CRC Report No. DP-04-17

CRC INTERNAL DIESEL INJECTOR DEPOSIT (IDID) TEST: HARDWARE, FUEL, AND ADDITIVE EVALUATIONS

September 2019

COORDINATING RESEARCH COUNCIL, INC.

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CRC Internal Diesel Injector Deposit (IDID) Test: Hardware, Fuel, and Additive Evaluations

CRC Project No. DP-04-17

FINAL REPORT

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EXECUTIVE SUMMARY

The objective of this project was to establish and demonstrate a new test system to evaluate internal diesel injector deposits. This methodology is a combination of an injector deposit test rig and a novel, spectroscopic technique to measure deposit thickness. The project was not designed to be a comprehensive study of the factors that affect injector deposit formation.

- A new IDID test system, based on previously published work, was assembled.
- Thirteen tests were performed to demonstrate that the assembled test rig could rank fuels similarly to results from previous rig and engine tests. Results from these tests were:
  1) Test rig capability to discriminate between fuels with and without contaminants/additives.
  2) Capability to discriminate between high and normal additive levels.
  3) Discrimination was demonstrated using both visual rating and VASE deposit thickness measurement methods.
  4) Longer rig run time (21 hr vs. 7 hr) produced thicker deposits for fuel with normal additive/contaminant treat rates, as expected.
  5) Discrimination between additive/contaminant levels was demonstrated at both 21 hr and 7 hr run times.
- Seventy tests were conducted using fuels blended to a designed experimental plan. The fuels were blends of a base diesel fuel (clay-treated to remove additives) and combinations of eight different contaminants and/or fuel additives.
- Using the Variable Angle Spectroscopic Ellipsometer (VASE), pintle deposits as thin as 10 nanometers were measurable. Deposits of this thickness are not discernable to the unaided eye.
- Statistical analysis of the VASE/deposit results showed:
  - There were no statistical outliers.
  - Regarding deposit by location on the injector pintles:
    - No significant axial location differences.
    - No significant radial location differences.
  - Sodium increases deposit thickness.
  - No significant corrosion inhibitor and cetane number improver differences.
  - Detergent additive reduces deposit thickness in fuels without biodiesel.
  - Sodium increases deposit thickness in fuels without:
    - Detergent additive.
    - Glycerin.
    - Mono-acid lubricity additive.
  - Conductivity additive increases deposit thickness in fuel without:
    - Biodiesel.
    - Glycerin.
  - Conductivity additive increases deposit thickness in fuel with mono-acid lubricity additive.

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ACKNOWLEDGEMENTS

The authors wish to acknowledge the support of the Coordinating Research Council for this work. We also greatly appreciate the statistical analyses performed by Jo Martinez of Chevron. Special acknowledgement is also given to Delphi Technologies Ltd for providing the test method that was the basis for the test rig and test conditions.

ACRONYMS & ABBREVIATIONS

°	degree
%	percent
µm(b)	micron (b)
F	Fahrenheit
g	grams
GPM	gallons per minute
kPa	kilopascals
L/sec	liters per second
mg/L	milligrams per liter
psi	pounds per square inch
psid	pounds per square inch, differential
AFLRF	Army Fuels and Lubricants Research Facility (SwRI)
ATR	Attenuated Total Reflectance
CARB	California Air Resources Board
CLyy-xxxx	SwRI Chemistry Lab Sample ID (yy = year, xxxx = sample number)
CRC	Coordinating Research Council
DDSA	Dodecyl Succinic Acid
DPG	Diesel Performance Group (CRC)
EMRE	ExxonMobil Research and Engineering
EPA	Environmental Protection Agency
FTIR	Fourier Transform Infrared Spectrometry
HDD	Heavy Duty Diesel
IDID	Internal Diesel Injector Deposit
MTxx	Matrix Test (xx = test number)
ND	Non-Destructive
PTxx	Proof Test (xx = test number)
RFP	Request for Proposal
SwRI	Southwest Research Institute
VASE	Variable Angle Spectroscopic Ellipsometer

1.0 INTRODUCTION AND OBJECTIVE

Since 2012 three studies related to diesel internal injector deposits/sticking have been conducted under the Diesel Performance Group of the Coordinating Research Council (CRC).[1,2,3] The work done under the 2016 project established a reasonable correlation between the Delphi-designed Internal Diesel Injector Deposit (IDID) rig and an actual commercial heavy-duty engine. This correlation showed that the Delphi rig had the ability to discriminate between fuels that result in internal injector sticking and those that do not. The 2016 project was designed to evaluate the rig capability only, it did not investigate the specific effects of fuels, additives, or impurities.

In addition to the work on the IDID approach, CRC organized a small proof of concept program with ExxonMobil Research and Engineering (EMRE) to evaluate the potential use of ellipsometry to provide a more sensitive measurement of internal deposits than can be done visually. This program showed it was possible to map the deposits that form on the fuel injector pintle, a key capability that allows more precise and sensitive quantitation of fuel deposits.

Since the 2016 IDID rig work demonstrated a meaningful correlation, between the rig and the engine, and the EMRE tests showed a promise of a breakthrough analysis technique, the CRC Diesel Performance Group (DPG) agreed that both avenues should be pursued under a single project. Therefore, the CRC issued a request for proposal (RFP) for a project to 1) set up the IDID rig at a U.S. research facility and 2) develop a novel injector deposit evaluation system for evaluation of fuels and additives, and impurities.

The objective of CRC project DP-04-17 was to establish and demonstrate this combination of capabilities to generate and measure IDID. It was not designed to be a comprehensive study of the factors that affect IDID.

2.0 TEST RIG

2.1 Test Rig

The CRC Request for Proposal (RFP) directed that the contractor should set up the test rig according to the description provided in the "Test Methodology for IDID Apparatus" that was attached to the RFP. According to the RFP, the rig was designed to accelerate formation of internal injector deposits. The operating parameters of the rig simulate severe engine operating conditions for light duty vehicle, high pressure, common rail systems. It was anticipated that test results would be useful for HDD, heavy duty diesel, engines as well.

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[1] "Scoping Study to Evaluate Two Rig Tests for Internal Injector Sticking," CRC Project DP-04, July 2012.
[2] "Internal Injector Deposits; A Scoping Study to Evaluate the Delphi Test Rig," CRC Project DP-04-13b, August 2013.
[3] "Internal Injector Deposits; Correlation of the Delphi Test Rig with Production Engines," CRC Project DP-04-10, March 2016.

The rig was mounted on an electric motor-driven test stand. Injected fuel was not recirculated. The operating conditions were selected to continuously reproduce conditions that mimicked the severe thermal soak back conditions similar to that which would briefly occur during idle, immediately following extended operations at full power on an engine or vehicle. To achieve this, elevated temperatures were maintained using an electrical heater to replicate combustion heat combined with high injection pressures. A slow injection rate was used, similar to that observed during engine idle operation, which gave time for fuel deposit-forming reactions to occur and also minimized fuel consumption. It was a continuous replication of transient shut down condition. Injection pressure and temperature were high. Injected volume was low. This resulted in providing maximum stress to the fuel with minimum fuel flow.

Although Delphi injectors were used in the current study, the rig is not specific to any fuel injection equipment (FIE) design or brand. Neither the test program nor the apparatus were intended for evaluation of FIE design or construction. Electric heaters were used to replicate combustion temperature.

Figure 1 is a schematic diagram of the test rig and Figure 2 is a photograph of the rig constructed under this project.

