to the reactor and tubing, along with confirmation that the upcoming experiment would be employing properly functioning equipment. During these controls, the DNAN solution effluent was recycled into the 250 mL volumetric flask to conserve stock solution required for follow-on AOP experiments. A checklist was used in all procedures to ensure powered devices were turned on (stir plates and the peristaltic pump) and effluent tubing was correctly positioned (i.e., effluent tubing discharging into the 250 mL volumetric flask for controls vice the waste container for AOP experiments). Sampling for these localized controls was accomplished by extracting the effluent tubing at time intervals of 0, 10, 20, 30, 40, 50, and 60 minutes. The effluent tube was quickly placed in a 10 mL syringe with the plunger removed for 45 seconds. The plunger was then reinserted into the syringe to filter the effluent directly into an amber vial which was subsequently capped and mixed as in

samples in the same manner described for calibration curve samples. Collecting a sample volume for 45 seconds resulted in approximately 1 mL of filtered effluent in the amber vials.

3.2.2 AOP Experiments

Trials for each molar ratio were executed immediately following the associated control experiment. An essential note pertains to estimation of the initial concentration for the AOP experiment. This was calculated by averaging the untreated effluent concentrations over one hour via the samples taken during the corresponding control experiment. This initial concentration (C_0) for the AOP experiment and was used to calculate relative concentrations (C_t/C_0). An average was used for the initial concentration due to random variability observed over the one-hour control where no treatment (no UV light) occurred. Generally, the DNAN concentrations appeared to increase slightly up to 40 minutes, then decrease slightly up to 60 minutes. The starting concentration mean and standard deviation was 9.6226 and 0.1835 ppm, respectively. Appendix E provides further insight on this occurrence. A potential explanation for this involves imperfectly representative samples collected in the syringe (i.e. non-ideal mixing).

A timer was used via cellular device for countdown intervals between sampling and a wristwatch was synchronized to provide redundancy and keep track of overall time elapsed. The effluent tube was placed in the waste container and the timer was started as soon as the power supply to the UV-LED reactor was turned on. Samples were taken by removing the effluent tube from the waste container and emitting the treated DNAN solution into the 10 mL syringe via the same method as the controls described previously.

Samples were taken at 5, 10, 15, 20, 25, 35, 45, and 60-minute intervals. Following completion of the 60-minute sample, the reactor power supply and peristaltic pump were immediately turned off and the remaining samples were mixed on the vortex mixing unit. All 2 mL amber vials were secured in a .45 caliber ammunition container which served as a practical vessel for transport to HPLC instrumental analysis.

The treated effluent collected in the waste container was photographed for visual comparison to stock DNAN solution and then properly disposed of. The reactor and tube network were flushed with DI water in the same manner as priming the system to ensure all DNAN solution was removed from the reactor and supply lines. All glassware was rinsed with DI water and then cleaned with soap and tap water.

3.3 Data Collection and Analysis

3.3.1 DNAN Quantification

An Agilent Technologies 1260 Infinity HPLC system with a G1351C UV-VIS diode array detector (DAD) (Agilent Technologies, Santa Clara, CA) measuring absorbance at 253 nm was used to quantify DNAN concentrations for each AOP experiment sample.

A 1.8 μm , 2.1x50 mm, C18 column (Model #: 827700-902, SN: USWEY 12941, Agilent Technologies, USA) was used for separation of DNAN in the treated effluent. The mobile phase consisted of acetonitrile and water (0.1% formic acid) in the ratio of 60:40 at a flow rate of 0.6 mL/min. Under these conditions, DNAN elutes at approximately 1.1 minutes. The methodology provided sufficient DNAN peak resolution when expedited run times were desired. Quality control checks were conducted three

times on calibration curve samples (60% DNAN stock solution) for each experiment with a target of less than 10% relative error. Agilent Technologies ChemStation Rec B.04.03-SP1 software was used to integrate chromatogram peaks produced from the HPLC-DAD analysis. Manual integration was used only when the automatic integration software incorrectly quantified peaks due to software glitches. Chromatogram features for calibration curve samples provided relative quantification for treated DNAN samples. Appendix F details each control and AOP experiment calibration curve, chromatogram integration data, and corresponding DNAN concentrations over the course of the experiment.

3.3.2 Byproduct Analysis

The HPLC-MS makes qualitative analysis possible since each analyte (potential byproduct) has a unique mass spectrum (Kenkel, 2014). A 6130-quadrupole mass spectrometer (MS) was used for byproduct analysis following DNAN quantification in an effort to propose OBPs and explain prospective reaction mechanisms. Mass spectrum data was collected for each molar ratio experiment except 50:1. The single ion mass (SIM) spectrum was set to 240 atomic mass units (amu). This method assumed one acetonitrile molecule (41 g/mol) would be attached to DNAN (198 g/mol). The MS resolution was set to 1 atomic mass unit.

3.3.3 Rate Constant Computation

The reactor was modeled as a CSTR. The residence time is computed using Equation 2 and the mass balance in Equation 3 (Tchobanoglous et al., 2014) results in Equation 4 as described by Duckworth et al., (2015).

$$\tau = \frac{V}{Q} \quad (2)$$

τ : residence time (hydraulic retention time)

V : reactor volume = 35 mL

$$Q = \text{flow rate} = 2 \frac{\text{mL}}{\text{min}}$$

$$\text{mass}_{\text{accumulated}} = \text{mass}_{\text{in}} - \text{mass}_{\text{out}} - \text{mass}_{\text{degradation}} \quad (3)$$

$$\frac{C}{C_o} = \frac{\tau k_s e^{-t(k_s + \frac{1}{\tau})} + 1}{\tau k_s + 1} \quad (4)$$

C = DNAN concentration at time (t)

C_o = DNAN initial concentration ($t = 0$)

k_s = apparent first – order degradation rate constant

t = time of sample taken

Pseudo first-order rate constants (k_s) were retrieved by curve-fitting using MATLAB (ver. R2020a) as the computational platform. Relative DNAN concentrations over the course of AOP experiments served as input matrices. Raw data for DNAN degradation in terms of relative concentration can be found in Appendix F. The mathematical basis of the curve fit was a non-steady state solution for a CSTR with the first-order equation found in Equation 4. A prospective first order rate constant is selected by the code which is subsequently entered into the derivative of Equation 4. Following integration, the solution is compared to the modeled data until an appropriate fit is

realized. Appendix G contains all code, organized by data files and the iterative process of generating best-fit curves. Graphs were also created using MATLAB to provide comparative illustrations of DNAN degradation for all molar ratios.

3.4 Statistical Analysis

An outlier analysis was conducted upon retrieval of rate constants by subjecting each of the three molar ratio trials to the Q-test. This statistical test for rejection of data is appropriate for small data sets ($3 \leq n \leq 10$) where the suspect outlier is rejected for calculated Q-values greater than published values (Harvey, 2000) at a particular confidence level (Kenkel, 2014). Upon acceptance, the three rate constants for each molar ratio were averaged. The mean degradation across the three trials for each time interval were also averaged for further plotting and curve fitting in MATLAB. Appendix H details all outlier analysis calculations and data corresponding to average molar ratio rate constants.

A one-way analysis of variance (ANOVA) was conducted for each molar ratio to determine whether any two molar ratios possessed rate constants which were statistically significantly different. A significance level of 0.05 was selected, corresponding to a 95% confidence level. The ANOVA was coded in Python® via Jupyter Notebook's interactive, web-based environment. The model used molar ratios as treatments and rate constants as the response. The null hypothesis for the ANOVA states that all five molar ratios have equal mean rate constants. If the F-test conducted during the ANOVA results in a p-value lower than the chosen level of significance (0.05), the null hypothesis will be

rejected meaning two or more molar ratios possess mean rate constants which are statistically different.

Tukey's method uses pairwise comparisons when all sample sizes are equal and it was employed to determine which individual molar ratios possess statistically significant mean rate constants. This is a crucial step which accounts for the variability associated with each mean rate constant and provides the answer to research objective 1. The null hypothesis for Tukey's method states there is not a statistically significant difference between the two treatments (molar ratios) under consideration. Therefore, non-rejection (indicated by "False" in Python® output) of the null hypothesis indicates that two molar ratios do not have significantly different mean rate constants. An output of "True" indicates that a statistical difference does exist.

To employ parametric statistics and the ANOVA F-test associated with the methods described above, the data must meet three assumptions: (1) The samples are randomly and independently selected from the treatment populations, (2) all sampled populations have approximately normal distributions, and (3) the sample populations have equal variances (Mcclave et al., 2016). Shapiro-Wilk and Bartlett's test were used to confirm whether the assumptions were met for approximately normal distributions and equal variances, respectively. Appendix I provides all code used for statistical analysis of pseudo first-order rate constants.

Correlation between kinetic rate constants and molar ratios, pH values, starting concentrations, and measured DNAN masses were visually inspected via scatter plots then evaluated using Microsoft® Excel for plotting and calculation of Pearson correlation coefficients (r) and coefficients of determination (r^2). A positive or negative Pearson

coefficient near 1 indicates a relationship exists between the two variables under consideration, while a value near zero suggests the variables are independent of each other (Christian, 2004). Equation 5 is used to calculate the Pearson correlation coefficient.

$$r = \frac{\sum (x_i - \bar{x})(y_i - \bar{y})}{n s_x s_y} \quad (5)$$

r = correlation coefficient

n = number of observations

s_{x,y} = standard deviation of x or y

x_i or y_i = individual values of x or y

$\bar{x}$ or $\bar{y}$ = mean of all x_i or y_i values

A linear regression analysis was used to describe the effect of molar peroxide ratio manipulation on pseudo first-order rate constant. The statistical analysis tools available in Microsoft® Excel and Python® were employed to create linear and quadratic equations with associated predictive power. The adjusted coefficient of determination (R_a^2) was used due to its ability to incorporate both the sample size (n) and the number of parameters (β) included in the model. The R_a^2 is generally preferred when choosing a measure of model adequacy due to its conservative nature (Mcclave et al., 2016). Equation 6 describes R_a^2 calculation procedures.

$$R_a^2 = 1 - \left[\frac{n-1}{n-(k+1)} \right] \frac{SSE}{SS_{yy}} \quad (6)$$

$R_a^2 = \text{adjusted coefficient of determination}$

$n = \text{number of observations}$

$k = \text{number of predictor variables}$

$SSE = \text{sum of squared errors}$

$SS_{yy} = \text{total variability}$

Python® was used to test the four assumptions for the residuals associated with the model: (1) mean equaling zero, (2) constant variance (Breusch-Pagan test), (3) normally distributed (Shapiro-Wilk Test), and (4) independence (Durbin-Watson Test). Appendix N provides all code and Excel spreadsheets used for the regression analysis. The root mean squared error (RMSE) was calculated for each model constructed. This allows for measurement of model forecast error and can be used to evaluate the accuracy of the forecast for a given model, with lower RMSE values corresponding to better fits (Mcclave et al., 2016). Equation 7 provides RMSE calculation procedures.

$$RMSE = \sqrt{\frac{\sum(\text{measured } k_s - \text{predicted } k_s)^2}{n}} \quad (7)$$

$RMSE = \text{root mean squared error}$

$\text{measured } k_s = \text{experimental rate constant value}$

$\text{predicted } k_s = \text{modeled rate constant value}$

$n = \text{number of observations}$

IV. Results and Discussion

This section follows a pattern of describing figure elements followed by discussion of key insights. Data comprising all figures in this section has had suspect outlier values removed. The first experiment for the 1000:1 molar ratio appeared to be an outlier, resulting in a repeat experiment and resulting rate constant which passed the Q-test. A pipette error was suspected as a cause for the outlier. The outlier is not included in the plots below nor the statistical analysis of rate constants. Appendices H and F provide all raw data for the outlier and Appendix J details the three molar ratio trials on one plot to better illustrate the variability and curve fitting for each experiment. An experimental error occurred during the second trial of the 100:1 molar ratio experiments resulting in only 45 minutes of sample collection. Due to the DNAN degradation achieving nearly steady-state conditions after approximately 35 minutes, this experiment was retained and shown to not be an outlier.

4.1 The Effect of Molar Peroxide Ratio on DNAN Degradation

Figure 5 illustrates the removal of DNAN as a function of molar peroxide ratio in the AOP. The x-axis and y-axis show the time of the experiment over sixty minutes and relative DNAN concentration, respectively. The relative concentration allows for comparison of trials regardless of variability associated with initial DNAN concentrations (C_0) which are provided in Appendix E. A non-linear removal rate of DNAN was observed at every molar peroxide ratio. The curves align with a pseudo first-order model and are fit to the average degradation over each molar ratio's three distinct trials. Error bars represent one standard deviation above and below mean rate constants.

The extent of DNAN degradation depended on the molar peroxide ratio. At a molar peroxide ratio of 50:1, the relative concentration decreased from 1.0 to approximately 0.78 (22% DNAN removal). The DNAN relative concentration continued to decrease (corresponding to higher AOP efficacy) as the molar peroxide ratio increased up to a ratio of 500:1. Molar peroxide ratios of 100:1, 250:1, and 500:1 possessed final DNAN relative concentrations of approximately 0.73 (27% DNAN removal) 0.66 (34% DNAN removal), and 0.63 (37% DNAN removal), respectively. However, when the molar peroxide ratio was increased above 500:1 to 1000:1, the relative concentration upon conclusion of treatment was approximately 0.72 (28% DNAN removal). The 500:1 molar ratio achieved the highest overall degradation with a mean rate constant of 0.0320 min^{-1} and approximately 37% DNAN removal over 60 minutes. Notably, the molar ratio 250:1 was very close to the 500:1 mean rate constant, possessing a mean k_s of 0.0307 min^{-1} . Both 100:1 and 1000:1 molar peroxide ratios possessed identical mean rate constants of 0.0233 min^{-1} , while the 50:1 mean rate constant was found to be 0.0180 min^{-1} . These results agree with Stubbs (2017) concerning the 500:1 molar ratio constituting a promising ratio in UV-LED experiments for the degradation of various organic chemicals.

As expected, the control experiment (0:1 molar ratio) maintained a rate constant of nearly zero at 0.001 min^{-1} . This confirms that the addition of hydrogen peroxide is required to induce rapid degradation of DNAN via hydroxyl radicals and the effect of photochemical degradation alone is a slow process, agreeing with the only other UV/H₂O₂ AOP which tested DNAN at a molar ratio of 0:1 (Yang et al., 2018). Although DNAN may be slowly degraded by absorbing light (Rao et al., 2013), this control

experiment confirms that while hydrogen peroxide is photochemically degraded over 60 minutes, DNAN is not.

Results in Figure 5 show that, when molar peroxide ratios were between 500:1 and 1000:1, the number of hydroxyl radicals available to react with DNAN was not increased by adding more hydrogen peroxide. This finding strongly suggests radical scavenging, which occurs when radicals are consumed by competing reactions. Subsequently, this negatively impacts DNAN degradation. Conversely, results from molar peroxide ratios of 50:1 and 100:1 indicate peroxide-limitation occurs due to insufficient radical production, thus prematurely terminating DNAN oxidation reactions. This finding supports Hypothesis #1 that DNAN removal kinetics are influenced by both hydroxyl radical scavenging and peroxide-limiting reactions.

Due to experiments only utilizing DI water, hydrogen peroxide, and DNAN, potential radical scavengers are limited to bicarbonate, hydrogen peroxide, and hydroxyl radicals. Reactions between hydroxyl radicals (radical-radical) are the most thermodynamically favorable, with an activation energy of 8 KJ/mol. Radical-hydrogen peroxide and radical-bicarbonate reactions are less thermodynamically favorable, with activation energies of 14 and 21.1 KJ/mol, respectively (Buxton et al., 1988). This suggests radical-radical reactions constitute a primary inhibitor for oxidation of DNAN in the AOP experiments, though molar peroxide ratios above 500:1 may be subject to significant radical-hydrogen peroxide scavenging.

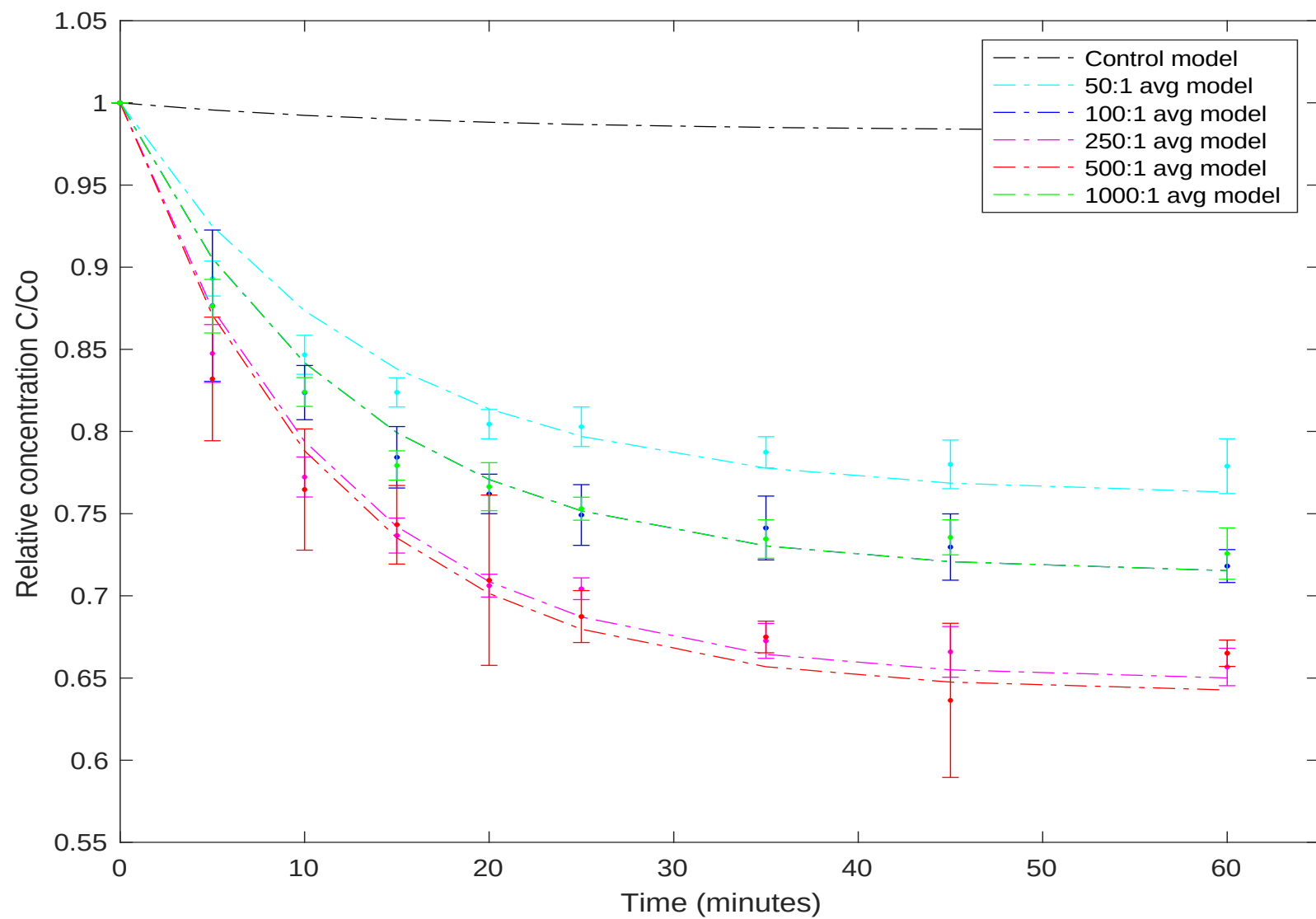


Figure 5: The effect of molar peroxide ratio on DNAN removal

Figure 6a tabulates each rate constant for individual trials while Figure 6b and 6c provide plots and a regression analysis which further inform the previous discussion in Figure 5. Figure 6b shows the molar peroxide ratio on the x-axis and the kinetic rate constant on the y-axis. The individual blue data points relate to each trial for corresponding molar ratios. Figure 6b shows the highest pseudo first-order rate constant achieved for all experiments occurred at the 500:1 molar ratio with a value of 0.034 min^{-1} . The lowest k_s observed was 0.017 min^{-1} during a 50:1 trial. Based on Figure 6b, it appears the 500:1 molar ratio performs slightly better than the 250:1 molar ratio, with an average rate constant 0.0013 min^{-1} greater than that of 250:1. Further statistical analysis is required to determine whether the variability associated with each group of molar ratio experiments warrants a statistical difference between any or all molar ratios tested. Figure 6b indicates the AOP increasingly oxidizes DNAN from 50 to 500:1 molar ratios, with negative impacts as the dosage surpassed 500:1 and increased to a 1000:1 ratio. Minimal gains were realized by doubling the molar ratio from 250 to 500:1. This may be attributed to hydroxyl scavenging transpiring at molar ratios greater than 500:1 and premature termination of $\text{OH}\cdot$ reactions below a molar ratio of 250:1. This conclusion is further confirmed by considering the average rate constants for the 100:1 and 1000:1 molar ratios are identical.

The three curves labeled “Linear”, “Quadratic 1”, and “Quadratic 2” shown in Figure 6b were generated from a regression analysis. As depicted graphically in Figure 6b and by the R_a^2 value of 0.496 in Figure 6c, the relationship between molar ratio and k_s does not correspond to a linear fit over the entire range of molar ratios tested. It is possible k_s may be predicted linearly up to a molar ratio of 250:1, which yielded a R_a^2

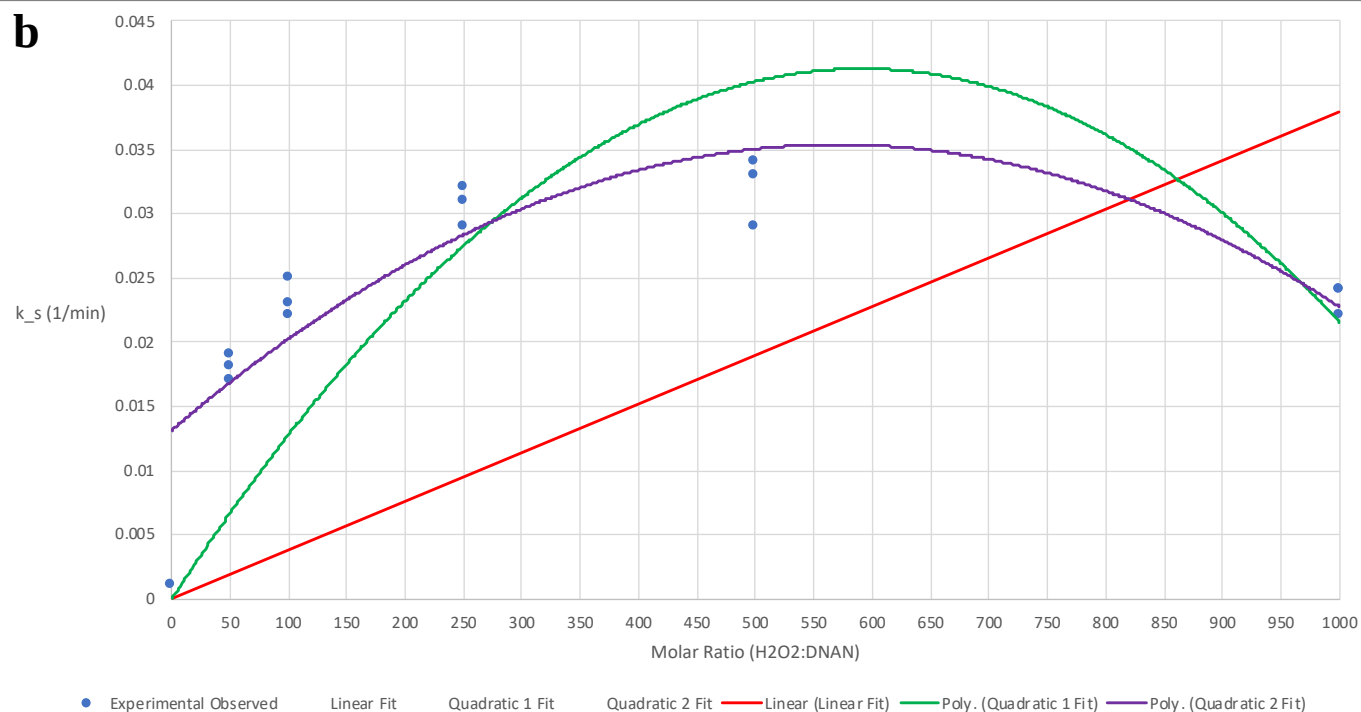
value of 0.762 (Appendix N). A quadratic relationship appears to more accurately describe the relationship between an increase in molar ratio and corresponding pseudo first-order rate constants. The green curve labeled “Quadratic 1” possesses a favorable R_a^2 value of 0.824; however, the predictive power of this statistic is deceiving upon visual inspection and scrutiny of the residuals and RMSE associated with the regression analysis. The Quadratic 1 model clearly underestimates and overestimates k_s values for molar ratios below and above 250:1, respectively. The purple curve labeled “Quadratic 2” has a R_a^2 value of 0.707 and appears to more accurately represent the relationship while reducing residual error (RMSE of 0.00397). Molar ratios below 50:1 are heavily overestimated. The Quadratic 2 model meets three of the four assumptions required for a valid regression analysis. The mean of all residuals is equal to approximately zero ($-1.32\text{E-}15$), the residuals possess constant variance (p-value of 0.349 for Breusch-Pagan test), and the random errors are independent of one another (Durban-Watson value of 1.26). The assumption of the residuals being normally distributed was not met, with a p-value of 0.0033 for the Shapiro-Wilk test. This is not surprising upon visual inspection of the curve in Figure 6b. The model’s residual errors are lower than the curve up to 250:1, after which the model overpredicts k_s values. Of the four assumptions required for a valid regression analysis, the assumption that the random errors are normally distributed is the least restrictive and McClave et al., (2016) states regression analysis is robust with respect to nonnormal errors. Figure 6c provides corresponding equations for each model allowing for various molar ratios not tested (i.e. 300:1) to be predicted, though caution should be applied based on aforementioned residual normality issues.

The regression analysis indicates the degradation of DNAN in the AOP may quadratically relate to the molar ratio employed. More sophisticated curve fitting may allow for greater predictive power. A key takeaway pertains to the observation that the rate at which DNAN is oxidized in the AOP is positively correlated to the amount of hydrogen peroxide and corresponding $\text{OH}\cdot$ generation up to a certain molar ratio (i.e., 250:1). Passing this threshold value, which will be particular to each reactor and experimental methodology, will result in minimal or diminishing returns. Appendix N provides all raw data generated from the MS Excel regression analysis as well as Python® code for regression assumption validation demonstrated for the Quadratic 2 model.

a

Molar Ratio (H ₂ O ₂ :DNAN)	Rate Constant (min ⁻¹)	Avg. Rate Constant (min ⁻¹)
0	0.001	0.001
50	0.019	0.0180
50	0.018	
50	0.017	
100	0.025	0.0233
100	0.022	
100	0.023	
250	0.032	0.0307
250	0.029	
250	0.031	
500	0.033	0.0320
500	0.029	
500	0.034	
1000	0.024	0.0233
1000	0.024	
1000	0.022	

b



c

Fit	Equation	R_a^2	RMSE
Linear (red)	$k_s = \text{molar ratio} \times 3.79\text{E-}5 + 0$	0.496	1.667E-02
Quadratic 1 (green)	$k_s = [\text{molar ratio} \times 1.396\text{E-}4] + [(\text{molar ratio})^2 \times -1.18\text{E-}7] + 0$	0.824	7.876E-03
Quadratic 2 (purple)	$k_s = [\text{molar ratio} \times 7.803\text{E-}5] + [(\text{molar ratio})^2 \times -6.841\text{E-}8] + 0.0131$	0.707	3.971E-03

Figure 6: The relationship between molar peroxide ratio and pseudo first-order rate constants

Figure 7 compares results to optimal molar ratios and rate constant values reported in Su et al., (2019). The x-axis and y-axis display molar ratio and kinetic rate constant (min^{-1}), respectively. Blue data points represent current research results while orange data points comprise results from Su et al., (2019). Tabulated values of all molar ratios and corresponding kinetic rate constants are provided for both studies in the lower-right corner of Figure 7. First-order rate constants for Su et al., (2019) were calculated using MATLAB due to the authors only reporting zero-order kinetics. A similar method was used for retrieval of rate constants as described in the current research, and all MATLAB code used for retrieval of Su et al., (2019) rate constants can be found in Appendix K. The molar ratios employed, and observed k_s , were substantially lower for Su et al. (2019). A common trend between studies was found in identification of an optimal molar ratio where DNAN degradation peaks and then slows upon further addition of H_2O_2 . Su et al. (2019) found this to occur at a molar ratio of approximately 70:1, while the current research suggests it occurs around 500:1. Yang et al. (2018) did not provide details on kinetic rate constants, only noting DNAN degradation increased from 50 to 125:1 and decreased from 125 to 250:1. Results from the current research agree with the overall premise of both studies concerning gradual increases in DNAN degradation followed by reduced performance, though each study disagrees on when such an optimal ratio is realized. This is likely attributed to previously discussed variations in methodologies, reactor designs, and irradiation sources between each study in the literature review. A comparison of initial conditions is provided in Appendix K. Results from this research appear to be the first to test molar ratios above 250:1 and further expound on trends seen in Su et al., (2019) and Yang et al., (2018).

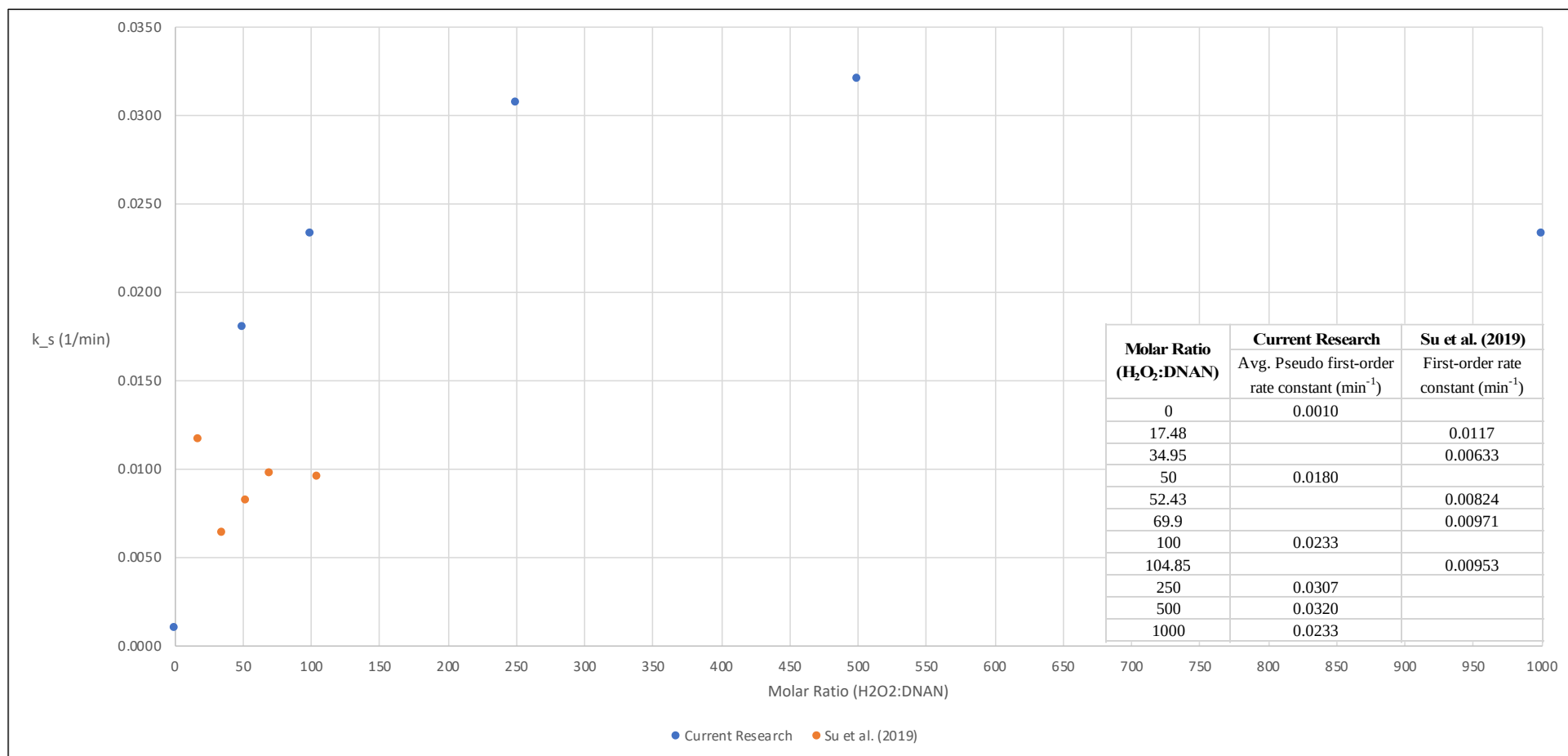


Figure 7: Results compared to Su et al. (2019)

4.2 Statistical Analysis of First-Order Rate Constants

Figure 8 illustrates the variability of first-order rate constants retrieved for each molar peroxide ratio. The x and y-axis provide values of different molar ratios and k_s , respectively. Box and whisker plots encompass each molar ratio which provide a qualitative, visual representation of the variance associated with the three trials comprising each group of molar ratio experiments. The wider the boxes are in a vertical orientation, the greater the variability. Whiskers extending vertically describe the upper and lower bounds and any outliers present are shown by single black dots representing each data point which may be an outlier. The green horizontal line passing through each box plot represents the median rate constant for each molar ratio. Each individual rate constant for the five molar peroxide ratios examined were subjected to the Q-test at a 95% confidence level. All passed the Q-test and specific Q-test values for each molar ratio are found in Appendix H along with 95% confidence intervals. This is further confirmed by the box plots in Figure 8 which show no individual “dots” representing data points for suspect outliers.

The control (0:1 molar ratio) experiment does not contain a box plot due to only one trial being conducted. The variability is greatest at the 500:1 molar ratio, though no general trends can be shown from the box plots alone concerning a positive correlation between variability and molar ratio. The one-way ANOVA of k_s resulted in a F-statistic of 36.05 and a p-value of 7×10^{-6} , which is approximately zero and results in rejection of the null hypothesis. The null hypothesis states that all five molar ratios (50, 100, 250, 500, 1000:1) possess equal mean rate constants when considering the variability

associated with each experiment. This indicates a high confidence that molar peroxide ratio is a statistically significant predictor of the first order rate constant. Each molar ratio passed the Shapiro Wilk test ($p\text{-values} > 0.05$) for normality except for 1000:1. This is expected due to the 1000:1 molar ratio possessing two identical rate constant values of 0.024 min^{-1} . McClave et al. (2016) shows ANOVA to be a very robust method when the assumption of normality is not satisfied exactly. Therefore, the 1000:1 molar ratio was retained for evaluation with existing data. Bartlett's test yielded a p-statistic of 0.73, resulting in a failure to reject the null hypothesis that equal variances exist across all treatments (molar peroxide ratios). Python® ANOVA table outputs and statistical tests for assumptions displaying these values are provided in Appendix L.

The alternative hypothesis for the F-test states at least two molar peroxide ratios possess statistically different mean rate constants. Tukey analysis of k_s by molar ratio showed no statistically significant differentiation at a 95% confidence level between the molar ratios 100:1 and 1000:1, along with 250:1 and 500:1. Comparison of the following molar ratio's mean k_s values showed a statistical difference: 50:1 & 100:1, 50:1 & 250:1, 50:1 & 500:1, 50:1 & 1000:1, 100:1 & 250:1, 100:1 & 500:1, 250:1 & 1000:1, and 500:1 & 1000:1. The Tukey multiple comparison of means confirms that 100 and 1000:1 molar ratios perform similarly. Likewise, the 250 and 500:1 mean k_s values are not statistically different, indicating the 250:1 molar ratio is optimal due to employing half the hydrogen peroxide and still generating sufficient radicals to achieve high levels of DNAN degradation. This informs research objective 1 and shows that not only is molar peroxide ratio a reliable predictor variable of DNAN degradation in the UV-LED/H₂O₂ AOP, but a best-case ratio appears to be a non-extreme value of 250:1. This supports Stubbs (2017)

findings of molar ratios in vicinity of 500:1 being well suited for the degradation of many organic chemicals in the UV-LED AOP. Appendix L shows the Python® output for all mean rate constants compared individually against one another for respective molar ratio experiments.

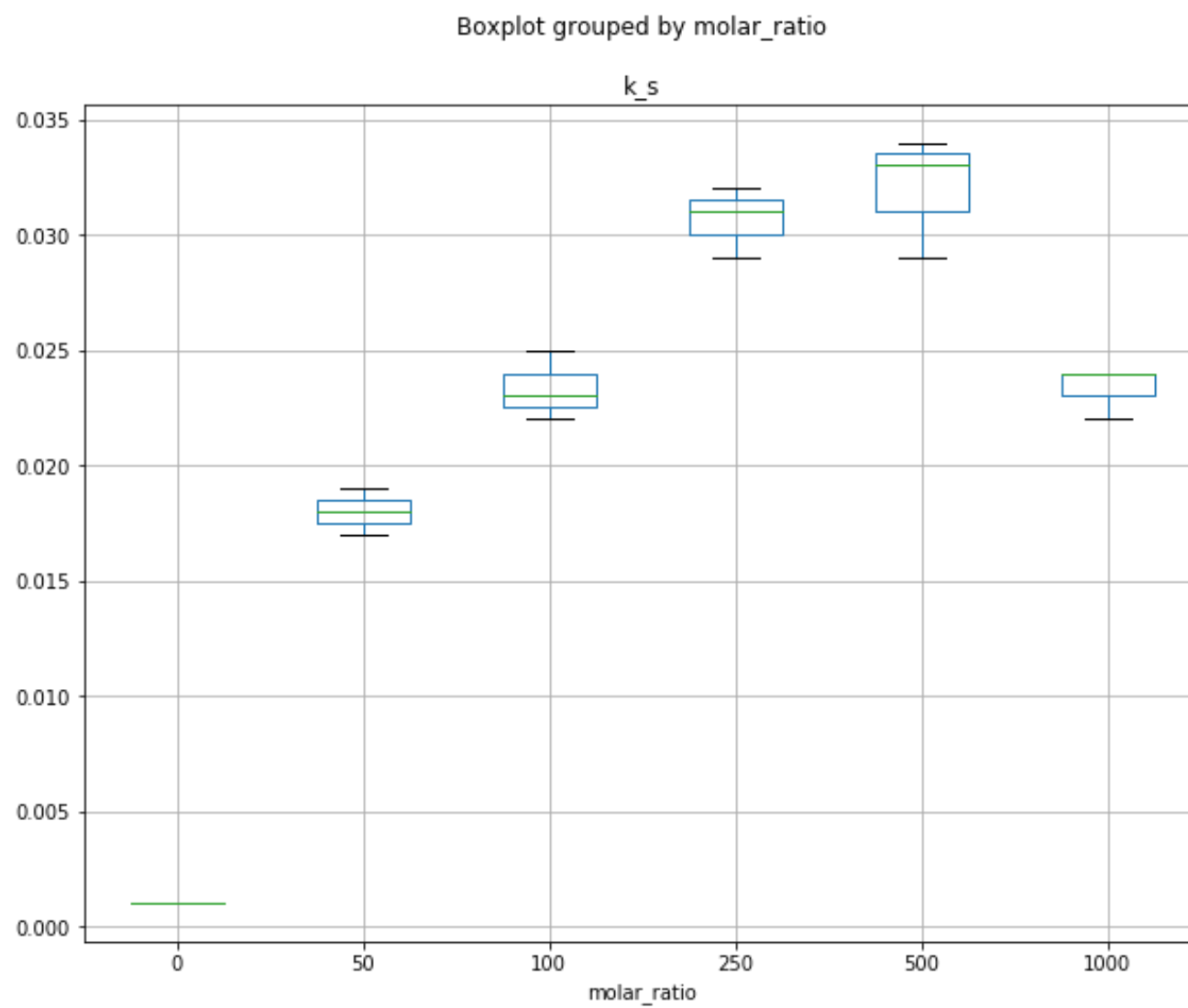


Figure 8: ANOVA of pseudo first-order rate constants for molar peroxide ratios

The pH, measured DNAN mass (from solution preparation), and starting concentration (C_0) showed no significant correlation with regards to effect on kinetic rate constant. Pearson correlation coefficient values for each were 0.40, 0.02, and -0.12, respectively. Christian (2004) describes any r -value less than 0.9 as a very poor fit due to both the dependent and independent variables being assigned equal weight. The r^2 value is more conservative, and further reinforces minimal correlation between rate constant dependence on any variables other than the molar peroxide ratio. Appendix L provides all correlation coefficient calculations and associated plots (i.e., pH vs. k_s). Concerning the effect of pH, these results are consistent with Su et al. (2019) and Yang et al. (2018) in that molar peroxide ratio retains much greater significance than pH manipulation. Still, a positive correlation is observed in the current research and may warrant further investigation.

4.3 DNAN Oxidation Byproduct Analysis

Figure 9 displays a chromatogram produced from the HPLC-DAD analysis for the first (trial 1) 500:1 molar peroxide ratio experiment. Figure 9a and 9b illustrate features detected by the DAD at a 5-minute sampling time. The x and y-axis display retention time (minutes) and UV-VIS DAD signal intensity (absorbance), respectively. Proceeding from left to right on Figure 9a, the first large feature with a retention time of 0.358 minutes is representative of the solvent peak. This feature is a result of the HPLC methodology employed and is caused by the difference in the refractive index between the sample injected and the mobile phase composition. This peak was present in pure DI water as displayed in Appendix M and also in every control (with H_2O_2 and no UV-light).