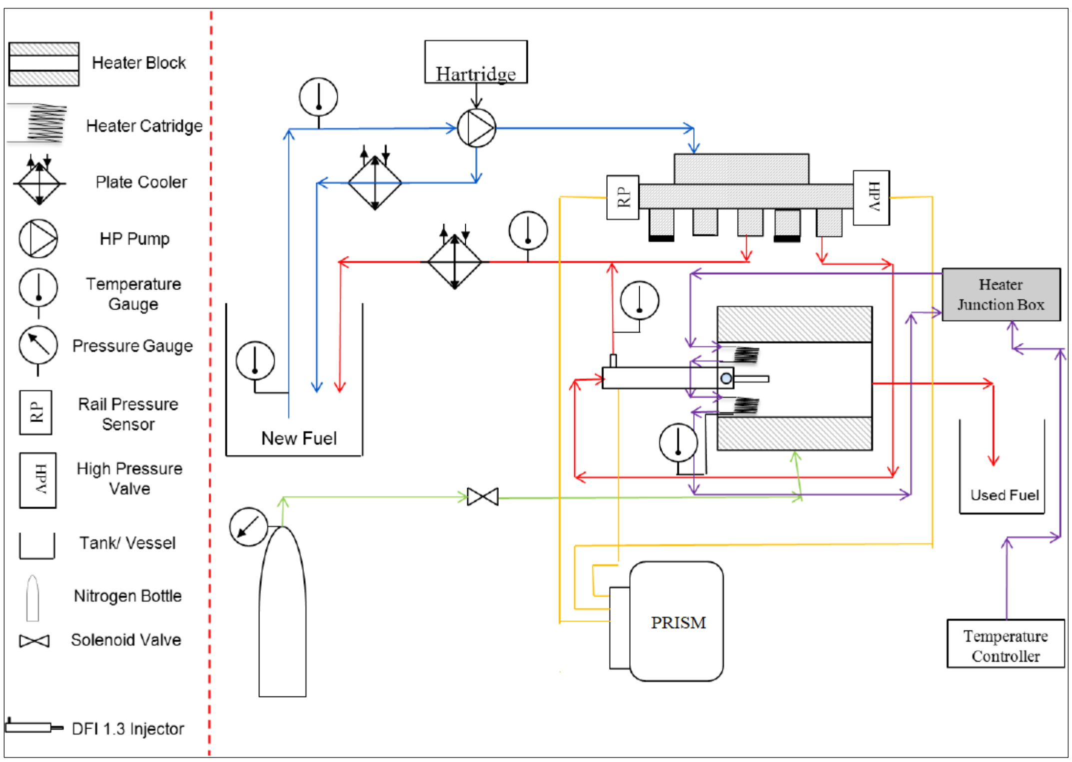


Figure 1. Test Rig Schematic

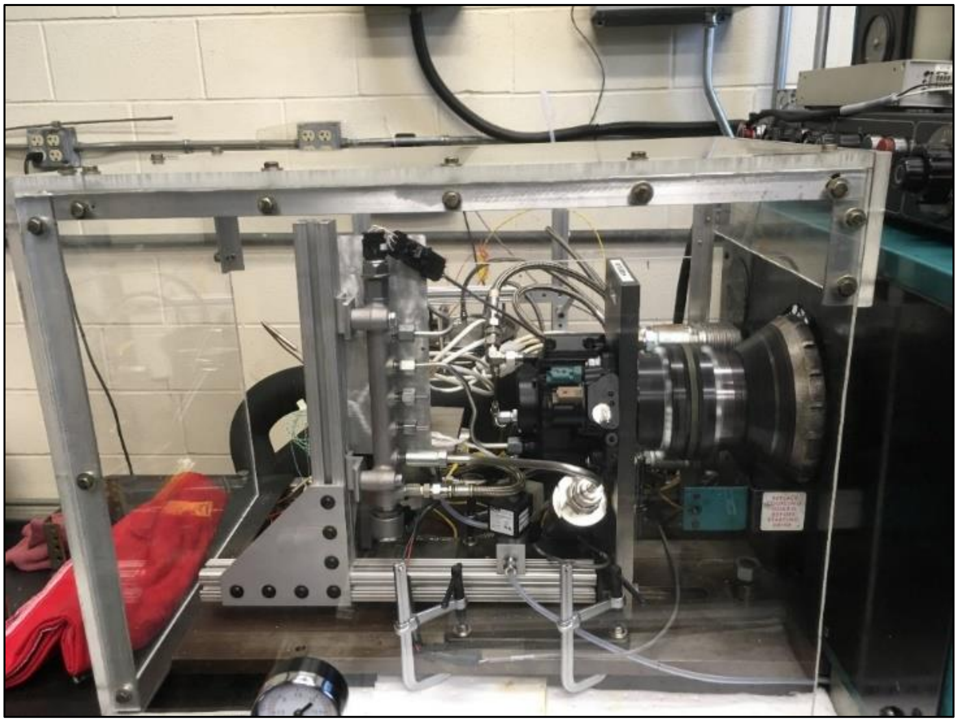


Figure 2. IDID Test Rig

2.2 Test Fuels, Additives, Contaminants, and Treat Rates

The CRC, Diesel Performance Group, Deposit Panel provided specific instructions regarding all the test fuels, additives, contaminants, and treat rates to be used in this project. The two base fuels and the B100 were all provided through the deposit panel. All fuel additives were likewise provided to the project through the deposit panel. Additives were provided by several additive companies, through the American Chemistry Council, and final selection was made by an American Chemistry Council representative. SwRI agreed not to identify the specific additives that were used nor to do any analysis of the additives. This additive policy is in keeping with the intent of the project to demonstrate the capability and not perform an in-depth study of fuel or additive effects. The sodium and glycerin were purchased from chemical supply companies as reagents.

The first 13 tests conducted were Proof Tests (PT01 through PT13). These tests were intended to demonstrate that the SwRI test rig would discriminate the deposit-forming tendencies of fuels similarly to the Delphi test rig. The test fuels used in the Proof Tests used the same fuels, additives, and contaminants used in the Delphi rig testing (see Section 2.3 for additional information). Below is a list of base fuels, additives, contaminants, and treat rates used in these Proof Tests.

- CARB No. 2 ULSD (donated by a major oil company)
- EPA No. 2 ULSD (donated by a major oil company)
- DDSA provided through CRC Deposit Panel (Normal Use Rate: 1 mg/kg) (Higher Concentration: 44.0 mg/kg)

- Sodium as sodium naphthenate (Reagent Grade, TCI America) (3.55 mg/kg mass)

Following the Proof Tests, 64 Matrix Tests were conducted using a specific test plan provided by CRC. Below is a list of the test fuels, additive types, and contaminants used in the matrix tests. The test fuels were clay-filtered, to remove additives, prior to preparation of test blends.

- CARB No. 2 ULSD (donated by a major oil company)
- EPA No. 2 ULSD (donated by a major oil company)
- B100 biodiesel (meets D6751, Rancimat induction period 7.5 hours) (20 volume %, i.e. used to prepare a B20 blend)
- Sodium as sodium naphthenate (Reagent Grade, TCI America) (1 ppm mass)
- Glycerin (Reagent Grade, LabChem, Fisher Scientific Catalogue No. LC148502) (0.004 mass %)
- Corrosion inhibitor additive (supplied by major additive manufacturer) (20 ppm mass)
- Diesel fuel lubricity additive (supplied by major additive manufacturer) (200 ppm mass)
- Detergent additive (supplied by major additive manufacturer) (425 ppm mass)
- Cetane improver additive (supplied by major additive manufacturer) (4000 ppm mass)
- Static dissipator (conductivity improver) additive (supplied by major additive manufacturer) (3 ppm mass)

2.3 Test Rig Proof Testing

Once the rig was assembled and ready for testing, the next phase, per the CRC statement of work, was to conduct a small matrix of tests called the proof tests. The proof tests were intended to demonstrate that the rig would be able to discriminate between various test fuel blends and would also rank fuels similarly to testing conducted previously,[4] as well as explore some other aspects of the test method. A total of 13 proof tests were conducted and the results are presented in Tables 1 and 2. Table 1 presents the visual rating results for the pintles. Table 2 presents the deposit thickness on the pintles, as measured with the VASE instrument (the VASE instrument is discussed later in this report). The first six proof tests (PT01-PT06) were conducted to evaluate the precision of the test rig and its ability to discriminate fuels. The visual rating scale is:

1 = very little deposit
2 = some deposit
3 = heavy deposit, stiff
4 = heavy deposit, stuck

It is noted at this point that the previously reported CRC work used visual assessments of the level of deposit, along with reporting when the pintle was stiff or stuck. No deposit thickness measurements were conducted during that testing. The purpose of the proof tests was to confirm

[4] "Internal Injector Deposits; Correlation of the Delphi Test Rig with Production Engines," CRC Project DP-04-10, March 2016.

that testing with the same test fuels and test conditions would result in the same visual rating as reported in CRC DP-04-10. After reviewing the results, the deposit panel concluded that the results were comparable and that the work should continue with the matrix tests.