The retention time for this peak remains consistent throughout each experiment. Any non-prominent features present before the solvent peak are likely resultant from prior experiment samples (“ghost peaks”) or minor contaminants from handling procedures. The second large feature in Figure 9a represents DNAN eluting from the column at a retention time of 1.104 minutes. Figure 9b magnifies a smaller feature associated with a retention time of 0.83 minutes. A consistent method of manual integration was used to quantify the prospective OBP features as seen in Figure 9b.

DNAN appears to degrade into OBPs as represented by features eluting prior to the prominent DNAN peak on the chromatogram as evidenced by Figure 9b. The small features eluting before DNAN with a retention time of 0.637 and 0.831 minutes are not seen in control experiments and warranted further study by HPLC-MS to identify potential molecular structures. These features are consistent for the majority of experiments and found to have a retention time near 0.6 and 0.8 minutes for numerous molar peroxide ratios. It is also possible DNAN transformation products are present in the solvent peak due to not being retained by the HPLC column. Appendix M provides chromatograms for blank samples, calibration curve samples, controls, and every sampling interval for both 250:1 and 500:1 molar peroxide ratios. Reference Appendix F for a complete list of features identified outside of DNAN for all experiments.

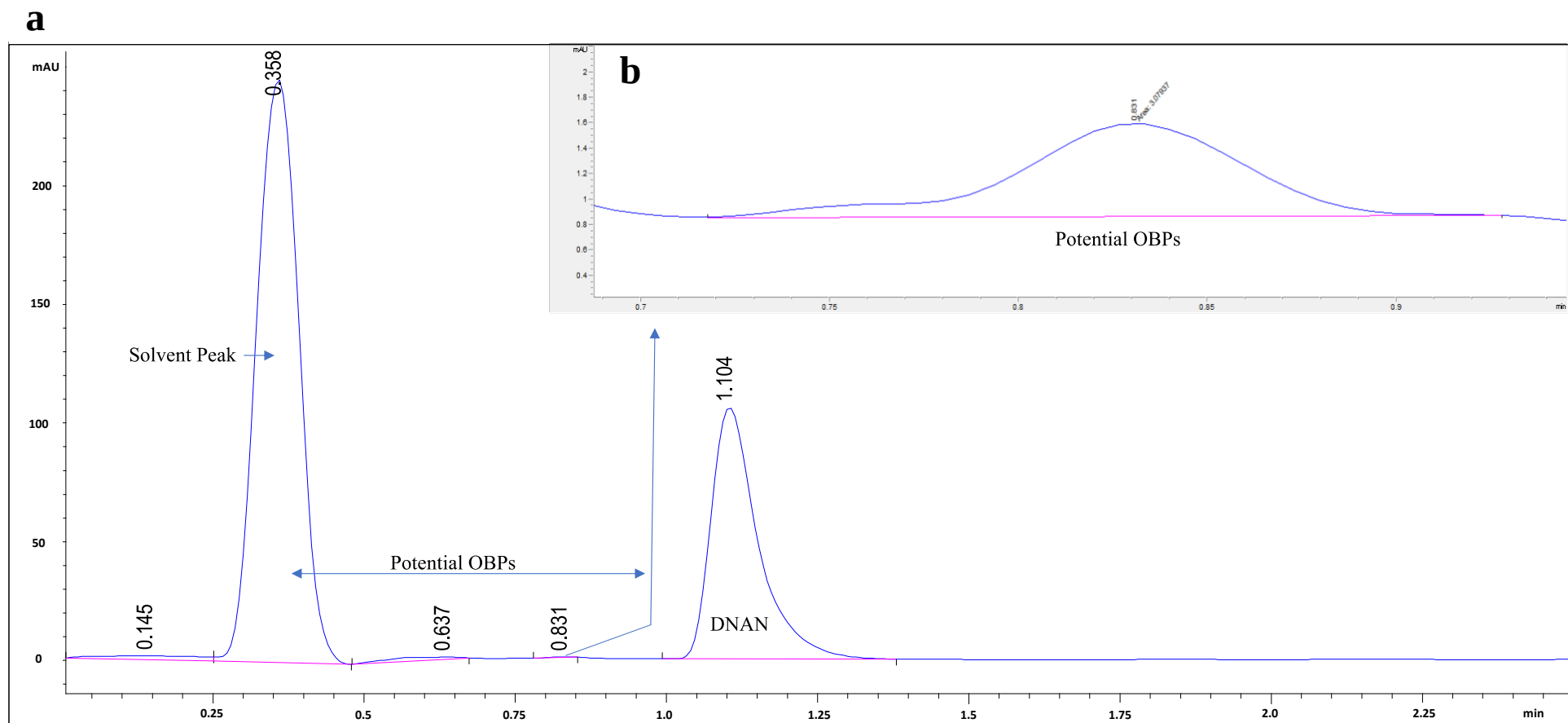


Figure 9: DNAN transformation in AOP for 500:1 molar peroxide ratio

Figure 10 illustrates the potential for byproduct growth over the duration of experiments for 250 and 500:1 molar peroxide ratios. These ratios were selected due to maximum DNAN degradation observed, corresponding to a potentially higher yield of OBPs. An increase in feature area over the 60-minute AOP experiment may correspond to OBP generation and inform follow-on mass spectroscopy analyses. The x and y-axis for each plot represent the time in minutes and UV-VIS DAD-signal in absorbance units (AU), respectively. Each plot contains data from each molar ratio's triplicate experiments, represented by orange, blue, and grey data points. Figure 10a shows chromatogram peak fluctuations for the 250:1 molar ratio at retention times ranging from 0.821 to 0.827 minutes. Figure 10b and 10c show chromatogram peak fluctuations for the 500:1 molar ratio at retention times ranging from 0.831 to 0.844 minutes and 0.583 to 0.650 minutes, respectively. Appendix F provides integrated chromatogram peak areas identified for all experiments not included in Figure 10.

Chromatogram features constituting potential OBPs appear to generally increase over the duration of the AOP experiment as seen in Figure 10. In nearly every 250 and 500:1 experiment, Figure 10a, 10b, and 10c illustrate how features are slightly larger at 60 minutes than at 5 minutes. It should be noted that these incremental increases are relatively small when compared to DNAN concentrations. The results from Figure 10 are meaningful in the sense that DNAN is observably oxidized in the AOP to various compounds which not only remain throughout the experiment, but potentially increase in concentration.

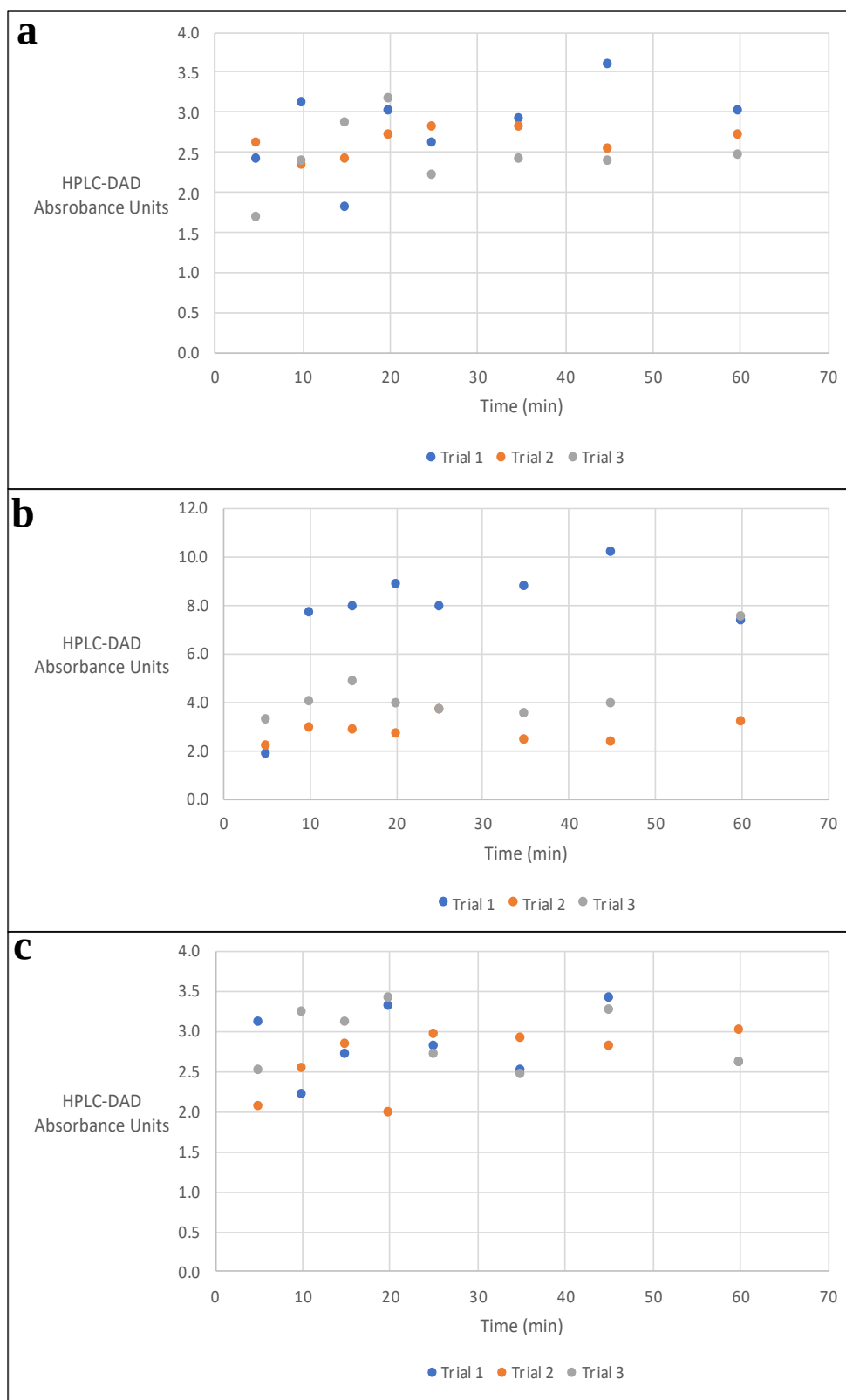


Figure 10: Byproduct Growth Potential

In every experiment, treated DNAN solution demonstrated a persistent yellow color consistent with literature investigating hydrolysis, photo-transformation, and advanced oxidation of DNAN. In the present research, the interpretation of DNAN OBP identities (and subsequent reaction mechanisms) remains challenging due to the HPLC mobile phase and mass spectrometry methodology creating nonideal conditions for byproduct analyses. A brief list of OBPs is proposed based on the analysis from a 500:1 (trial 1) molar peroxide ratio experiment.

Figure 11 illustrates various masses present in the spectra. Figures 11a and 11b correspond to a mass of 167 atomic mass units (amu) while Figures 11c and 11d correspond to a mass of 184 amu. Figures 11a and 11c show extracted ion chromatograms. The x and y-axes represent the retention time (minutes) and MS signal response, respectively. Figures 11b and 11d show the mass-to-charge ratio on the x-axis and the signal intensity on the y-axis. The spectrum indicates a potential presence of 1,3-dinitrobenzene, with signals present at 167 (Figure 11b) amu. The MS resolution was maintained at 1 amu; therefore, a mass of 168 amu is possible and corresponds with 1,3-dinitrobenzene. The red rectangle present in Figure 11b highlights this mass-to-charge ratio. Zhou et al., (2018) describes this reaction occurring through a series of hydrogen abstraction and dehydration reactions in a similar manner to TNT in AOPs. Prior to the potential formation of 1,3-dinitrobenzene, Zhou et al., (2018) also proposes the combination of a radical intermediate with $\text{OH}\cdot$ to form 2,4-dinitrobenzoic acid (212 amu). This corresponds to +2-charged dinitrobenzene with a carboxylic acid. In an acidic environment, the carboxylic acid could dissociate a hydrogen atom resulting in a mass corresponding to half of 2,4-dinitrobenzoic acid (106 amu). Considering the MS

resolution of 1 amu, a mass-to-charge ratio of 105 is feasible and was identified (Appendix O) which may correspond to the molecular structure consistent with 2,4-dinitrobenzoic acid. The potential presence of 2,4-dinitrobenzoic acid or 1,3-dinitrobenzene contributes evidence to hydrogen abstraction reaction mechanisms. A molecular weight of 184 amu was identified as shown in Figure 11c and 11d. The red rectangle present in Figure 11d highlights this mass-to-charge ratio which may be associated with the formation of 2,4-DNP and methanol via substitution of DNAN's methoxy group with a hydroxyl group (Rao et al., 2013; Yang et al., 2018). Appendix O provides additional chromatograms and evidence of DNAN molecules bonding to acetonitrile upon entering the mobile phase (240 amu).

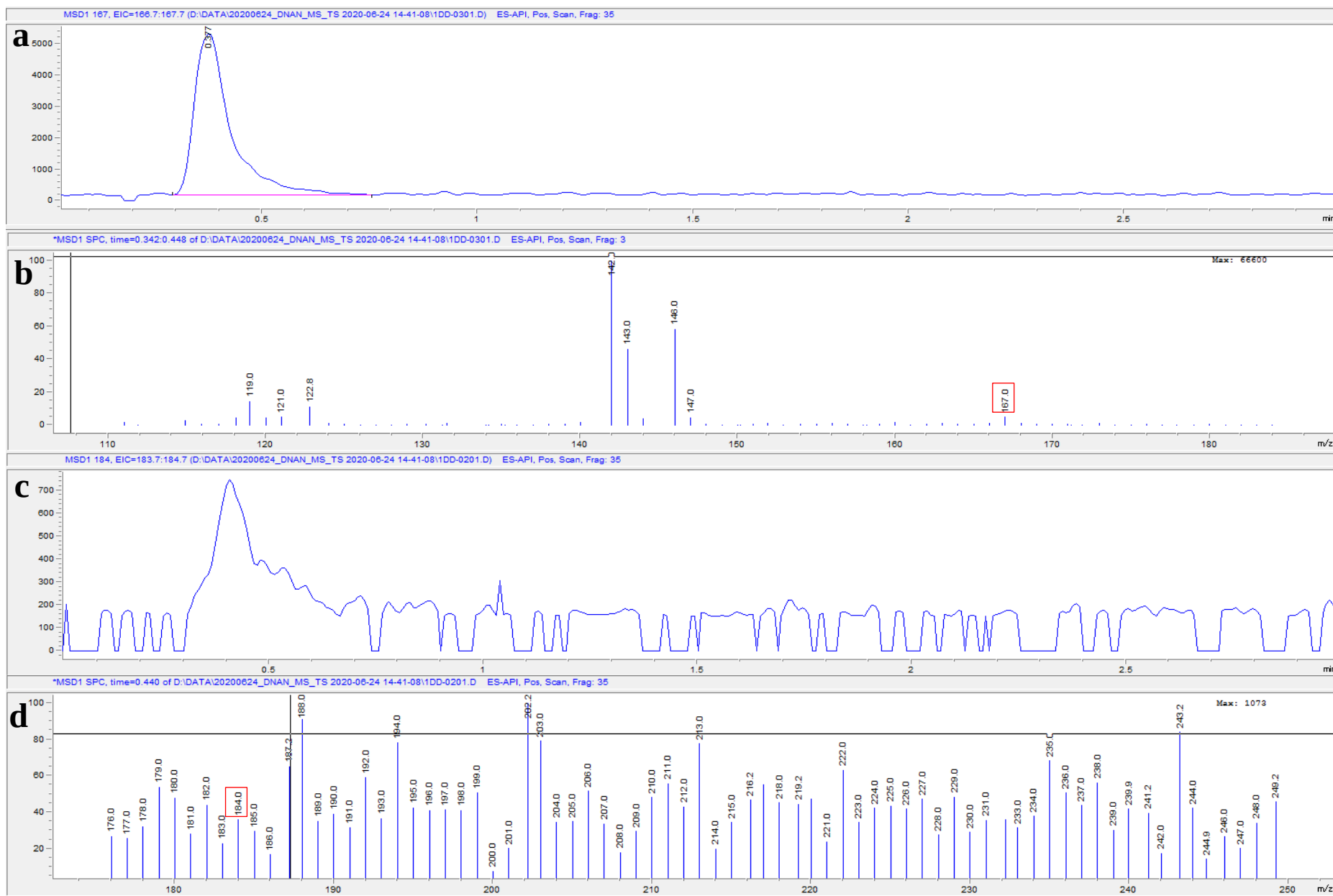


Figure 11: Mass Spectrum for DNAN Degradation

It should be noted that multiple masses detected led to convoluted molecular structures which decreased the confidence associated with OBP proposals. The consistent observation of discolored DNAN effluent confirms transformation of DNAN into subsequent degradation products. Nevertheless, Figure 11 exemplifies that not only is DNAN forming OBPs, but the processes (HPLC-DAD and MS) used to quantify and identify such analytes may impose degradation not attributable to the AOP. The numerous masses present in the spectrum require meticulous examination before a detailed byproduct structure summary may be composed. This task has been reserved for future research. The mass spectrum data collected in this research may still be useful in follow-on studies to identify trends present in various experimental conditions. Research objective 2 requires further study to fully answer the question of DNAN OBP identities and reaction mechanisms for DNAN degradation; however, this research confirms the presence of numerous mass-to-charge ratios which could be attributable to the AOP and provides data which may be further explored. Section 5.3 provides greater detail concerning future recommendations for identification of DNAN AOP byproducts.

4.4 Investigative Questions Answered

The first research objective required explanation of how the concentration of hydrogen peroxide influenced the degradation of DNAN in the UV-LED AOP. The associated hypothesis was that both peroxide-limiting reactions (low molar peroxide ratios) and hydroxyl radical scavenging (high molar peroxide ratios) occur over the range of ratios tested. Hypothesis #1 was supported by this research by demonstrating the mean rate constant increased from 50 to 500:1 molar peroxide ratios. This was followed by a

decrease in DNAN degradation from 500 to 1000:1 ratios. These results provide evidence that the number of hydroxyl radicals available to react with DNAN was not increased by adding more H_2O_2 than a 500:1 ratio and that radical scavenging occurs, negatively impacting DNAN removal in the AOP. Research objective 1 was further informed by the identification of the 250:1 molar peroxide ratio being optimal. This was due to a non-statistically significant difference between the mean k_s values for 250 (0.0307 min^{-1}) and 500:1 (0.032 min^{-1}) molar ratios. The differences between each molar ratio's pseudo first-order rate constant were statistically significant except for pairwise comparisons of 250 & 500:1 and 100 & 1000:1.

The second research objective inquired how DNAN is transformed in the AOP with the associated hypothesis that numerous OBPs would result from oxidation of DNAN. The oxidation of DNAN via hydroxyl radicals appears to yield numerous OBPs as observed by the mass spectroscopy analysis. This research indicates that not only are OBPs generated, but they may increase during the experiment and persist, not being degraded over a 60-minute treatment interval. The formation of 1,3-dinitrobenzene through hydrogen abstraction reactions and 2,4-DNP via radical substitution were proposed as possible DNAN OBPs. Data collected in this study may allow for follow-on proposal of OBP molecular structures and accompanying evidence supporting reaction mechanism(s) present during DNAN oxidation in the AOP.

V. Conclusions and Recommendations

5.1 Conclusions of Research

Key outcomes from this research are summarized below:

- The relative concentration of DNAN was reduced from 1 to approximately 0.63 over a range of molar ratios. The pseudo first-order rate constant for DNAN was statistically and positively correlated with molar peroxide ratio up to 500:1, after which negative effects were observed. A quadratic model appears to fit the relationship between H₂O₂ dosage and DNAN degradation over range of molar ratios spanning from 0 to 1000:1. There was no statistically significant difference between pseudo first-order rate constants of the molar ratios 250 and 500:1, resulting in 250:1 being characterized as optimal with a k_s of 0.0307 min⁻¹.
- Oxidation byproduct analysis indicated that DNAN transforms into numerous degradation compounds. These OBPs persist from the start of DNAN treatment in the AOP and may increase in concentration over the course of oxidation. The chemicals 1,3-dinitrobenzene and 2,4-dinitrophenol may constitute DNAN OBPs.

5.2 Significance of Research

This research provides a baseline for comparison of DNAN degradation in AOPs when other elements (i.e., IMX-101 constituents) are present in the water matrix. It also serves future studies as a point of reference when manipulating variables such as LED power output, longer treatment periods, and intermittent H₂O₂ dosages. Furthermore, it

contributes to sparse scientific literature comprising both UV-LED induced AOPs and advanced oxidation of insensitive munitions.

This research described how H_2O_2 dosage affects the degradation of DNAN in a UV-LED AOP. It is part of a collaborative effort constituting the first use of LEDs to produce hydroxyl radicals for the advanced oxidation of DNAN. The dependence of DNAN degradation kinetics on H_2O_2 concentration was demonstrated over a wider range of molar peroxide ratios than previous studies, finding that ratios up to 500:1 do not appear to induce hydroxyl scavenging. A regression model was proposed which described the quadratic relationship between molar ratio and degradation of DNAN. Finally, DNAN may transform into multiple byproducts, including 1,3-dinitrobenzene and 2,4-DNP, which appear to endure the AOP treatment process and warrant further study to determine toxicity and persistence of DNAN OBPs.

These results offer evidence to the DoD that advanced oxidation of DNAN is promising, specifically with LEDs as an alternative to traditional mercury lamps. Munitions manufacturing plants dependent on GAC are potential benefactors of this research along with range training area remediation efforts.

5.3 Recommendations for Future Research

Future research can be divided into manipulation of experimental conditions and byproduct analysis:

- A pressing requirement appears to pertain to the treatment of IM-producing wastewater at munitions manufacturing facilities. Advanced oxidation of DNAN will be affected by the presence of IMX-101 and

IMX-104 constituents (i.e., NQ and NTO); therefore, future research should seek to treat replicate mixtures of IMX wastewater consistent with IM concentrations present in the effluent. A matured understanding of reaction mechanisms, byproduct structures, and IM degradation kinetics associated with mixtures will provide evidence for whether pilot-scale testing is justified. The effect of pH on the oxidation of DNAN does not appear significant; however, controlled manipulation of this variable would provide further insight into ideal operating conditions which have proven important in oxidation of other organic chemicals in the UV-LED AOP.

- Instrumental analysis must consider both quantification of DNAN along with identification of OBPs. The HPLC-DAD and MS methodology allowed for rapid data analysis, accurate quantification of DNAN, and instrumental longevity. This method also degraded the ability to identify OBPs in the mass spectrum. A different mobile phase and MS methodology is recommended, along with increased run times to allow for enhanced peak resolution. Acetonitrile and water are endorsed for continued use in the mobile phase, though determination of ideal operating conditions requires further testing before specific parameters can be recommended. The time-dependent transformation of DNAN to 2,4-DNP has been described in previous studies and should be quantified for future UV-LED AOP research. Therefore, standards of 2,4-DNP and DNAN

should be procured to enable enhanced accuracy, DNAN quantification, and OBP identification.

5.4 Summary

Development of diverse water treatment technologies is crucial to the DoD and LED-induced AOPs offer a potential solution to current IM wastewater treatment inefficiencies. This study found H_2O_2 dosage significantly affects DNAN degradation kinetics. The DNAN degradation can be described by pseudo first-order rate constants and a quadratic relationship over a sufficient range of molar peroxide ratios, with both radical-limiting reactions and hydroxyl scavenging occurring. DNAN degrades into various compounds upon AOP treatment and may form 1,3-dinitrobenzene and 2,4-dinitrophenol.

Appendix A – Experiment Schedule

Experiment Schedule		
Date	Molar Ratio	Lab Notes
5/27/20	0:1 (controls)	
6/3/20	100:1	
6/10/20	100:1	experiment error resulted in sampling up to 45 min vice 60
6/17/20	100:1	
6/24/20	500:1	
7/1/20	500:1	
7/8/20	500:1	pH calibration error
7/14/20	1000:1	outlier
7/21/20	1000:1	
7/28/20	1000:1	
8/4/20	250:1	
8/4/20	250:1	
8/11/20	250:1	
8/11/20	50:1	
8/18/20	50:1	
8/18/20	50:1	
8/25/20	1000:1	repeat for 1000:1 outlier on 7/14/20

Appendix B – Stock DNAN Solution Concentrations

Researcher	Date	Molar Ratio	weigh boat measurements (empty) (g)				average (g)	weigh boat + DNAN measurements (g)				average (g)	mass obtained (g)	experiment concentration (ppm)
Dr. A. Burdsall	5/22/20	0:1 (control)	0.595920	0.595924	0.595922	0.595922		0.598420	0.598424	0.598432	0.598425		0.002503	10.013333
Dr. A. Burdsall	5/29/20	100:1	0.638126	0.638127	0.638133	0.638129		0.640633	0.640641	0.640656	0.640643		0.002515	10.058667
Dr. A. Burdsall	6/5/20	100:1	0.788224	0.788224	0.788220	0.788223		0.790723	0.790726	0.790721	0.790723		0.002501	10.002667
Dr. A. Burdsall	6/11/20	100:1	0.651493	0.651493	0.651489	0.651492		0.653992	0.653998	0.653995	0.653995		0.002503	10.013333
Dr. A. Burdsall	6/19/20	500:1	0.629599	0.629600	0.629604	0.629601		0.632101	0.632104	0.632107	0.632104		0.002503	10.012000
Dr. A. Burdsall	6/26/20	500:1	0.531593	0.531596	0.531599	0.531596		0.534099	0.534098	0.534104	0.534100		0.002504	10.017333
Dr. A. Burdsall	7/2/20	500:1	0.647139	0.647140	0.647139	0.647139		0.649637	0.649640	0.649642	0.649640		0.002500	10.001333
T. Searcy	7/10/20	1000:1	0.648295	0.648295	0.648296	0.648295		0.650793	0.650800	0.650806	0.650800		0.002504	10.017333
T. Searcy	7/16/20	1000:1	0.641818	0.641824	0.641821	0.641821		0.644319	0.644321	0.644321	0.644320		0.002499	9.997333
T. Searcy	7/23/20	1000:1	0.789774	0.789774	0.789775	0.789774		0.792272	0.792273	0.792277	0.792274		0.002500	9.998667
T. Searcy	7/30/20	250:1	0.657322	0.657323	0.657322	0.657322		0.659821	0.659825	0.659822	0.659823		0.002500	10.001333
T. Searcy	7/30/20	250:1	0.694844	0.694845	0.694845	0.694845		0.697347	0.697346	0.697344	0.697346		0.002501	10.004000
T. Searcy	8/6/20	250:1	0.599244	0.599246	0.599246	0.599245		0.601747	0.601746	0.601748	0.601747		0.002502	10.006667
T. Searcy	8/6/20	50:1	0.670763	0.670761	0.670762	0.670762		0.673265	0.673265	0.673265	0.673265		0.002503	10.012000
T. Searcy	8/13/20	50:1	0.653940	0.653940	0.653941	0.653940		0.656442	0.656441	0.656443	0.656442		0.002502	10.006667
T. Searcy	8/13/20	50:1	0.606212	0.606213	0.606213	0.606213		0.608713	0.608713	0.608713	0.608713		0.002500	10.001333
T. Searcy	8/20/20	1000:1	0.740718	0.740716	0.740717	0.740717		0.743215	0.743217	0.743217	0.743216		0.002499	9.997333

Appendix C – Hydrogen Peroxide Dosage Calculations

Lab H₂O₂ Solution = 30% by weight (70% water)

$$\rho_{H_2O_2} = 1.121 \frac{g}{cm^3} \text{ at } 4^\circ C \text{ and } 30\% H_2O_2 \text{ (Schumb et al., 1953)}$$

$$MW_{H_2O_2} = 2 \left(1.0079 \frac{g}{mol} \right) + 2 \left(15.999 \frac{g}{mol} \right) = 34.0138 \frac{g}{mol}$$

$$MW_{DNAN} = 198.135 \frac{g}{mol}$$

- Determine the concentration of H₂O₂ in lab stock solution (30% H₂O₂ by wt):

$$\begin{aligned} \text{Concentration}_{H_2O_2} &= \rho_{H_2O_2} * MW_{H_2O_2} \\ &= 1.121 \frac{g}{cm^3} * \left(\frac{1 \text{ mol}}{34.0138 \text{ g}} \right) * 30\% * \left(\frac{1 \times 10^3 \text{ cm}^3}{1 \text{ L}} \right) * \left(\frac{1 \text{ L}}{1 \times 10^3 \text{ mL}} \right) \\ &= 0.009887 \frac{\text{mol } H_2O_2}{\text{mL solution}} = 9.887 \frac{\text{mmol } H_2O_2}{\text{mL solution}} = 9.887 \frac{\mu\text{mol } H_2O_2}{\mu\text{L solution}} \end{aligned}$$

- Determine moles of DNAN present in 250 mL solution with a concentration of 10 ppm (mg/L) DNAN:

$$\begin{aligned} m_{DNAN} &= 250 \text{ mL DNAN solution} * \left(\frac{10 \text{ mg DNAN}}{L} \right) * \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right) \\ &* \left(\frac{1 \text{ mol DNAN}}{198.135 \text{ g DNAN}} \right) * \left(\frac{1 \text{ g}}{1000 \text{ mg}} \right) = 1.2618 \times 10^{-5} \text{ moles DNAN} \\ &= 12.618 \mu\text{mol DNAN} \end{aligned}$$

- Determine volume of H₂O₂ required for a molar ratio of 100:1 (same method for all molar ratios):

$$\frac{100 \mu\text{mol } H_2O_2}{1 \mu\text{mol DNAN}} = \frac{? \mu\text{mol } H_2O_2}{12.618 \mu\text{mol DNAN}} \rightarrow 1261.8 \mu\text{mol } H_2O_2 \text{ required}$$

$$1261.8 \mu\text{mol } H_2O_2 * \left(\frac{1 \mu\text{L } H_2O_2 \text{ stock solution}}{9.887 \mu\text{mol } H_2O_2} \right) = 127.62 \mu\text{L } H_2O_2 \text{ stock solution}$$

* Pipette 128 μL H₂O₂ stock solution into 250mL volumetric flask containing 10ppm DNAN

Molar Ratio Desired (H ₂ O ₂ : DNAN)	H ₂ O ₂ required (umol)	lab H ₂ O ₂ solution required (ul)	Pipet this volume directly from refrigerated lab H ₂ O ₂ solution into the 250 mL DNAN Solution (ul)
100:1	1261.766	127.617	128
500:1	6308.830	638.083	638
1000:1	12617.660	1276.166	1276
250:1	3154.415	319.041	319
50:1	630.883	63.808	64

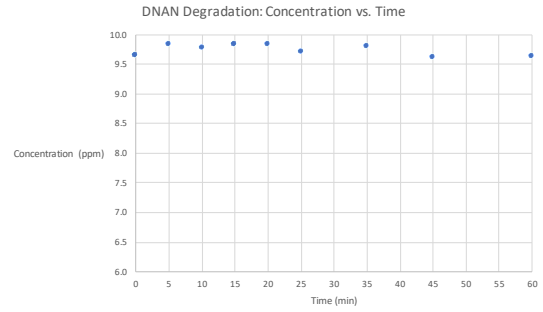
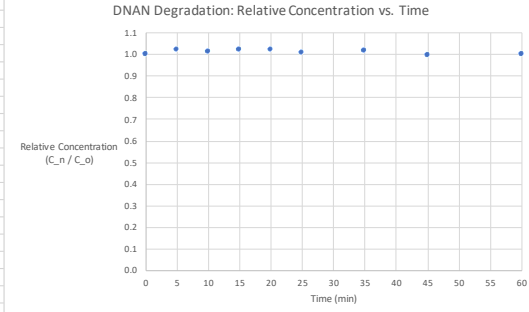
Appendix D – pH Meter Calibration Procedure

1. Prepare solution for treatment in the AOP (mix H_2O_2 into DNAN solution) and transfer to a smaller vessel for pH measurement.
2. Turn pH meter on.
3. Remove pH meter from the pH 7 buffer solution where it resides when not in use. Use Kimtech Kimwipe ® to dry pH meter.
4. Place pH meter in pH=4 solution (pink solution) and press “cal.” Wait until screen settles on pH value of 4. Remove from pink solution and clean residual liquid with Kimtech Kimwipe ®. Repeat for pH=7 (yellow solution) and pH=10 (blue solution).
5. Upon completion of pH=10 solution calibration; press “end” followed by “save.”
6. Place pH meter in pH=7 (yellow) solution to ensure calibration was effective.
7. Measure pH of DNAN solution. Rinse pH meter with DI water into waste container and dry with Kimtech Kimwipe ®.
8. Return meter to original solution where it resides until future use.

Appendix E – Starting Concentrations of DNAN for AOP Experiments

Starting Concentration Variability (ppm)																			
HPLC Type	Sample Time (min)	Controls	100:1				500:1			1000:1				250:1			50:1		
		27-May	3-Jun	10-Jun	17-Jun	24-Jun	1-Jul	8-Jul	14-Jul	21-Jul	28-Jul	25-Aug	4-Aug	4-Aug	11-Aug	11-Aug	18-Aug	18-Aug	
C1	0	9.3244	9.3136	8.9525	9.5362	9.4444	9.1241	9.5582	9.2345	9.5574	9.5313	9.8813	9.3510	9.6679	9.5835	9.5616	10.0297	9.5422	
C2	10		9.6583	9.1827	9.6901	9.6256	9.4279	9.8171	9.2120	9.6480	9.5257	9.4540	9.5541	9.7324	9.6425	9.8020	9.9606	9.5770	
C3	20	9.5378	9.6969	9.0615	9.6577	9.7468	9.5702	9.8384	9.5458	9.6480	9.6676	9.5978	9.6163	9.8124	9.5931	9.7527	9.9772	9.6995	
C4	30		9.7741	9.2863	9.6658	9.5796	9.4115	9.8327	9.3901	9.6650	9.6426	9.6860	9.7364	9.8602	9.6891	9.8127	9.9578	9.7078	
C5	40	10.0641	9.6626	9.2298	9.8062	9.5629	9.3211	9.7204	9.4869	9.6508	9.7163	9.7131	9.5823	9.8559	9.6932	9.8343	9.9620	9.7051	
C6	50		9.8385	9.1813	9.6995	9.5935	9.4032	9.8029	9.4715	9.5787	9.7163	9.6453	9.6089	9.8363	9.6754	9.7788	9.9606	9.7176	
C7	60	9.6465	9.6669	9.1517	9.6172	9.5824	9.3540	9.8398	9.3298	9.6777	9.6537	9.8447	9.5660	9.8447	9.6246	9.7619	9.8099	9.6870	
	mean	9.6432	9.6587	9.1494	9.6675	9.5907	9.3731	9.7728	9.3815	9.6322	9.6362	9.6889	9.5736	9.8014	9.6431	9.7577	9.9511	9.6623	mean
	std. dev.	0.3109	0.1665	0.1110	0.0823	0.0894	0.1350	0.1033	0.1286	0.0455	0.0789	0.1457	0.1152	0.0733	0.0449	0.0911	0.0673	0.0715	std. dev.
	z-score	0.1	0.2	-2.6	0.2	-0.2	-1.4	0.8	-1.3	0.1	0.1	0.4	-0.3	1.0	0.1	0.7	1.8	0.2	

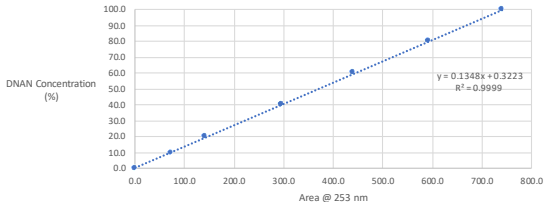
Appendix F – AOP Experiment Data

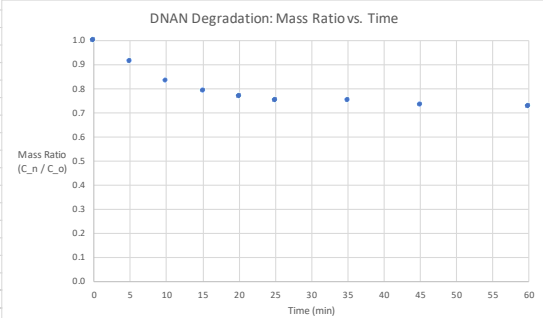
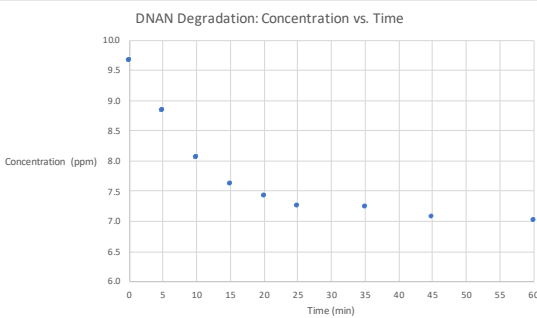
Data File Name		20200529_DNAN_A							
DNAN Concentration (mg/L or ppm)		10.013333							
pH		6.885							
Calibration Curve									
	Concentration (%)	Concentration (ppm)	RT (min)	Area (meas. @ 253 nm)					
	0.0000	0.0000	0.000	0.0					
	10.0000	1.0013	1.154	72.5					
	20.0000	2.0027	1.149	143.3					
	40.0000	4.0053	1.155	290.4					
	60.0000	6.0080	1.153	437.5					
	80.0000	8.0107	1.151	574.1					
	100.0000	10.0133	1.154	770.2					
	Slope	0.1324							
	y-intercept	1.1014							
Control # 1: No H2O2, No UV Light									
HPLC Type	Sample Time (min)	Concentration (%)	Concentration (ppm)	RT (min)	Area (meas. @ 253 nm)	C_o = Avg Ctrl Conc. (ppm)			
C1	0	93.1194	9.3244	1.151	695.0	9.6432			
C2	20	95.2511	9.5378	1.152	711.1				
C3	40	100.5074	10.0641	1.150	750.8				
C4	60	96.3368	9.6465	1.151	719.3				
Control #2: No H2O2, With UV Light applied									
DNAN									
HPLC Type	Sample Time (min)	Concentration (%)	Concentration (ppm)	RT (min)	Area (meas. @ 253 nm)	Other	RT (min)	Area (meas. @ 253 nm)	Mass Ratio (C_n / C_o)
C_o (starting Conc)	0		9.6432			None Observed			1.0000
R1	5	98.1506	9.8281	1.106	733.0				1.0192
R2	10	97.5813	9.7711	1.106	728.7				1.0133
R3	15	98.2036	9.8335	1.106	733.4				1.0197
R4	20	98.1109	9.8242	1.107	732.7				1.0188
R5	25	96.9061	9.7035	1.106	723.6				1.0063
R6	35	97.7005	9.7831	1.104	729.6				1.0145
R7	45	95.9131	9.6041	1.104	716.1				0.9959
R8	60	96.1779	9.6306	1.106	718.1				0.9987
DNAN Degradation: Concentration vs. Time						DNAN Degradation: Relative Concentration vs. Time			
									
Quality Control Checks: QC 60%									
Line	Area	Relative Error (< 10%)							
9	470.1	7.4514							
14	466.0	6.5143							
24	467.9	6.9486							

Data File Name		20200603_DNAN																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																									
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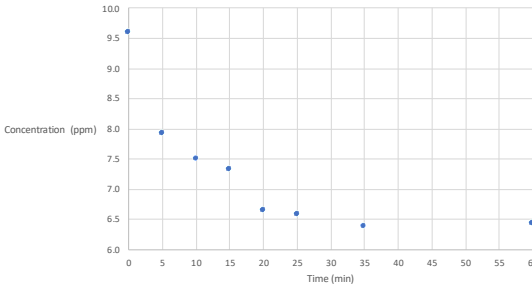
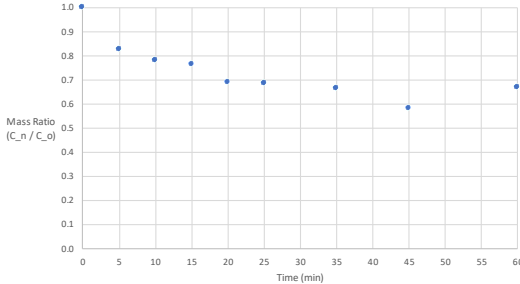
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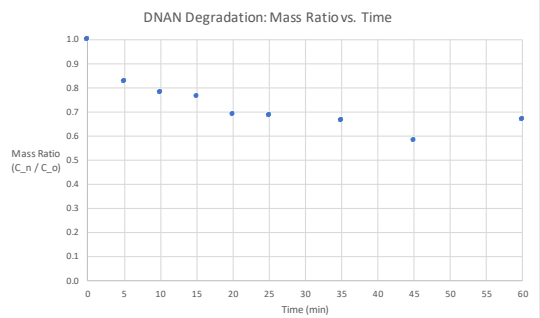
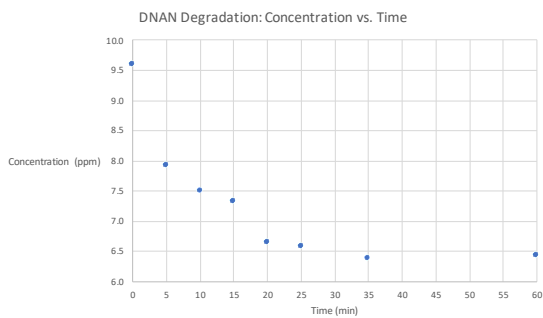
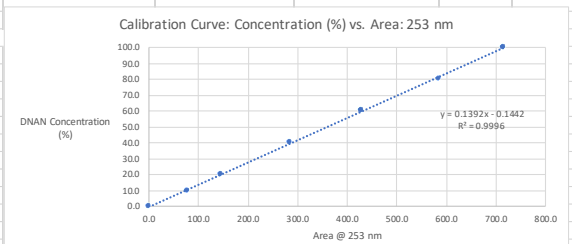
* This was the experiment where the peristaltic pump malfunctioned and readings were only taken up to 45 minutes.

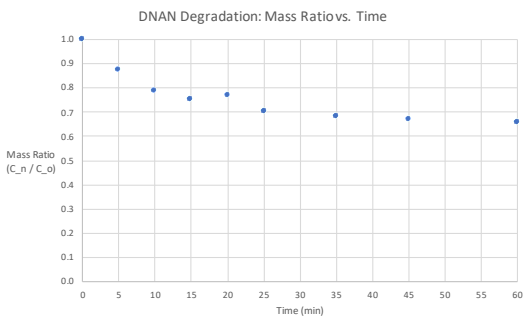
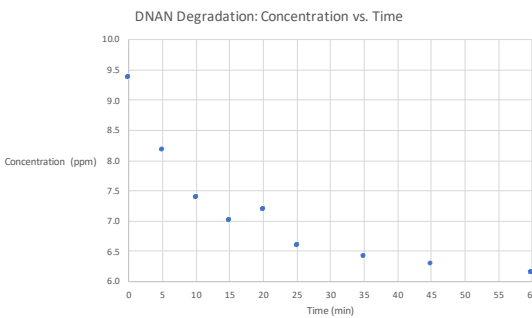
Data File Name		20200617A_DNAN															
DNAN Concentration (mg/L or ppm)		10.013333															
pH		6.687															
														Calibration Curve			
		Concentration (%)		Concentration (ppm)		RT (min)		Area (meas. @ 253 nm)									
		0.0000		0.0000		0.000		0.0									
		10.0000		1.0013		1.142		72.3									
		20.0000		2.0027		1.146		141.7									
		40.0000		4.0053		1.143		296.6									
		60.0000		6.0080		1.144		440.4									
		80.0000		8.0107		1.143		592.1									
		100.0000		10.0133		1.14		739.9									
		Slope		0.1348													
		y-intercept		0.3223													
														Calibration Curve: Concentration (%) vs. Area: 253 nm			
																	
Control Experiment																	
HPLC Type		Sample Time (min)		Concentration (%)		Concentration (ppm)		RT (min)		Area (meas. @ 253 nm)		C_o = Avg Ctrl Conc. (ppm)					
C1		0		95.2350		9.5362		1.141		704.1		9.6675					
C2		10		96.7717		9.6901		1.142		715.5							
C3		20		96.4482		9.6577		1.143		713.1							
C4		30		96.5291		9.6658		1.143		713.7							
C5		40		97.9310		9.8062		1.142		724.1							
C6		50		96.8661		9.6995		1.144		716.2							
C7		60		96.0438		9.6172		1.144		710.1							
Experiment: 100:1 (3 of 3)																	
DNAN																	
HPLC Type		Sample Time (min)		Concentration (%)		Concentration (ppm)		RT (min)		Area (meas. @ 253 nm)		RT (min)		Area (meas. @ 253 nm)			
C_o (starting Conc)		0				9.6675											
R1		5		88.3063		8.8424		1.145		652.7							
R2		10		80.3935		8.0501		1.143		594.0							
R3		15		76.0799		7.6181		1.144		562.0							
R4		20		74.1388		7.4238		1.142		547.6							
R5		25		72.4807		7.2577		1.141		535.3							
R6		35		72.3459		7.2442		1.143		534.3							
R7		45		70.5666		7.0661		1.144		521.1							
R8		60		70.0139		7.0107		1.144		517.0							
Other																	
None Observed																	



Quality Control Checks: QC 60%		
Line	Area	Relative Error (< 10%)
9	445.2	1.0899
17	442.5	0.4768
27	449.0	1.9528

Data File Name		20200624_DNAN_TS						
DNAN Concentration (mg/L or ppm)		10.012000						
pH		7.154						
Calibration Curve								
	Concentration (%)	Concentration (ppm)	RT (min)	Area (meas. @ 253 nm)				
	0.0000	0.0000	0.000	0.0				
	10.0000	1.0012	0.998	76.1				
	20.0000	2.0024	1.027	144.9				
	40.0000	4.0048	1.05	284.9				
	60.0000	6.0072	1.074	427.6				
	80.0000	8.0096	1.07	585.2				
	100.0000	10.0120	1.051	714.9				
	Slope		0.1392					
	y-intercept		-0.1442					
Control Experiment								
HPLC Type	Sample Time (min)	Concentration (%)	Concentration (ppm)	RT (min)	Area (meas. @ 253 nm)	C_o = Avg Ctrl Conc. (ppm)		
C1	0	94.3308	9.4444	1.038	678.7	9.5907		
C2	10	96.1404	9.6256	1.046	691.7			
C3	20	97.3515	9.7468	1.058	700.4			
C4	30	95.6811	9.5796	1.069	688.4			
C5	40	95.5140	9.5629	1.078	687.2			
C6	50	95.8203	9.5935	1.085	689.4			
C7	60	95.7089	9.5824	1.093	688.6			
Experiment: 500:1 (1 of 3)								
DNAN								
HPLC Type	Sample Time (min)	Concentration (%)	Concentration (ppm)	RT (min)	Area (meas. @ 253 nm)	RT (min)	Area (meas. @ 253 nm)	Mass Ratio (C_n / C_o)
C_o (starting Conc)	0		9.5907					1.0000
R1	5	79.1163	7.9211	1.104	569.4	0.640	1.8	0.8259
						0.831	3.1	
R2	10	74.9403	7.5030	1.111	539.4	0.584	7.6	0.7823
						0.835	2.2	
R3	15	73.1585	7.3246	1.115	526.6	0.584	7.9	0.7637
						0.837	2.7	
R4	20	66.3934	6.6473	1.120	478.0	0.585	8.8	
						0.844	3.3	0.6931
R5	25	65.7670	6.5846	1.122	473.5	0.584	7.9	
						0.843	2.8	0.6866
R6	35	63.7347	6.3811	1.117	458.9	0.583	8.7	
						0.837	2.5	0.6653
R7	45	55.8560	5.5923	1.121	402.3	0.584	10.1	
						0.843	3.4	0.5831
R8	60	64.2080	6.4285	1.124	462.3	0.585	7.3	0.6703
						0.842	2.6	
DNAN Degradation: Concentration vs. Time						DNAN Degradation: Mass Ratio vs. Time		
								
Quality Control Checks: QC 60%								
Line	Area	Relative Error (< 10%)						
9	426.5	0.2572						
17	429.7	0.4911						
27	426.6	0.2339						

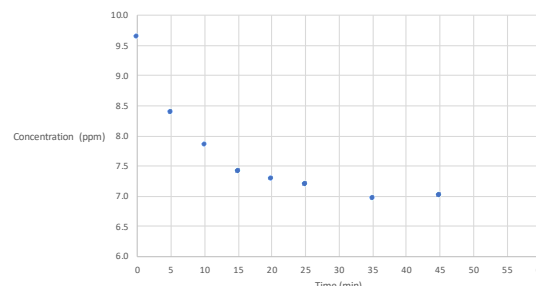
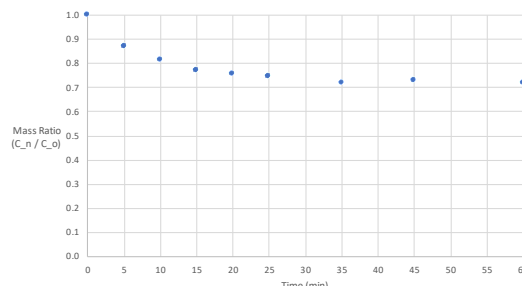


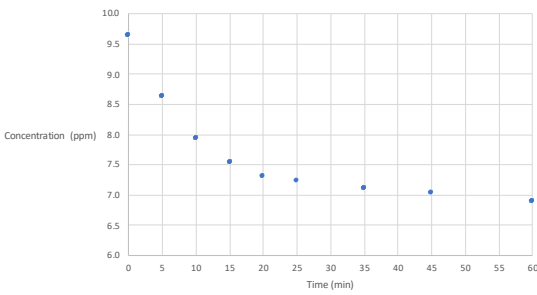
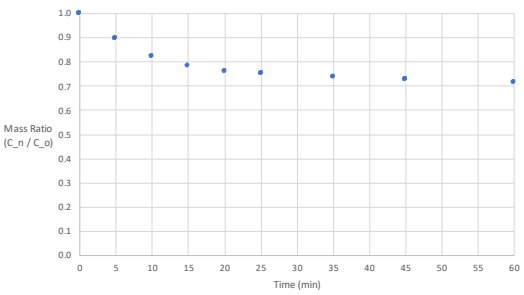
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Data File Name		20200708_DNAN_TS																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																								</
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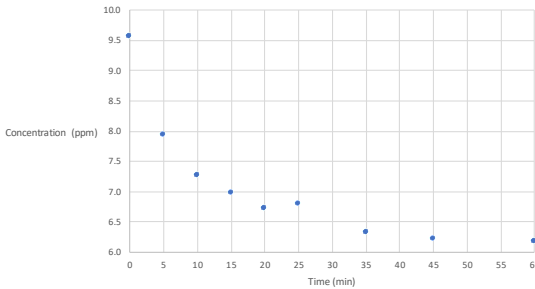
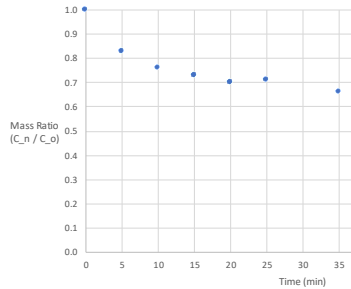
Data File Name		20200714_DNAN_TS														
DNAN Concentration (mg/L or ppm)		10.017333														
pH		6.202														
Calibration Curve																
		Concentration (%)	Concentration (ppm)	RT (min)	Area (meas. @ 253 nm)											
		0.0000	0.0000	0.000	0.0											
		10.0000	1.0017	1.062	69.0											
		20.0000	2.0035	1.062	144.1											
		40.0000	4.0069	1.066	276.5											
		60.0000	6.0104	1.084	429.5											
		80.0000	8.0139	1.104	577.3											
		100.0000	10.0173	1.112	708.1											
		Slope	0.1400													
		y-intercept	0.1909													
Control Experiment																
HPLC Type	Sample Time (min)	Concentration (ppm)	Concentration (ppm)	RT (min)	Area (meas. @ 253 nm)	C_o = Avg Ctrl Conc. (ppm)										
C1	0	92.1849	9.2345	1.118	657.1	9.3815										
C2	10	91.9609	9.2120	1.121	655.5											
C3	20	95.2929	9.5458	1.119	679.3											
C4	30	93.7389	9.3901	1.119	668.2											
C5	40	94.7049	9.4869	1.122	675.1											
C6	50	94.5509	9.4715	1.121	674.0											
C7	60	93.1369	9.3298	1.121	663.9											
Experiment: 1000:1 (1 of 3)																
		DNAN						Other								
HPLC Type	Sample Time (min)	Concentration (%)	Concentration (ppm)	RT (min)	Area (meas. @ 253 nm)	RT (min)	Area (meas. @ 253 nm)	Mass Ratio (C_n / C_o)								
C_o (starting Conc)	0		9.3815					1.0000								
R1	5	79.7109	7.9849	1.118	568.0	0.837	2.9	0.8511								
R2	10	71.5909	7.1715	1.116	510.0	0.839	3.2	0.7644								
R3	15	67.0829	6.7199	1.121	477.8	0.842	3.0	0.7163								
R4	20	65.0109	6.5124	1.119	463.0	0.845	2.8	0.6942								
R5	25	63.8629	6.3974	1.120	454.8	0.840	3.0	0.6819								
R6	35	61.0209	6.1127	1.119	434.5	0.841	2.6	0.6516								
R7	45	60.5029	6.0608	1.118	430.8	0.841	3.0	0.6460								
R8	60	60.8109	6.0916	1.118	433.0	0.838	3.0	0.6493								
DNAN Degradation: Concentration vs. Time																
DNAN Degradation: Mass Ratios vs. Time																
Quality Control Checks: QC 60%																
Line	Area	Relative Error (< 10%)														
9	416.0	3.1432														
17	425.1	1.0244														
27	432.1	0.6054														

*This is the 1000:1 outlier experiment. A pipette error is suspected.

Data File Name		20200721_DNAN_TS																			
DNAN Concentration (mg/L or ppm)		9.997333																			
pH		6.185																			
Calibration Curve																					
		Concentration (%)	Concentration (ppm)	RT (min)	Area (meas. @ 253 nm)																
		0.0000	0.0000	0.000	0.0																
		10.0000	0.9997	1.094																	
		20.0000	1.9995	1.094	141.4																
		40.0000	3.9989	1.095	281.9																
		60.0000	5.9984	1.095	424.5																
		80.0000	7.9979	1.096	566.8																
		100.0000	9.9973	1.095	705.8																
		Slope	0.1415																		
		y-intercept	0.0025																		
Control Experiment																					
HPLC Type	Sample Time (min)	Concentration (%)	Concentration (ppm)	RT (min)	Area (meas. @ 253 nm)	C_o = Avg Ctrl Conc. (ppm)															
C1	0	95.5999	9.5574	1.095	675.6	9.6322															
C2	10	96.5055	9.6480	1.096	682.0																
C3	20	96.5055	9.6480	1.096	682.0																
C4	30	96.6753	9.6650	1.096	683.2																
C5	40	96.5338	9.6508	1.096	682.2																
C6	50	95.8122	9.5787	1.096	677.1																
C7	60	96.8027	9.6777	1.095	684.1																
Experiment: 1000:1 (2 of 3)																					
		DNAN						Other													
HPLC Type	Sample Time (min)	Concentration (%)	Concentration (ppm)	RT (min)	Area (meas. @ 253 nm)	RT (min)	Area (meas. @ 253 nm)	Mass Ratio (C_n / C_o)													
C_o (starting Conc)	0		9.6322					1.0000													
R1	5	83.8837	8.3861	1.096	592.8	none	none	0.8706													
R2	10	78.5492	7.8528	1.097	555.1	0.823	2.1	0.8153													
R3	15	74.1202	7.4100	1.097	523.8	0.825	2.5	0.7693													
R4	20	72.9741	7.2955	1.096	515.7	0.823	2.2	0.7574													
R5	25	71.9694	7.1950	1.096	508.6	0.827	2.6	0.7470													
R6	35	69.5498	6.9531	1.097	491.5	0.830	2.2	0.7219													
R7	45	70.2431	7.0224	1.098	496.4	0.826	1.9	0.7291													
R8	60	69.2951	6.9277	1.098	489.7	0.827	2.5	0.7192													
DNAN Degradation: Concentration vs. Time												DNAN Degradation: Mass Ratios. Time									
																					
Quality Control Checks: QC 60%																					
Line	Area	Relative Error (< 10%)																			
9	420.9	0.8481																			
17	421.4	0.7303																			
27	424.6	0.0236																			

Data File Name		20200728_DNAN_TS																			
DNAN Concentration (mg/L or ppm)		9.998667																			
pH		6.210																			
Calibration Curve																					
		Concentration (%)	Concentration (ppm)	RT (min)	Area (meas. @ 253 nm)																
		0.0000	0.0000	0.000	0.0																
		10.0000	0.9999	1.070	72.9																
		20.0000	1.9997	1.080	141.9																
		40.0000	3.9995	1.082	287.1																
		60.0000	5.9992	1.082	429.7																
		80.0000	7.9989	1.082	576.0																
		100.0000	9.9987	1.083	718.9																
		Slope		0.1391																	
		y-intercept		0.0560																	
Control Experiment																					
HPLC Type	Sample Time (min)	Concentration (%)	Concentration (ppm)	RT (min)	Area (meas. @ 253 nm)	C_o = Avg Ctrl Conc. (ppm)															
C1	0	95.3256	9.5313	1.092	684.9	9.6362															
C2	10	95.2700	9.5257	1.092	684.5																
C3	20	96.6888	9.6676	1.094	694.7																
C4	30	96.4384	9.6426	1.095	692.9																
C5	40	97.1756	9.7163	1.096	698.2																
C6	50	97.1756	9.7163	1.098	698.2																
C7	60	96.5497	9.6537	1.097	693.7																
Experiment: 1000:1 (3 of 3)																					
DNAN						Other															
HPLC Type	Sample Time (min)	Concentration (%)	Concentration (ppm)	RT (min)	Area (meas. @ 253 nm)	RT (min)	Area (meas. @ 253 nm)	Mass Ratio (C_n / C_o)													
C_o (starting Conc)	0		9.6362					1.0000													
R1	5	86.2285	8.6217	1.095	619.5	0.824	1.8	0.8947													
R2	10	79.3986	7.9388	1.096	570.4	0.826	1.9	0.8239													
R3	15	75.4343	7.5424	1.097	541.9	0.825	2.3	0.7827													
R4	20	73.0974	7.3088	1.096	525.1	0.824	2.4	0.7585													
R5	25	72.4158	7.2406	1.094	520.2	0.822	2.0	0.7514													
R6	35	71.0248	7.1015	1.096	510.2	0.823	2.6	0.7370													
R7	45	70.3293	7.0320	1.098	505.2	0.826	2.6	0.7297													
R8	60	68.8410	6.8832	1.097	494.5	0.824	1.9	0.7143													
DNAN Degradation: Concentration vs. Time																					
																					
DNAN Degradation: Mass Ratios vs. Time																					
																					
Quality Control Checks: QC 60%																					
Line	Area	Relative Error (< 10%)																			
9	429.1	0.1396																			
17	429.8	0.0233																			
27	428.3	0.3258																			

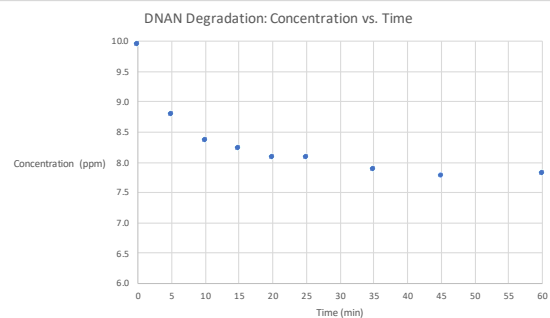
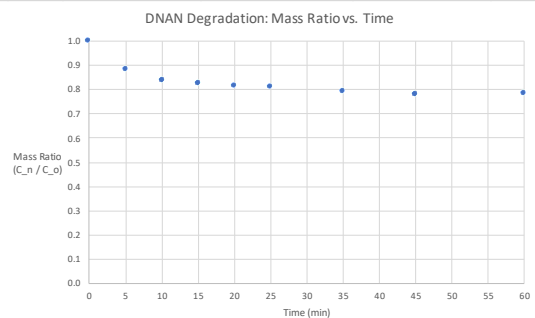
Data File Name		20200825_DNAN_A_TS							
DNAN Concentration (mg/L or ppm)		9.997333							
pH		5.270							
		Calibration Curve							
		Concentration (%)	Concentration (ppm)	RT (min)	Area (meas. @ 253 nm)				
		0.0000	0.0000	0.000	0.0				
		10.0000	0.9997	1.088	69.2				
		20.0000	1.9995	1.091	145.8				
		40.0000	3.9989	1.088	297.4				
		60.0000	5.9984	1.089	441.5				
		80.0000	7.9979	1.090	586.1				
		100.0000	9.9973	1.089	735.7				
		Slope	0.1357						
		y-intercept	0.1587						

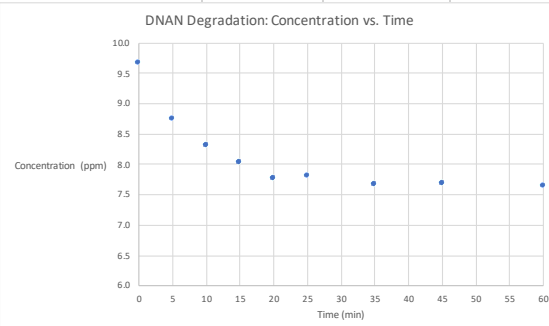
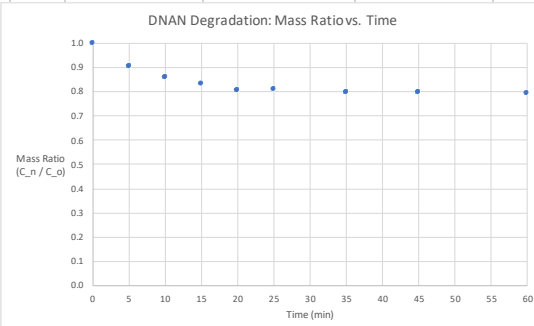
Data File Name		20200804_DNAN_TS																	
DNAN Concentration (mg/L or ppm)		10.001333																	
pH		6.277																	
Calibration Curve																			
		Concentration (%)		Concentration (ppm)		RT (min)		Area (meas. @ 253 nm)											
		0.0000		0.0000		0.000		0.0											
		10.0000		1.0001		1.095		66.6											
		20.0000		2.0003		1.097		132.7											
		40.0000		4.0005		1.097		269.2											
		60.0000		6.0008		1.097		402.0											
		80.0000		8.0011		1.097		542.5											
		100.0000		10.0013		1.096		671.9											
		Slope		0.1482															
		y-intercept		0.1319															
Control Experiment																			
HPLC Type		Sample Time (min)		Concentration (ppm)		Concentration (ppm)		RT (min)		Area (meas. @ 253 nm)		C_o = Avg Ctrl Conc. (ppm)							
C1		0		93.4979		9.3510		1.097		630.0		9.5736							
C2		10		95.5282		9.5541		1.097		643.7									
C3		20		96.1507		9.6163		1.093		647.9									
C4		30		97.3511		9.7364		1.094		656.0									
C5		40		95.8098		9.5823		1.095		645.6									
C6		50		96.0766		9.6089		1.096		647.4									
C7		60		95.6468		9.5660		1.097		644.5									
Experiment: 250:1 (1 of 3)																			
				DNAN								Other							
HPLC Type		Sample Time (min)		Concentration (%)		Concentration (ppm)		RT (min)		Area (meas. @ 253 nm)		RT (min)		Area (meas. @ 253 nm)		Mass Ratio (C_n / C_o)			
C_o (starting Conc)		0				9.5736										1.0000			
R1		5		79.3596		7.9370		1.096		534.6		0.821		2.4		0.8291			
R2		10		72.6165		7.2626		1.096		489.1		0.823		3.1		0.7586			
R3		15		69.6970		6.9706		1.097		469.4		0.823		1.8		0.7281			
R4		20		67.2369		6.7246		1.095		452.8		0.824		3.0		0.7024			
R5		25		67.9630		6.7972		1.096		457.7		0.821		2.6		0.7100			
R6		35		63.2503		6.3259		1.097		425.9		0.823		2.9		0.6608			
R7		45		62.1240		6.2132		1.097		418.3		0.824		3.6		0.6490			
R8		60		61.9017		6.1910		1.096		416.8		0.822		3.0		0.6467			
DNAN Degradation: Concentration vs. Time																			
																			
DNAN Degradation: Mass Ratio vs. Time																			
																			
Quality Control Checks: QC 60%																			
Line		Area		Relative Error (< 10%)															
9		403.5		0.3731															
17		400.2		0.4478															
27		402.1		0.0749															

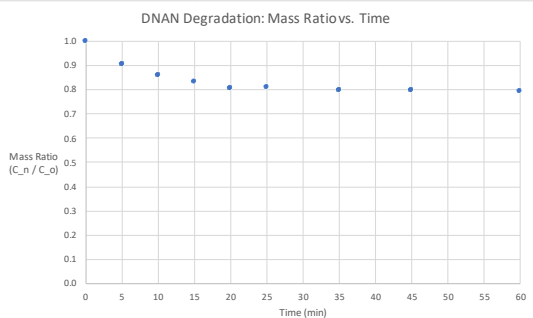
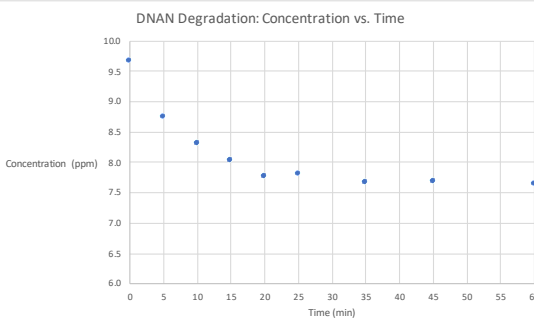
Data File Name		20200804_2_DNAN_TS									
DNAN Concentration (mg/L or ppm)		10.004000									
pH		5.563									
Calibration Curve											
		Concentration (%)	Concentration (ppm)	RT (min)	Area (meas. @ 253 nm)						
		0.0000	0.0000	0.000	0.0						
		10.0000	1.0004	1.101	71.6						
		20.0000	2.0008	1.099	142.7						
		40.0000	4.0016	1.102	279.9						
		60.0000	6.0024	1.098	427.8						
		80.0000	8.0032	1.097	567.5						
		100.0000	10.0040	1.099	714.1						
		Slope	0.1403								
		y-intercept	0.1136								
Control Experiment											
HPLC Type	Sample Time (min)	Concentration (%)	Concentration (ppm)	RT (min)	Area (meas. @ 253 nm)	C_o = Avg Ctrl Conc. (ppm)					
C1	0	96.6400	9.6679	1.095	688.0	9.8014					
C2	10	97.2854	9.7324	1.098	692.6						
C3	20	98.0851	9.8124	1.102	698.3						
C4	30	98.5621	9.8602	1.102	701.7						
C5	40	98.5200	9.8559	1.098	701.4						
C6	50	98.3236	9.8363	1.100	700.0						
C7	60	98.4078	9.8447	1.098	700.6						
Experiment: 250:1 (2 of 3)											
DNAN						Other					
HPLC Type	Sample Time (min)	Concentration (%)	Concentration (ppm)	RT (min)	Area (meas. @ 253 nm)	RT (min)	Area (meas. @ 253 nm)	Mass Ratio (C_n / C_o)			
C_o (starting Conc)	0		9.8014					1.0000			
R1	5	84.6584	8.4692	1.098	602.6	0.824	2.6	0.8641			
R2	10	76.6052	7.6636	1.097	545.2	0.822	2.3	0.7819			
R3	15	73.3502	7.3380	1.098	522.0	0.824	2.4	0.7487			
R4	20	69.9690	6.9997	1.097	497.9	0.823	2.7	0.7142			
R5	25	69.1552	6.9183	1.098	492.1	0.825	2.8	0.7058			
R6	35	66.7280	6.6755	1.097	474.8	0.822	2.8	0.6811			
R7	45	66.5457	6.6572	1.097	473.5	0.823	2.5	0.6792			
R8	60	65.5636	6.5590	1.098	466.5	0.824	2.7	0.6692			
DNAN Degradation: Concentration vs. Time											
DNAN Degradation: Mass Ratio vs. Time											
Quality Control Checks: QC 60%											
Line	Area	Relative Error (< 10%)									
9	423.7	0.9584									
17	426.5	0.3039									
27	423.4	1.0285									

[illegible]

Data File Name		20200811_BB_DNAN_TS																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																					
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Data File Name		20200818_A_DNAN_TS						
DNAN Concentration (mg/L or ppm)		10.006667						
pH		5.030						
Calibration Curve								
		Concentration (%)	Concentration (ppm)	RT (min)	Area (meas. @ 253 nm)			
		0.0000	0.0000	0.000	0.0			
		10.0000	1.0007	1.096	72.7			
		20.0000	2.0013	1.094	139.5			
		40.0000	4.0027	1.093	288.1			
		60.0000	6.0040	1.091	434.0			
		80.0000	8.0053	1.093	572.1			
		100.0000	10.0067	1.092	725.5			
		Slope	0.1382					
		y-intercept	0.2153					
Control Experiment								
HPLC Type	Sample Time (min)	Concentration (%)	Concentration (ppm)	RT (min)	Area (meas. @ 253 nm)	C_o = Avg Ctrl Conc. (ppm)		
C1	0	100.2306	10.0297	1.096	723.7	9.9511		
C2	10	99.5396	9.9606	1.095	718.7			
C3	20	99.7055	9.9772	1.095	719.9			
C4	30	99.5120	9.9578	1.094	718.5			
C5	40	99.5535	9.9620	1.092	718.8			
C6	50	99.5396	9.9606	1.092	718.7			
C7	60	98.0333	9.8099	1.091	707.8			
Experiment: 50:1 (2 of 3)								
DNAN								
HPLC Type	Sample Time (min)	Concentration (%)	Concentration (ppm)	RT (min)	Area (meas. @ 253 nm)	RT (min)	Area (meas. @ 253 nm)	Mass Ratio (C_n / C_o)
C_o (starting Conc)	0		9.9511					1.0000
R1	5	87.9032	8.7962	1.092	634.5	0.820	1.9	0.8839
R2	10	83.4117	8.3467	1.093	602.0	0.819	2.8	0.8388
R3	15	82.1541	8.2209	1.093	592.9	0.819	2.3	0.8261
R4	20	80.8412	8.0895	1.095	583.4	0.821	2.2	0.8129
R5	25	80.6892	8.0743	1.095	582.3	0.820	2.3	0.8114
R6	35	78.6991	7.8752	1.095	567.9	0.821	2.7	0.7914
R7	45	77.6211	7.7673	1.095	560.1	0.821	2.4	0.7805
R8	60	78.0495	7.8102	1.095	563.2	0.820	2.4	0.7849
DNAN Degradation: Concentration vs. Time						DNAN Degradation: Mass Ratio vs. Time		
								
Quality Control Checks: QC 60%								
Line	Area	Relative Error (< 10%)						
9	443.5	2.1889						
17	440.0	1.3825						
27	433.0	0.7304						

Data File Name		20200818_B_DNAN_TS														
DNAN Concentration (mg/L or ppm)		10.001333														
pH		4.853														
Calibration Curve																
		Concentration (%)	Concentration (ppm)	RT (min)	Area (meas. @ 253 nm)											
		0.0000	0.0000	0.000	0.0											
		10.0000	1.0001	1.093	80.2											
		20.0000	2.0003	1.094	144.7											
		40.0000	4.0005	1.094	290.2											
		60.0000	6.0008	1.091	436.6											
		80.0000	8.0011	1.092	578.8											
		100.0000	10.0013	1.093	720.2											
		Slope	0.1392													
		y-intercept	-0.4580													
Control Experiment																
HPLC Type	Sample Time (min)	Concentration (%)	Concentration (ppm)	RT (min)	Area (meas. @ 253 nm)	C_o = Avg Ctrl Conc. (ppm)										
C1	0	95.4090	9.5422	1.092	688.7	9.6623										
C2	10	95.7570	9.5770	1.091	691.2											
C3	20	96.9820	9.6995	1.093	700.0											
C4	30	97.0655	9.7078	1.092	700.6											
C5	40	97.0377	9.7051	1.095	700.4											
C6	50	97.1630	9.7176	1.095	701.3											
C7	60	96.8567	9.6870	1.095	699.1											
Experiment: 50:1 (3 of 3)																
DNAN						Other										
HPLC Type	Sample Time (min)	Concentration (%)	Concentration (ppm)	RT (min)	Area (meas. @ 253 nm)	RT (min)	Area (meas. @ 253 nm)	Mass Ratio (C_n / C_o)								
C_o (starting Conc)	0		9.6623					1.0000								
R1	5	87.4050	8.7417	1.095	631.2	0.821	0.9	0.9047								
R2	10	83.1177	8.3129	1.094	600.4	0.822	2.1	0.8603								
R3	15	80.3198	8.0330	1.096	580.3	0.822	1.5	0.8314								
R4	20	77.8142	7.7825	1.094	562.3	0.821	1.9	0.8054								
R5	25	78.0647	7.8075	1.094	564.1	0.820	2.4	0.8080								
R6	35	76.7284	7.6739	1.094	554.5	0.820	2.1	0.7942								
R7	45	76.7562	7.6766	1.095	554.7	0.821	2.2	0.7945								
R8	60	76.5057	7.6516	1.094	552.9	0.819	1.9	0.7919								
DNAN Degradation: Concentration vs. Time																
																
DNAN Degradation: Mass Ratios vs. Time																
																
Quality Control Checks: QC 60%																
Line	Area	Relative Error (< 10%)														
9	432.8	0.8704														
17	433.3	0.7558														
27	436.1	0.1145														



Appendix G – MATLAB Code for Rate Constant Retrieval

1. Data file for individual rate constant retrieval and curve fitting

File Name: searcyDNANdata2020

Code:

```
%June 2020 - AFIT
%Author: W. Harper
%Project: 2019-20 UV LED project

global Cinit realdata10 realdata11 realdata12 realdata13 realdata14
realdata15 realdata16 realdata17 realdata17redo realdata18 realdata19
realdata110 realdata111 realdata112 realdata113 realdata114 realdata115
realdata20 realdata21 realdata22 realdata23 realdata24 realdata25
realdata26 realdata27 realdata27redo realdata28 realdata29 realdata210
realdata211 realdata212 realdata213 realdata214 realdata215

%this is a data file
%realdata1* entries are time in minutes
%realdata2* entries are relative concentration
%Cinit is the matrix of initial concentrations
%
%
Cinit = [9.6587 %100:1 #1-updated
9.1494 %100:1 #2-updated
9.6675 %100:1 #3-updated
9.5907 %500:1 #1-updated
9.3731 %500:1 #2-updated
9.7728 %500:1 #3-updated
9.3815 %this is the outlier 1000:1 #1-updated
9.6322 %1000:1 #2-updated
9.6362 %1000:1 #3-updated
9.5736 %250:1 #1-updated
9.8014 %250:1 #2-updated
9.6431 %250:1 #3-updated
9.7577 %50:1 #1-updated
9.9511 %50:1 #2-updated
9.6623 %50:1 #3-updated
9.6889 %this is the repeat experiment (1000:1 #4)-updated
9.6432]; % 0:1 Control Experiment-updated
%
%
%
%
%molar ratio = 0:1
%Control Experiment
%time data:
realdata10 = [0
5
10
```



```
%Experiment #2 of 3
```

```
%time data:
```

```
realdata12 = [0
```

```
45];
```

%Note: This was the experiment where a 60min reading was not taken.

```
realdata22 = [1.0000
```

0.8253

0.8338

0.8009

0.7698

0.7669

0.7554

```
0.7494];
```

```
%Experiment #3 of 3
```

```
%time data:
```

```
realdata13 = [0
```

```
realdata23 = [1.0000
```

0.9147

0.8327

0.7880

0.7679

```
0.7507
0.7493
0.7309
0.7252];
```

```
%
```

```
%
```

```
%molar ratio = 500:1
%Experiment #1 of 3
%time data:
realdata14 = [0
5
10
15
20
25
35
45
60];
```

```
%relative concentration C/Co
realdata24 = [1.0000
0.8259
0.7823
0.7637
0.6931
0.6866
0.6653
0.5831
0.6703];
```

```
%
```

```
%
```

```
%molar ratio = 500:1
%Experiment #2 of 3
%time data:
realdata15 = [0
5
10
15
20
25
35
45
60];
```

```
%relative concentration C/Co
realdata25 = [1.0000
0.8723
```

```
0.7895
0.7493
0.7676
0.7035
0.6845
0.6714
0.6559];
```

```
%
```

```
%
```

```
%molar ratio = 500:1
%Experiment #3 of 3
%time data:
realdata16 = [0
5
10
15
20
25
35
45
60];
```

```
%relative concentration C/Co
realdata26 = [1.0000
0.7979
0.7224
0.7170
0.6679
0.6720
0.6752
0.6548
0.6691];
```

```
%
```

```
%
```

```
%molar ratio = 1000:1: This is the outlier
%Experiment #1 of 3
%time data:
realdata17 = [0
5
10
15
20
25
35
45
60];
```



```
35
45
60];
```

```
%relative concentration C/Co
realdata28 = [1.0000
0.8706
0.8153
0.7693
0.7574
0.7470
0.7219
0.7291
0.7192];
%
```

```
%
```

```
%molar ratio = 1000:1
%Experiment #3 of 3
%time data:
realdata19 = [0
5
10
15
20
25
35
45
60];
```

```
%relative concentration C/Co
realdata29 = [1.0000
0.8947
0.8239
0.7827
0.7585
0.7514
0.7370
0.7297
0.7143];
```

```
%
```

```
%
```

```
%molar ratio = 250:1
%Experiment #1 of 3
%time data:
realdata110 = [0
5
```

```
10
15
20
25
35
45
60];
```

```
%relative concentration C/Co
realdata210 = [1.0000
0.8291
0.7586
0.7281
0.7024
0.7100
0.6608
0.6490
0.6467];
```

```
%
```

```
%
```

```
%molar ratio = 250:1
%Experiment #2 of 3
%time data:
realdata111 = [0
5
10
15
20
25
35
45
60];
```

```
%relative concentration C/Co
realdata211 = [1.0000
0.8641
0.7819
0.7487
0.7142
0.7058
0.6811
0.6792
0.6692];
```

```
%
```

```
%
```

```
%molar ratio = 250:1
%Experiment #3 of 3
```

```
%time data:
realdata112 = [0
5
10
15
20
25
35
45
60];
```

```
%relative concentration C/Co
realdata212 = [1.0000
0.8493
0.7764
0.7332
0.7020
0.6970
0.6760
0.6694
0.6544];
```

```
%
```

```
%
```

```
%molar ratio = 50:1
%Experiment #1 of 3
%time data:
realdata113 = [0
5
10
15
20
25
35
45
60];
```

```
%relative concentration C/Co
realdata213 = [1.0000
0.8905
0.8409
0.8139
0.7951
0.7891
0.7765
0.7650
0.7601];
```

```
%
```

```

%


---




---


%


---


%relative concentration C/Co
realdata114 = [0
5
10
15
20
25
35
45
60];

%relative concentration C/Co
realdata214 = [1.0000
0.8839
0.8388
0.8261
0.8129
0.8114
0.7914
0.7805
0.7849];
%


---




---


%


---




---


%


---


%relative concentration C/Co
realdata115 = [0
5
10
15
20
25
35
45
60];

%relative concentration C/Co
realdata215 = [1.0000
0.9047
0.8603
0.8314
0.8054
0.8080
0.7942
0.7945
0.7919];

```

```
%
%
%
%
%
```

2. Curve fitting for individual rate constant retrieval and curve fitting

File Name: searcyDNAN5.m

Code:

```
%June, 2020
%Author: W. Harper
%Project: UV LED Project
%This program is used to model DNAN removal in a UV LED reactor

%the clock is here to help determine the runtime. It does not affect
the process simulation
tstart = clock;

%global declarations - the purpose of these declarations is to make
these parameter values
%available to light3.

%global declarations
global rateconstant reactorvolume flow xo Cinit
global realdata10 realdata11 realdata12 realdata13 realdata14
realdata15 realdata16 realdata17 realdata17redo realdata18 realdata19
realdata110 realdata111 realdata112 realdata113 realdata114 realdata115
realdata20 realdata21 realdata22 realdata23 realdata24 realdata25
realdata26 realdata27 realdata27redo realdata28 realdata29 realdata210
realdata211 realdata212 realdata213 realdata214 realdata215

%The parameters in the matrix are respectively:
%effluent concentration of DNAN (1)

%the units of the rateconstant are inverse time (1/min)

%the units of volume are ml
reactorvolume = 35;
%this reactor volume takes into account the stir bar volume in the
reactor
%during experiments.

%the units of flow are ml/minutes
```

```

flow = 2.0;
%this flow rate value was measured by Dr. Burdsall

tau = reactorvolume./flow;

%parameters needed for simulation
alpha = 0.001;
beta = 0.001;
gamma = 0.05;

%additional matrices needed for data processing
nnn = 100000;
ZZZ1 = zeros(7,nnn);
BEST = zeros(6,1);
BEST1 = zeros(1,1);
ZZZ2 = zeros(7,nnn);
BEST2 = zeros(1,1);
ZZZ3 = zeros(7,nnn);
BEST3 = zeros(1,1);
ZZZ4 = zeros(7,nnn);
BEST4 = zeros(1,1);
ZZZ5 = zeros(7,nnn);
BEST5 = zeros(1,1);
ZZZ6 = zeros(7,nnn);
BEST6 = zeros(1,1);
ZZZ7 = zeros(7,nnn);
BEST7 = zeros(1,1);
ZZZ8 = zeros(7,nnn);
BEST8 = zeros(1,1);
ZZZ9 = zeros(7,nnn);
BEST9 = zeros(1,1);
ZZZ10 = zeros(7,nnn);
BEST10 = zeros(1,1);
ZZZ11 = zeros(7,nnn);
BEST11 = zeros(1,1);
ZZZ12 = zeros(7,nnn);
BEST12 = zeros(1,1);
ZZZ13 = zeros(7,nnn);
BEST13 = zeros(1,1);
ZZZ14 = zeros(7,nnn);
BEST14 = zeros(1,1);
ZZZ15 = zeros(7,nnn);
BEST15 = zeros(1,1);
ZZZ16 = zeros(7,nnn); %this is the repeat experiment (1000:1 #4)
BEST16 = zeros(1,1); %this is the repeat experiment (1000:1 #4)
ZZZ17 = zeros(7,nnn); %this is the CONTROL experiment (0:1)
BEST17 = zeros(1,1); %this is the CONTROL experiment (0:1)

%the following are process parameters
to = 0;
%the units are minutes
tf = 60;

searcyDNANdata2020