SwRI operated the rig proof tests following the procedures previously outlined by Delphi, performing each 21-hour test over three consecutive 7-hour test days. Approximately 12.6 L of EPA test fuel was utilized for each 21-hour procedure without the fuel filters. For operating the filtered test the fuel quantity was increased to 15 L, to allow for more flush fuel and the filter canister volume.

Proof tests PT07 and PT08 were the same as PT03 and PT04 with the addition of an inline fuel filter (CAT 1R-0750, 2 micron rating, advanced efficiency). The fuel filter was added to aid CRC in determining if the discrepancy between the Cummins and the John Deere engine correlation in the 2016 CRC program (CRC Project DP-04-10) was due to one of the engines running on filtered fuel. During the 2016 work, both engine participants reported having difficulty keeping the contaminants in solution. One of the engines used an inline fuel filter to remove the particles ahead of the engine and one did not. When differences in pintle ratings were seen, the use of the filter was thought to be the source of the differences by removing contaminants ahead of the engine. Under the current project, SwRI found that the visual rating results both with and without a filter, were equivalent. It should also be noted that we saw no visible evidence of contaminant insolubility in any of the test fuels. The deposit thickness for PT04, 07, and 08 were also of similar magnitude. The deposit thickness for PT03 was somewhat lower than the other three. We believe this is due to accidentally switching pintles PT03 and PT05 in the time between taking the visual rating and the VASE analysis.

The first filter run, Proof Test 7, terminated at 20-hours and 18-minutes due to a fuel shortage. During testing the test rig shut down 3-times due to power outages. The re-establishment of test conditions after the shutdowns utilized excess fuel. The injector pintle at the conclusion of Proof Test 7 was stuck, a rating of 4. The second filter run, Proof Test 8 completed 21-hours of testing. The injector pintle at the conclusion of Proof Test 8 was stuck, a rating of 4.

Proof tests PT09-PT12 were the same as PT02-PT05 with one exception. These tests were run for only 7 hours rather than the 21 hours used for the other PT tests. These four tests were conducted to confirm that the test rig, combined with the VASE method of measuring deposits, is able to differentiate fuels with a 7-hour test as opposed to a 21-hour test. The original rig-test method, as developed by Delphi, was seven hours long. The test duration was lengthened to 21 hours for the CRC correlation study.[5] The additional test time was added in order to develop sufficient deposits on the injector pintles to allow visual rating of the deposits with the test fuels that were used. CRC approved the SwRI recommendation to do only two 21-hour tests with filters and to devote the other four proof tests to exploring 7-hr tests. Both of the tests (PT10 & PT11) with the elevated DDSA + Na resulted in stuck pintles. The tests with normal DDSA (PT09 & PT12) had light

[5] "Internal Injector Deposits; Correlation of the Delphi Test Rig with Production Engines," CRC Project DP-04-10, March 2016.

deposits. At the end of these tests, the deposit panel concluded that 7-hour tests, combined with VASE analysis, would give acceptable results and the matrix tests were conducted as 7-hour tests.

Proof test PT13 was a repeat of PT05 because the average deposit depth result for PT05 appeared to be unusually high. The average deposit depth for PT13 was more in line with expected results. It appears that the average deposit depth for PT05 was incorrect or that two pintles (PT03 and PT05) had been accidentally switched prior to VASE analysis. Unfortunately, there was no means to confirm if the pintles had been switched. In order to keep this from happening again, SwRI etched each pintle with a unique number at the completion of the rig test and before any additional analysis of the pintle (see Figure 3Figure 3).

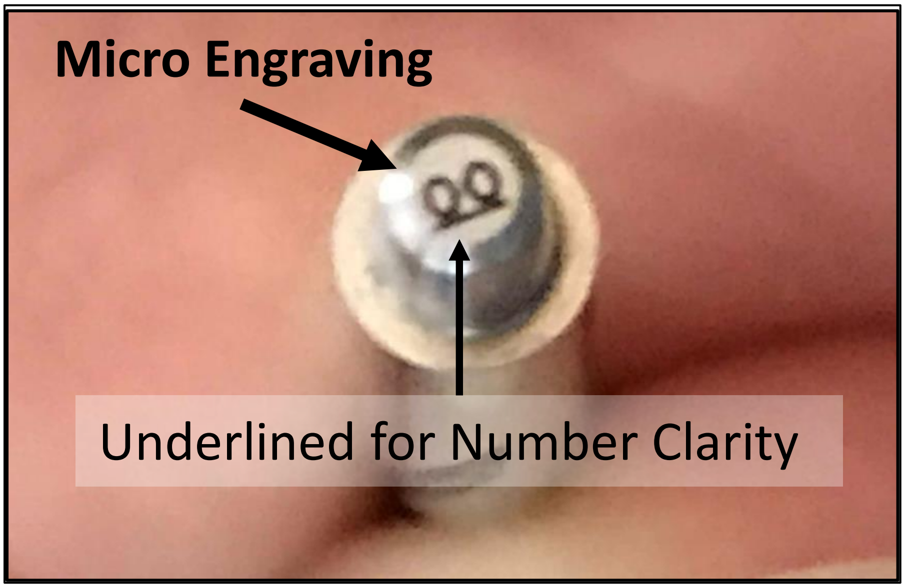


Figure 3. Engraved Identification Number on Pintle

Table 1. Proof Tests -- Rating of Injector Pintles Using CRC Guidelines

Test	Fuel (see Sec 2.2 for details)	Rating* (1:clean to 4:stuck)
PT01 (21-hour)	CARB	1.5
PT02 (21-hour)	EPA + Normal Use Rate DDSA + Na	2
PT03 (21-hour)	EPA + Higher Concentration DDSA + Na	3, sticky, sluggish
PT04 (21-hour)	EPA + Higher Concentration DDSA + Na	4, stuck
PT05 (21-hour)	EPA + Normal Use Rate DDSA + Na	2
PT06 (21-hour)	CARB	1.75
PT07 (21-hour)	EPA + Higher Concentration DDSA + Na with In-Line Fuel Filter	4, stuck
PT08 (21-hour)	EPA + Higher Concentration DDSA + Na with In-Line Fuel Filter	4, stuck
PT09 (7-hour)	EPA + Normal Use Rate DDSA + Na	2
PT10 (7-hour)	EPA + Higher Concentration DDSA + Na	4, stuck
PT11 (7-hour)	EPA + Higher Concentration DDSA + Na	4, stuck
PT12 (7-hour)	EPA + Normal Use Rate DDSA + Na	2
PT13 (21-hour)	EPA + Normal Use Rate DDSA + Na (PT05 repeat)	2
* Non-integer ratings indicate a rating judged to fall between two integer ratings.		

Table 2. Proof Tests -- Average Pintle Deposit Thickness per VASE (Pintle Region 1-B)

Test No.	Base Fuel	Additive/Contaminant (see Sec 2.2 for details)	Notes	Avg. Deposit Thickness, nm
PT01	CARB	None	21-hr. no filter	64.2
PT02	EPA	Normal use rate DDSA + Na	21-hr. no filter	169.8
PT03	EPA	Higher concentration DDSA + Na	21-hr. no filter	180.5
PT04	EPA	Higher concentration DDSA + Na	21-hr. no filter	456.3
PT05	EPA	Normal use rate DDSA + Na	21-hr. no filter	355.8
PT06	CARB	None	21-hr. no filter	23.8
PT07	EPA	Higher concentration DDSA + Na	21-hr. with filter	592.0
PT08	EPA	Higher concentration DDSA + Na	21-hr. with filter	395.1
PT09	EPA	Normal use rate DDSA + Na	7-hr. no filter	25.4
PT10	EPA	Higher concentration DDSA + Na	7-hr. no filter	478.7
PT11	EPA	Higher concentration DDSA + Na	7-hr. no filter	573.4
PT12	EPA	Normal use rate DDSA + Na	7-hr. no filter	37.0
PT13	EPA	Normal use rate DDSA +Na (rerun of #5)	21-hr. no filter	140

The results of the proof tests were statistically analyzed during a panel meeting held at SwRI to review the proof tests. Below is a summary of that statistical analysis:

7-hr no filter – 4 runs

There's significant difference between the two fuels.