```

```

%aaa is needed to determine the best parameter combination
aaa1 = 10000000000;
aaa2 = aaa1;
aaa3 = aaa1;
aaa4 = aaa1;
aaa5 = aaa1;
aaa6 = aaa1;
aaa7 = aaa1;
aaa8 = aaa1;
aaa9 = aaa1;
aaa10 = aaa1;
aaa11 = aaa1;
aaa12 = aaa1;
aaa13 = aaa1;
aaa14 = aaa1;
aaa15 = aaa1;
aaa16 = aaa1; %this is the repeat experiment (1000:1 #4)
aaa17 = aaa1; %this is the CONTROL experiment (0:1)

%this is a counter
counttt = 1;

%the simulation logic begins here

%This is for the first experimental data set: 100:1 #1
for rateconstant = alpha:beta:gamma
%
%Initial Conditions Matrix
xo = Cinit(1,1);
%Solve the differential equations
[t,x] = ode45('light3',realdata11,xo,[],tau);

MMM1 = abs((realdata21 - x(:,1)./Cinit(1,1))).^2;
ttt1 = cumsum(MMM1);
bbb1 = ttt1(end)./size(realdata21,1);
rrr1 = ((bbb1)^(0.5))./max(realdata21);

ZZZ1(1,counttt) = rrr1;
ZZZ1(2,counttt) = rateconstant;

if ZZZ1(1,counttt) < aaa1
    aaa1 = ZZZ1(1,counttt);
    BEST(1,1) = rateconstant;
    zipa = x(:,1)./Cinit(1,1);
    zipat = t;
end
counttt = counttt + 1;
end

counttt = 1;

```

```

%This is for the second experimental data set: 100:1 #2
for rateconstant = alpha:beta:gamma
%
%Initial Conditions Matrix
xo = Cinit(2,1);
%Solve the differential equations
[t,x] = ode45('light3',realdata12,xo,[],tau);

MMM2 = abs((realdata22 - x(:,1)./Cinit(2,1))).^2;
ttt2 = cumsum(MMM2);
bbb2 = ttt2(end)./size(realdata22,1);
rrr2 = ((bbb2)^(0.5))./max(realdata22);

ZZZ2(1,counttt) = rrr2;
ZZZ2(2,counttt) = rateconstant;

if ZZZ2(1,counttt) < aaa2
    aaa2 = ZZZ2(1,counttt);
    BEST(2,1) = rateconstant;
    zipb = x(:,1)./Cinit(2,1);
    zipbt = t;
end
counttt = counttt + 1;
end

counttt = 1;

%This is for the third experimental data set: 100:1 #3
for rateconstant = alpha:beta:gamma
%
%Initial Conditions Matrix
xo = Cinit(3,1);
%Solve the differential equations
[t,x] = ode45('light3',realdata13,xo,[],tau);

MMM3 = abs((realdata23 - x(:,1)./Cinit(3,1))).^2;
ttt3 = cumsum(MMM3);
bbb3 = ttt3(end)./size(realdata23,1);
rrr3 = ((bbb3)^(0.5))./max(realdata23);

ZZZ3(1,counttt) = rrr3;
ZZZ3(2,counttt) = rateconstant;

if ZZZ3(1,counttt) < aaa3
    aaa3 = ZZZ3(1,counttt);
    BEST(3,1) = rateconstant;
    zipc = x(:,1)./Cinit(3,1);
    zipct = t;
end
counttt = counttt + 1;
end

counttt = 1;

```

```

%This is for the fourth experimental data set: 500:1 #1
for rateconstant = alpha:beta:gamma
%
%Initial Conditions Matrix
xo = Cinit(4,1);
%Solve the differential equations
[t,x] = ode45('light3',realdata14,xo,[],tau);

MMM4 = abs((realdata24 - x(:,1)./Cinit(4,1))).^2;
ttt4 = cumsum(MMM4);
bbb4 = ttt4(end)./size(realdata24,1);
rrr4 = ((bbb4)^(0.5))./max(realdata24);

ZZZ4(1,counttt) = rrr4;
ZZZ4(2,counttt) = rateconstant;

if ZZZ4(1,counttt) < aaa4
    aaa4 = ZZZ4(1,counttt);
    BEST(4,1) = rateconstant;
    zipd = x(:,1)./Cinit(4,1);
    zipdt = t;
end
counttt = counttt + 1;
end

counttt = 1;

%This is for the fifth experimental data set: 500:1 #2
for rateconstant = alpha:beta:gamma
%
%Initial Conditions Matrix
xo = Cinit(5,1);
%Solve the differential equations
[t,x] = ode45('light3',realdata15,xo,[],tau);

MMM5 = abs((realdata25 - x(:,1)./Cinit(5,1))).^2;
ttt5 = cumsum(MMM5);
bbb5 = ttt5(end)./size(realdata25,1);
rrr5 = ((bbb5)^(0.5))./max(realdata25);

ZZZ5(1,counttt) = rrr5;
ZZZ5(2,counttt) = rateconstant;

if ZZZ5(1,counttt) < aaa5
    aaa5 = ZZZ5(1,counttt);
    BEST(5,1) = rateconstant;
    zipe = x(:,1)./Cinit(5,1);
    zipet = t;
end
counttt = counttt + 1;
end

```

```

counttt = 1;

%This is for the sixth experimental data set: 500:1 #3
for rateconstant = alpha:beta:gamma
%
%Initial Conditions Matrix
xo = Cinit(6,1);
%Solve the differential equations
[t,x] = ode45('light3',realdata16,xo,[],tau);

MMM6 = abs((realdata26 - x(:,1)./Cinit(6,1))).^2;
ttt6 = cumsum(MMM6);
bbb6 = ttt6(end)./size(realdata26,1);
rrr6 = ((bbb6)^(0.5))./max(realdata26);

ZZZ6(1,counttt) = rrr6;
ZZZ6(2,counttt) = rateconstant;

if ZZZ6(1,counttt) < aaa6
    aaa6 = ZZZ6(1,counttt);
    BEST(6,1) = rateconstant;
    zipf = x(:,1)./Cinit(6,1);
    zipft = t;
end
counttt = counttt + 1;
end

%This is for the seventh experimental data set: 1000:1 #1
%NOTE: This is the outlier trial and Dr. Harper advised you to
eliminate it
%from the body of your thesis but include it in your appendix. Ensure
you
%discuss it in the methodology / results portion.
for rateconstant = alpha:beta:gamma
%
%Initial Conditions Matrix
xo = Cinit(7,1);
%Solve the differential equations
[t,x] = ode45('light3',realdata17,xo,[],tau);

MMM7 = abs((realdata27 - x(:,1)./Cinit(7,1))).^2;
ttt7 = cumsum(MMM7);
bbb7 = ttt7(end)./size(realdata27,1);
rrr7 = ((bbb7)^(0.5))./max(realdata27);

ZZZ7(1,counttt) = rrr7;
ZZZ7(2,counttt) = rateconstant;

if ZZZ7(1,counttt) < aaa7
    aaa7 = ZZZ7(1,counttt);
    BEST(7,1) = rateconstant;
    zipg = x(:,1)./Cinit(7,1);
    zipgt = t;
end
end

```

```

counttt = counttt + 1;
end

%This is for the eighth experimental data set: 1000:1 #2
for rateconstant = alpha:beta:gamma
%
%Initial Conditions Matrix
xo = Cinit(8,1);
%Solve the differential equations
[t,x] = ode45('light3',realdata18,xo,[],tau);

MMM8 = abs((realdata28 - x(:,1)./Cinit(8,1))).^2;
ttt8 = cumsum(MMM8);
bbb8 = ttt8(end)./size(realdata28,1);
rrr8 = ((bbb8)^(0.5))./max(realdata28);

ZZZ8(1,counttt) = rrr8;
ZZZ8(2,counttt) = rateconstant;

if ZZZ8(1,counttt) < aaa8
    aaa8 = ZZZ8(1,counttt);
    BEST(8,1) = rateconstant;
    ziph = x(:,1)./Cinit(8,1);
    zipht = t;
end
counttt = counttt + 1;
end

%This is for the ninth experimental data set: 1000:1 #3
for rateconstant = alpha:beta:gamma
%
%Initial Conditions Matrix
xo = Cinit(9,1);
%Solve the differential equations
[t,x] = ode45('light3',realdata19,xo,[],tau);

MMM9 = abs((realdata29 - x(:,1)./Cinit(9,1))).^2;
ttt9 = cumsum(MMM9);
bbb9 = ttt9(end)./size(realdata29,1);
rrr9 = ((bbb9)^(0.5))./max(realdata29);

ZZZ9(1,counttt) = rrr9;
ZZZ9(2,counttt) = rateconstant;

if ZZZ9(1,counttt) < aaa9
    aaa9 = ZZZ9(1,counttt);
    BEST(9,1) = rateconstant;
    zipi = x(:,1)./Cinit(9,1);
    zipit = t;
end
counttt = counttt + 1;
end

```

```

%This is for the tenth experimental data set: 250:1 #1
for rateconstant = alpha:beta:gamma
%
%Initial Conditions Matrix
xo = Cinit(10,1);
%Solve the differential equations
[t,x] = ode45('light3',realdata110,xo,[],tau);

MMM10 = abs((realdata210 - x(:,1)./Cinit(10,1))).^2;
ttt10 = cumsum(MMM10);
bbb10 = ttt10(end)./size(realdata210,1);
rrr10 = ((bbb10)^(0.5))./max(realdata210);

ZZZ10(1,counttt) = rrr10;
ZZZ10(2,counttt) = rateconstant;

if ZZZ10(1,counttt) < aaa10
    aaa10 = ZZZ10(1,counttt);
    BEST(10,1) = rateconstant;
    zipj = x(:,1)./Cinit(10,1);
    zipjt = t;
end
counttt = counttt + 1;
end

%This is for the eleventh experimental data set: 250:1 #2
for rateconstant = alpha:beta:gamma
%
%Initial Conditions Matrix
xo = Cinit(11,1);
%Solve the differential equations
[t,x] = ode45('light3',realdata111,xo,[],tau);

MMM11 = abs((realdata211 - x(:,1)./Cinit(11,1))).^2;
ttt11 = cumsum(MMM11);
bbb11 = ttt11(end)./size(realdata211,1);
rrr11 = ((bbb11)^(0.5))./max(realdata211);

ZZZ11(1,counttt) = rrr11;
ZZZ11(2,counttt) = rateconstant;

if ZZZ11(1,counttt) < aaa11
    aaa11 = ZZZ11(1,counttt);
    BEST(11,1) = rateconstant;
    zipk = x(:,1)./Cinit(11,1);
    zipkt = t;
end
counttt = counttt + 1;
end

%This is for the twelfth experimental data set: 250:1 #3
for rateconstant = alpha:beta:gamma
%
%Initial Conditions Matrix

```

```

xo = Cinit(12,1);
%Solve the differential equations
[t,x] = ode45('light3',realdata112,xo,[],tau);

MMM12 = abs((realdata212 - x(:,1)./Cinit(12,1))).^2;
ttt12 = cumsum(MMM12);
bbb12 = ttt12(end)./size(realdata212,1);
rrr12 = ((bbb12)^(0.5))./max(realdata212);

ZZZ12(1,counttt) = rrr12;
ZZZ12(2,counttt) = rateconstant;

if ZZZ12(1,counttt) < aaa12
    aaa12 = ZZZ12(1,counttt);
    BEST(12,1) = rateconstant;
    zipl = x(:,1)./Cinit(12,1);
    ziplt = t;
end
counttt = counttt + 1;
end

%This is for the thirteenth experimental data set: 50:1 #1
for rateconstant = alpha:beta:gamma
%
%Initial Conditions Matrix
xo = Cinit(13,1);
%Solve the differential equations
[t,x] = ode45('light3',realdata113,xo,[],tau);

MMM13 = abs((realdata213 - x(:,1)./Cinit(13,1))).^2;
ttt13 = cumsum(MMM13);
bbb13 = ttt13(end)./size(realdata213,1);
rrr13 = ((bbb13)^(0.5))./max(realdata213);

ZZZ13(1,counttt) = rrr13;
ZZZ13(2,counttt) = rateconstant;

if ZZZ13(1,counttt) < aaa13
    aaa13 = ZZZ13(1,counttt);
    BEST(13,1) = rateconstant;
    zipm = x(:,1)./Cinit(13,1);
    zipmt = t;
end
counttt = counttt + 1;
end

%This is for the fourteenth experimental data set: 50:1 #2
for rateconstant = alpha:beta:gamma
%
%Initial Conditions Matrix
xo = Cinit(14,1);
%Solve the differential equations
[t,x] = ode45('light3',realdata114,xo,[],tau);

```

```

MMM14 = abs((realdata214 - x(:,1)./Cinit(14,1))).^2;
ttt14 = cumsum(MMM14);
bbb14 = ttt14(end)./size(realdata214,1);
rrr14 = ((bbb14)^(0.5))./max(realdata214);

ZZZ14(1,counttt) = rrr14;
ZZZ14(2,counttt) = rateconstant;

if ZZZ14(1,counttt) < aaal4
    aaal4 = ZZZ14(1,counttt);
    BEST(14,1) = rateconstant;
    zipn = x(:,1)./Cinit(14,1);
    zipnt = t;
end
counttt = counttt + 1;
end

%This is for the fifteenth experimental data set: 50:1 #3
for rateconstant = alpha:beta:gamma
%
%-----
%Initial Conditions Matrix
xo = Cinit(15,1);
%Solve the differential equations
[t,x] = ode45('light3',realdata115,xo,[],tau);

MMM15 = abs((realdata215 - x(:,1)./Cinit(15,1))).^2;
ttt15 = cumsum(MMM15);
bbb15 = ttt15(end)./size(realdata215,1);
rrr15 = ((bbb15)^(0.5))./max(realdata215);

ZZZ15(1,counttt) = rrr15;
ZZZ15(2,counttt) = rateconstant;

if ZZZ15(1,counttt) < aaal5
    aaal5 = ZZZ15(1,counttt);
    BEST(15,1) = rateconstant;
    zipo = x(:,1)./Cinit(15,1);
    zipot = t;
end
counttt = counttt + 1;
end

%This is for the REPEAT (16th) experimental data set: 1000:1 REPEAT of
#1
for rateconstant = alpha:beta:gamma
%
%-----
%Initial Conditions Matrix
xo = Cinit(16,1);
%Solve the differential equations
[t,x] = ode45('light3',realdata17redo,xo,[],tau);

MMM16 = abs((realdata27redo - x(:,1)./Cinit(16,1))).^2;

```

```

t16 = cumsum(M16);
b16 = t16(end)./size(realdata27redo,1);
r16 = ((b16)^(0.5))./max(realdata27redo);

ZZ16(1,countt) = r16;
ZZ16(2,countt) = rateconstant;

if ZZ16(1,countt) < aa16
    aa16 = ZZ16(1,countt);
    BEST(16,1) = rateconstant;
    zip1 = x(:,1)./Cinit(16,1);
    zip1t = t;
end
countt = countt + 1;
end

%This is for the CONTROL experimental data set: 0:1 molar ratio
for rateconstant = alpha:beta:gamma
%
%Initial Conditions Matrix
xo = Cinit(17,1);
%Solve the differential equations
[t,x] = ode45('light3',realdata10,xo,[],tau);

M17 = abs((realdata10 - x(:,1)./Cinit(17,1))).^2;
t17 = cumsum(M17);
b17 = t17(end)./size(realdata20,1);
r17 = ((b17)^(0.5))./max(realdata20);

ZZ17(1,countt) = r17;
ZZ17(2,countt) = rateconstant;

if ZZ17(1,countt) < aa17
    aa17 = ZZ17(1,countt);
    BEST(17,1) = rateconstant;
    zip2 = x(:,1)./Cinit(17,1);
    zip2t = t;
end
countt = countt + 1;
end

%End of calculations and use of ODE45 function
%
%
%These are individual (each trial for each experiment) plots:

figure(1)
plot(realdata11,realdata21,'bd',zipat,zipa(:,1),'k-.')
title('DNAN Removal, Molar Ratio 100:1, 1 of 3')
xlabel('Time (minutes)')

```

```

ylabel('Relative concentration C/Co')
legend('data','model')
axis([0 60 0.55 1.05])

figure(2)
plot(realdata12,realdata22,'bd',zipbt,zipb(:,1),'k-.')
title('DNAN Removal, Molar Ratio 100:1, 2 of 3')
xlabel('Time (minutes)')
ylabel('Relative concentration C/Co')
legend('data','model')
axis([0 60 0.55 1.05])

figure(3)
plot(realdata13,realdata23,'bd',zipct,zipc(:,1),'k-.')
title('DNAN Removal, Molar Ratio 100:1, 3 of 3')
xlabel('Time (minutes)')
ylabel('Relative concentration C/Co')
legend('data','model')
axis([0 60 0.55 1.05])

figure(4)
plot(realdata14,realdata24,'bd',zipdt,zipd(:,1),'k-.')
title('DNAN Removal, Molar Ratio 500:1, 1 of 3')
xlabel('Time (minutes)')
ylabel('Relative concentration C/Co')
legend('data','model')
axis([0 60 0.55 1.05])

figure(5)
plot(realdata15,realdata25,'bd',zipet,zipc(:,1),'k-.')
title('DNAN Removal, Molar Ratio 500:1, 2 of 3')
xlabel('Time (minutes)')
ylabel('Relative concentration C/Co')
legend('data','model')
axis([0 60 0.55 1.05])

figure(6)
plot(realdata16,realdata26,'bd',zipft,zipf(:,1),'k-.')
title('DNAN Removal, Molar Ratio 500:1, 3 of 3')
xlabel('Time (minutes)')
ylabel('Relative concentration C/Co')
legend('data','model')
axis([0 60 0.55 1.05])

figure(7)
plot(realdata17,realdata27,'bd',zipgt,zipg(:,1),'k-.')
title('DNAN Removal, Molar Ratio 1000:1, 1 of 3')
xlabel('Time (minutes)')
ylabel('Relative concentration C/Co')
legend('data','model')
axis([0 60 0.55 1.05])

figure(77)%This is the 1000:1 repeat experiment
plot(realdata17redo,realdata27redo,'bd',zippt,zipp(:,1),'k-.')

```

```

title('DNAN Removal, Molar Ratio 1000:1, Repeat Experiment (#4)')
xlabel('Time (minutes)')
ylabel('Relative concentration C/Co')
legend('data','model')
axis([0 60 0.55 1.05])

figure(8)
plot(realdata18,realdata28,'bd',zipht,zipht(:,1),'k-.')
title('DNAN Removal, Molar Ratio 1000:1, 2 of 3')
xlabel('Time (minutes)')
ylabel('Relative concentration C/Co')
legend('data','model')
axis([0 60 0.55 1.05])

figure(9)
plot(realdata19,realdata29,'bd',zipit,zipit(:,1),'k-.')
title('DNAN Removal, Molar Ratio 1000:1, 3 of 3')
xlabel('Time (minutes)')
ylabel('Relative concentration C/Co')
legend('data','model')
axis([0 60 0.55 1.05])

figure(10)
plot(realdata110,realdata210,'bd',zipjt,zipjt(:,1),'k-.')
title('DNAN Removal, Molar Ratio 250:1, 1 of 3')
xlabel('Time (minutes)')
ylabel('Relative concentration C/Co')
legend('data','model')
axis([0 60 0.55 1.05])

figure(11)
plot(realdata111,realdata211,'bd',zipkt,zipkt(:,1),'k-.')
title('DNAN Removal, Molar Ratio 250:1, 2 of 3')
xlabel('Time (minutes)')
ylabel('Relative concentration C/Co')
legend('data','model')
axis([0 60 0.55 1.05])

figure(12)
plot(realdata112,realdata212,'bd',ziplt,ziplt(:,1),'k-.')
title('DNAN Removal, Molar Ratio 250:1, 3 of 3')
xlabel('Time (minutes)')
ylabel('Relative concentration C/Co')
legend('data','model')
axis([0 60 0.55 1.05])

figure(13)
plot(realdata113,realdata213,'bd',zipmt,zipmt(:,1),'k-.')
title('DNAN Removal, Molar Ratio 50:1, 1 of 3')
xlabel('Time (minutes)')
ylabel('Relative concentration C/Co')
legend('data','model')
axis([0 60 0.55 1.05])

```

```

figure(14)
plot(realdata114,realdata214,'bd',zipnt,zipn(:,1),'k-.')
title('DNAN Removal, Molar Ratio 50:1, 2 of 3')
xlabel('Time (minutes)')
ylabel('Relative concentration C/Co')
legend('data','model')
axis([0 60 0.55 1.05])

```

```

figure(15)
plot(realdata115,realdata215,'bd',zipot,zipo(:,1),'k-.')
title('DNAN Removal, Molar Ratio 50:1, 3 of 3')
xlabel('Time (minutes)')
ylabel('Relative concentration C/Co')
legend('data','model')
axis([0 60 0.55 1.05])

```

```

figure(16)
plot(realdata10,realdata20,'bd', zipqt,zipq(:,1),'k-.')
title('DNAN Removal, Control Experiment, Molar Ratio 0:1')
xlabel('Time (minutes)')
ylabel('Relative concentration C/Co')
legend('data','model')
axis([0 60 0.55 1.05])

```

```
%
```

```
%These are plots categorized by molar ratio with x3 trials plotted:
```

```

%Note: there was only one control experiment ran where a molar ratio of
0:1
%was used. Therefore it does not have a graph with multiple curves and
it
%does not have an average degradation curve either.

```

```

figure(100)
plot(realdata11,realdata21,'bd',zipat,zipa(:,1),'b-.')
title('DNAN Removal, Molar Ratio 100:1, 3 Trials')
xlabel('Time (minutes)')
ylabel('Relative concentration C/Co')
axis([0 60 0.55 1.05])
hold on
plot(realdata12,realdata22,'rd',zipbt,zipb(:,1),'r-.')
plot(realdata13,realdata23,'gd',zipct,zipc(:,1),'g-.')
legend('Trial 1','Model 1','Trial 2','Model 2','Trial 3','Model 3')
hold off

```

```

figure(500)
plot(realdata14,realdata24,'bd',zipdt,zipd(:,1),'b-.')
title('DNAN Removal, Molar Ratio 500:1, 3 Trials')
xlabel('Time (minutes)')
ylabel('Relative concentration C/Co')

```

```

axis([0 60 0.55 1.05])
hold on
plot(realdata15,realdata25,'rd',zipet,zipet(:,1),'r-.')
plot(realdata16,realdata26,'gd',zipft,zipf(:,1),'g-.')
legend('Trial 1','Model 1','Trial 2','Model 2','Trial 3','Model 3')
hold off

figure(1000) %This plot includes the repeat experiment and the outlier
from the graph
plot(realdata17,realdata27,'bd',zipgt,zipg(:,1),'b-.')
title('DNAN Removal, Molar Ratio 1000:1, 4 Trials')
xlabel('Time (minutes)')
ylabel('Relative concentration C/Co')
axis([0 60 0.55 1.05])
hold on
plot(realdata18,realdata28,'rd',zipht,zipht(:,1),'r-.')
plot(realdata19,realdata29,'gd',zipit,zipi(:,1),'g-.')
plot(realdata17redo,realdata27redo,'cd',zippt,zippt(:,1),'c-.')
text(35,0.62,'Outlier (Trial 1): Pipette Error Suspected')
legend('Trial 1','Model 1','Trial 2','Model 2','Trial 3','Model 3',
'Trial 4 (Repeat)','Model 4 (Repeat)')
hold off

figure(250)
plot(realdata110,realdata210,'bd',zipjt,zipj(:,1),'b-.')
title('DNAN Removal, Molar Ratio 250:1, 3 Trials')
xlabel('Time (minutes)')
ylabel('Relative concentration C/Co')
axis([0 60 0.55 1.05])
hold on
plot(realdata111,realdata211,'rd',zipkt,zipk(:,1),'r-.')
plot(realdata112,realdata212,'gd',ziplt,zipk(:,1),'g-.')
legend('Trial 1','Model 1','Trial 2','Model 2','Trial 3','Model 3')
hold off

figure(50)
plot(realdata113,realdata213,'bd',zipmt,zipm(:,1),'b-.')
title('DNAN Removal, Molar Ratio 50:1, 3 Trials')
xlabel('Time (minutes)')
ylabel('Relative concentration C/Co')
axis([0 60 0.55 1.05])
hold on
plot(realdata114,realdata214,'rd',zipnt,zipn(:,1),'r-.')
plot(realdata115,realdata215,'gd',zipot,zipo(:,1),'g-.')
legend('Trial 1','Model 1','Trial 2','Model 2','Trial 3','Model 3')
hold off

%


---




---



%Rate Constants to Excel:

xlswrite('DNANregressions.xls',zipa,'sheet1','B6');

```

```

xlswrite('DNANregressions.xls',zipat,'sheet1','C6');
xlswrite('DNANregressions.xls',zipb,'sheet2','B6');
xlswrite('DNANregressions.xls',zipbt,'sheet2','C6');
xlswrite('DNANregressions.xls',zipc,'sheet3','B6');
xlswrite('DNANregressions.xls',zipct,'sheet3','C6');
xlswrite('DNANregressions.xls',zipd,'sheet4','B6');
xlswrite('DNANregressions.xls',zipdt,'sheet4','C6');
xlswrite('DNANregressions.xls',zipe,'sheet5','B6');
xlswrite('DNANregressions.xls',zipet,'sheet5','C6');
xlswrite('DNANregressions.xls',zipf,'sheet6','B6');
xlswrite('DNANregressions.xls',zipft,'sheet6','C6');
xlswrite('DNANregressions.xls',zipg,'sheet7','B6');
xlswrite('DNANregressions.xls',zipgt,'sheet7','C6');
xlswrite('DNANregressions.xls',ziph,'sheet8','B6');
xlswrite('DNANregressions.xls',zipht,'sheet8','C6');
xlswrite('DNANregressions.xls',zipi,'sheet9','B6');
xlswrite('DNANregressions.xls',zipit,'sheet9','C6');
xlswrite('DNANregressions.xls',zipj,'sheet10','B6');
xlswrite('DNANregressions.xls',zipjt,'sheet10','C6');
xlswrite('DNANregressions.xls',zipk,'sheet11','B6');
xlswrite('DNANregressions.xls',zipkt,'sheet11','C6');
xlswrite('DNANregressions.xls',zipl,'sheet12','B6');
xlswrite('DNANregressions.xls',ziplt,'sheet12','C6');
xlswrite('DNANregressions.xls',zipm,'sheet13','B6');
xlswrite('DNANregressions.xls',zipmt,'sheet13','C6');
xlswrite('DNANregressions.xls',zipn,'sheet14','B6');
xlswrite('DNANregressions.xls',zipnt,'sheet14','C6');
xlswrite('DNANregressions.xls',zipo,'sheet15','B6');
xlswrite('DNANregressions.xls',zipot,'sheet15','C6');
xlswrite('DNANregressions.xls',zipp,'sheet16','B6');
xlswrite('DNANregressions.xls',zippt,'sheet16','C6');
xlswrite('DNANregressions.xls',zipq,'sheet17','B6');
xlswrite('DNANregressions.xls',zipqt,'sheet17','C6');

```

```

xlswrite('DNANregressions.xls',BEST(:,1),'sheet18','C6');
%

```

```

%the following block is needed to calculate and display the runtime.
tstop = clock;
runtime = etime(tstop,tstart)./60;
disp('length of run in minutes:')
disp(runtime)

```

3. Data file for average rate constant retrieval and curve fitting

File Name: searcyDNANdataavg2020.m

Code:

```
%June 2020 - AFIT
```



```

0.0461
0.0165
0.0187
0.0120
0.0185
0.0194
0.0202
0.0100];
%

```

```

%

```

```

% molar ratio = 500:1
% Average Degradation
% time data:
realdata500_avg1 = [0
5
10
15
20
25
35
45
60];

% relative concentration C/Co
realdata500_avg2 = [1.0000
0.8320
0.7647
0.7433
0.7095
0.6874
0.6750
0.6364
0.6651];

% Error Bars: Standard Deviations for each time increment over the
course of
% the three experiments
err500 = [0.0000
0.0376
0.0369
0.0239
0.0518
0.0158
0.0096
0.0469
0.0080];
%

```

```
%relative concentration C/Co
realdata250_avg2 = [1.0000
0.8475
0.7723
0.7367
0.7062
0.7043
0.6726
0.6659
0.6567];
```

[illegible]

```
%relative concentration C/Co
realdata50_avg2 = [1.0000
0.8931
0.8467
0.8238
0.8045
0.8029
0.7874
0.7800
```

```
0.7789];
```

```
%Error Bars: Standard Deviations for each time increment over the  
course of
```

```
%the three experiments
```

```
err50 = [0.0000
```

```
0.0106
```

```
0.0119
```

```
0.0089
```

```
0.0089
```

```
0.0120
```

```
0.0095
```

```
0.0148
```

```
0.0167];
```

```
%
```

```
%
```

4. Curve fitting for average rate constant retrieval and curve fitting

File Name: searcyDNAN5avg.m

Code:

```
%June, 2020
```

```
%Author: W. Harper
```

```
%Project: UV LED Project
```

```
%This program is used to model DNAN removal in a UV LED reactor
```

```
%the clock is here to help determine the runtime. It does not affect  
the process simulation
```

```
tstart = clock;
```

```
%global declarations - the purpose of these declarations is to make  
these parameter values
```

```
%available to light3.
```

```
%global declarations
```

```
global rateconstant reactorvolume flow xo Cinit_avg
```

```
global realdata10 realdata100_avg1 realdata500_avg1 realdata1000_avg1
```

```
realdata250_avg1 realdata20 realdata50_avg1 realdata100_avg2
```

```
realdata500_avg2 realdata1000_avg2 realdata250_avg2 realdata50_avg2
```

```
err50 err100 err250 err500 err1000
```

```
%The parameters in the matrix are respectively:
```

```
%effluent concentration of DNAN (1)
```

```
%the units of the rateconstant are inverse time (1/min)
```

```

%the units of volume are ml
reactorvolume = 35;

%the units of flow are ml/minutes
flow = 2.0;

tau = reactorvolume./flow;

%parameters needed for simulation
alpha = 0.001;
beta = 0.001;
gamma = 0.05;

%additional matrices needed for data processing
nnn = 100000;
ZZZ100AVG = zeros(7,nnn);
BEST = zeros(6,1);
BEST100AVG = zeros(1,1);
ZZZ500AVG = zeros(7,nnn);
BEST500AVG = zeros(1,1);
ZZZ1000AVG = zeros(7,nnn);
BEST1000AVG = zeros(1,1);
ZZZ250AVG = zeros(7,nnn);
BEST250AVG = zeros(1,1);
ZZZ50AVG = zeros(7,nnn);
BEST50AVG = zeros(1,1);

%the following are process parameters
to = 0;
%the units are minutes
tf = 60;

searcyDNANdata2020avg

%aaa is needed to determine the best parameter combination
aaa1 = 100000000000;
aaa100avg = aaa1;
aaa500avg = aaa1;
aaa1000avg = aaa1;
aaa250avg = aaa1;
aaa50avg = aaa1;

%this is a counter
counttt = 1;

%the simulation logic begins here

%This is for the Avg. Rate Constant of the 100:1 experimental data sets
for rateconstant = alpha:beta:gamma
%


---


%Initial Conditions Matrix
xo = Cinit_avg(1,1);

```

```

%Solve the differential equations
[t,x] = ode45('light3',realdata100_avg1,xo,[],tau);

MMM100AVG = abs((realdata100_avg2 - x(:,1)./Cinit_avg(1,1))).^2;
ttt100avg = cumsum(MMM100AVG);
bbb100avg = ttt100avg(end)./size(realdata100_avg2,1);
rrr100avg = ((bbb100avg)^(0.5))./max(realdata100_avg2);

ZZZ100AVG(1,counttt) = rrr100avg;
ZZZ100AVG(2,counttt) = rateconstant;

if ZZZ100AVG(1,counttt) < aaa100avg
    aaa100avg = ZZZ100AVG(1,counttt);
    BEST(1,1) = rateconstant;
    zip100avg = x(:,1)./Cinit_avg(1,1);
    zip100avgt = t;
end
counttt = counttt + 1;
end

counttt = 1;

%This is for the Avg. Rate Constant of the 500:1 experimental data sets
for rateconstant = alpha:beta:gamma
%
%-----
%Initial Conditions Matrix
xo = Cinit_avg(2,1);
%Solve the differential equations
[t,x] = ode45('light3',realdata500_avg1,xo,[],tau);

MMM500AVG = abs((realdata500_avg2 - x(:,1)./Cinit_avg(2,1))).^2;
ttt500avg = cumsum(MMM500AVG);
bbb500avg = ttt500avg(end)./size(realdata500_avg2,1);
rrr500avg = ((bbb500avg)^(0.5))./max(realdata500_avg2);

ZZZ500AVG(1,counttt) = rrr500avg;
ZZZ500AVG(2,counttt) = rateconstant;

if ZZZ500AVG(1,counttt) < aaa500avg
    aaa500avg = ZZZ500AVG(1,counttt);
    BEST(2,1) = rateconstant;
    zip500avg = x(:,1)./Cinit_avg(2,1);
    zip500avgt = t;
end
counttt = counttt + 1;
end

counttt = 1;

%This is for the Avg. Rate Constant of the 1000:1 experimental data
sets
%NOTE: This Avg. Rate Constant eliminates the outlier data point.
Therefore

```

```

%this produces the rate constant based on the average degradation of
trial
%2, trial 3, and the repeat trial.
for rateconstant = alpha:beta:gamma
%
%Initial Conditions Matrix
xo = Cinit_avg(3,1);
%Solve the differential equations
[t,x] = ode45('light3',realdata1000_avg1,xo,[],tau);

MMM1000AVG = abs((realdata1000_avg2 - x(:,1)./Cinit_avg(3,1))).^2;
ttt1000avg = cumsum(MMM1000AVG);
bbb1000avg = ttt1000avg(end)./size(realdata1000_avg2,1);
rrr1000avg = ((bbb1000avg)^(0.5))./max(realdata1000_avg2);

ZZZ1000AVG(1,counttt) = rrr1000avg;
ZZZ1000AVG(2,counttt) = rateconstant;

if ZZZ1000AVG(1,counttt) < aaa1000avg
    aaa1000avg = ZZZ1000AVG(1,counttt);
    BEST(3,1) = rateconstant;
    zip1000avg = x(:,1)./Cinit_avg(3,1);
    zip1000avgt = t;
end
counttt = counttt + 1;
end

counttt = 1;

%This is for the Avg. Rate Constant of the 250:1 experimental data sets
for rateconstant = alpha:beta:gamma
%
%Initial Conditions Matrix
xo = Cinit_avg(4,1);
%Solve the differential equations
[t,x] = ode45('light3',realdata250_avg1,xo,[],tau);

MMM250AVG = abs((realdata250_avg2 - x(:,1)./Cinit_avg(4,1))).^2;
ttt250avg = cumsum(MMM250AVG);
bbb250avg = ttt250avg(end)./size(realdata250_avg2,1);
rrr250avg = ((bbb250avg)^(0.5))./max(realdata250_avg2);

ZZZ250AVG(1,counttt) = rrr250avg;
ZZZ250AVG(2,counttt) = rateconstant;

if ZZZ250AVG(1,counttt) < aaa250avg
    aaa250avg = ZZZ250AVG(1,counttt);
    BEST(4,1) = rateconstant;
    zip250avg = x(:,1)./Cinit_avg(4,1);
    zip250avgt = t;
end
counttt = counttt + 1;
end

```

```

countttt = 1;

%This is for the Avg. Rate Constant of the 50:1 experimental data sets
for rateconstant = alpha:beta:gamma
%
%Initial Conditions Matrix
xo = Cinit_avg(5,1);
%Solve the differential equations
[t,x] = ode45('light3',realdata50_avg1,xo,[],tau);

MMM50AVG = abs((realdata50_avg2 - x(:,1)./Cinit_avg(5,1))).^2;
ttt50avg = cumsum(MMM50AVG);
bbb50avg = ttt50avg(end)./size(realdata50_avg2,1);
rrr50avg = ((bbb50avg)^(0.5))./max(realdata50_avg2);

ZZZ50AVG(1,countttt) = rrr50avg;
ZZZ50AVG(2,countttt) = rateconstant;

if ZZZ50AVG(1,countttt) < aaa50avg
    aaa50avg = ZZZ50AVG(1,countttt);
    BEST(5,1) = rateconstant;
    zip50avg = x(:,1)./Cinit_avg(5,1);
    zip50avgt = t;
end
countttt = countttt + 1;
end

countttt = 1;

%
%
%
%

%Plot with Data Points
figure(1)
plot(realdata10,realdata20,'kd', zipqt,zipq(:,1),'k-.')
title('DNAN Removal, Molar Ratios 50, 100, 250, 500, 1000:1, Avg. Degradation')
xlabel('Time (minutes)')
ylabel('Relative concentration C/Co')
axis([0 65 0.55 1.05])
hold on
plot(realdata50_avg1,realdata50_avg2,'cd',zip50avgt,zip50avg(:,1),'c-')
plot(realdata100_avg1,realdata100_avg2,'bd',zip100avgt,zip100avg(:,1),'b-')
plot(realdata250_avg1,realdata250_avg2,'md',zip250avgt,zip250avg(:,1),'m-')
plot(realdata500_avg1,realdata500_avg2,'rd',zip500avgt,zip500avg(:,1),'r-')

```

```

plot(realdata1000_avg1,realdata1000_avg2,'gd',zip1000avgt,zip1000avg(:,
1),'g-.')
text(25,0.95,'Control 0:1; k_s=0.001 min^-^1')
text(30,0.81,'50:1; k_s=0.018 min^-^1')
text(30,0.755,'100:1 & 1000:1; k_s=0.023 min^-^1')
text(30,0.695,'250:1; k_s=0.031 min^-^1')
text(30,0.64,'500:1; k_s=0.032 min^-^1')
legend('Control data','Control model','50:1 avg data','50:1 avg
model','100:1 avg data','100:1 avg model','250:1 avg data','250:1 avg
model','500:1 avg data','500:1 avg model','1000:1 avg data','1000:1
avg model')
hold off

%Plot w/o Data Points (just the model for each molar ratio)
figure(2)
plot(zipqt,zipq(:,1),'k-.')
title('DNAN Removal, Molar Ratios 50, 100, 250, 500, 1000:1, Avg.
Degradation')
xlabel('Time (minutes)')
ylabel('Relative concentration C/Co')
axis([0 65 0.55 1.05])
hold on
plot(zip50avgt,zip50avg(:,1),'c-.')
plot(zip100avgt,zip100avg(:,1),'b-.')
plot(zip250avgt,zip250avg(:,1),'m-.')
plot(zip500avgt,zip500avg(:,1),'r-.')
plot(zip1000avgt,zip1000avg(:,1),'g-.')
%text(30,0.81,'50:1; k_s=0.018 min^-^1')
%text(30,0.755,'100:1 & 1000:1; k_s=0.023 min^-^1')
%text(30,0.695,'250:1; k_s=0.031 min^-^1')
%text(30,0.64,'500:1; k_s=0.032 min^-^1')
%text(15,0.87,'Error bars encompass 1 Std. Dev. around Avg.
Degradation')
errorbar(realdata50_avg1, realdata50_avg2, err50, '' , 'c.')
errorbar(realdata100_avg1, realdata100_avg2, err100, '' , 'b.')
errorbar(realdata250_avg1, realdata250_avg2, err250, '' , 'm.')
errorbar(realdata500_avg1, realdata500_avg2, err500, '' , 'r.')
errorbar(realdata1000_avg1, realdata1000_avg2, err1000, '' , 'g.')
legend('Control model','50:1 avg model','100:1 avg model','250:1 avg
model','500:1 avg model','1000:1 avg model')
hold off

xlswrite('DNANregressionsavg.xls',zip100avg,'sheet1','B6');
xlswrite('DNANregressionsavg.xls',zip100avgt,'sheet1','C6');
xlswrite('DNANregressionsavg.xls',zip500avg,'sheet2','B6');
xlswrite('DNANregressionsavg.xls',zip500avgt,'sheet2','C6');
xlswrite('DNANregressionsavg.xls',zip1000avg,'sheet3','B6');
xlswrite('DNANregressionsavg.xls',zip1000avgt,'sheet3','C6');
xlswrite('DNANregressionsavg.xls',zip250avg,'sheet4','B6');
xlswrite('DNANregressionsavg.xls',zip250avgt,'sheet4','C6');
xlswrite('DNANregressionsavg.xls',zip50avg,'sheet5','B6');
xlswrite('DNANregressionsavg.xls',zip50avgt,'sheet5','C6');

xlswrite('DNANregressionsavg.xls',BEST(:,1),'sheet6','C6');

```

```
%the following block is needed to calculate and display the runtime.
tstop = clock;
runtime = etime(tstop,tstart)./60;
disp('length of run in minutes:')
disp(runtime)
```

5. Differential equation for use in ODE45 function

File Name: light3.m.

Code:

```
function xdot = light3(t,~,~,tau)
%this function simulates UV LED/H2O2 degradation of DNAN

%xdot is the matrix of differential expressions (ie dC/dt,
dX/dt,etc...)
%x is the matrix of parameters (ie C, X, etc...)

%global declarations
global rateconstant xo

%The parameters in the matrix are respectively:
%effluent concentration of DNAN (1)

%math
%reactions/equations
xdot = xo.*(tau.*rateconstant.*(exp(-1.*t.*(rateconstant +
1./tau))).*(-1.*(rateconstant + 1./tau)))./(tau.*rateconstant + 1);
```

Appendix H – Average Molar Ratio Rate Constant Calculations and Outlier Analysis

	DNAN Degradation: C/Co																												
	100:1					500:1					1000:1					250:1					50:1								
	Trial					Trial					Trial					Trial					Trial								
Time (min)	1	2	3	Avg	Std. Dev.	1	2	3	Avg	Std. Dev.	1:Outlier	2	3	4: Repeat of #1	Avg	Std. Dev.	1	2	3	Avg	Std. Dev.	1	2	3	Avg	Std. Dev.			
0	1.0000	1.0000	1.0000	1.0000	0.0000	1.0000	1.0000	1.0000	1.0000	0.0000	1.0000	1.0000	1.0000	1.0000	1.0000	0.0000	1.0000	1.0000	1.0000	1.0000	0.0000	1.0000	1.0000	1.0000	1.0000	0.0000			
5	0.8896	0.8253	0.9147	0.8765	0.0461	0.8259	0.8723	0.7979	0.8320	0.0376	0.8511	0.8706	0.8947	0.8636	0.8763	0.0163	0.8291	0.8641	0.8493	0.8475	0.0176	0.8905	0.8839	0.9047	0.8931	0.0106			
10	0.8046	0.8338	0.8327	0.8237	0.0165	0.7823	0.7895	0.7224	0.7647	0.0369	0.7644	0.8153	0.8239	0.8329	0.8240	0.0088	0.7586	0.7819	0.7764	0.7723	0.0122	0.8409	0.8388	0.8603	0.8467	0.0119			
15	0.7641	0.8009	0.7880	0.7843	0.0187	0.7637	0.7493	0.7170	0.7433	0.0239	0.7163	0.7693	0.7827	0.7860	0.7793	0.0089	0.7281	0.7487	0.7332	0.7367	0.0107	0.8139	0.8261	0.8314	0.8238	0.0089			
20	0.7482	0.7698	0.7679	0.7620	0.0120	0.6931	0.7676	0.6679	0.7095	0.0518	0.6942	0.7574	0.7585	0.7832	0.7664	0.0146	0.7024	0.7142	0.7020	0.7062	0.0069	0.7951	0.8129	0.8054	0.8045	0.0089			
25	0.7300	0.7669	0.7507	0.7492	0.0185	0.6866	0.7035	0.6720	0.6874	0.0158	0.6819	0.7470	0.7514	0.7607	0.7530	0.0070	0.7100	0.7058	0.6970	0.7043	0.0066	0.7891	0.8114	0.8080	0.8029	0.0120			
35	0.7192	0.7554	0.7493	0.7413	0.0194	0.6653	0.6845	0.6752	0.6750	0.0096	0.6516	0.7219	0.7370	0.7450	0.7346	0.0117	0.6608	0.6811	0.6760	0.6726	0.0106	0.7765	0.7914	0.7942	0.7874	0.0095			
45	0.7090	0.7494	0.7309	0.7297	0.0202	0.5831	0.6714	0.6548	0.6364	0.0469	0.6460	0.7291	0.7297	0.7479	0.7356	0.0107	0.6490	0.6792	0.6694	0.6659	0.0154	0.7650	0.7805	0.7945	0.7800	0.0148			
60	0.7110		0.7252	0.7181	0.0100	0.6703	0.6559	0.6691	0.6651	0.0080	0.6493	0.7192	0.7143	0.7435	0.7257	0.0156	0.6467	0.6692	0.6544	0.6567	0.0114	0.7601	0.7849	0.7919	0.7789	0.0167			
Starting Concentration (ppm)	9.6587	9.1494	9.6675	9.4919	0.2966	9.5907	9.3731	9.7728	9.5789	0.2001	9.3815	9.6322	9.6362	9.6889	9.6524	0.0316	9.5736	9.8014	9.6431	9.6727	0.1168	9.7577	9.9511	9.6623	9.7904	0.1472			
MATLAB Rate Constant modeled (min ⁻¹)	0.025	0.022	0.023	0.0233	0.0015	0.033	0.029	0.034	0.0320	0.0026	0.033	0.024	0.024	0.022	0.0233	0.0012	0.032	0.029	0.031	0.0307	0.0015	0.019	0.018	0.017	0.0180	0.0010			
MATLAB Avg. Rate Constant Modeled (min ⁻¹)				0.023					0.032						0.023				0.031						0.018				
Q TEST (95% Conf.)																													
Ordered K _s (left to right)	0.022	0.023	0.025			0.029	0.033	0.034			0.022	0.024	0.024	0.033			0.029	0.031	0.032			0.017	0.018	0.019					
gap (use larger)	0.001		0.002			0.004		0.001			0.002			0.009			0.002		0.001			0.001		0.001					
Q=gap/range			0.667			0.800					Advise to reject and include data for outlier in appendix.			0.818			0.667					0.5		0.5					
Confidence Interval	n	t-statistic	95% Conf Int			95% Conf Int			95% Conf Int			95% Conf Int			95% Conf Int			95% Conf Int			95% Conf Int			95% Conf Int			95% Conf Int		
95% Conf Int for sample mean	3	4.303	0.0195	0.0271			0.0254			0.0386	0.0205			0.0262			0.0269			0.0345			0.0155			0.0205			

Appendix I – Statistical Analysis Python® Code

```
#!/usr/bin/env python
# coding: utf-8

# # Statistical Analysis: The Effect of Molar Peroxide Ratio on the Oxidation of 2,4
Dinitroanisole in an Ultraviolet Light Emitting Diode Advanced Oxidation Process
#
# ### Statistical Analysis for Thesis Research
# ### Capt Troy Searcy
# ### Note: Original Code and Python functions were provided by Maj Timothy
Anderson during STAT 535 Class in the Winter of 2020.
# ### Experimental Values from Jun - Aug 2020

# In[1]:
import seaborn as sns
import numpy as np
import pandas as pd
from scipy.stats import shapiro, bartlett, kruskal, friedmanchisquare, mannwhitneyu,
boxcox
import statsmodels.api as sm
import statsmodels.stats.api as sms
from statsmodels.formula.api import ols
from statsmodels.graphics.factorplots import interaction_plot
from statsmodels.stats.stattools import durbin_watson
from statsmodels.sandbox.stats.runs import runstest_1samp
from statsmodels.stats.diagnostic import kstest_normal
from statsmodels.stats.outliers_influence import summary_table
from statsmodels.sandbox.regression.predstd import wls_prediction_std
import matplotlib.pyplot as plt
get_ipython().run_line_magic('matplotlib', 'inline')

### 1.1. Reading in the Data
# Data has been compiled from experiments conducted from 27 May - 25 Aug 2020.
# Add in column names to make the analysis easier.

# In[3]:
dnan_df = pd.read_csv('dnan.csv')
dnan_df.columns = ['date', 'molar_ratio', 'k_s', 'pH', 'Meas. DNAN Conc.', 'Starting
Conc.', 'HPLC 100% CC']
dnan_df.head()

# In[4]:
dnan_df.tail()
```

```

# In[7]:
dnan2_df = pd.read_csv('dnan2.csv')
dnan2_df.columns = ['date', 'molar_ratio', 'k_s', 'pH', 'Meas. DNAN Conc.', 'Starting
Conc.', 'HPLC 100% CC']
dnan2_df.head()

## 2. Descriptive Statistics

# In[38]:
print(dnan_df.columns)
print(dnan_df.describe())

# In[39]:
dnan_describe_df = pd.read_csv('dnan_describe.csv')
dnan_describe_df.columns = ['0:1 k_s', '50:1 k_s', '100:1 k_s', '250:1 k_s', '500:1 k_s',
'1000:1 k_s']
print(dnan_describe_df.columns)
print(dnan_describe_df.describe())

### 2.1 Histograms

# In[9]:
dnan_df.hist(column='k_s', figsize=(10,8))
plt.show()

# In[10]:
dnan_df.hist(column='k_s', by='molar_ratio', figsize=(10,8))
plt.show()

# In[11]:
dnan_df.hist(column='Meas. DNAN Conc.', figsize=(10,8))
plt.show()

### 2.2. Boxplots

# In[12]:
dnan_df.boxplot('k_s', figsize=(10,8))
plt.show()

# In[14]:
dnan_df.boxplot('k_s', by='molar_ratio', figsize=(10,8))
plt.show()

# In[15]:
dnan_df.boxplot('Meas. DNAN Conc.', figsize=(10,8))

```

```
plt.show()
```

```
# In[16]:  
dnan_df.boxplot('Meas. DNAN Conc.', by='molar_ratio', figsize=(10,8))  
plt.show()
```

```
# In[17]:  
dnan_df.boxplot('Starting Conc.', figsize=(10,8))  
plt.show()
```

```
# In[18]:  
dnan_df.boxplot('Starting Conc.', by='molar_ratio', figsize=(10,8))  
plt.show()
```

2.3. Scatter Plots

```
# In[19]:  
plt.scatter(x=dnan_df["molar_ratio"], y=dnan_df["k_s"])  
plt.ylim(ymin=0, ymax=.04)
```

```
# In[20]:  
plt.scatter(x=dnan_df["pH"], y=dnan_df["k_s"])  
plt.ylim(ymin=0, ymax=.04)
```

```
# In[21]:  
plt.scatter(x=dnan_df["Meas. DNAN Conc."], y=dnan_df["k_s"])  
plt.ylim(ymin=0, ymax=.04)
```

```
# In[22]:  
plt.scatter(x=dnan_df["Starting Conc."], y=dnan_df["k_s"])  
plt.ylim(ymin=0, ymax=.04)
```

```
# In[23]:  
plt.scatter(x=dnan_df["Starting Conc."], y=dnan_df["Meas. DNAN Conc."])  
plt.ylim(ymin=9.90, ymax=10.08)
```

```
# In[24]:  
plt.scatter(x=dnan_df["Meas. DNAN Conc."], y=dnan_df["HPLC 100% CC"])  
plt.ylim(ymin=600, ymax=800)
```

Use pairplot command to inform decisions - Any trends?

```
# In[25]:  
sns.pairplot(dnan_df)
```

3. Quantitative Test for Normality

In[27]:

```
for molar_ratio in dnan2_df.molar_ratio.unique():
    tempV1_df = dnan2_df[dnan2_df["molar_ratio"] == molar_ratio]
    print(molar_ratio)
    print(shapiro(tempV1_df["k_s"]))
    print("")
```

-For the Shapiro Wilk test, the null hypothesis states the data appears normal. If the calculated p-value is less than the chosen level of significance (0.05 = alpha), then the null hypothesis is rejected and the assumption of normality is not met.

#

-Quantitative Check: For a significance level (alpha) of .05, the null hypothesis is not rejected since the p-values (except for 1000:1) are greater than the chosen level of significance (p-value < alpha = reject null). The null states that the errors are approximately normal distribution.

#

-After running the Shapiro-Wilk Test for normality we would fail to reject the null hypothesis for each p-value except the 1000:1 molar ratio (each p-value is larger than the chosen alpha level of 0.05 except the 1000:1 molar ratio, which is less than 0.05). Based on these test statistics and p-value we would not reject the null hypothesis which means that the data does appear to be normal EXCEPT for the 1000:1 molar ratio. However, because ANOVA is robust against normality we continue on with parametric testing as long as the assumption for equal variance (Bartlett's Test is satisfied).

4. Quantitative Test for Equal Variance

In[29]:

```
test_array = list()
for molar_ratio in dnan2_df.molar_ratio.unique():
    test_array.append(list(dnan2_df[dnan2_df["molar_ratio"] == molar_ratio]["k_s"]))
print(bartlett(*test_array))
```

-For Bartlett's Test, the null hypothesis states that equal variances exist across all treatments (molar ratios).

#

-Bartlett's Test yielded a high p-value (greater than alpha = 0.05) resulting in non-rejection of the null hypothesis (p-value < alpha = reject null). This satisfies the assumption required to continue the analysis of variance with parametric methods.

5. ANOVA

5.1 One-way ANOVA model using molar ratios as the factor levels and the rate constants (k_s) as the response.

```
# In[30]:
dnan2_model = ols('k_s ~ C(molar_ratio)', data=dnan2_df).fit()
dnan2_anova_table = sm.stats.anova_lm(dnan2_model, typ=2)
print(dnan2_anova_table)
```

-This model uses molar ratios as treatments and the rate constants as the response which results in a low p-value leading to a rejection of the null hypothesis (p-value < alpha = reject null).

#

-This null hypothesis states that all five molar ratios have equal mean rate constants. We know this is not true since we have calculated the means, however, by doing the ANOVA we incorporate the variance to see if there is a statistically significant difference between the means when the variance is accounted for and we can put associate a level of confidence with the fact that the means are not the same (taking the variance into account) and also determine which are individually different using Tukey's test.

#

-The F-test lead to the rejection of the null hypothesis that the treatment means are equal. The null hypothesis is rejected for the ANOVA test in favor of the alternative hypothesis. The alternative hypothesis states that at least two of the molar ratios have different mean rate constant values. At this point, we know that at least two of the molar ratio's mean rate constants are different from each other. However, we currently do not know which, or how many, are different from each other.

5.2. Tukey Analysis

Calculate the pairwise comparisons for the different molar ratios to determine which rate constants for each individual trial for each molar ratio are significantly different

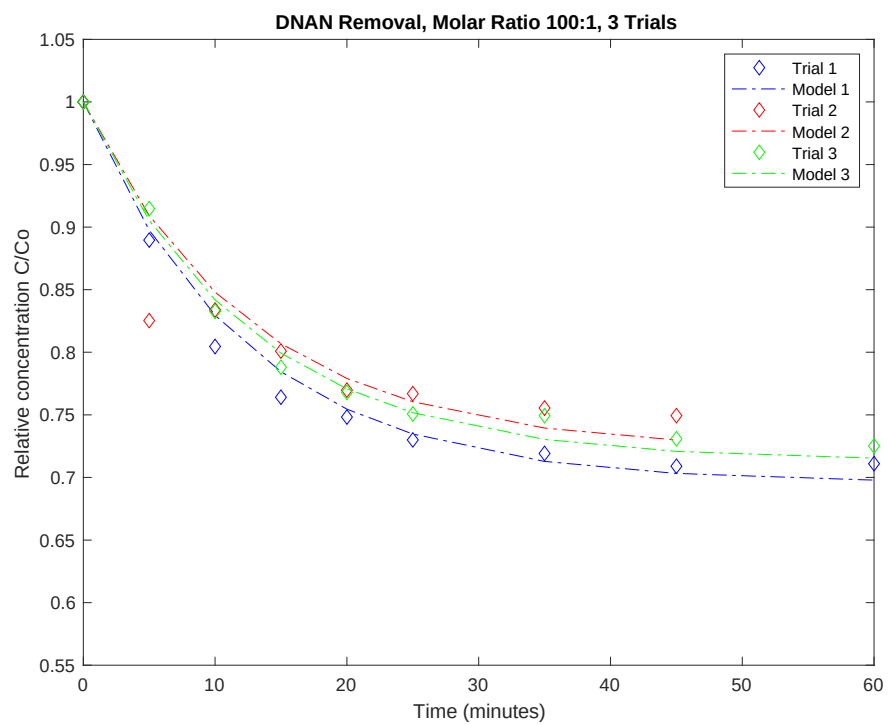
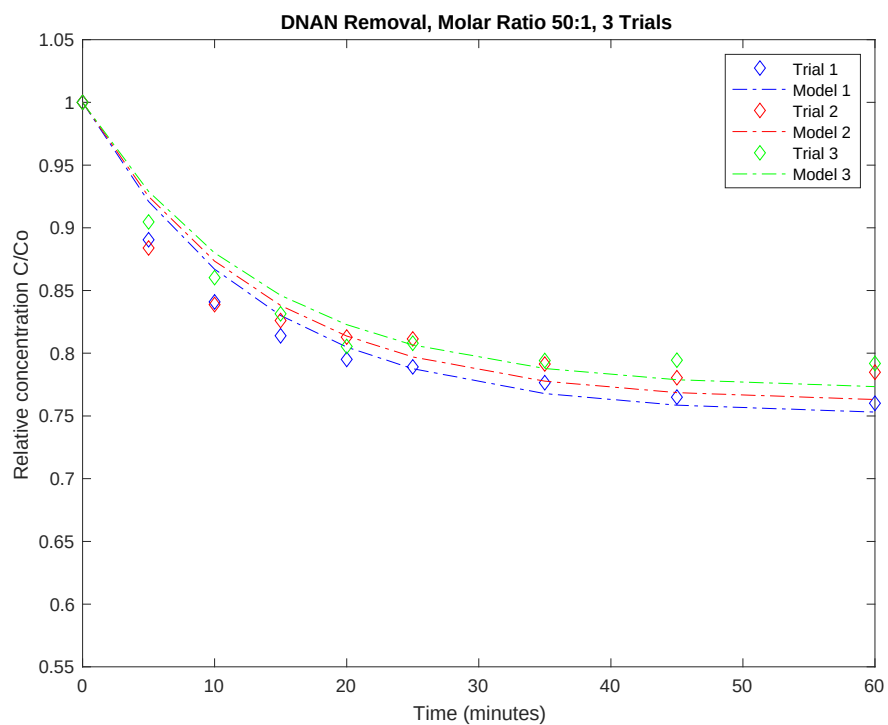
```
# In[31]:
dnan2_tukey = sm.stats.multicomp.pairwise_tukeyhsd(dnan2_df['k_s'],
dnan2_df['molar_ratio'], .05)
print(dnan2_tukey)
```

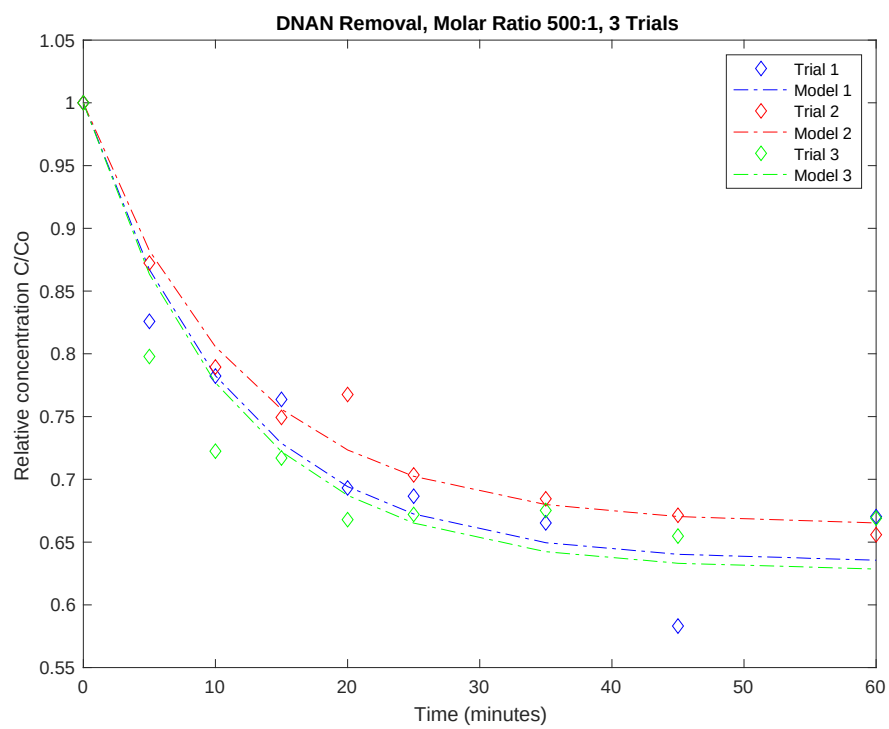
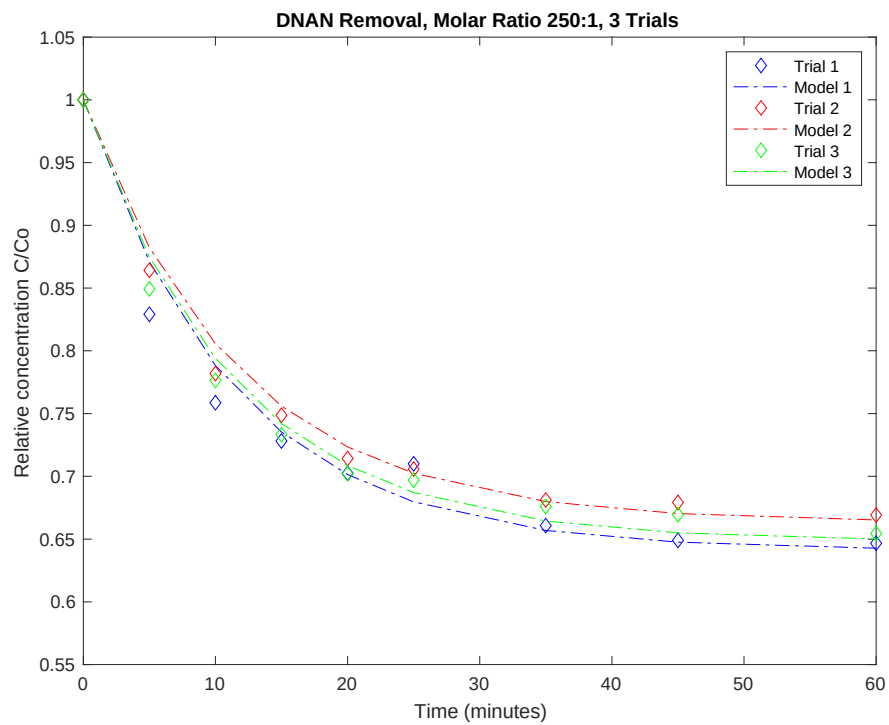
-The null hypothesis for Tukey's Method states that there is NOT a statistically significant difference in the mean rate constants between the different molar ratios (so the mean rate constants are the same if you fail to reject). Rejection of the null equates to the mean rate constants under consideration being statistically different at a .05 level of significance.

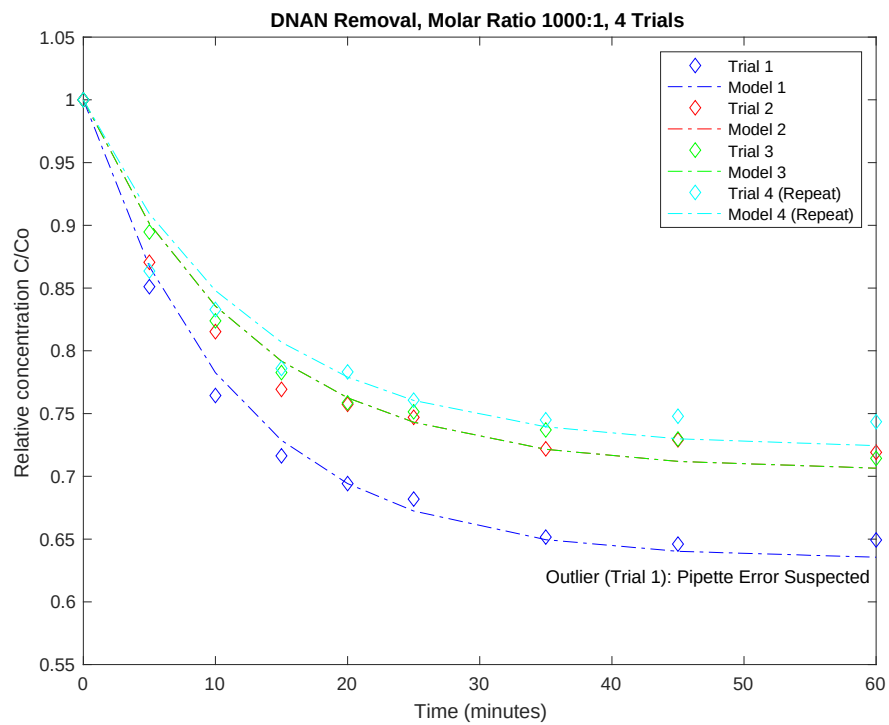
-NOTE: "False" under the reject column equates to NOT rejecting (fail to reject) the null hypothesis.

-Conclusion: Based off pairwise comparisons, the mean rate constants appear to be different for all molar ratios except for the combination 100:1 / 1000:1 (which makes sense because we know the average rate constants for 100:1 and 1000:1 experiments were very close) and for the combination 250:1 / 500:1 (which makes sense since we know that these two molar ratios have average rate constants which are very similar).

Appendix J – DNAN Degradation Plots by Molar Ratio





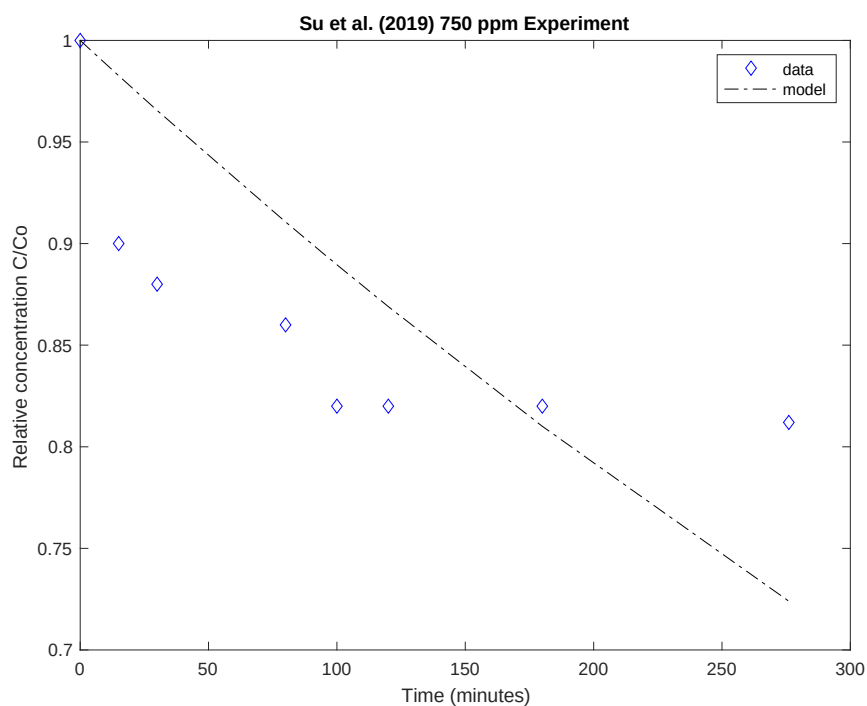


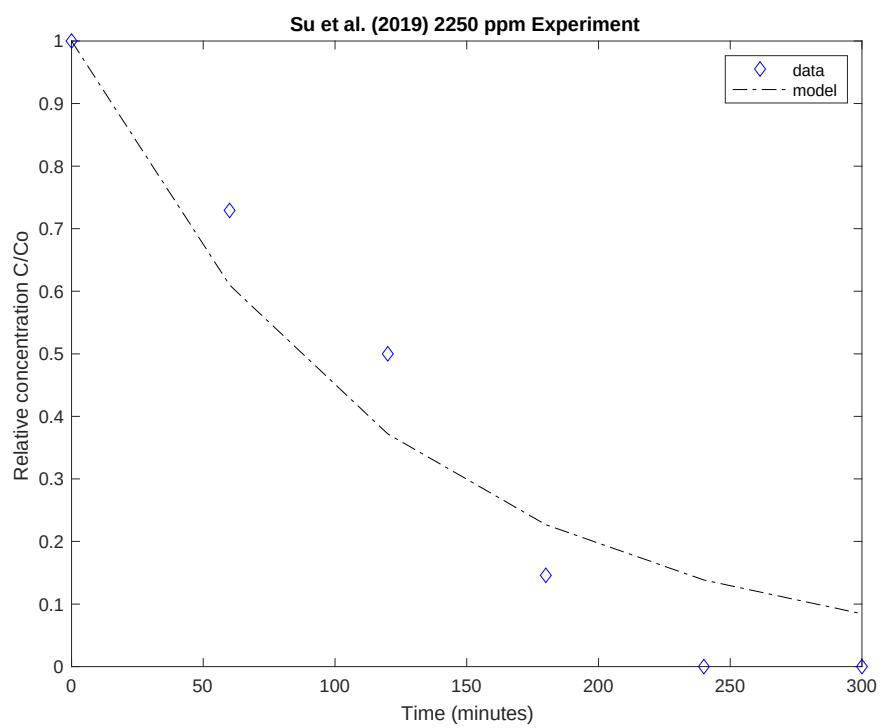
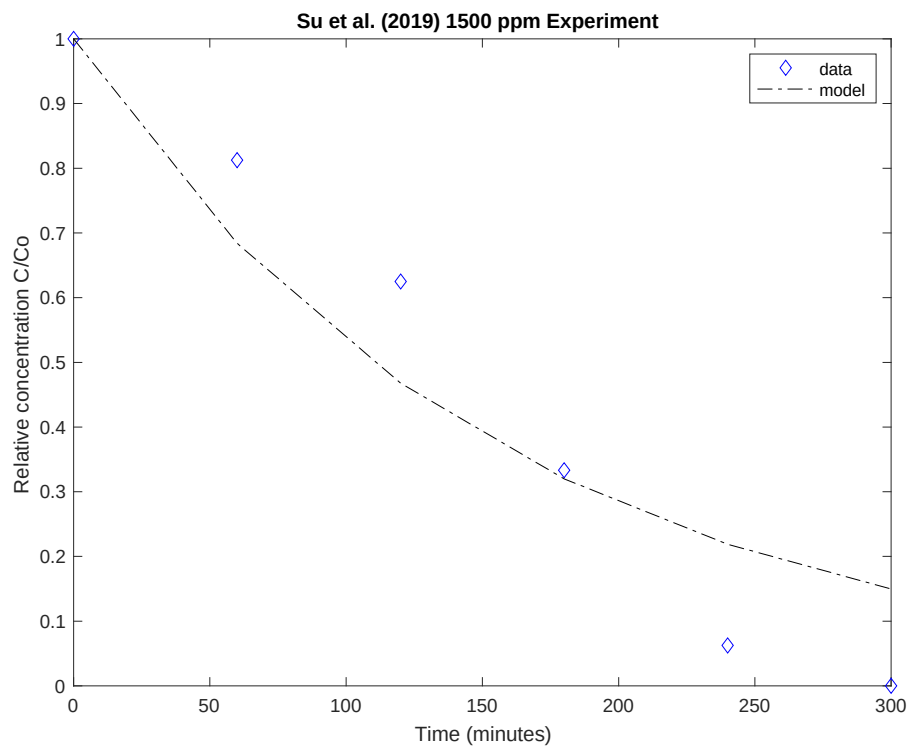
Appendix K – Comparison of Conditions and Results in Relevant Studies

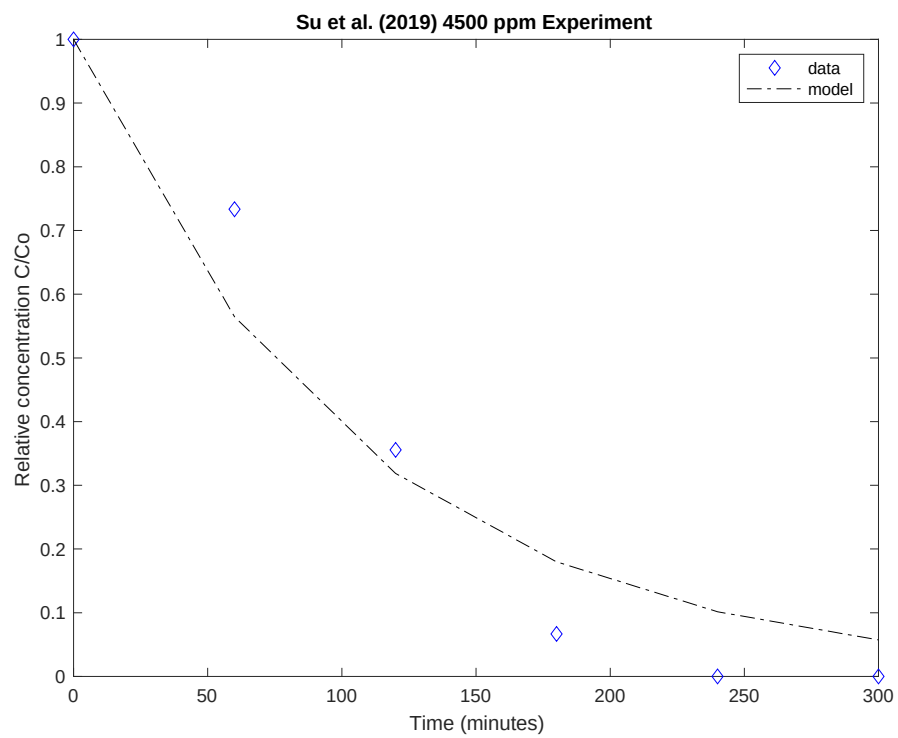
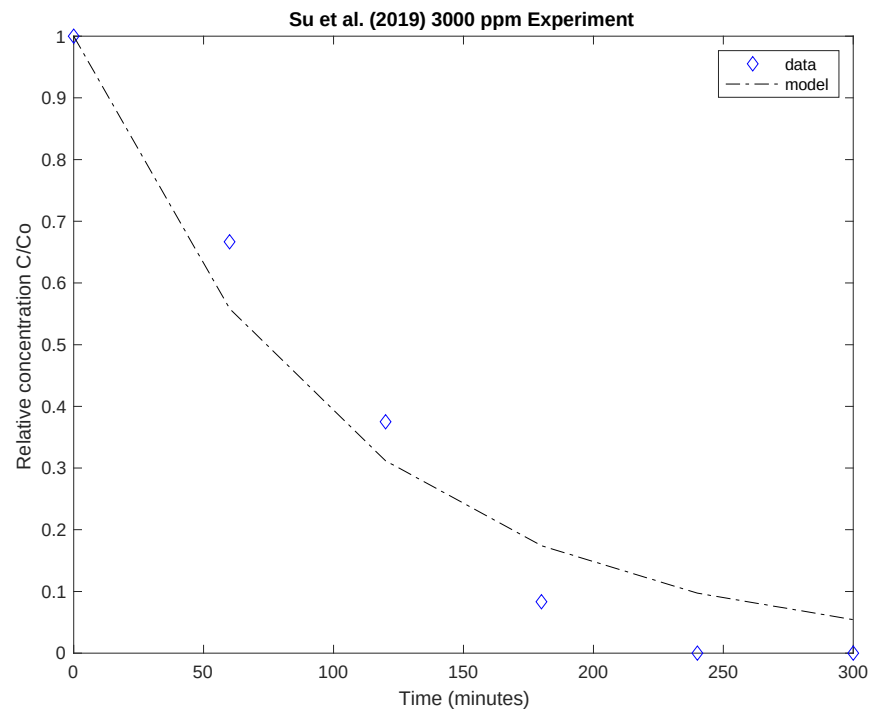
1. Initial conditions, reported values, and calculated rate constants:

Current Research							
DNAN concentration	mg/L (ppm)	10					
	uM	50.48					
H ₂ O ₂ Concentration	mM	0	2.524	5.048	12.620	25.240	50.480
Molar Ratio	H ₂ O ₂ :DNAN	0	50	100	250	500	1000
Avg. Rate Constant (pseudo first-order)	min ⁻¹	0	0.0180	0.0233	0.0307	0.0320	0.0233
Yang et al. (2018)							
DNAN concentration	uM (reported)	40					
	mg/L (ppm)	7.9254					
	mol/L	0.00004					
H ₂ O ₂ Concentration	mM (reported)	0	2	5	10		
	mol/L (M)	0	0.002	0.005	0.01		
Molar Ratio	H ₂ O ₂ :DNAN	0	50	125	250		
Su et al. (2019)							
DNAN concentration	mg/L (ppm - reported)	250					
	mol/L (M)	0.001261766					
H ₂ O ₂ Concentration	mg/L (ppm - reported)	750	1500	2250	3000	4500	
	mol/L (M)	0.0220	0.0441	0.0661	0.0882	0.1323	
Molar Ratio	H ₂ O ₂ :DNAN	17.48	34.95	52.43	69.90	104.85	
Rate Constant (zero-order)	hour ⁻¹ (reported)	not tested	56.76	61.88	73.72	70.76	
Rate Constant (pseudo first-order)	min ⁻¹	0.0117	0.00633	0.00824	0.00971	0.00953	

2. First-order fits for Su et al. (2019)







```
%Nov 2020 - AFIT
%Author: W. Harper
%Project: 2019-20 UV LED project

global realdata11 realdata12 realdata13 realdata14 realdata15
realdata21 realdata22 realdata23 realdata24 realdata25

%this is a data file taken from Su et al 2019
%realdata1* entries are time in minutes
%realdata2* entries are relative concentration
%


---


%


---


%molar ratio = 17.48
%time data,
realdata11 = [0
15
30
80
100
120
180
276];

%relative concentration C/Co
realdata21 = [1
0.9
0.88
0.86
0.82
0.82
0.82
0.812];
%


---


%


---


%


---


%molar ratio = 34.95
%time data,
realdata12 = [0
60
120
180
240
300];

%relative concentration C/Co
realdata22 = [1
0.8125
0.625
```

0.333333333

0.0625

0];

%

%

%molar ratio = 52.53

%time data,

realdata13 = [0

60

120

180

240

300];

%relative concentration C/Co

realdata23 = [1

0.729166667

0.5

0.145833333

0

0];

%

%

%molar ratio = 69.90

%time data,

realdata14 = [0

60

120

180

240

300];

%relative concentration C/Co

realdata24 = [1

0.666666667

0.375

0.083333333

0

0];

%

%

%molar ratio = 104.85

%time data,


```

%additional matrices needed for data processing
nnn = 100000;
ZZZ1 = zeros(7,nnn);
BEST = zeros(5,1);
BEST1 = zeros(1,1);
ZZZ2 = zeros(7,nnn);
BEST2 = zeros(1,1);
ZZZ3 = zeros(7,nnn);
BEST3 = zeros(1,1);
ZZZ4 = zeros(7,nnn);
BEST4 = zeros(1,1);
ZZZ5 = zeros(7,nnn);
BEST5 = zeros(1,1);
ZZZ6 = zeros(7,nnn);
BEST6 = zeros(1,1);
ZZZ7 = zeros(7,nnn);
BEST7 = zeros(1,1);
ZZZ8 = zeros(7,nnn);
BEST8 = zeros(1,1);
ZZZ9 = zeros(7,nnn);
BEST9 = zeros(1,1);

%the following are process parameters
to = 0;
%the units are minutes
tf = 300;

SuetaldataNov2020

%aaa is needed to determine the best parameter combination
aaa1 = 100000000000;
aaa2 = aaa1;
aaa3 = aaa1;
aaa4 = aaa1;
aaa5 = aaa1;
aaa6 = aaa1;
aaa7 = aaa1;
aaa8 = aaa1;
aaa9 = aaa1;
aaa10 = aaa1;
aaa11 = aaa1;

%this is a counter
counttt = 1;

%the simulation logic begins here
%Note that this code corresponds to a batch reactor rather than a CSTR.
Su
%et al. (2019) employed a batch reactor. The equation is different for
this
%code than what was employed for AFIT experiments.

%This is for the first experimental data set

```

```

for rateconstant = alpha:beta:gamma
%
%Initial Conditions Matrix
Cinit(1,1) = 250;
xo = Cinit(1,1);
%Solve the differential equations
[t,x] = ode45('light4',realdata11,xo,[],rateconstant);

MMM1 = abs((realdata21 - x(:,1)./Cinit(1,1))).^2;
ttt1 = cumsum(MMM1);
bbb1 = ttt1(end)./size(realdata21,1);
rrr1 = ((bbb1)^(0.5))./max(realdata21);

ZZZ1(1,counttt) = rrr1;
ZZZ1(2,counttt) = rateconstant;

if ZZZ1(1,counttt) < aaa1
    aaa1 = ZZZ1(1,counttt);
    BEST(1,1) = rateconstant;
    zipa = x(:,1)./Cinit(1,1);
    zipat = t;
end
counttt = counttt + 1;
end

%
%

counttt = 1;

%This is for the second experimental data set
for rateconstant = alpha:beta:gamma
%
%Initial Conditions Matrix
Cinit(2,1) = 240;
xo = Cinit(2,1);
%Solve the differential equations
[t,x] = ode45('light4',realdata12,xo,[],rateconstant);

MMM2 = abs((realdata22 - x(:,1)./Cinit(2,1))).^2;
ttt2 = cumsum(MMM2);
bbb2 = ttt2(end)./size(realdata22,1);
rrr2 = ((bbb2)^(0.5))./max(realdata22);

ZZZ2(1,counttt) = rrr2;
ZZZ2(2,counttt) = rateconstant;

if ZZZ2(1,counttt) < aaa2
    aaa2 = ZZZ2(1,counttt);
    BEST(2,1) = rateconstant;
    zipb = x(:,1)./Cinit(2,1);
    zipbt = t;
end

```

```

end
counttt = counttt + 1;
end

counttt = 1;

%This is for the third experimental data set
for rateconstant = alpha:beta:gamma
%
%Initial Conditions Matrix
Cinit(3,1) = 240;
xo = Cinit(3,1);
%Solve the differential equations
[t,x] = ode45('light4',realdata13,xo,[],rateconstant);

MMM3 = abs((realdata23 - x(:,1)./Cinit(3,1))).^2;
ttt3 = cumsum(MMM3);
bbb3 = ttt3(end)./size(realdata23,1);
rrr3 = ((bbb3)^(0.5))./max(realdata23);

ZZZ3(1,counttt) = rrr3;
ZZZ3(2,counttt) = rateconstant;

if ZZZ3(1,counttt) < aaa3
    aaa3 = ZZZ3(1,counttt);
    BEST(3,1) = rateconstant;
    zipc = x(:,1)./Cinit(3,1);
    zipct = t;
end
counttt = counttt + 1;
end

counttt = 1;

%This is for the fourth experimental data set
for rateconstant = alpha:beta:gamma
%
%Initial Conditions Matrix
Cinit(4,1) = 240;
xo = Cinit(4,1);
%Solve the differential equations
[t,x] = ode45('light4',realdata14,xo,[],rateconstant);

MMM4 = abs((realdata24 - x(:,1)./Cinit(4,1))).^2;
ttt4 = cumsum(MMM4);
bbb4 = ttt4(end)./size(realdata24,1);
rrr4 = ((bbb4)^(0.5))./max(realdata24);

ZZZ4(1,counttt) = rrr4;
ZZZ4(2,counttt) = rateconstant;

if ZZZ4(1,counttt) < aaa4
    aaa4 = ZZZ4(1,counttt);

```

```

        BEST(4,1) = rateconstant;
        zipd = x(:,1)./Cinit(4,1);
        zipdt = t;
    end
    countttt = countttt + 1;
end

countttt = 1;

%This is for the fifth experimental data set
for rateconstant = alpha:beta:gamma
%
%-----
%Initial Conditions Matrix
Cinit(5,1) = 225;
xo = Cinit(5,1);
%Solve the differential equations
[t,x] = ode45('light4',realdata15,xo,[],rateconstant);

MMM5 = abs((realdata25 - x(:,1)./Cinit(5,1))).^2;
ttt5 = cumsum(MMM5);
bbb5 = ttt5(end)./size(realdata25,1);
rrr5 = ((bbb5)^(0.5))./max(realdata25);

ZZZ5(1,countttt) = rrr5;
ZZZ5(2,countttt) = rateconstant;

if ZZZ5(1,countttt) < aaa5
    aaa5 = ZZZ5(1,countttt);
    BEST(5,1) = rateconstant;
    zipe = x(:,1)./Cinit(5,1);
    zipet = t;
end
countttt = countttt + 1;
end

figure(1)
%plot(realdata11,realdata21,'bd',zipat,zipa(:,1),'k-
.',zipat,zipa(:,2),'kd.')
plot(realdata11,realdata21,'bd',zipat,zipa(:,1),'k-.')
title('First')
xlabel('Time (minutes)')
ylabel('Relative concentration C/Co')
legend('data','model')
%axis([0 120 0.3 1])

figure(2)
plot(realdata12,realdata22,'bd',zipbt,zipb(:,1),'k-.')
title('Second')
xlabel('Time (minutes)')
ylabel('Relative concentration C/Co')
legend('data','model')

figure(3)
plot(realdata13,realdata23,'bd',zipct,zipc(:,1),'k-.')