Summary of Fit

RSquare	0.989312
RSquare Adj	0.983968
Root Mean Square Error	0.208618
Mean of Response	4.842081
Observations (or Sum Wgts)	4

Analysis of Variance

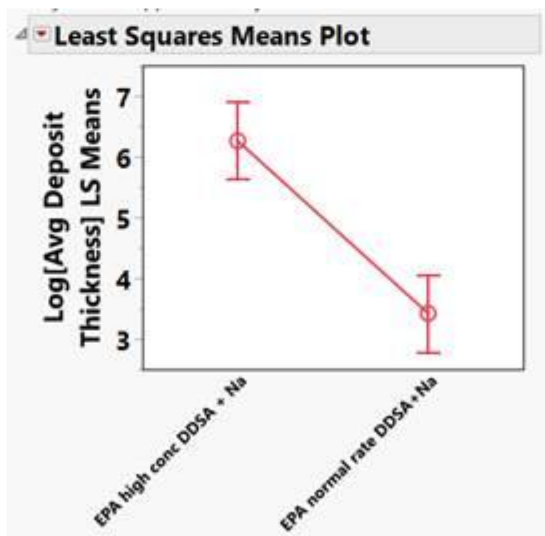
Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	8.0570555	8.05706	185.1275
Error	2	0.0870433	0.04352	Prob > F
C. Total	3	8.1440988		0.0054*

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	4.8420812	0.104309	46.42	0.0005*
Fuel[EPA high conc DDSA + Na]	1.4192476	0.104309	13.61	0.0054*

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Fuel	1	1	8.0570555	185.1275	0.0054*



21-hr no filter – 7 runs

There's significant difference between the CARB and the EPA fuels.

Summary of Fit

RSquare	0.76989
RSquare Adj	0.654834
Root Mean Square Error	0.593131
Mean of Response	4.943029
Observations (or Sum Wgts)	7

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	2	4.7081804	2.35409	6.6915
Error	4	1.4072160	0.35180	Prob > F
C. Total	6	6.1153964		0.0530

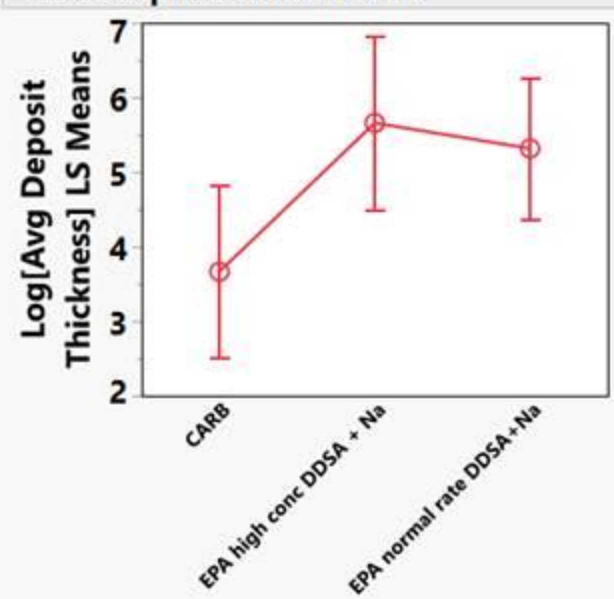
Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	4.8807208	0.228296	21.38	<.0001*
Fuel[CARB]	-1.214876	0.332796	-3.65	0.0218*
Fuel[EPA high conc DDSA + Na]	0.7787198	0.332796	2.34	0.0794

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Fuel	2	2	4.7081804	6.6915	0.0530

Least Squares Means Plot



EPA high conc DDSA + Na – 4 runs

There's no significant difference between with or without filter

Summary of Fit

RSquare	0.592089
RSquare Adj	0.388133
Root Mean Square Error	135.4304
Mean of Response	378.175
Observations (or Sum Wgts)	4

Analysis of Variance

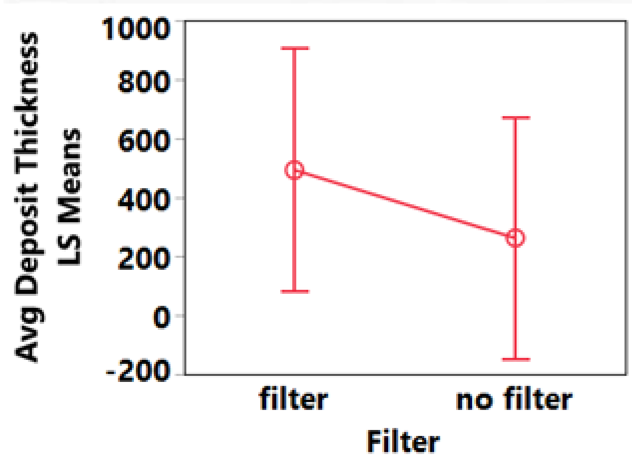
Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	53245.563	53245.6	2.9030
Error	2	36682.805	18341.4	Prob > F
C. Total	3	89928.368		0.2305

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	378.175	67.71522	5.58	0.0306*
Filter[filter]	115.375	67.71522	1.70	0.2305

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Filter	1	1	53245.563	2.9030	0.2305



The proof tests demonstrated:

1) Test rig capability to discriminate between fuels with and without contaminants/additives.
2) Capability to discriminate between high and normal additive levels.
3) Discrimination was demonstrated using both visual rating and VASE deposit thickness measurement methods.
4) Longer rig run time (21 hr vs. 7 hr) produced thicker deposits for fuel with normal additive/contaminant treat rates, as expected.
5) Discrimination between additive/contaminant levels was demonstrated at both 21 hr and 7 hr run times.

3.0 MATRIX TESTS

Based on the results of the proof tests, the CRC panel authorized SwRI to conduct the 64-test matrix as laid out in the RFP/Statement of Work. Additionally, the CRC panel gave permission to conduct 7-hour tests rather than 21-hour tests. Prior to the start of the test matrix, all heaters in the heating block were replaced. Additionally, the safety valve cracking pressure was adjusted and the jam nut wire tied. These adjustments were made because the cracking pressure of the safety valve had lowered due to vibration. In turn that caused variation in the rail pressure control which was witnessed towards the end of the proof testing.

The sixty four (64) test matrix, 7-hour, rig tests were completed without any operational issues. The matrix tests completed were numbered MT01 through MT64 as shown in Appendix B. Also shown in Appendix B are six additional matrix tests, MT65-MT70. These final six tests were selected by the CRC panel following completion of the first 64 matrix tests. These six tests are repeats of three previous matrix tests, run in duplicate. They were conducted as an evaluation of the precision of the test method. For all matrix tests the injector pintles and control valves were freely moving when the injectors were disassembled. The deposit thickness results from the matrix tests are discussed in Section 4 of this report.

Operating data are given in Appendix A. The data are the averages and standard deviations of the 1-Hz sampling for each of the 7-hour runs. They include rail pressure, fuel supply temperature, fuel inlet temperature, nozzle temperature, pump return temperature, system return temperature, injector return temperature, and pump speed. Also included is the weight of fuel utilized for each test. Appendix B gives the blend composition for each of the matrix test fuel blends.

Because each test fuel was blended individually, we used a specific protocol and work instruction for each blend in an attempt to maintain consistency. Also, each blend was prepared within 2 days of running and kept in cold storage until used. The test fuel was allowed to come to room temperature before it was used. This appears to have worked because there were no instances of particulate and/or crystalline pintle deposits in this test program, including the initial very high additive concentration runs

4.0 DEPOSIT THICKNESS MEASUREMENT AND MATRIX TEST INJECTOR DEPOSIT RESULTS

The most technically challenging part of the program had the least amount of definition. The RFP (request for proposal) simply stated:

> "Contracting laboratory will work closely with an expert in Variable Angle Spectroscopic Ellipsometry (VASE) analysis to apply this technique to the injector parts. Photos and FTIR also are required."

Referencing the available documents from CRC, the project final report of March 2016 and a follow up review of deposit evaluation technology of September 2016, provides some information. The former primarily defined the nature of the problem and documented the methods used, leading to justification of relying on the Delphi approach for the generation of deposits. Also mentioned are issues surrounding being able to visually judge the depth of the deposit acurately.

A presentation at the September 2016 meeting of the DPG[6] detailed the work of the group to outline the objectives that led to the RFP for this project. Included in that presentation was a presentation made by ExxonMobil Research and Engineering (EMRE), explaining their work on measuring injector deposits with ellipsometry.