```

```

title('Third')
xlabel('Time (minutes)')
ylabel('Relative concentration C/Co')
legend('data','model')

figure(4)
plot(realdata14,realdata24,'bd',zipdt,zipd(:,1),'k-.')
title('Fourth')
xlabel('Time (minutes)')
ylabel('Relative concentration C/Co')
legend('data','model')

figure(5)
plot(realdata15,realdata25,'bd',zipet,zipe(:,1),'k-.')
title('Fifth')
xlabel('Time (minutes)')
ylabel('Relative concentration C/Co')
legend('data','model')

%xlswrite('DNANregressions.xls',zipa,'sheet100','B6');
%xlswrite('DNANregressions.xls',zipat,'sheet100','C6');

%xlswrite('DNANregressions.xls',zipb,'sheet200','B6');
%xlswrite('DNANregressions.xls',zipbt,'sheet200','C6');

%xlswrite('DNANregressions.xls',zipc,'sheet300','B6');
%xlswrite('DNANregressions.xls',zipct,'sheet300','C6');

%xlswrite('DNANregressions.xls',zipd,'sheet400','B6');
%xlswrite('DNANregressions.xls',zipdt,'sheet400','C6');

%xlswrite('DNANregressions.xls',zipe,'sheet500','B6');
%xlswrite('DNANregressions.xls',zipet,'sheet500','C6');

xlswrite('DNANregressions.xls',BEST(:,1),'sheet33','C6');

%the following block is needed to calculate and display the runtime.
tstop = clock;
runtime = etime(tstop,tstart)./60;
disp('length of run in minutes:')
disp(runtime)



---


function xdot = light4(t,~,~,rateconstant)
%this function simulates UV LED/H2O2 degradation of DNAN

%xdot is the matrix of differential expressions (ie dC/dt,
dX/dt,etc...)
%x is the matrix of parameters (ie C, X, etc...)

%global declarations
global rateconstant xo

```

```

%The parameters in the matrix are respectively:
%effluent concentration of DNAN (1)

%math
    %reactions/equations
xdot = -1.*xo.*rateconstant.*exp(-1.*rateconstant.*t);

```

Appendix L – ANOVA, Tukey, and Correlation Statistics

1. One-way ANOVA model using molar ratios as factor levels and first-order rate constants as the response:

```
In [30]: dnan2_model = ols('k_s ~ C(molar_ratio)', data=dnan2_df).fit()
         dnan2_anova_table = sm.stats.anova_lm(dnan2_model, typ=2)
         print(dnan2_anova_table)
```

	sum_sq	df	F	PR(>F)
C(molar_ratio)	0.000404	4.0	36.047619	0.000007
Residual	0.000028	10.0	NaN	NaN

2. Shapiro Wilk Test for assumption of normal data distribution:

```
-----
In [27]: for molar_ratio in dnan2_df.molar_ratio.unique():
         tempV1_df = dnan2_df[dnan2_df["molar_ratio"] == molar_ratio]

         print(molar_ratio)
         print(shapiro(tempV1_df["k_s"]))
         print("") #prints out the test statistic and the p-value
```

```
50
(1.0, 0.9999986886978149)

100
(0.9642859101295471, 0.6368867754936218)

250
(0.9642855525016785, 0.6368849873542786)

500
(0.8928573727607727, 0.36311280727386475)

1000
(0.7500000596046448, -6.830188112871838e-07)
```

3. Bartlett's Test for equal variance among all molar ratio rate constant distributions:

```
In [29]: test_array = list()

         for molar_ratio in dnan2_df.molar_ratio.unique():
             test_array.append(list(dnan2_df[dnan2_df["molar_ratio"] == molar_ratio]["k_s"]))

         print(bartlett(*test_array))
```

```
BartlettResult(statistic=2.0331819060404994, pvalue=0.7296556895126242)
```

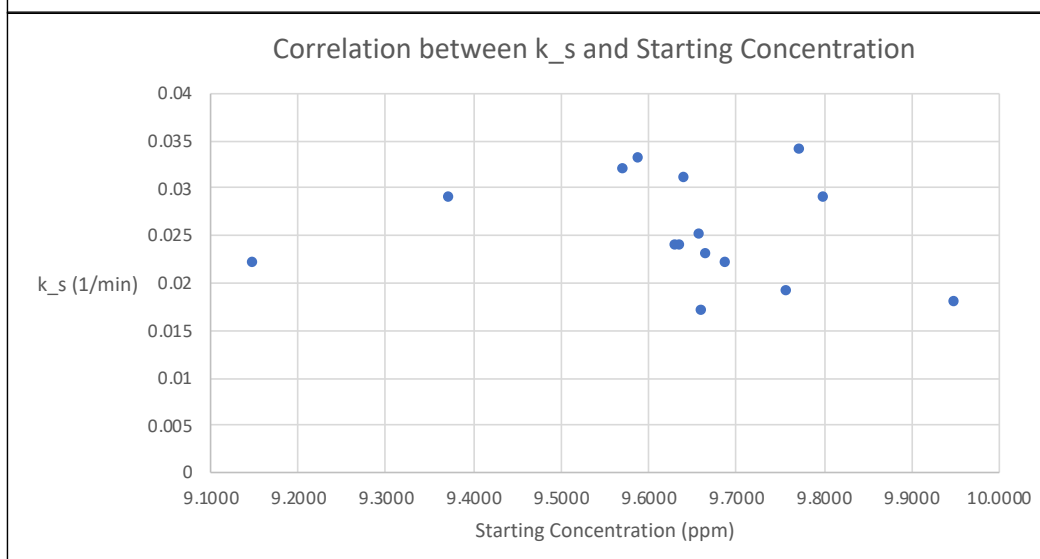
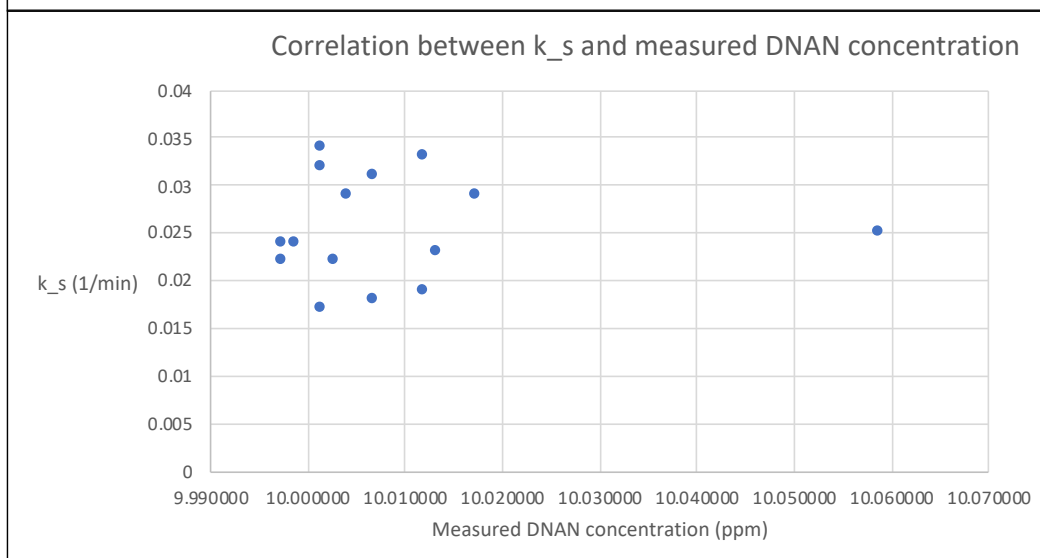
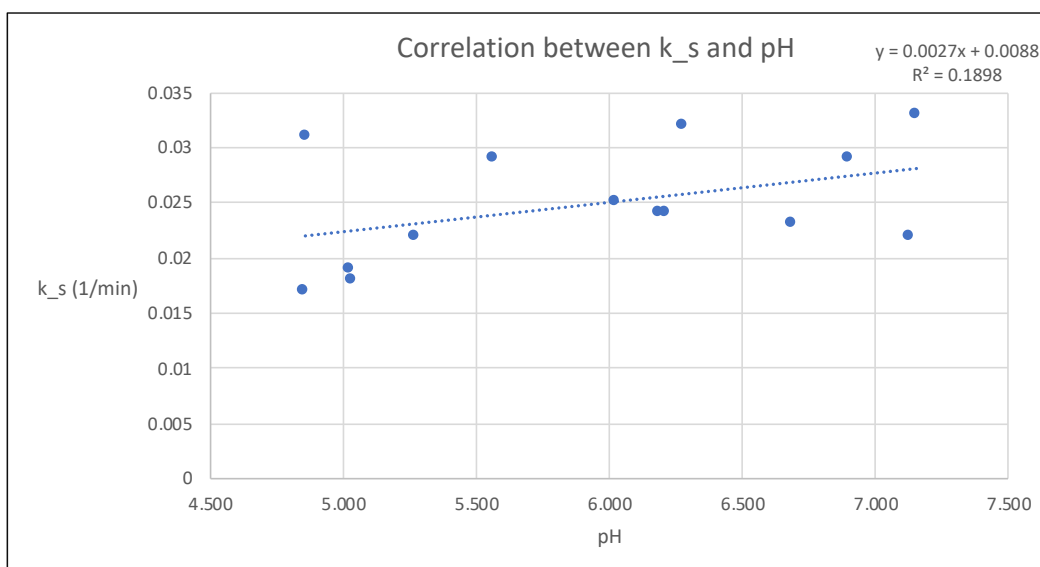
4. Tukey analysis: “False” indicates the individual molar ratios being compared do not possess statistically significant different mean rate constants.

```
In [31]: dnan2_tukey = sm.stats.multicomp.pairwise_tukeyhsd(dnan2_df['k_s'], dnan2_df['molar_ratio'],
print(dnan2_tukey)
```

```
Multiple Comparison of Means - Tukey HSD, FWER=0.05
=====
group1 group2 meandiff p-adj lower upper reject
=====
50 100 0.0053 0.0194 0.0008 0.0098 True
50 250 0.0127 0.001 0.0082 0.0172 True
50 500 0.014 0.001 0.0095 0.0185 True
50 1000 0.0053 0.0194 0.0008 0.0098 True
100 250 0.0073 0.0023 0.0028 0.0118 True
100 500 0.0087 0.001 0.0042 0.0132 True
100 1000 0.0 0.9 -0.0045 0.0045 False
250 500 0.0013 0.8478 -0.0032 0.0058 False
250 1000 -0.0073 0.0023 -0.0118 -0.0028 True
500 1000 -0.0087 0.001 -0.0132 -0.0042 True
=====
```

5. Determination of correlation between first-order rate constants and other variables not intentionally manipulated.

Date	Molar Ratio (H2O2 : DNAN)	k _s (min ⁻¹)	pH	k _s (min ⁻¹)	Meas. DNAN Conc. (mg/L)	Starting Conc. (ppm)
11-Aug	50	0.019	5.026	0.019	10.012000	9.7577
18-Aug	50	0.018	5.030	0.018	10.006667	9.9511
18-Aug	50	0.017	4.853	0.017	10.001333	9.6623
3-Jun	100	0.025	6.021	0.025	10.058667	9.6587
10-Jun	100	0.022	7.130	0.022	10.002667	9.1494
17-Jun	100	0.023	6.687	0.023	10.013333	9.6675
4-Aug	250	0.032	6.277	0.032	10.001333	9.5736
4-Aug	250	0.029	5.563	0.029	10.004000	9.8014
11-Aug	250	0.031	4.858	0.031	10.006667	9.6431
24-Jun	500	0.033	7.154	0.033	10.012000	9.5907
1-Jul	500	0.029	6.901	0.029	10.017333	9.3731
8-Jul	500			0.034	10.001333	9.7728
25-Aug	1000	0.022	5.270	0.022	9.997333	9.6889
21-Jul	1000	0.024	6.185	0.024	9.997333	9.6322
28-Jul	1000	0.024	6.210	0.024	9.998667	9.6362
	xbar		0.0249		0.0255	0.0255
	ybar		5.9404		10.0087	9.6373
	s _x		0.0052		0.0056	0.0056
	s _y		0.8427		0.0151	0.1846
	n		14		15	15
Pearson Correlation Coefficient		$r = \frac{\sum (x_i - \bar{x})(y_i - \bar{y})}{ns_x s_y}$				
	r-value	pH	Meas. DNAN Conc. (mg/L)		Starting Conc. (ppm)	
	r1	0.0870	-0.0169		-0.0507	
	r2	0.1014	0.0121		-0.1524	
	r3	0.1388	0.0496		-0.0138	
	r4	0.0002	-0.0185		-0.0007	
	r5	-0.0552	0.0166		0.1100	
	r6	-0.0225	-0.0090		-0.0049	
	r7	0.0391	-0.0383		-0.0271	
	r8	-0.0254	-0.0132		0.0377	
	r9	-0.1080	-0.0090		0.0021	
	r10	0.1606	0.0197		-0.0228	
	r11	0.0647	0.0242		-0.0607	
	r12		-0.0500		0.0752	
	r13	0.0311	0.0313		-0.0116	
	r14	-0.0034	0.0132		0.0005	
	r15	-0.0038	0.0117		0.0001	
	r	0.4046	0.0236		-0.1189	
	r ²	0.1637	0.0006		0.0141	



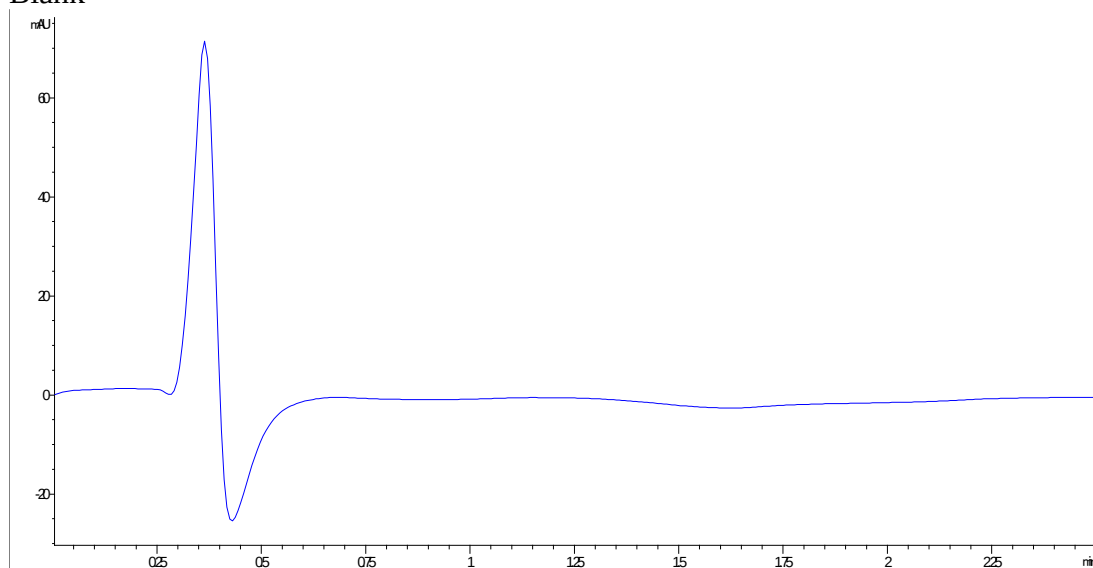
Appendix M – Chromatograms for DNAN Degradation in the AOP

500:1 Molar Ratio

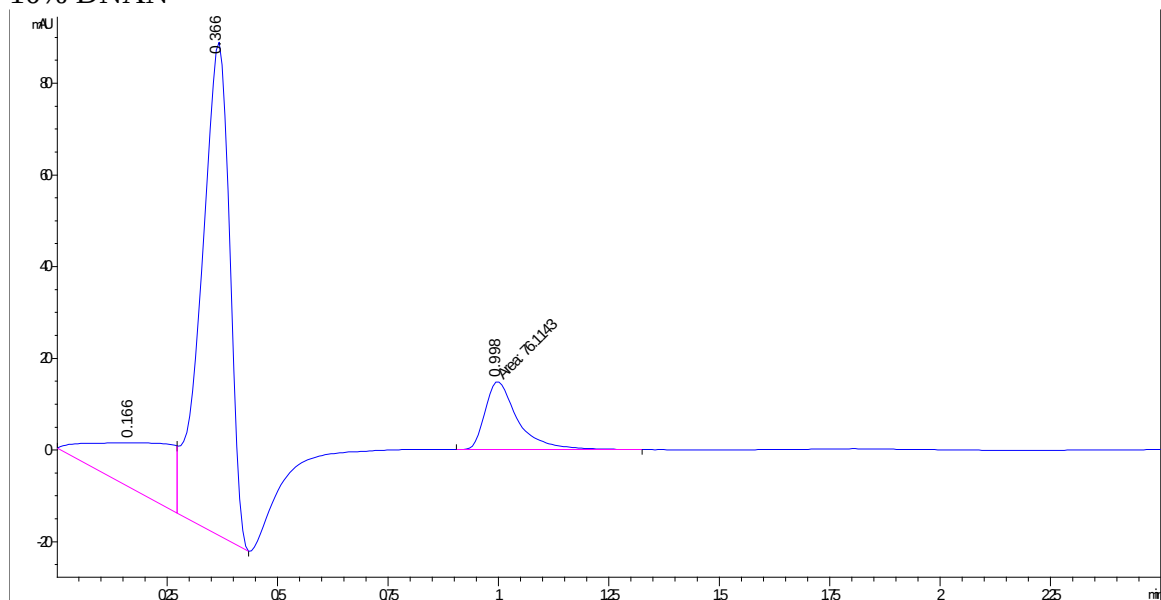
Trial 1 of 3

Calibration Curve Samples:

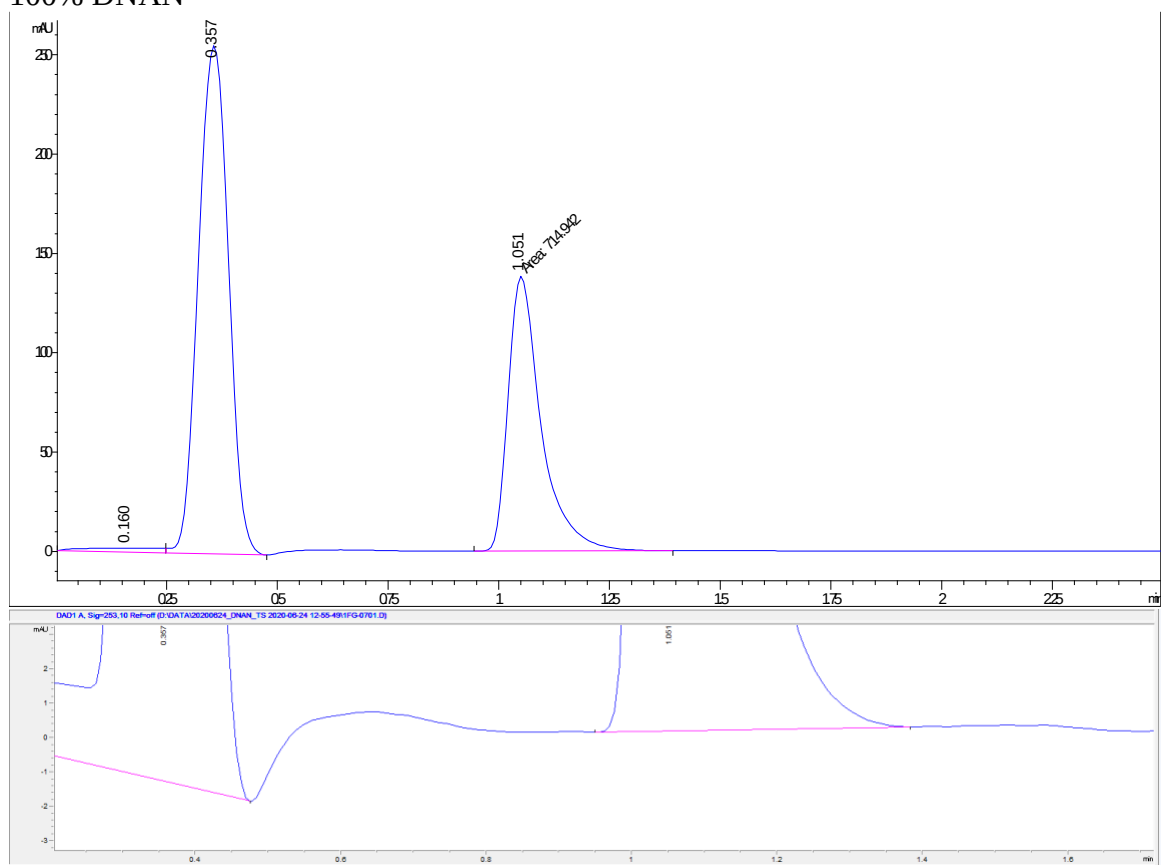
Blank



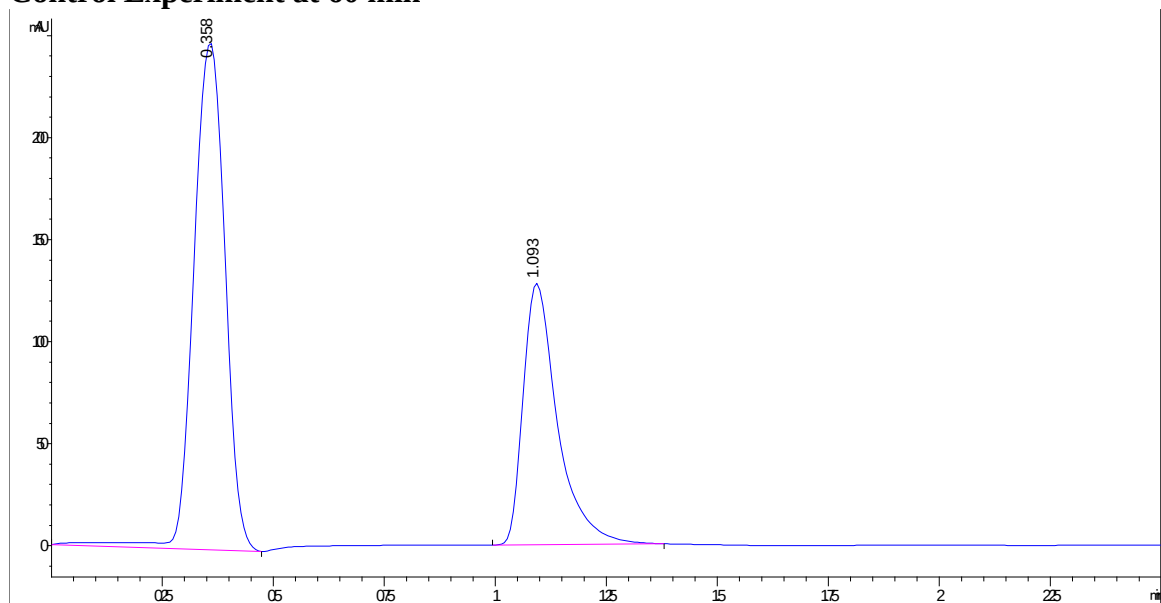
10% DNAN

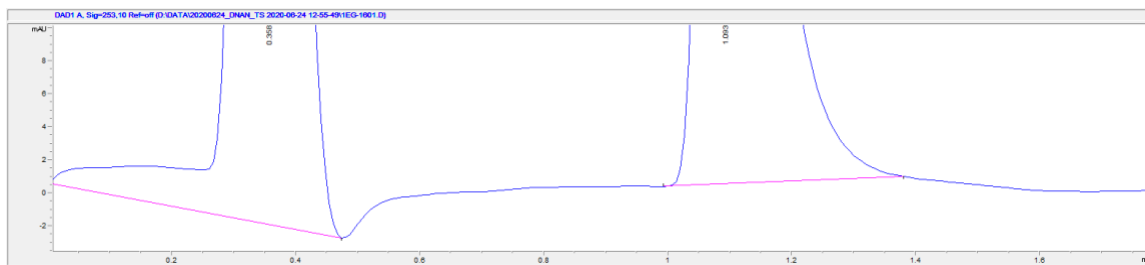


100% DNAN



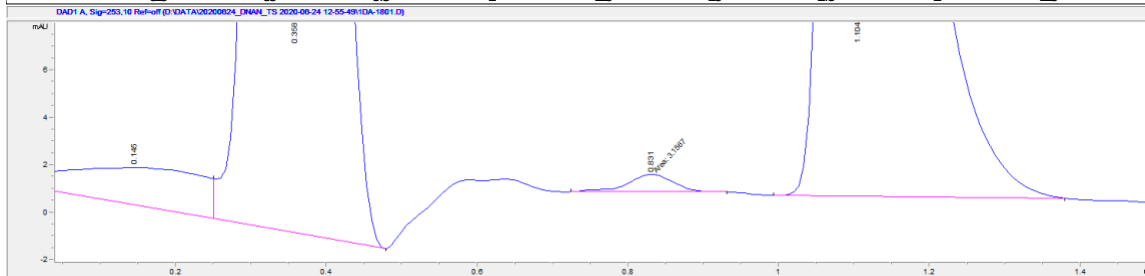
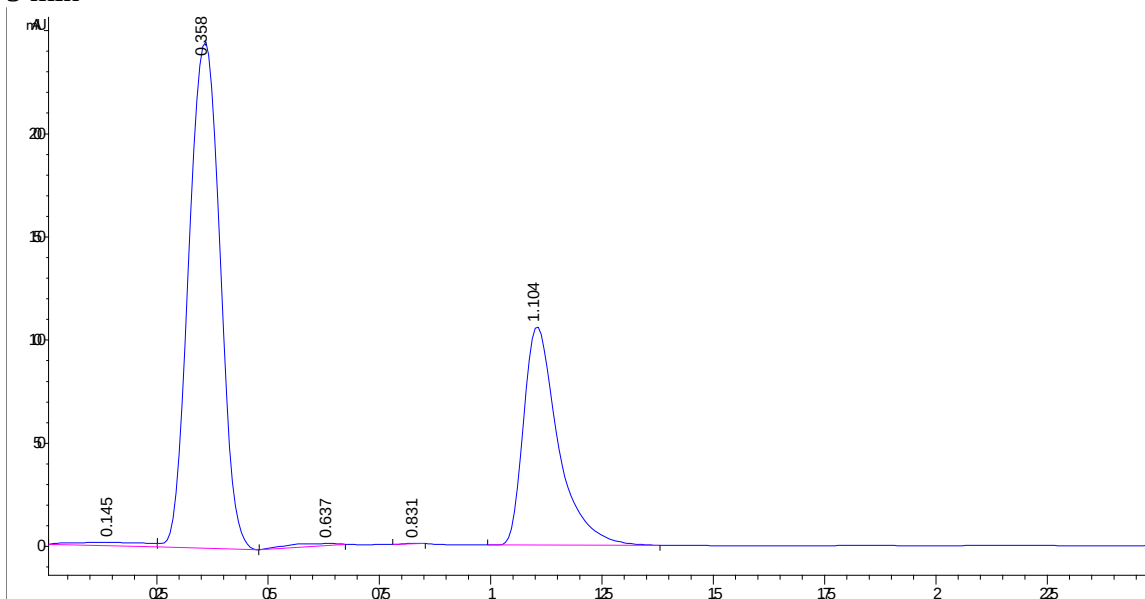
Control Experiment at 60 min



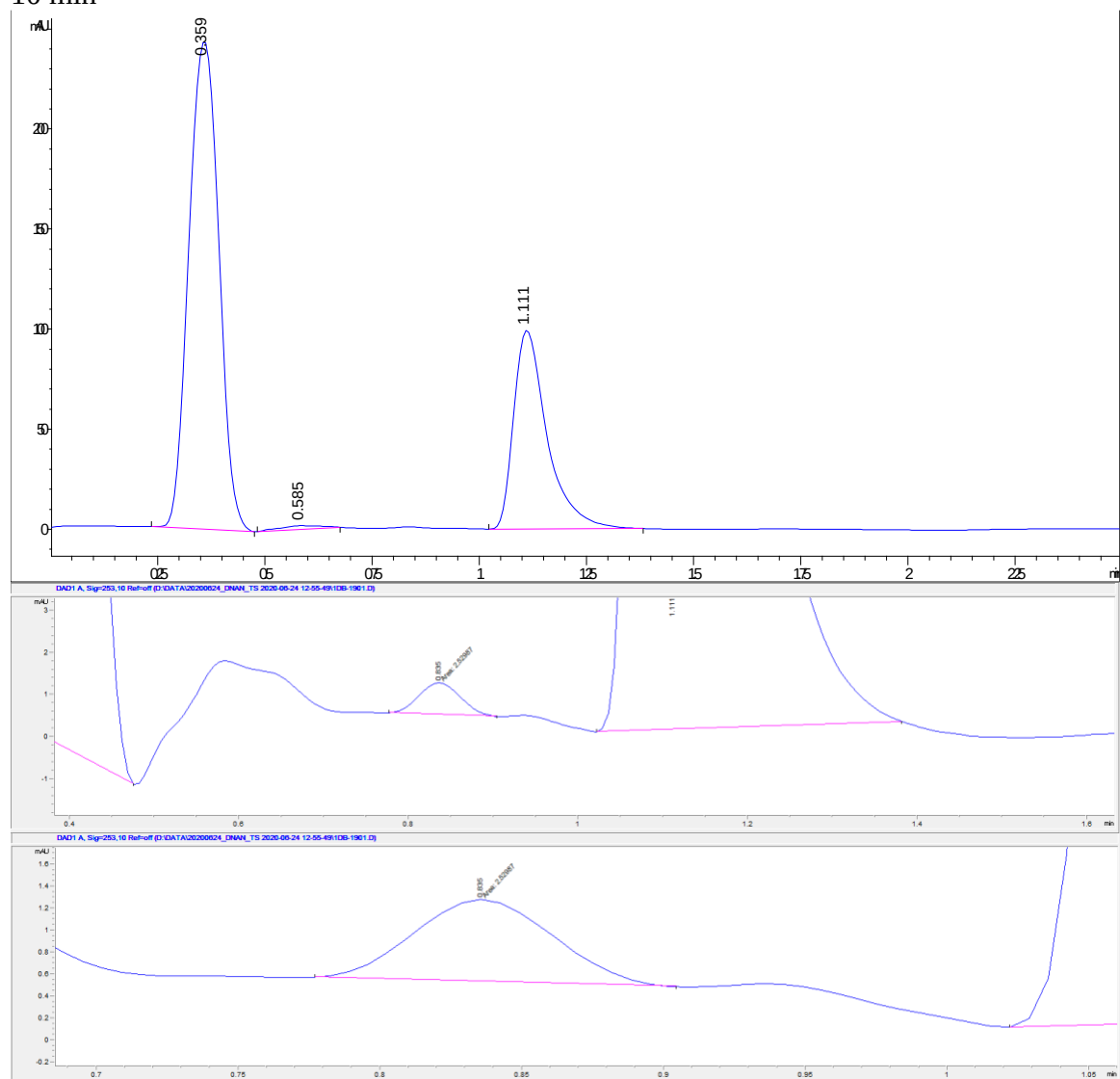


AOP Experiment Time Intervals:

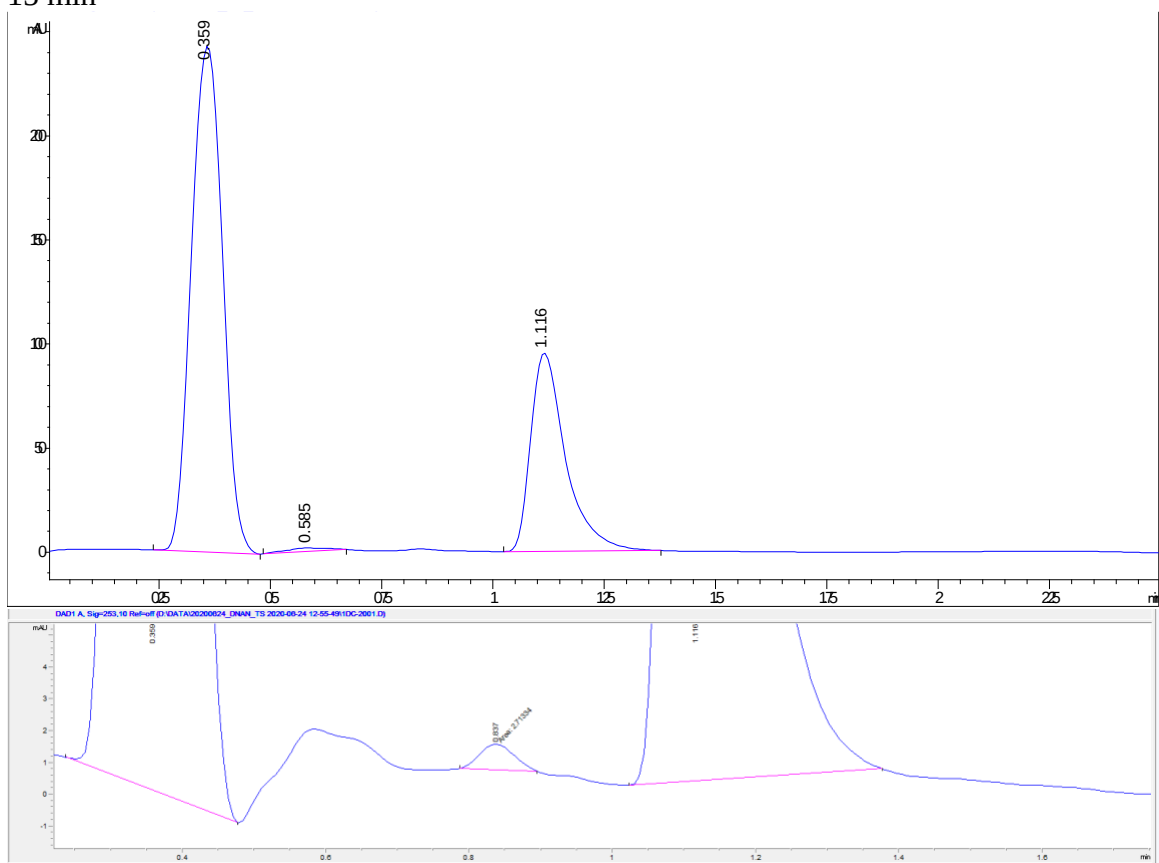
5 min



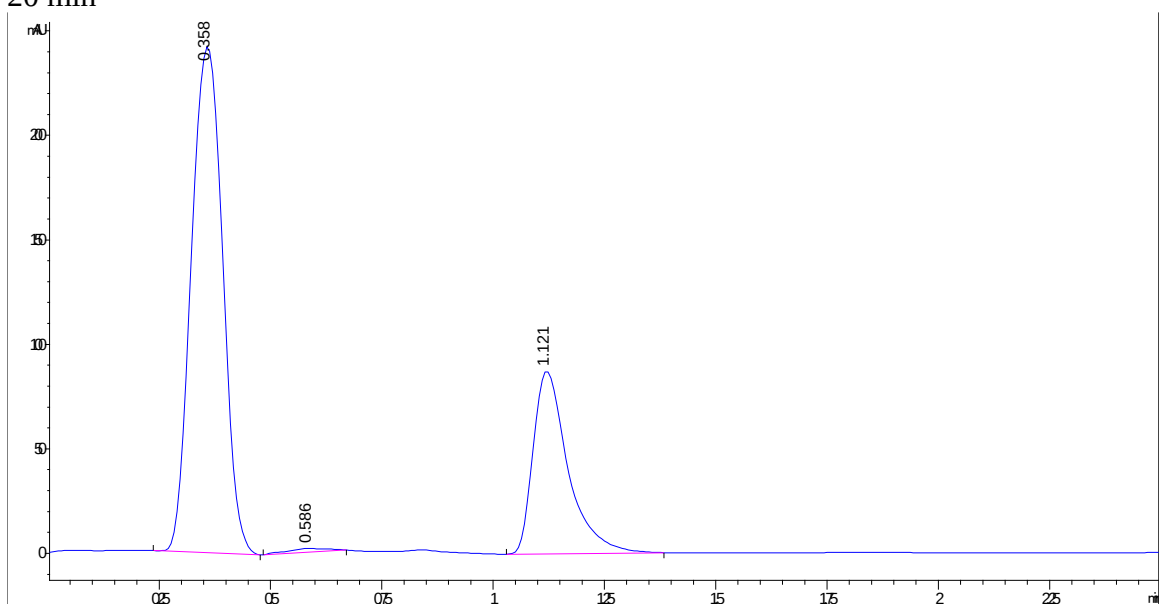
10 min

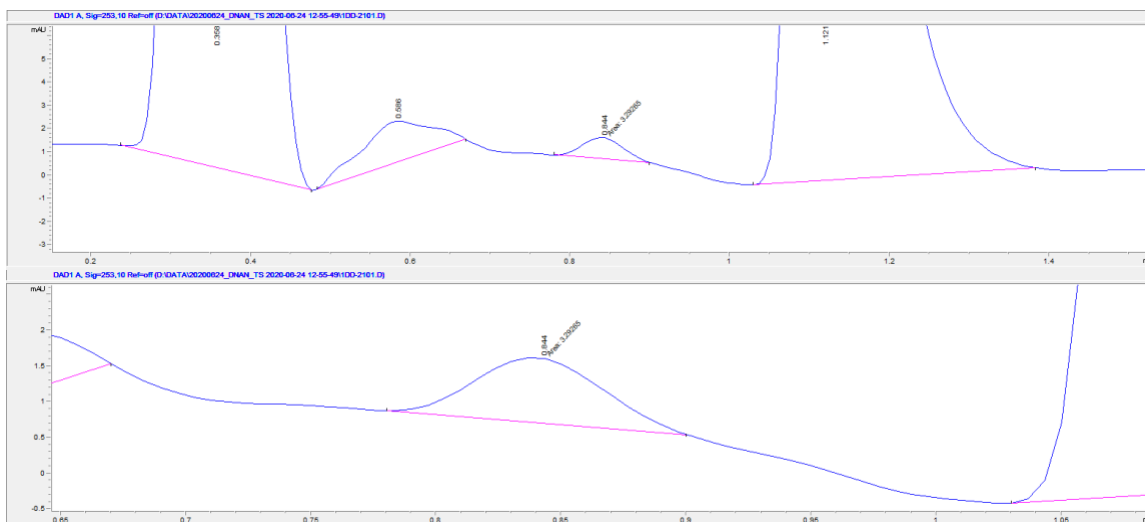


15 min

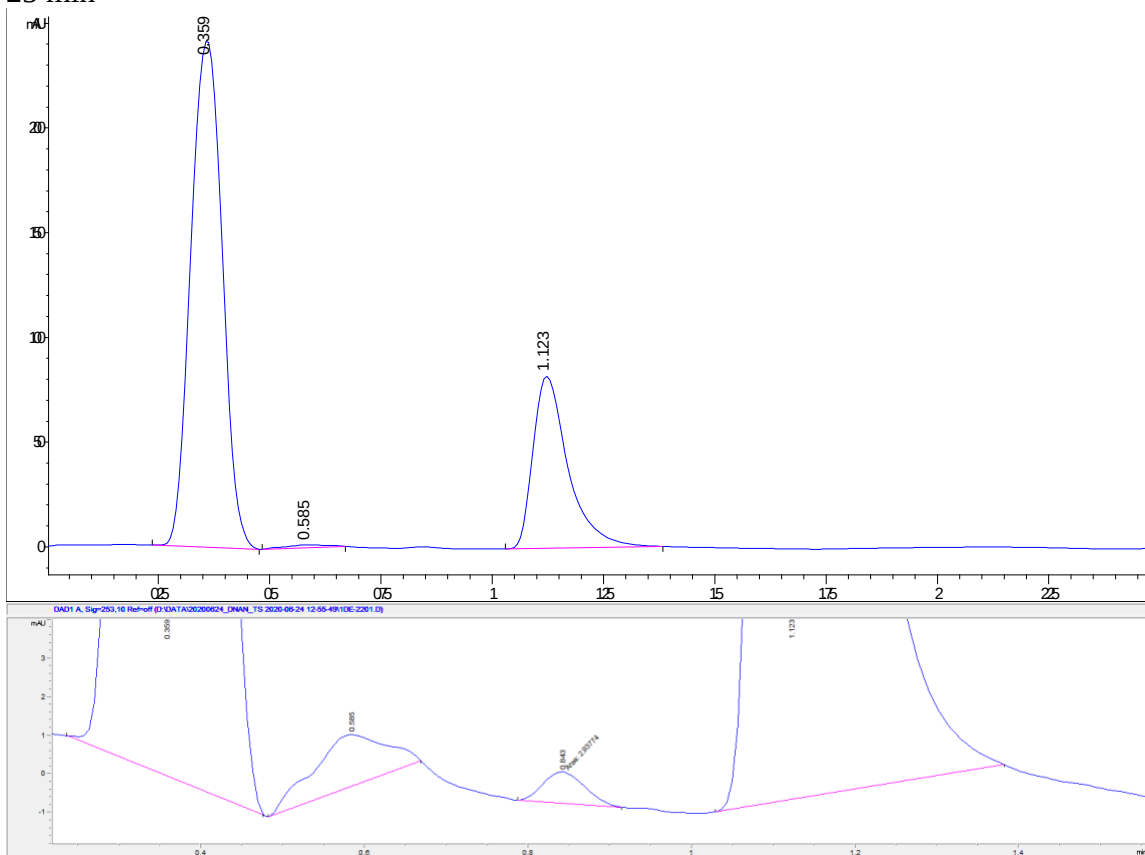


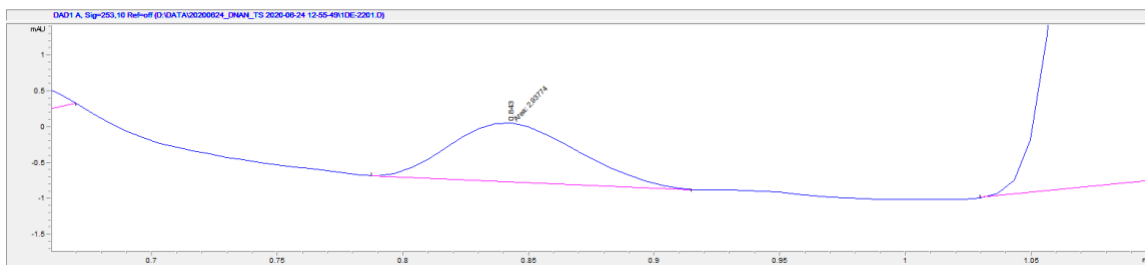
20 min



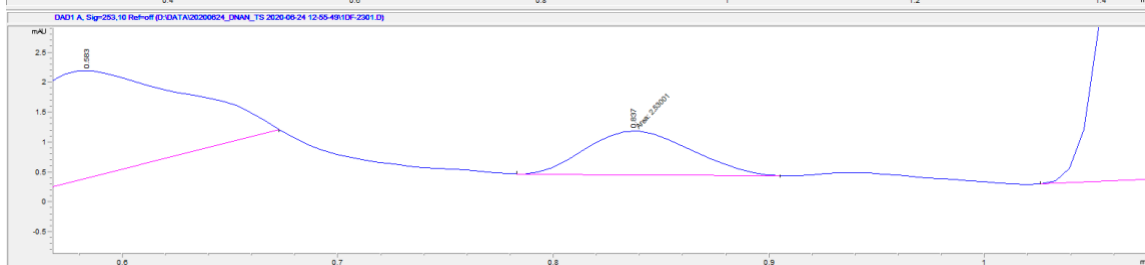
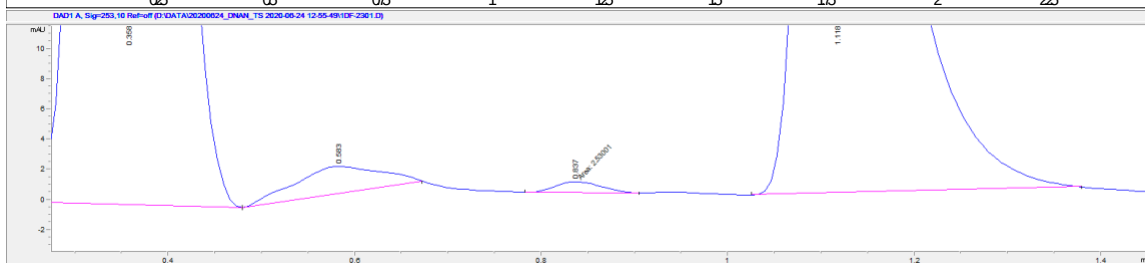
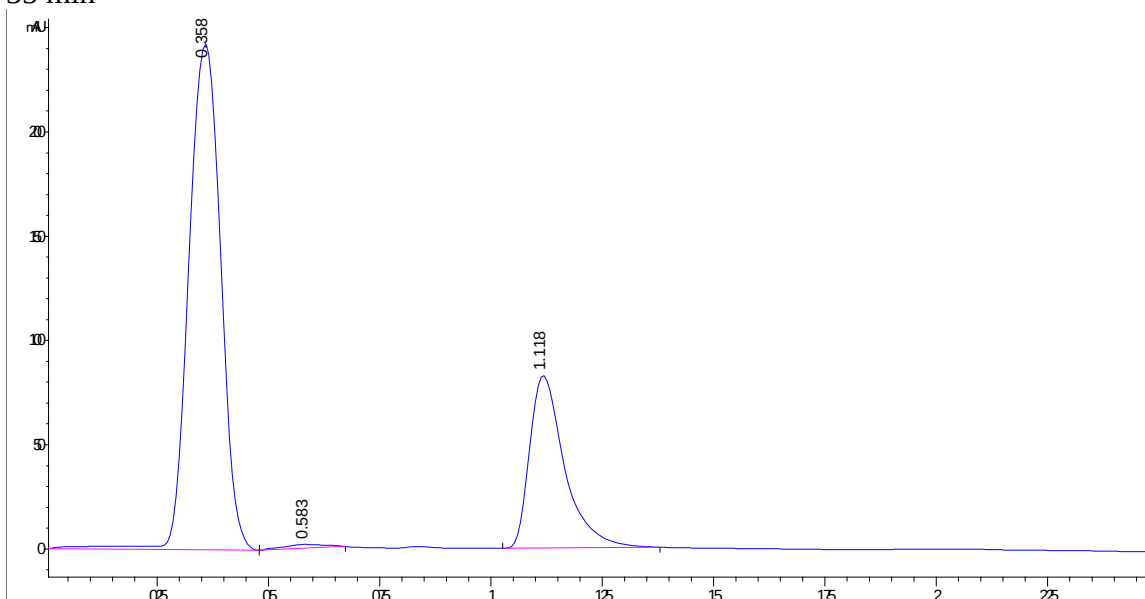


25 min

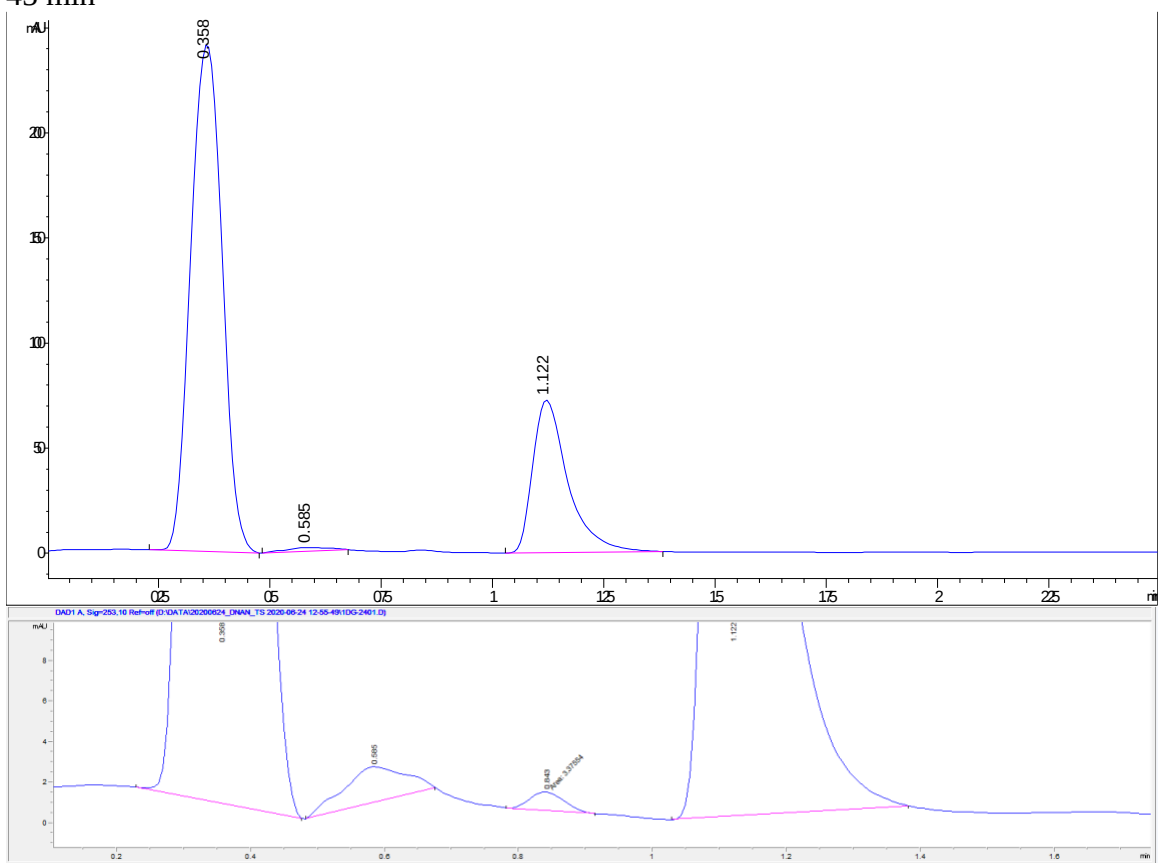




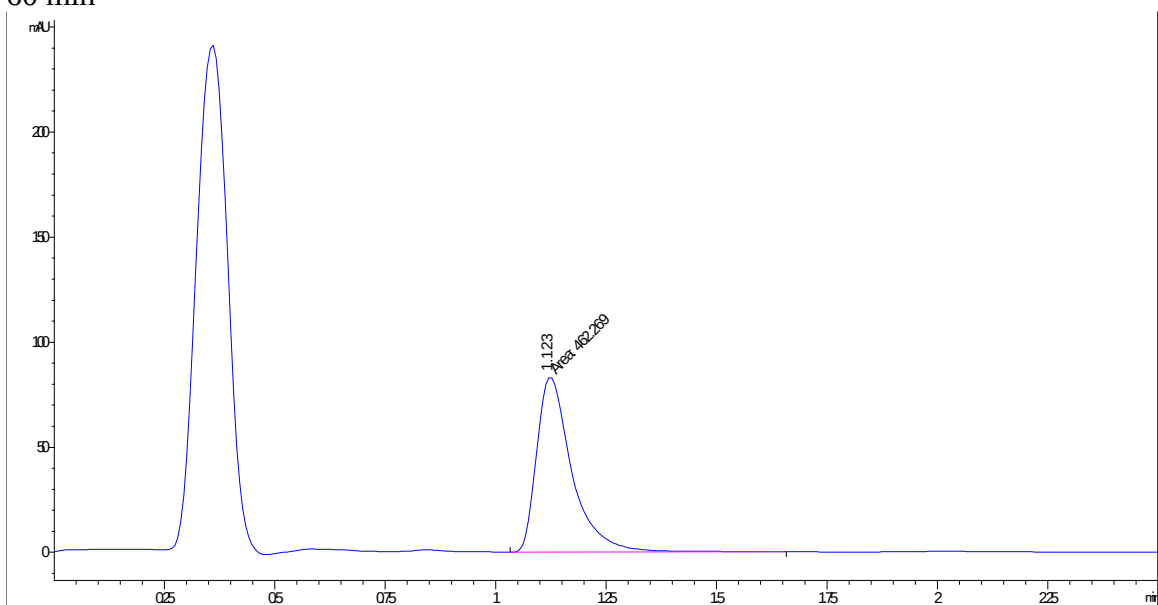
35 min

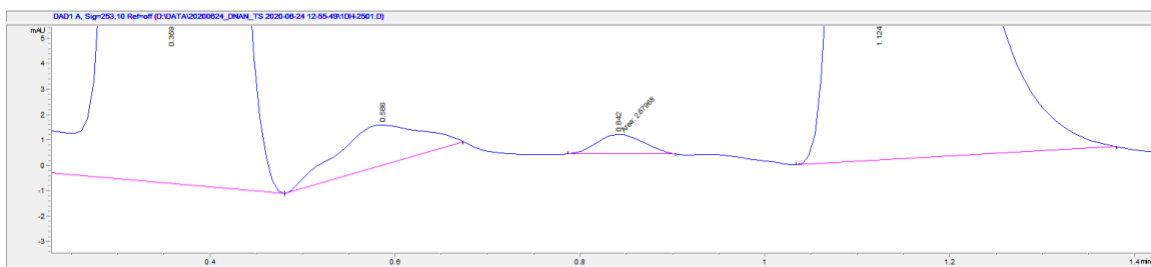


45 min



60 min



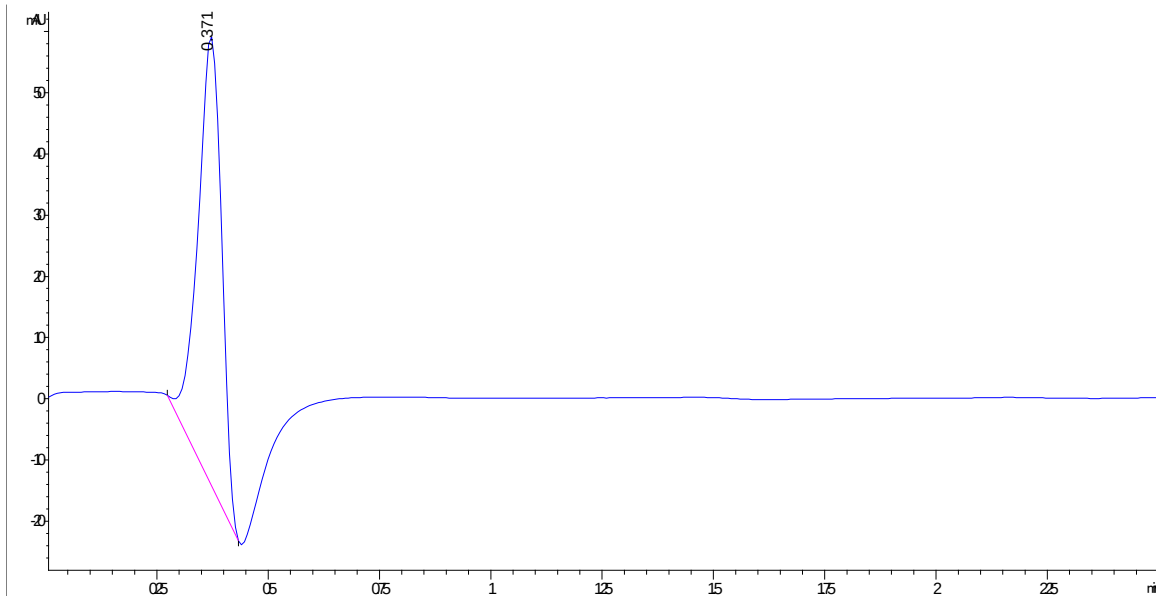


250:1 Molar Ratio

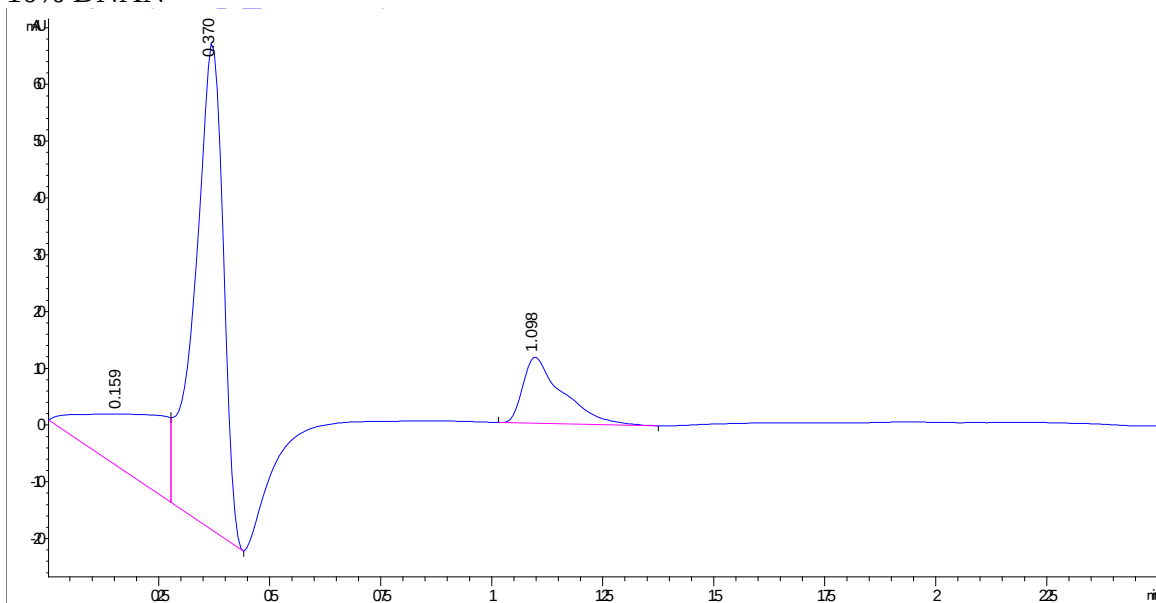
Trial 3 of 3

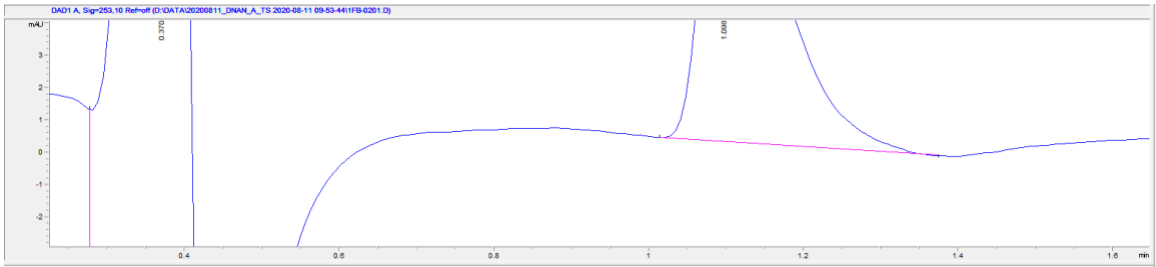
Calibration Curve Samples

Blank:

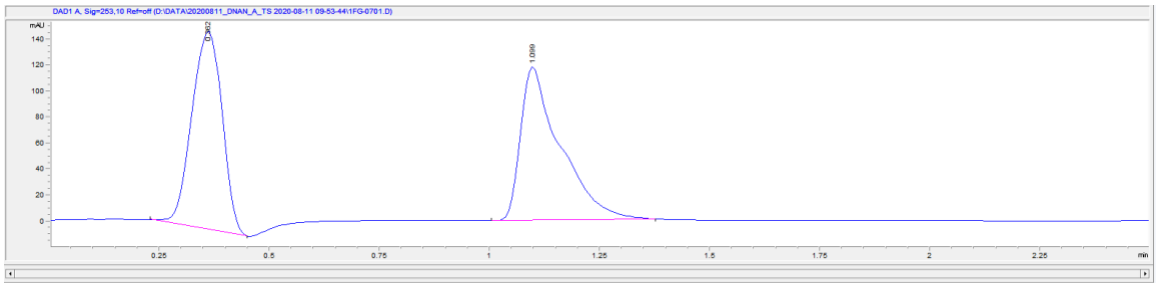


10% DNAN



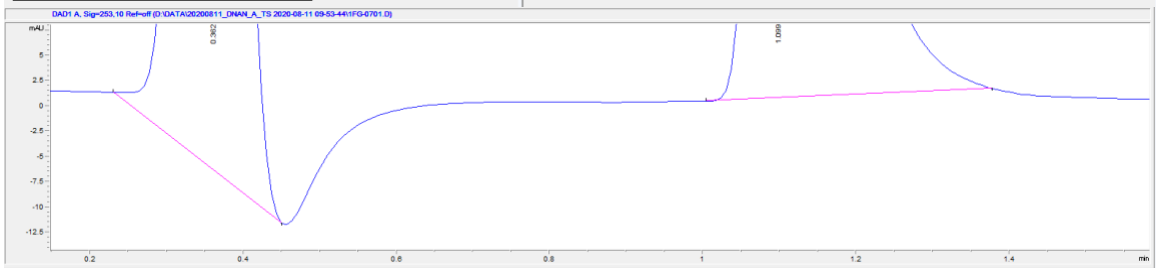


100% DNAN

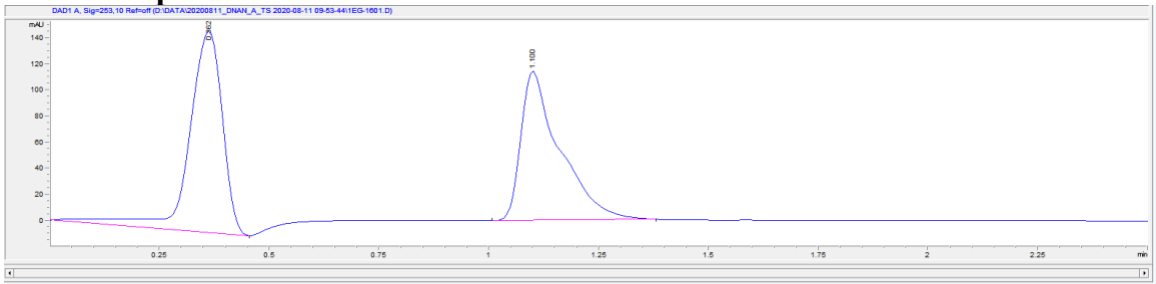


File Information	
LC File	FG-0701.D
File Path	D:\DATA\20200811_DNAN_A_TS 2020-08-11 09:53:44\
Date	11-Aug-20, 10:16:58
Sample	100%
Sample Info	
Barcode	
Operator	user
Method	20200220_BB_P_D_DAD_MS_DLF.M
Analysis Time	2.493 min
Sampling Rate	0.0067 min (0.402 sec), 375 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	0.362	721.1	152.5	0.0772	49.647	1.172
2	1.099	731.3	118.1	0.0882	50.353	0.403



Control Experiment at 60 min

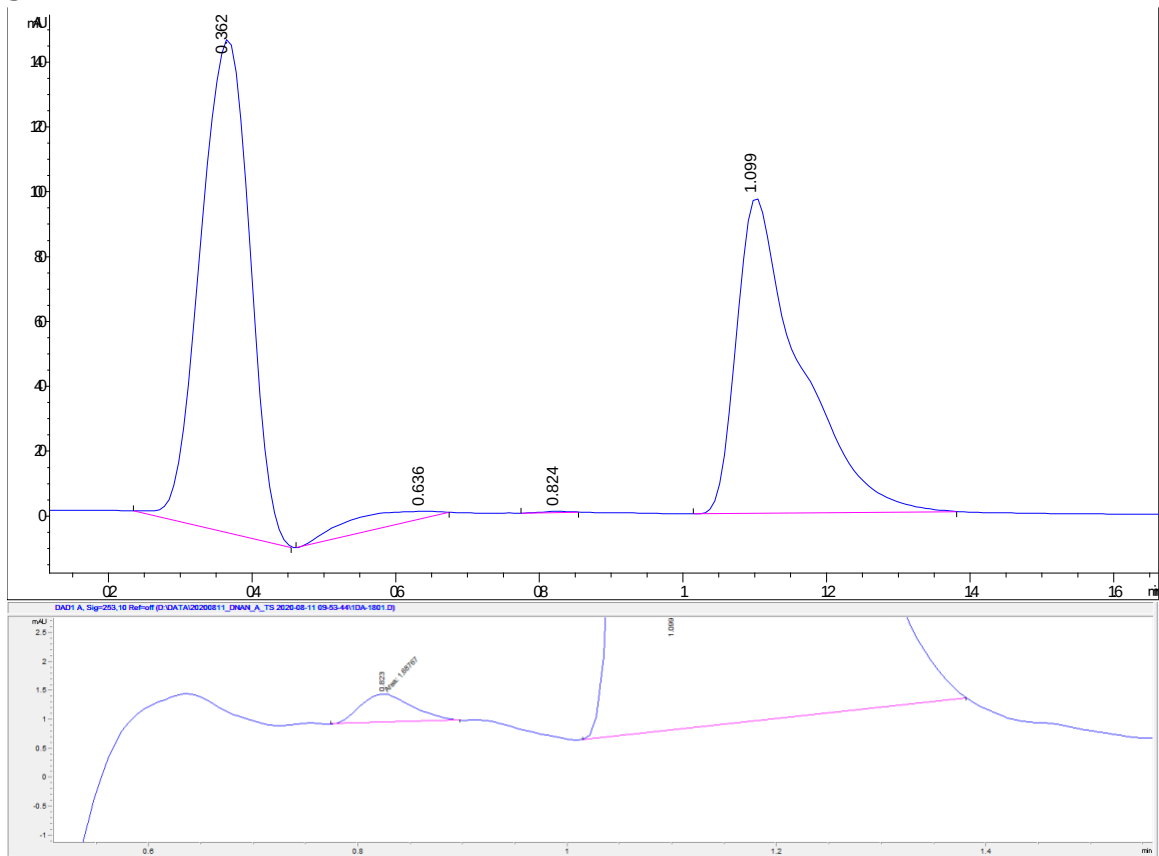


File Information	
LC File	FG-1001.D
File Path	D:\DATA\20200811_DNAN_A_TS 2020-08-11 09:53:44\
Date	11-Aug-20, 10:49:46
Sample	C7
Sample Info	60min
Barcode	
Operator	user
Method	20200220_BB_P_D_DAD_MS_DLF.M
Analysis Time	2.5 min
Sampling Rate	0.0067 min (0.402 sec), 376 datapoints

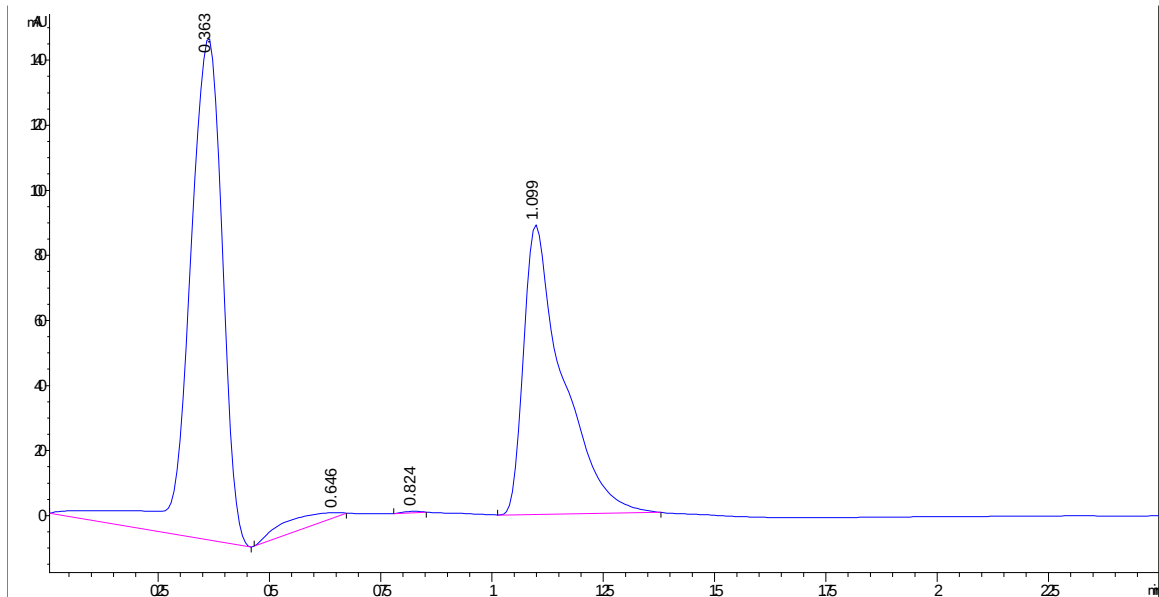
#	Time	Area	Height	Width	Area%	Symmetry
1	0.362	821.4	154.6	0.084	53.891	1.448
2	1.1	702.7	114.2	0.0878	46.109	0.403