The EMRE presentation showed how they used a VASE system to quantify deposits on components from a selection of injectors from multiple sources. The presentation was not detailed in regard to how it was done (other than it was done with the VASE system). SwRI personnel discussed the process with EMRE. While they were willing to provide some overview thoughts and discuss their results and concerns, they were not able to share specific EMRE techniques. They did provide a complete listing of the VASE system used for their work, which allowed SwRI to replicate the capability at SwRI.

SwRI asked CRC, as part of the RFP question and answer period, if there was a written method for VASE analysis of injector parts. EMRE stated, through CRC, that there was no formal method. They had been working on applying VASE techniques to fuel deposition for several years and applied that knowledge to make a simple proof of concept, no more. During subsequent consultations with EMRE, they reiterated some of the issues that would be important in developing an actual method, in particular they were concerned about potential deposits that were not amenable to the VASE process.

SwRI also sought clarification regarding exactly which parts, or areas of parts, should be measured. The implication of the RFP, and the associated committee documents, was that the injector pintle was the intended target of analysis. The reply from the deposit panel also clarified that this program is aimed at internal deposits, as would be found on the injector pintle. Based on this information,

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[6] Joan Axelrod and Manuch Nikanjam, "CRC Diesel Performance Group Deposit Panel," Tuesday 27 September 2016, Las Vegas, NV.

SwRI proposed the following analysis effort. It covered VASE ellipsometry, FTIR and visual analysis along with an intent to consider other surface analysis techniques that could be useful.

VASE Ellipsometry: VASE is a registered trademark of the J.A. Woollam Co (Woollam), Lincoln, NE. Dr. Woollam is the acknowledged industry leader in understanding the use of spectroscopic ellipsometry. The EMRE pro bono effort with the VASE system showed it was potentially the best solution for the work intended in this program. Upon receipt of the project, SwRI initiated the acquisition of a system identical to that used by EMRE.

The VASE was a long lead time item, 120 calendar days, however that did not put the project on hold. During that time SwRI worked with an expert in this technology from Woollam. SwRI negotiated a proposal with them that allowed initial elements of the program to be developed with their equipment while the SwRI unit was being built.

While Woollam was building the actual instrument, SwRI was constructing the needed fixture to ensure accurate reproduction of test data. Woollam supplied the requisite technical information on how to place specimens in their system and that was used to prepare a fixture. Building the fixture required the disassembly of a new injector of the specified type from which to extract the pintle. While that removed an injector from the inventory, it was still useful as a “clean” reference.

The Woollam system is highly automated and standardized so the process developed using their in-house equipment transferred directly to the SwRI unit. An SwRI researcher was trained in the system during build up period and collaborated with Woollam on the method development. This part of the program used the new pintle (this pintle was used during the construction of the fixture) to collect baseline properties for the pintle itself.

CRC provided two (2) used injector pintles of the designated type at this point. Since the actual analysis program had to be developed with deposited injector pintles, these pintles were very useful for developing the initial analysis program in conjunction with Woollam. Once the main evaluation program was commenced, SwRI, relying on advice from Woollam, considered the potential ways to scan the surface of the pintle.

SwRI initially scanned all of the areas shown in Figure 4. We then processed all of the scans in order to develop a protocol for subsequent analysis of the test pintles. SwRI determined that the last 4 mm of the main pintle body (area “B” in Figure 4, below) provided the most consistent results. Results from the scans outside of Area B tended to be far more varied and provided little to no additional information. During the program, it was noted that twenty one (21) data points over 4 mm resulted in some data overlap. That is true but this issue was covered in the development discussions with the Woollam technical support representative. Woollam’s stated that using the overlapping data provides a better picture of the structure of the deposit formation. Discreet data is still contained by simply skipping bridging data cells.

FTIR: The RFP requested that each pintle be scanned using Fourier Transform Infrared (FTIR) spectroscopy. These analyses were conducted using an attenuated total reflectance (ATR) method. This technique allows samples to be analyzed without removing the deposit from the pintle. During the analysis of the test pintles, it was determined that several had deposits that were too thin to be detected with our FTIR instrument (a Bruker Tensor 27 with an ATR cell). FTIR results are presented in Appendix C. All of the FTIR spectra are presented but several of them are not useful spectra. No analysis of the FTIR results was conducted because, presumably, at least some of the deposits could be caused by the presence or absence of certain additives in the fuel; and, we had agreed not to analyze any of the additives used in the project. Analysis of the spectra is left to the reader.

Photographic Record: While SwRI has experience with this type of documentation from nearly six decades of documenting engine tests, developing a good method for this effort was a challenge. The primary benefit of the test rig and methodology developed under this project was being able to run a 7-hour test and still measure deposits that were often unseen with the unaided eye. As such, photography of the pintles often failed to document the deposit thickness differences that were recorded with the VASE.

SwRI reviewed several approaches to photographing the pintles, ranging from photomicrographs to group pictures. After considering options, we decided to use individual pictures for system record and group pictures for comparison purposes in this report.

Visual Rating vs. VASE Analysis: In some of the earlier CRC projects there was evidence that some deposits could occur that would be too heavy for analysis by ellipsometry. There were photographic examples from previous studies that showed particulate and crystalline deposits on the injector pintle surface, substantiating this concern. As discussed earlier in this report, lacking another suitable method of deposit analysis/rating, visual rating was used. This meant that deposits needed to be sufficiently thick to be visible. That requirement leads to longer test times and also typically means higher than normal additive/contaminant treat rates, reducing the relevance of the results and potentially causing handling problems with the test fuel. Use of the VASE technique to measure deposits allows shorter test times and more realistic levels of additives and contaminants.

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4.1 Variable Angle Spectroscopic Ellipsometry (VASE) Analyses

The VASE is a non-destructive technique that uses polarized light to pass through and refract in a film or deposit at a specified angle of incidence. As the polarized light interacts with the film, the light depolarizes creating an ellipse. The information from the ellipse is then used to graph the experimental data in the form of ψ (amplitude component) and Δ (phase change) each plotted against multiple wavelengths (370 nm – 1687 nm). A data model is then generated to fit the experimental data to calculate the film thickness. Some of the variables utilized in the modeling are refractive index, UV contribution, and IR contribution.

The pintle deposit thickness data was measured as four radial readings at each of 21 axial measurement points over a 4-mm section of the pintle. Figure 4 is a photograph of a pintle showing the regions we scanned on each pintle. The scan data were recorded for each pintle but deposit thickness measurements/reporting were limited to a smaller region. As discussed earlier in this report, deposit thicknesses shown in Figures 5-12 are measurements in Region B.

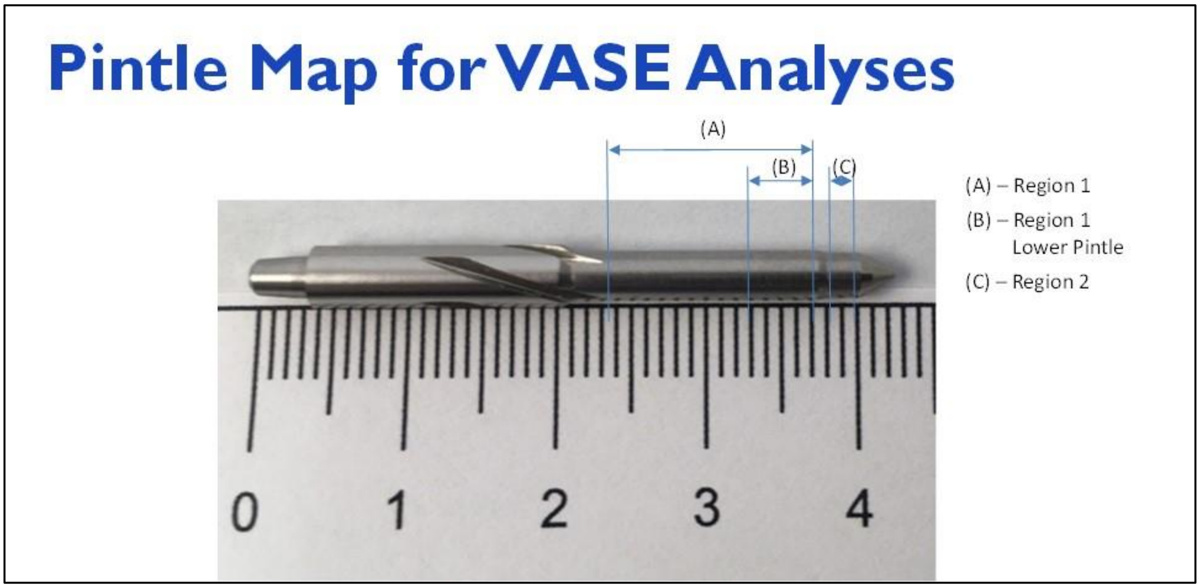


Figure 4. Injector Needle Showing Regions of Analysis (scale is millimeter/centimeter)

4.2 Deposit Measurement Results for Proof Tests

A total of 13 injector rig proof tests were completed, as described in Section 3. The pintles from each of the proof tests were analyzed using the VASE. Figure 5 and Figure 6 are plots of the deposit thickness measurement results.