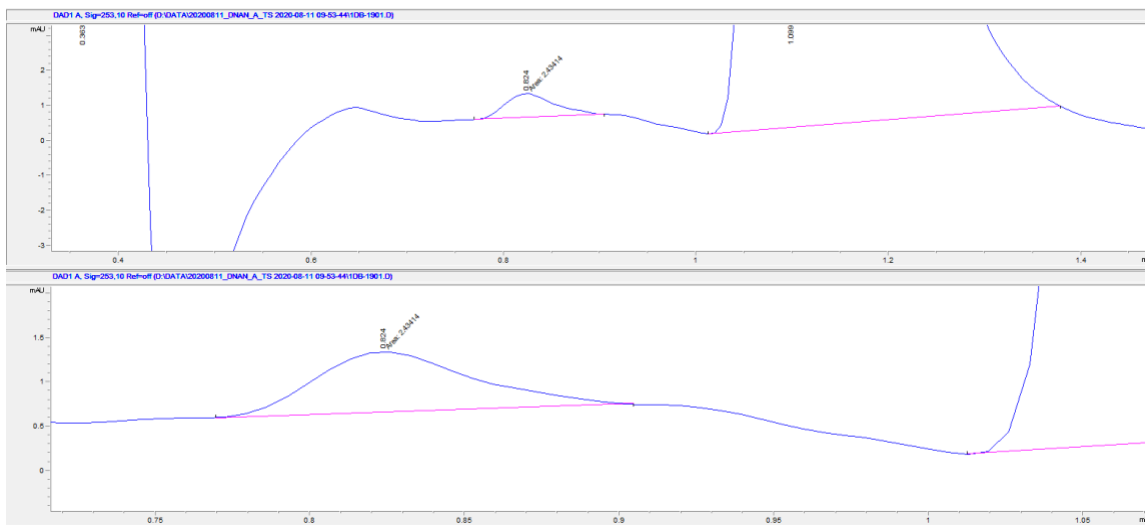
AOP Experiment Time Intervals

5 min

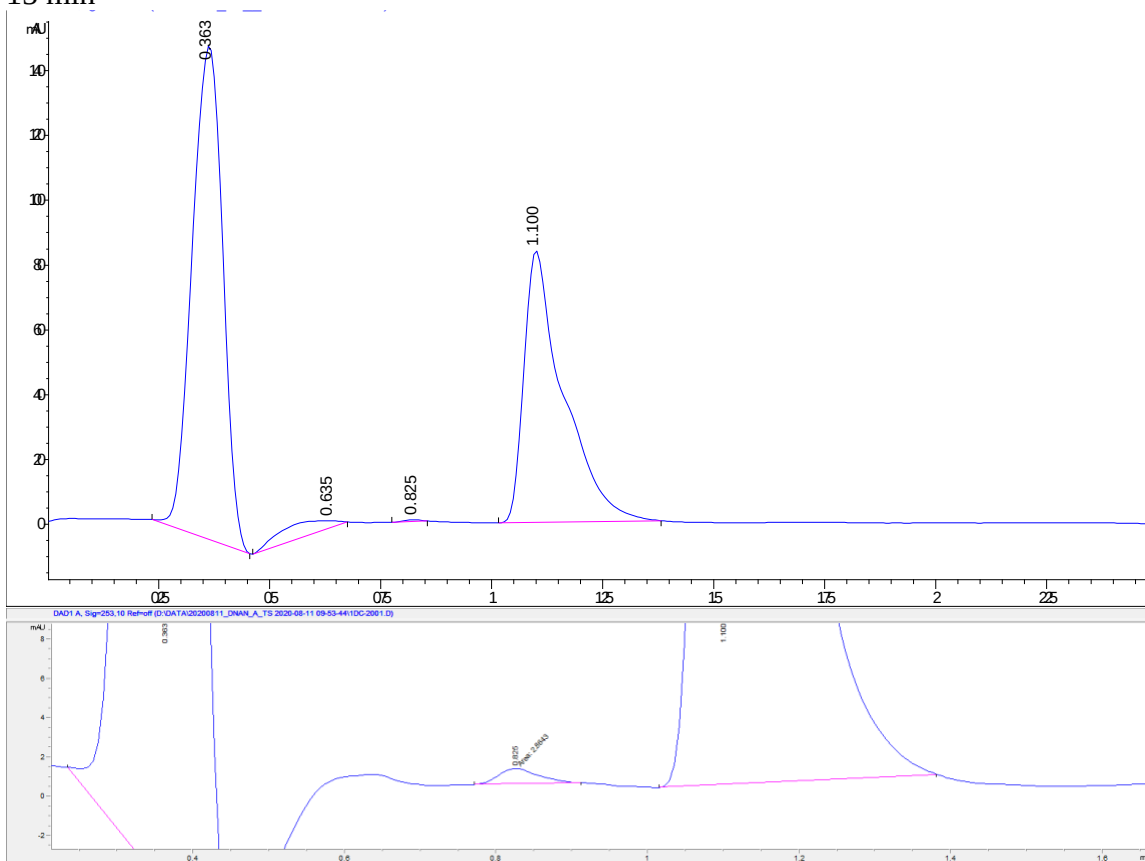


10 min

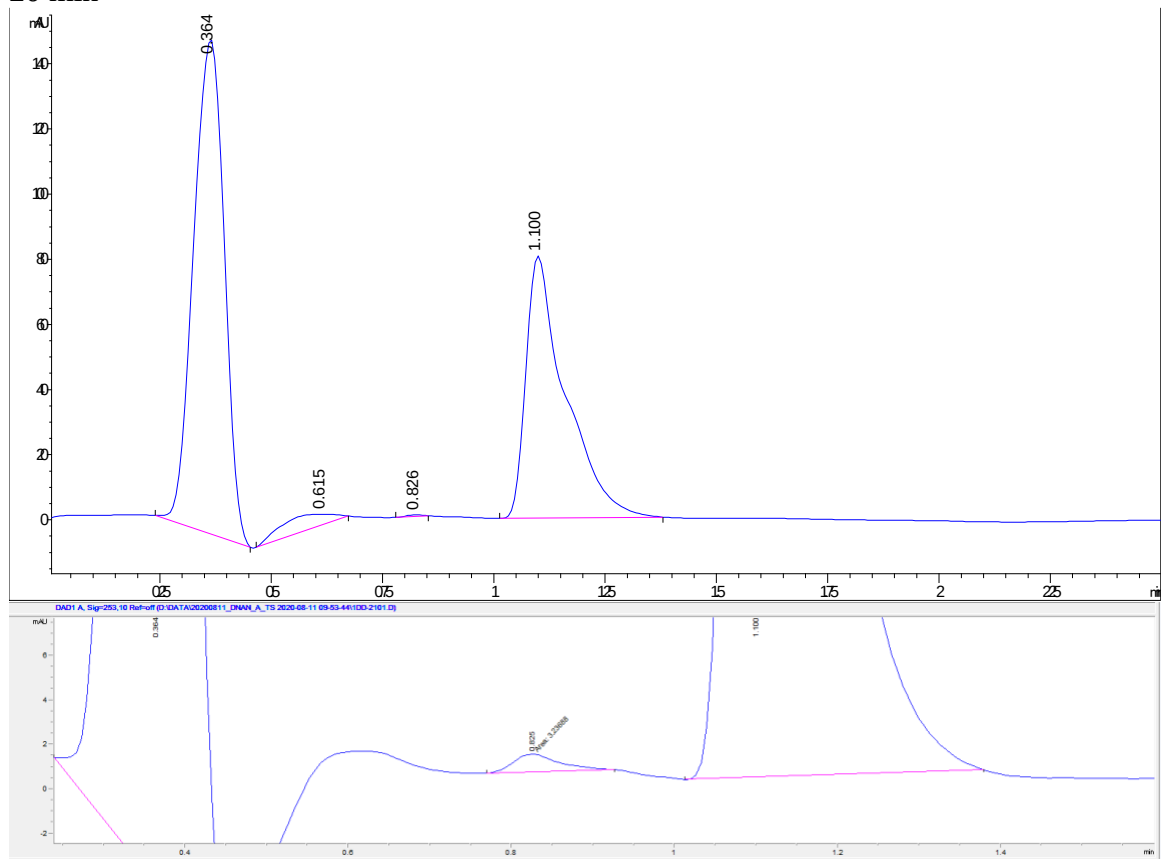




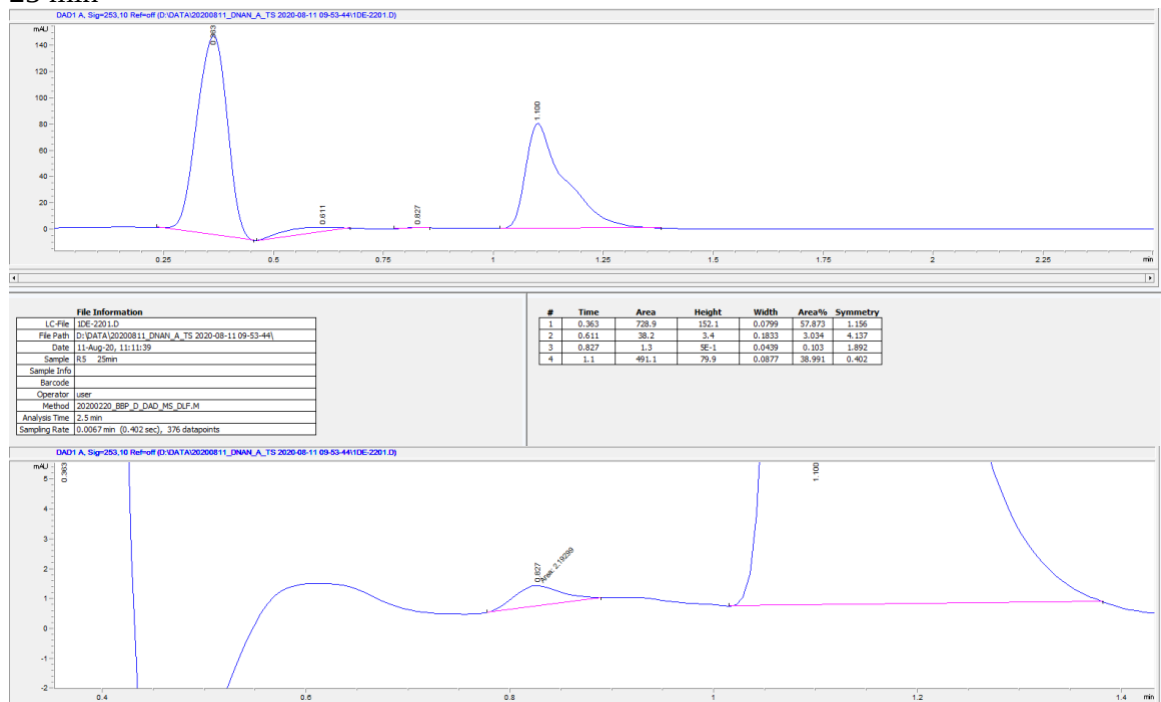
15 min

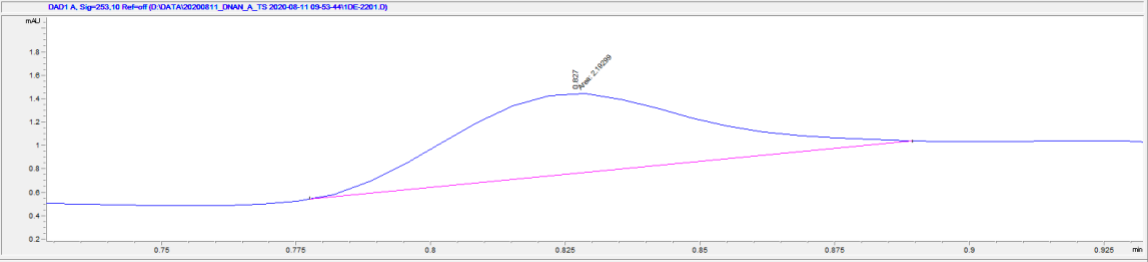


20 min

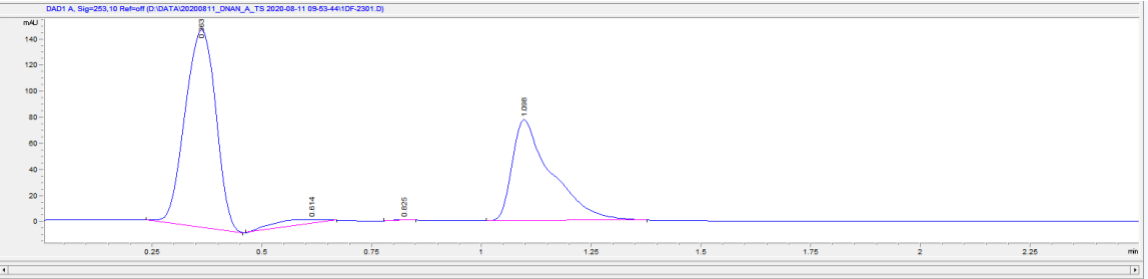


25 min

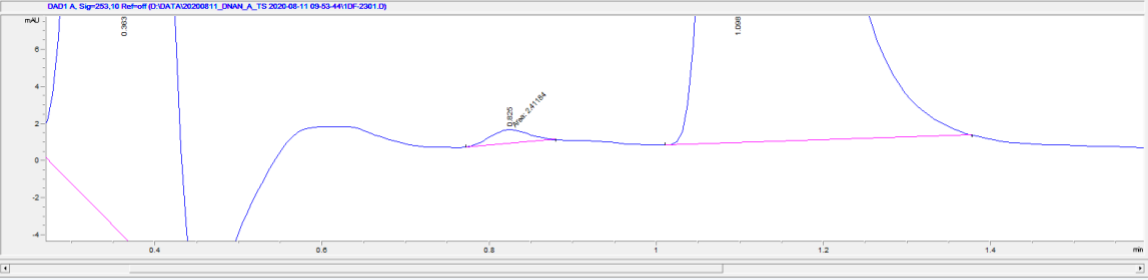




35 min

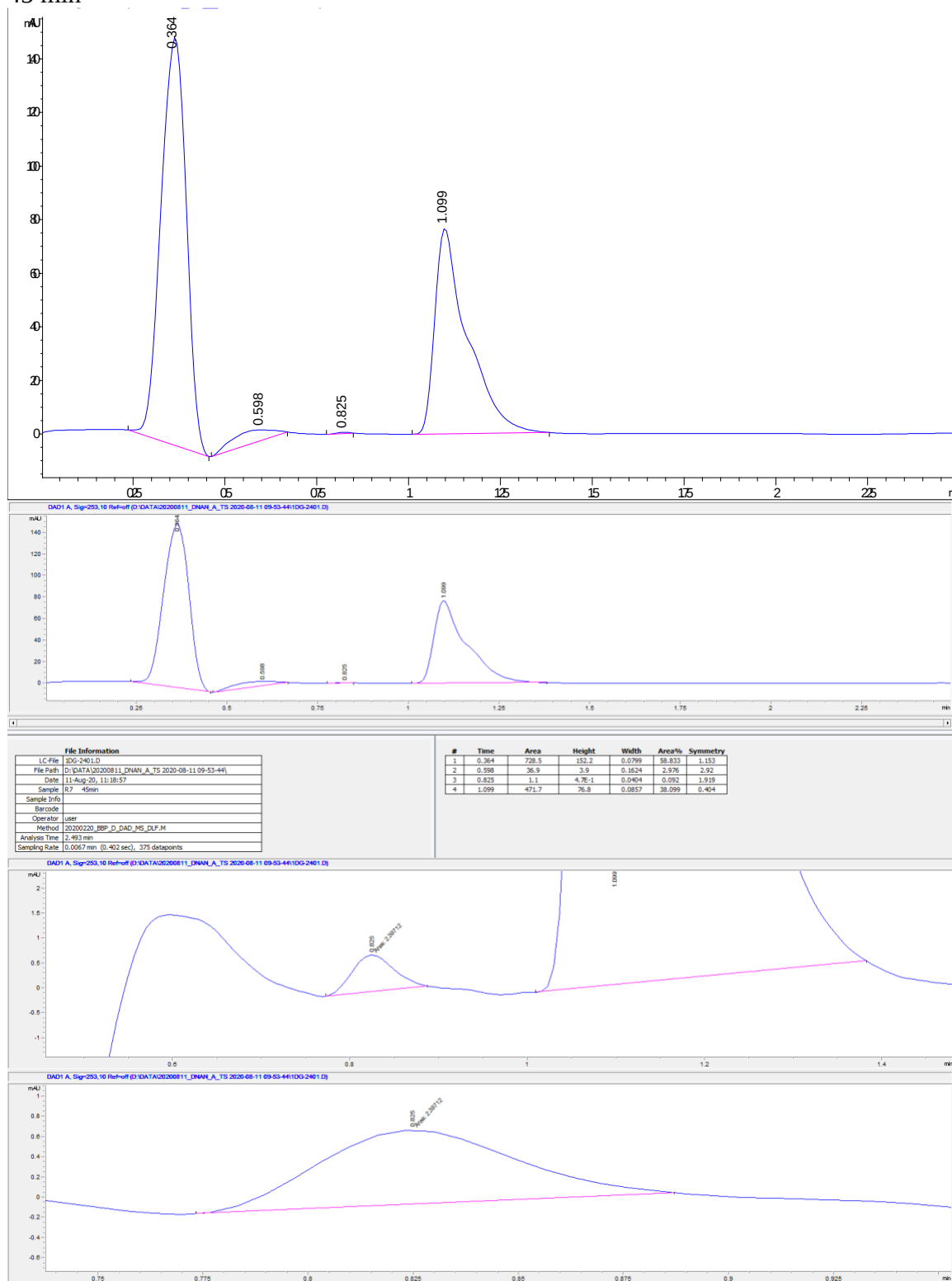


File Information		# Time Area Height Width Area% Symmetry						
LC File	10F-2301.D	1	0.363	726.3	152.1	0.0777	58.517	1.161
File Path	D:\DATA\20200811_DNAN_A_TS 2020-08-11 09:53:44\	2	0.614	37.2	3.2	0.1854	3.000	4.982
Date	11-Aug-20, 11:15:17	3	0.825	1.3	9E-1	0.0427	0.104	2.007
Sample	R6 35min	4	1.098	476.3	77.5	0.0877	38.379	0.405
Sample Info								
Barcode								
Operator	User							
Method	20200220_BBP_D_DAD_MS_DLF.M							
Analysis Time	2.493 min							
Sampling Rate	0.0067 min (0.402 sec), 375 datapoints							

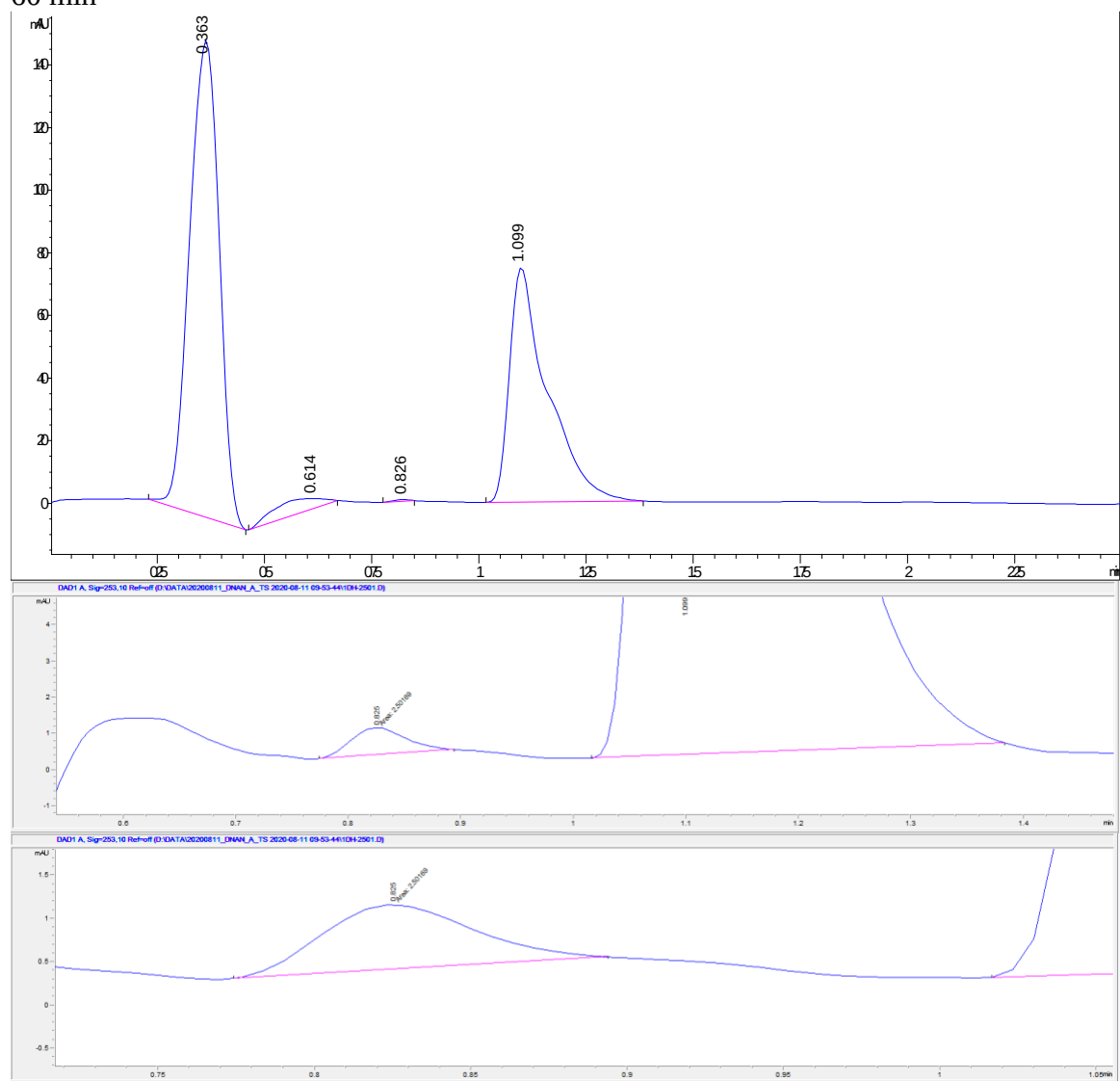


File Information		# Time Area Height Width Area% Symmetry						
LC File	10F-2301.D	1	0.363	726.3	152.1	0.0777	60.270	1.161
File Path	D:\DATA\20200811_DNAN_A_TS 2020-08-11 09:53:44\	2	0.825	2.4	7.6E-1	0.0529	0.200	1.065
Date	11-Aug-20, 11:15:17	3	1.098	476.3	77.5	0.0877	39.529	0.405
Sample	R6 35min							
Sample Info								
Barcode								
Operator	User							
Method	20200220_BBP_D_DAD_MS_DLF.M							
Analysis Time	2.493 min							
Sampling Rate	0.0067 min (0.402 sec), 375 datapoints							

45 min



60 min



Appendix N – Regression Analysis

1. Linear fit for all molar ratios tested.

Linear Regression - all molar ratios - y-intercept is forced through zero								
SUMMARY OUTPUT								
<i>Regression Statistics</i>								
Multiple R	0.749853564							
R Square	0.562280368							
Adjusted R Square	0.495613701							
Standard Error	0.017219503							
Observations	16							
<i>ANOVA</i>								
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>			
Regression	1	0.005713331	0.005713331	19.26851093	0.000617056			
Residual	15	0.004447669	0.000296511					
Total	16	0.010161						
	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	0	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
X Variable 1	3.79119E-05	8.63678E-06	4.389591203	0.000527798	1.95031E-05	5.63208E-05	1.95031E-05	5.63208E-05
RESIDUAL OUTPUT								
<i>Observation</i>	<i>Predicted Y</i>	<i>Residuals</i>						
1	0	0.001						
2	0.001895597	0.017104403						
3	0.001895597	0.016104403						
4	0.001895597	0.015104403						
5	0.003791195	0.021208805						
6	0.003791195	0.018208805						
7	0.003791195	0.019208805						
8	0.009477987	0.022522013						
9	0.009477987	0.019522013						
10	0.009477987	0.021522013						
11	0.018955975	0.014044025						
12	0.018955975	0.010044025						
13	0.018955975	0.015044025						
14	0.03791195	-0.01391195						
15	0.03791195	-0.01391195						
16	0.03791195	-0.01591195						

2. “Quadratic 1” Model: Quadratic fit for all molar ratios tested – intercept forced through origin.

"Quadratic 1" - all molar ratios for quadratic - y-intercept forced through zero.								
SUMMARY OUTPUT								
<i>Regression Statistics</i>								
Multiple R	0.949906669							
R Square	0.90232268							
Adjusted R Square	0.823917157							
Standard Error	0.008419786							
Observations	16							
<i>ANOVA</i>								
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>			
Regression	2	0.009168501	0.00458425	64.66453812	1.75478E-07			
Residual	14	0.000992499	7.08928E-05					
Total	16	0.010161						
	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	0	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
X Variable 1	0.000139621	1.51686E-05	9.204604253	2.58143E-07	0.000107087	0.000172154	0.000107087	0.000172154
X Variable 2	-1.18033E-07	1.69071E-08	-6.981257088	6.43621E-06	-1.54295E-07	-8.17708E-08	-1.54295E-07	-8.17708E-08
RESIDUAL OUTPUT								
<i>Observation</i>	<i>Predicted Y</i>	<i>Residuals</i>						
1	0	0.001						
2	0.006685957	0.012314043						
3	0.006685957	0.011314043						
4	0.006685957	0.010314043						
5	0.012781749	0.012218251						
6	0.012781749	0.009218251						
7	0.012781749	0.010218251						
8	0.027528134	0.004471866						
9	0.027528134	0.001471866						
10	0.027528134	0.003471866						
11	0.040302138	-0.007302138						
12	0.040302138	-0.011302138						
13	0.040302138	-0.006302138						
14	0.021587758	0.002412242						
15	0.021587758	0.002412242						
16	0.021587758	0.000412242						

3. “Quadratic 2” Model: Quadratic fit for all molar ratios tested – intercept allowing for best fit.

"Quadratic 2" - all molar ratios for quadratic - y-intercept not forced through zero. - These R^2 and coefficients align with "Basic Plots as well as Python Code"								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.863657865							
R Square	0.745904908							
Adjusted R Square	0.706813355							
Standard Error	0.004405421							
Observations	16							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	2	0.000740637	0.000370318	19.0809742	0.000135667			
Residual	13	0.000252301	1.94077E-05					
Total	15	0.000992938						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	0.013137416	0.002127273	6.175707811	3.34667E-05	0.008541722	0.01773311	0.008541722	0.01773311
X Variable 1	7.80266E-05	1.27461E-05	6.121622593	3.65078E-05	5.04904E-05	0.000105563	5.04904E-05	0.000105563
X Variable 2	-6.84151E-08	1.19502E-08	-5.725039737	6.9945E-05	-9.42319E-08	-4.25984E-08	-9.42319E-08	-4.25984E-08
RESIDUAL OUTPUT								
Observation	Predicted Y	Residuals						
1	0.013137416	-0.012137416						
2	0.016867707	0.002132293						
3	0.016867707	0.001132293						
4	0.016867707	0.000132293						
5	0.020255921	0.004744079						
6	0.020255921	0.001744079						
7	0.020255921	0.002744079						
8	0.028368112	0.003631888						
9	0.028368112	0.000631888						
10	0.028368112	0.002631888						
11	0.03504692	-0.00204692						
12	0.03504692	-0.00604692						
13	0.03504692	-0.00104692						
14	0.022748868	0.001251132						
15	0.022748868	0.001251132						
16	0.022748868	-0.000748868						

3.1 Python® code for testing assumptions and validation of Quadratic 2 model.

```
# In[3]:
import seaborn as sns
import numpy as np
import pandas as pd
from scipy.stats import shapiro, bartlett, kruskal, friedmanchisquare, mannwhitneyu,
boxcox
import statsmodels.api as sm
import statsmodels.stats.api as sms
from statsmodels.formula.api import ols
from statsmodels.graphics.factorplots import interaction_plot
from statsmodels.stats.stattools import durbin_watson
from statsmodels.sandbox.stats.runs import runstest_1samp
from statsmodels.stats.diagnostic import kstest_normal
from statsmodels.stats.outliers_influence import summary_table
from statsmodels.sandbox.regression.predstd import wls_prediction_std
import matplotlib.pyplot as plt
```

```

get_ipython().run_line_magic('matplotlib', 'inline')

# In[4]:
dnan_quad_df = pd.read_csv('dnan_quad.csv')
dnan_quad_df.columns = ['date', 'molar_ratio', 'molar_ratio_squared', 'k_s']
dnan_quad_df.head()

# In[5]:
dnan_quad_df.tail()

# In[6]:
n = dnan_quad_df.count()
intercept = np.ones(n[1])
dnan_quad_df["intercept"] = intercept
dnan_quad_df.head

# In[7]:
dnan_quad_df.molar_ratio.unique()

# In[8]:
X = dnan_quad_df[["intercept", "molar_ratio", 'molar_ratio_squared']]
Y = dnan_quad_df[["k_s"]]
dnan_quad_lm = sm.OLS(Y, X).fit()
dnan_quad_lm.summary()

# In[10]:
model_dnan_quad = ols('k_s ~ molar_ratio + molar_ratio_squared',
data=dnan_quad_df).fit()
anova_table_dnan_quad = sm.stats.anova_lm(model_dnan_quad, typ=1)
print(anova_table_dnan_quad)
model_dnan_quad.summary()

# In[15]:
sns.lmplot("molar_ratio", 'k_s', data=dnan_quad_df, fit_reg=True)
print()

# In[16]:
print(model_dnan_quad.params[0])
print(model_dnan_quad.params[1])
print(model_dnan_quad.params[2])

# In[17]:
resids = dnan_quad_lm.resid
pred = dnan_quad_lm.predict()
dnan_quad_df["residuals"] = resids

```

```

dnan_quad_df["fitted"] = pred
dnan_quad_df

# In[18]:
sns.distplot(model_dnan_quad.resid).set_title("Plot of the Residuals")
print()
print(np.mean(model_dnan_quad.resid))

# In[19]:
residuals_df = dnan_quad_lm.resid.to_frame('resid')
dnan_quad_df = dnan_quad_df.join(residuals_df)

predicted_values = 0.013137416182388426+(7.802656264413297e-
05*(dnan_quad_df.molar_ratio))+(-6.841511094081802e-
08*(dnan_quad_df.molar_ratio_squared))
predicted_df = predicted_values.to_frame('predict')
dnan_quad_df = dnan_quad_df.join(predicted_df)
print(dnan_quad_df.head())
sns.lmplot('resid', 'predict', data=dnan_quad_df, fit_reg=True)
print()
sms.het_breuschpagan(dnan_quad_lm.resid, dnan_quad_lm.model.exog)
# In[20]:
sns.distplot(dnan_quad_lm.resid).set_title("Plot of the Distribution of the Residuals")
print()
print(shapiro(dnan_quad_lm.resid))

# In[21]:
plt.scatter(x=range(len(dnan_quad_lm.resid)), y=dnan_quad_lm.resid)
plt.title("Residual Scatter Plot")
plt.xlabel("Index")
plt.ylabel("Residual")
plt.ylim(ymin=-.005, ymax=.005)
plt.show()
durbin_watson(dnan_quad_df.resid)

```

4. Linear fit for molar ratios ranging from 0:1 to 250:1.

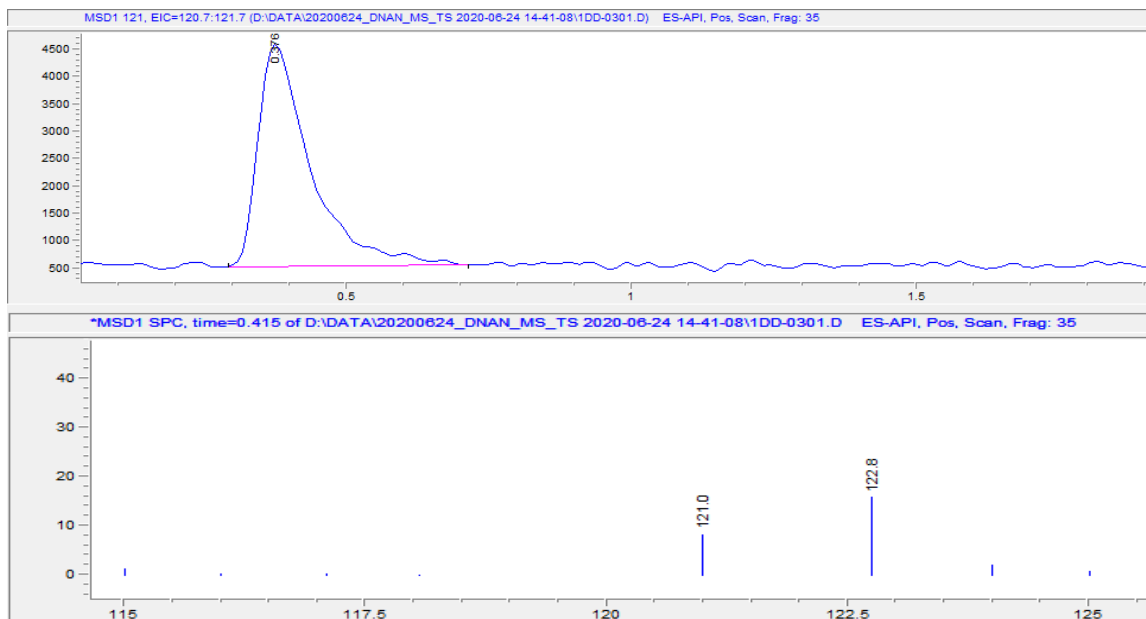
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.934753208							
R Square	0.873763559							
Adjusted R Square	0.762652448							
Standard Error	0.008734351							
Observations	10							
ANOVA								
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>			
Regression	1	0.0047524	0.0047524	62.2947859	4.81195E-05			
Residual	9	0.0006866	7.62889E-05					
Total	10	0.005439						
	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	0	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
X Variable 1	0.000145333	1.84136E-05	7.8927046	2.46522E-05	0.000103679	0.000186988	0.000103679	0.000186988
RESIDUAL OUTPUT								
<i>Observation</i>	<i>Predicted Y</i>	<i>Residuals</i>						
1	0	0.001						
2	0.007266667	0.011733333						
3	0.007266667	0.010733333						
4	0.007266667	0.009733333						
5	0.014533333	0.010466667						
6	0.014533333	0.007466667						
7	0.014533333	0.008466667						
8	0.036333333	-0.004333333						
9	0.036333333	-0.007333333						
10	0.036333333	-0.005333333						

Appendix O – Mass Spectrum Chromatograms

Potential Byproduct: Nitrobenzene

Molecular Mass: 121 amu

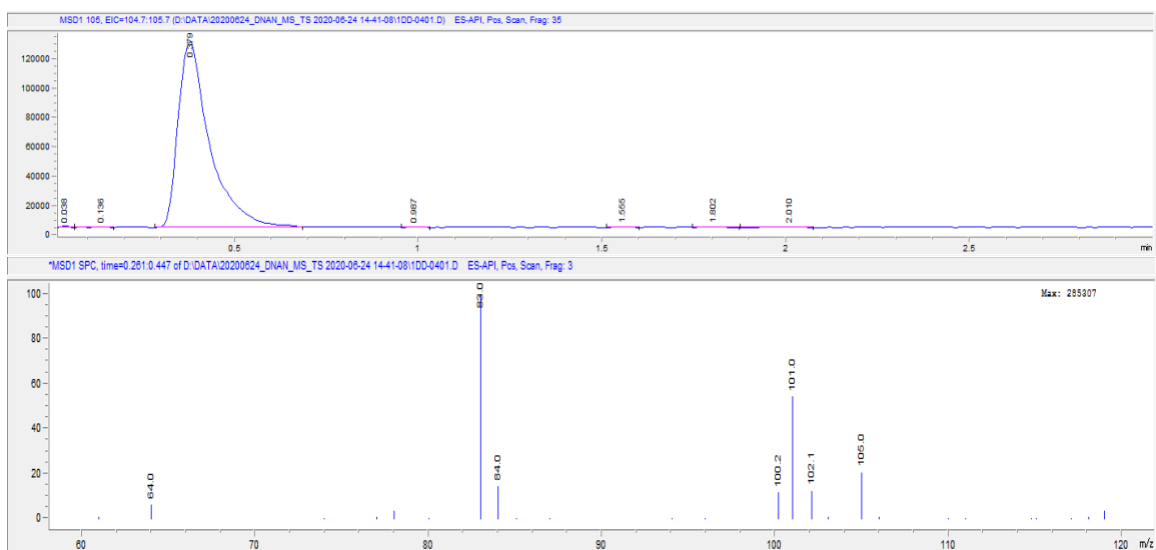
Retention Time: 0.376 minutes



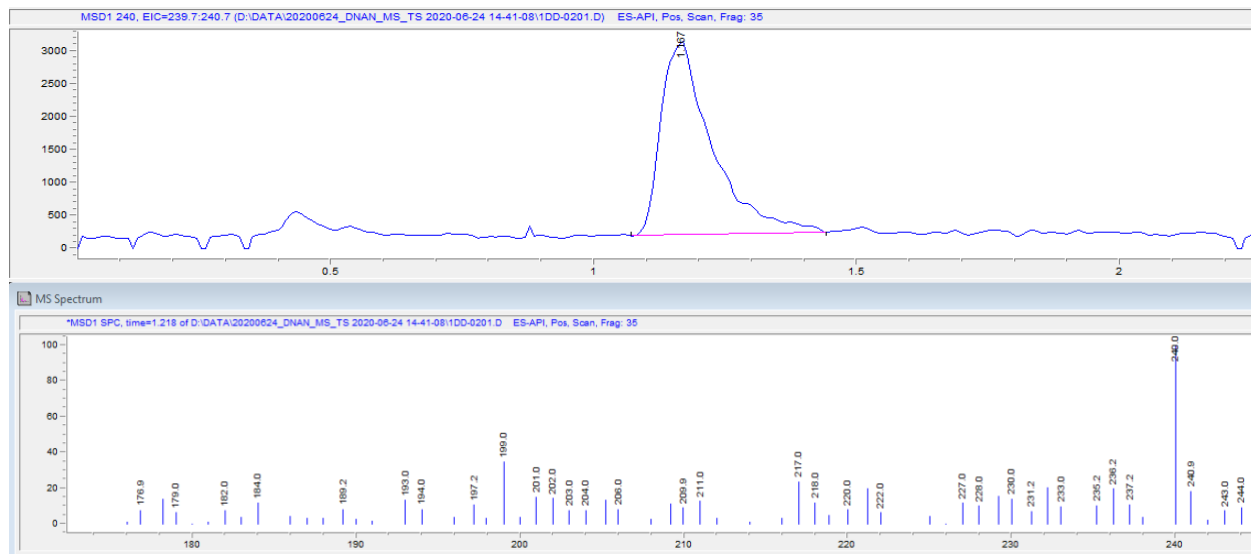
Potential Byproduct: 2,4-Dinitrobenzoic acid

Molecular Mass: 105 amu

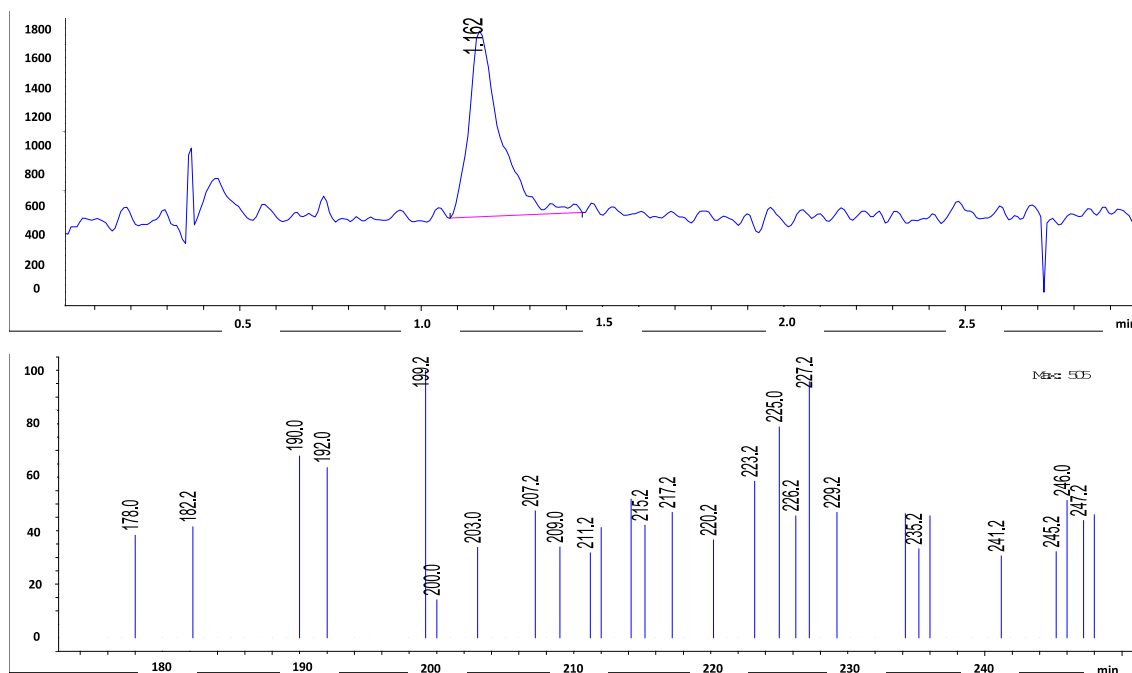
Retention Time: 0.379 minutes



Mass identified: DNAN+Acetonitrile
Molecular Mass: 240 amu
Retention Time: 1.167 minutes



Mass identified: DNAN
Molecular Mass: 199 amu
Retention Time: 1.162 minutes



Appendix P – Labsphere Calibration Procedure for LEDs

Equipment Setup

1. LED Preparation (if applicable)

- Turn on power supply, ensuring voltage is set to a low level (so LEDs are not overwhelmed when turned on repeatedly).
- Unsolder LEDs from their respective positions inside the reactor.
- Ensure LED contact points are clean and remove any residual solder from outer pins.

2. Labsphere Preparation

- Note: All Labsphere equipment and software is contained within the rolling cart and has a power source, chiller, the sphere itself, and a laptop to run the apparatus. The UV-LEDs must be connected to the same power supply and circuitry that was used during experiments.
- Connect the positive and negative labeled electrical wires from the Labsphere to their respective wires coming from the circuit board (which should be unattached from the reactor).
- Note the LED ID number on the back of the LED casing. This will be a letter followed by a number (i.e., I7).
- Remove the rectangular block from the side of the Labsphere module using a small hex-key wrench.
- Mount the LED in the three entry holes. Reattach the side to the sphere. Take care to not bend or break the fragile pins. If the pins are difficult to insert, it is likely due to residual solder that must be cleaned thoroughly.

3. Starting Labsphere

- Turn on the master power supply located underneath the cart (green toggle switch).
- Turn on the deuterium power supply (black toggle switch).
- Turn on Labsphere (large silver push-button).
- Turn on laptop
- Start Illumia Pro software on Laptop.
- Ensure the power supply used for experiments is “off.”
- Click “calibration.” This calibrates the deuterium lamp and will produce a calibration curve.
- Click “D 2000 lampfile.”
- When calibration of the deuterium lamp is complete, turn on the power supply used for experiments.
- Turn off the deuterium lamp (it will interfere with readings).

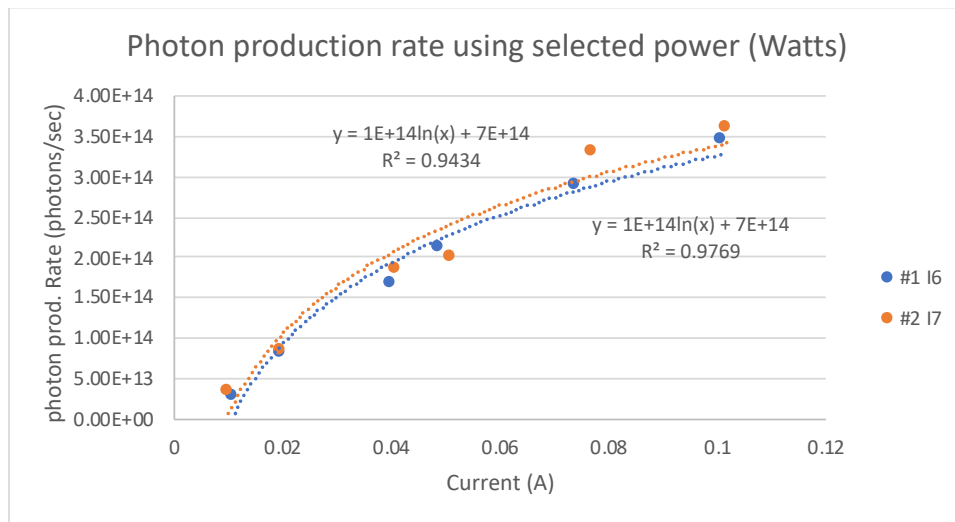
4. Calibrating LEDs

- The power supply can be adjusted manually up through the amplitude used during experiments.
- Several values will be displayed, including the center wavelength, lumens, purity, and others. A time lag occurs between changing voltages. Wait for output values to stabilize before recording.
- When finished with one LED, turn the power supply off and wait 3-4 minutes for the LED to cool before replacing it with another LED to calibrate.
- Switch out the LED and repeat previous steps in this section.
- When finished with all LEDs, close the Illumina Pro Software and shut down the laptop. Turn off the chiller, followed by the master power supply (last). Unhook all electrical wiring from the circuit board and return to the car

Labsphere Output Data

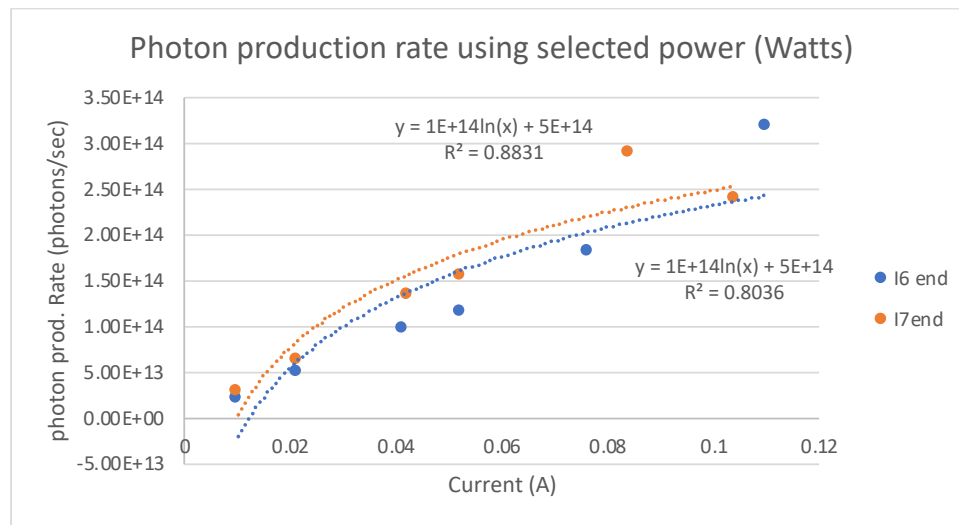
Prior to beginning experiments:

Light ID	Total power (W)	Selected power (W)	Center wavelength (nm)	Full width half max (nm)	Centroid wavelength (nm)	lumens	peak wavelength (nm)	purity	volts	amps	Energy (J)	electron volts (ev)	photon prod. Rate (photons/sec)		
#1 I6	2.16E-05	2.09E-05	264	11	264	6.63E-09	264	100	5.3	0.011	7.52955E-19	4.699573	2.78E+13		
#1 I6	6.38E-05	6.13E-05	264	12	264	1.01E-08	264	100	5.59	0.02	7.52955E-19	4.699573	8.15E+13		
#1 I6	1.32E-04	1.27E-04	264	12	264	1.63E-08	264	100	5.95	0.04	7.52955E-19	4.699573	1.69E+14		
#1 I6	1.67E-04	1.60E-04	264	12	264	1.86E-08	264	100	6.02	0.049	7.52955E-19	4.699573	2.13E+14		
#1 I6	1.56E-04	2.18E-04	264	12	264	2.46E-08	264	100	6.4	0.074	7.52955E-19	4.699573	2.90E+14		
#1 I6	2.72E-04	2.61E-04	264	12	264	2.80E-08	264	100	6.6	0.101	7.52955E-19	4.699573	3.46E+14		
														photons/L*s	lumens
#2 I7	2.93E-05	2.74E-05	264	11	263	7.29E-09	264	100	5.15	0.01	7.52955E-19	4.699573	3.63E+13	1.83E+15	1.39E-08
#2 I7	6.84E-05	6.49E-05	264	11	263	1.23E-08	264	100	5.38	0.02	7.52955E-19	4.699573	8.61E+13	4.79E+15	2.24E-08
#2 I7	6.47E-04	1.41E-04	264	12	264	1.88E-08	264	100	5.75	0.041	7.52955E-19	4.699573	1.87E+14	1.02E+16	3.51E-08
#2 I7	1.59E-04	1.52E-04	264	12	264	2.19E-08	264	100	5.89	0.051	7.52955E-19	4.699573	2.02E+14	1.19E+16	4.05E-08
#2 I7	2.60E-04	2.49E-04	264	12	264	2.79E-08	264	100	5.26	0.077	7.52955E-19	4.699573	3.31E+14	1.77E+16	5.25E-08
#2 I7	2.85E-04	2.72E-04	264	12	264	3.27E-08	264	100	6.6	0.102	7.52955E-19	4.699573	3.62E+14	2.02E+16	6.07E-08



Upon conclusion of experiments:

Light ID	Total power (W)	Selected power (W)	Center wavelength (nm)	Full width half max (nm)	Centroid wavelength (nm)	lumens	peak wavelength (nm)	purity	volts	amps	Energy (J)	electron volts (ev)	photon prod. Rate (photons/sec)		
I6 end	1.95E-05	1.55E-05	264	11	260	1.07E-08	265	100	5.09	0.01	7.52955E-19	4.699573	2.05E+13		
#1 I6	4.18E-05	3.75E-05	264	11	262	1.28E-08	264	100	5.36	0.021	7.52955E-19	4.699573	4.98E+13		
#1 I6	7.84E-05	7.23E-05	264	12	262	1.74E-08	264	100	5.36	0.041	7.52955E-19	4.699573	9.60E+13		
#1 I6	9.38E-05	8.72E-05	264	12	263	1.93E-08	264	100	5.78	0.052	7.52955E-19	4.699573	1.16E+14		
#1 I6	1.49E-04	1.37E-04	264	11	264	1.84E-08	264	100	6.35	0.076	7.52955E-19	4.699573	1.81E+14		
#1 I6	2.60E-04	2.39E-04	264	12	264	2.49E-08	264	100	6.66	0.11	7.52955E-19	4.699573	3.18E+14		
														photons/L*s	lumens
I7end	2.51E-05	2.14E-05	264	11	261	1.08E-08	264	100	5.13	0.01	7.52955E-19	4.699573	2.84E+13	1.40E+15	2.15E-08
#2 I7	5.22E-05	4.79E-05	264	11	262	1.44E-08	264	100	5.38	0.021	7.52955E-19	4.699573	6.36E+13	3.24E+15	2.72E-08
#2 I7	1.08E-04	1.00E-04	264	12	263	1.92E-08	264	100	5.72	0.042	7.52955E-19	4.699573	1.33E+14	6.55E+15	3.65E-08
#2 I7	1.24E-04	1.16E-04	264	12	264	2.08E-08	264	100	5.83	0.052	7.52955E-19	4.699573	1.54E+14	7.71E+15	4.01E-08
#2 I7	2.31E-04	2.17E-04	264	11	264	2.72E-08	264	100	6.35	0.084	7.52955E-19	4.699573	2.89E+14	1.34E+16	4.56E-08
#2 I7	1.91E-04	1.79E-04	265	12	264	2.39E-08	264	100	6.52	0.104	7.50113E-19	4.681838	2.38E+14	1.59E+16	4.88E-08



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14. ABSTRACT Insensitive munitions (IMs) are increasingly employed by the U.S. military to prevent unintended detonations associated with conventional munitions. One IM used extensively is 2,4 dinitroanisole (DNAN). This research employed an ultraviolet light emitting diode (LED) and hydrogen peroxide advanced oxidation process (AOP) to treat DNAN-contaminated water at the laboratory scale. Five molar peroxide ratios (50:1, 100:1, 250:1, 500:1, 1000:1) were evaluated using the observed pseudo first-order rate constant as the performance metric. Both peroxide-limiting reactions and radical scavenging were observed over the range of ratios tested, with overall removal of DNAN decreasing above a ratio of 500:1.					
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