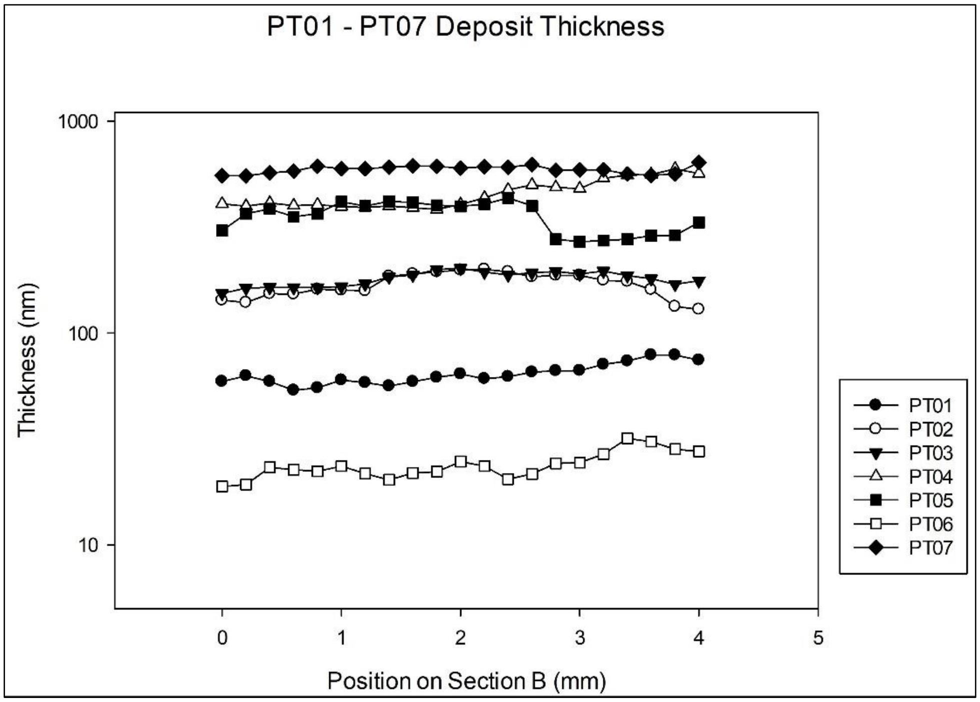


Figure 5. PT01 – PT07 Deposit Thickness Plots

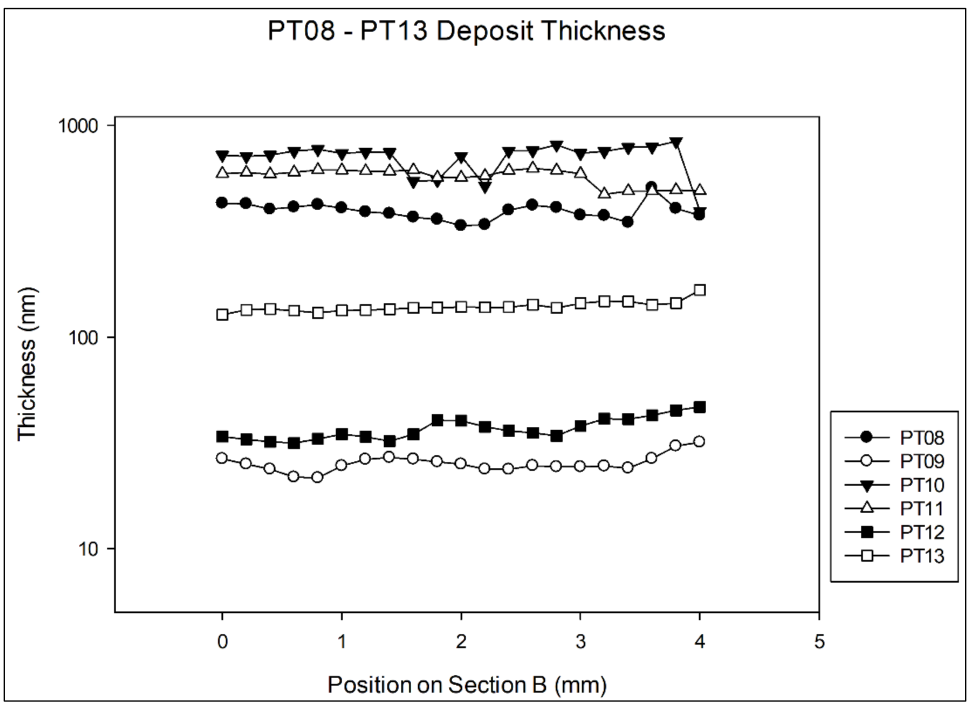


Figure 6. PT08 – PT13 Deposit Thickness Plots

4.3 Deposit Measurement Results for Matrix Tests

Figures 7 – Figure 13 are plots of the deposit thickness measurement results for the matrix tests. Data is presented on a log scale and limited to ten (10) pintles per graph for clarity.

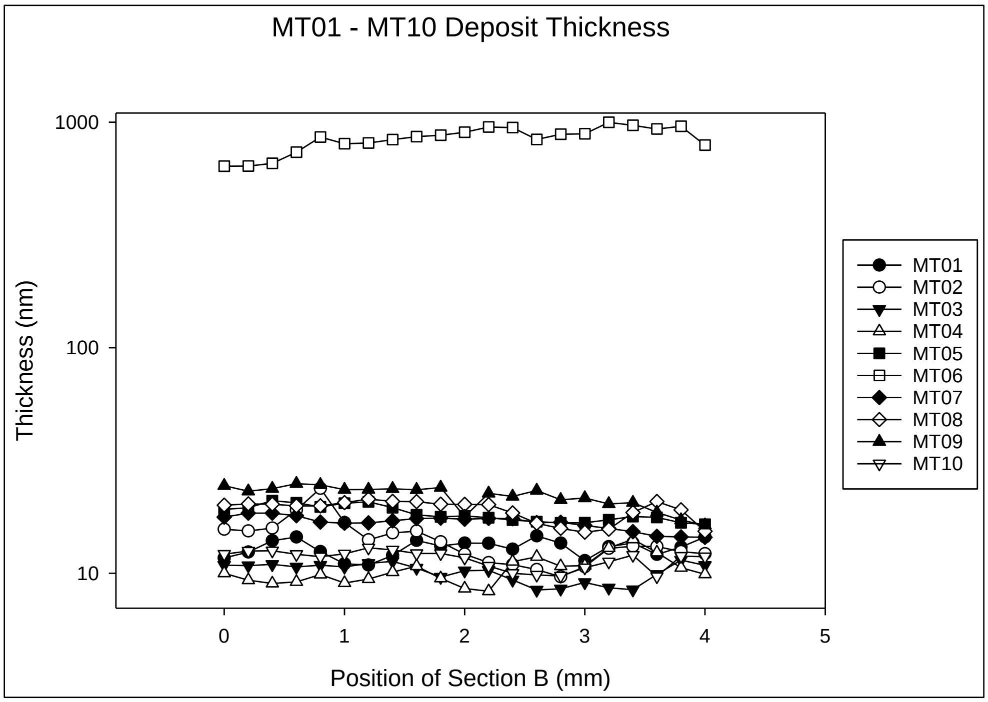


Figure 7. MT01 – MT10 Deposit Thickness Plots

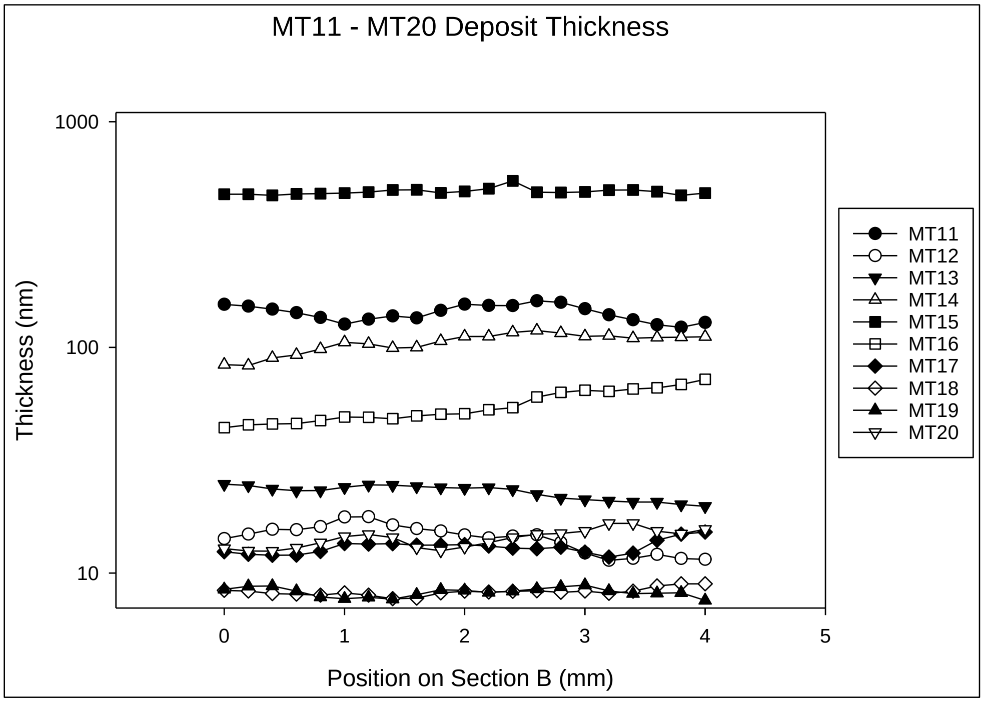


Figure 8. MT11 – MT20 Deposit Thickness Plots

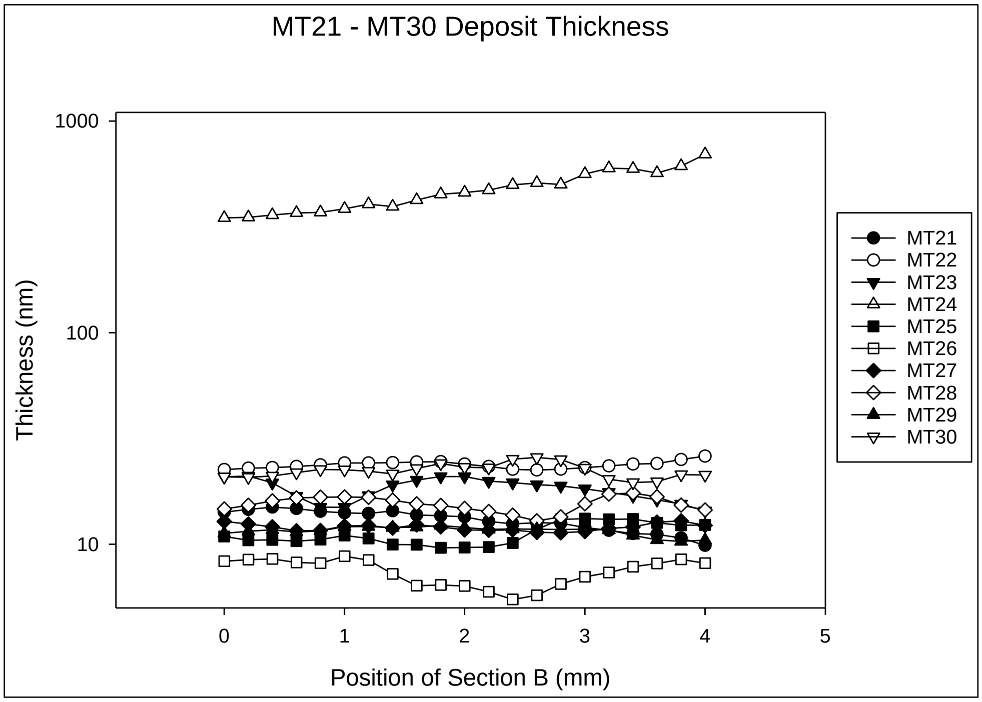


Figure 9. MT21 – MT30 Deposit Thickness Plots

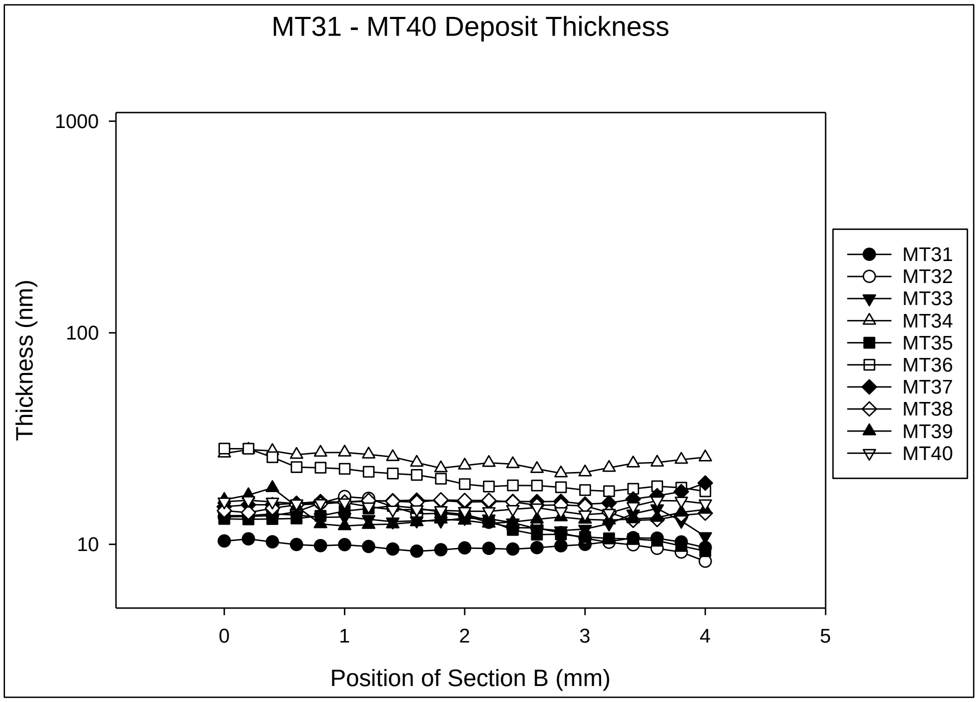


Figure 10. MT31 – MT40 Deposit Thickness Plots

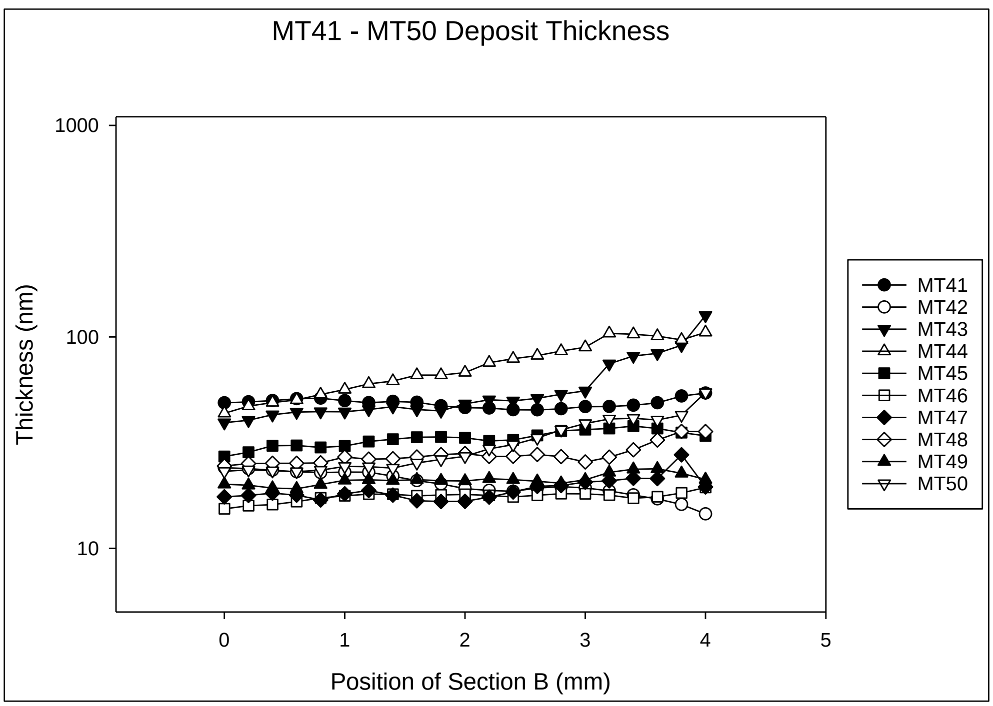


Figure 11. MT41 – MT50 Deposit Thickness Plots

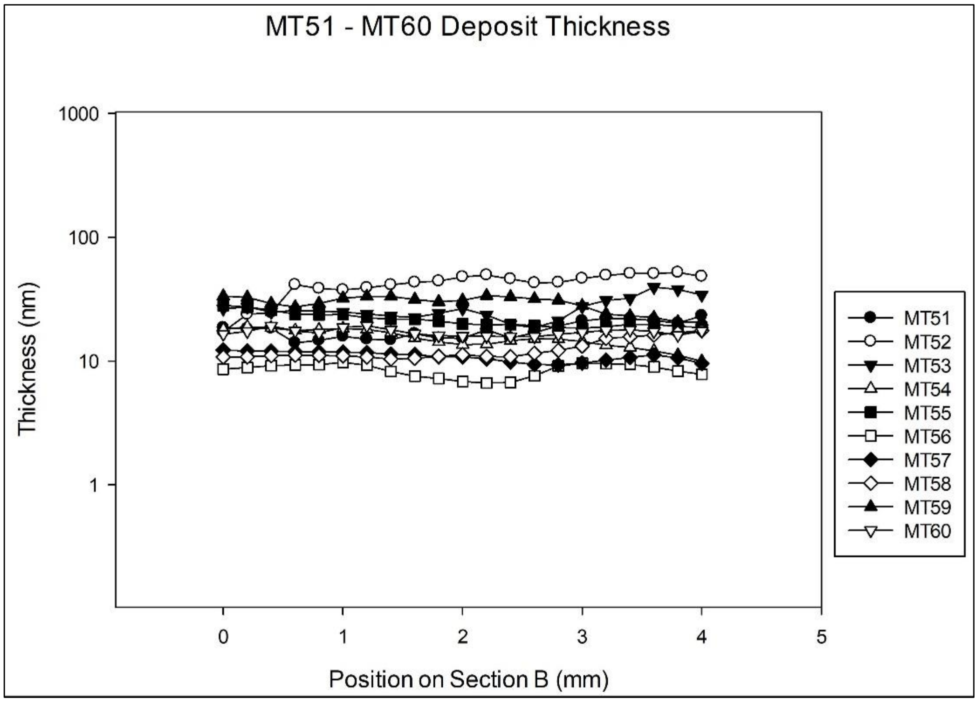


Figure 12. MT51 – MT60 Deposit Thickness Plots

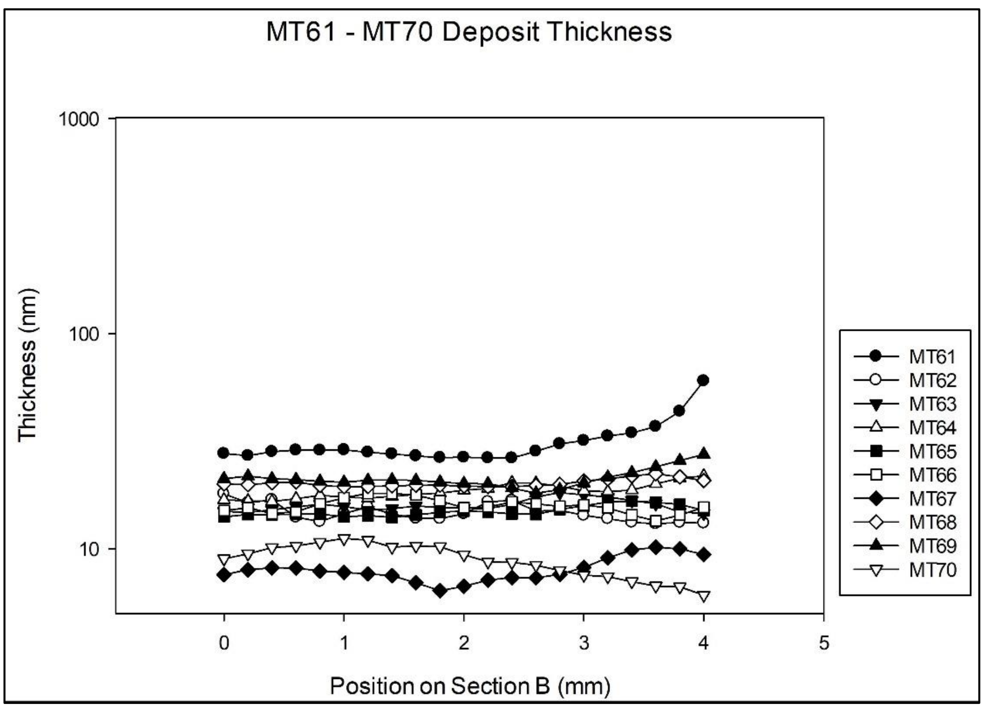


Figure 13. MT61 – MT70 Deposit Thickness Plots

4.4 Statistical Analysis of Deposit Results

4.4.1 Matrix Tests MT01 – MT64

The deposit depth data, for all of the matrix tests, were sent to Chevron for statistical analysis. The report of results for the first 64 tests in provided in Appendix E. In summary, the analysis showed:

- There were no statistical outliers.
- Regarding deposit by location on the injector pintle.
  - No significant axial location differences
  - No significant radial location differences
- Sodium increases deposit thickness
- No significant corrosion inhibitor and cetane number improver differences
- Detergent additive reduces deposit thickness in fuels without biodiesel
- Sodium increases deposit thickness in fuels without
  - Detergent additive
  - Glycerin
  - Mono-acid lubricity additive
- Conductivity additive increases deposit thickness in fuel without
  - Biodiesel
  - Glycerin
- Conductivity additive increases deposit thickness in fuel with mono-acid lubricity additive

4.4.2 Matrix Tests MT65 – MT70

These six tests were conducted as a measure of the test method repeatability. The tests fuels used in these analyses were chosen by the deposit panel. The results from these six tests were included in a separate statistical analysis conducted by Chevron statistician J. Martinez. The full presentation of the results is in Appendix E.

The results of the statistical analysis are summarized as follows (see presentation in Appendix E for full report):

"Based upon the estimated standard deviation (RMSE) and repeatability (r), there is no significant difference between deposit thickness results of

5nm and 14nm, or

10nm and 50nm, or

15nm and 140nm"

4.5 Matrix Deposit FTIR Results

Each pintle was scanned using an attenuated total reflectance (ATR) cell on a Bruker Fourier transform infrared spectrometer (FTIR). The FTIR spectra for the deposits on each pintle are given in Appendix C. As shown earlier in this report, the levels of deposits on the pintles varied greatly. For this reason, the FTIR spectra also vary widely. Some of the spectra give very little useful information. SwRI agreed not to analyze the additives used in this project and therefore conducted no analysis of the FTIR spectra. Any analysis of the FTIR spectra is left to the reader.

5.0 SUMMARY AND CONCLUSIONS

The objective of this CRC project was to establish and demonstrate a new system to evaluate internal diesel injector deposits. This system is a combination of an injector deposit test rig and a novel, spectroscopic technique to measure deposit thickness. The project was not designed to be a comprehensive study of the factors that affect injector deposit formation. The following is a summary of the results of CRC project DP-04-17.

- A new IDID test system, based on previously published work, was assembled.
- Thirteen tests were conducted to demonstrate that the test methodology could rank fuels similarly to results from previous rig and engine tests. The proof tests demonstrated: 1) Test rig capability to discriminate between fuels with and without contaminants/additives. 2) Capability to discriminate between high and normal additive levels. 3) Discrimination was demonstrated using both visual rating and VASE deposit thickness measurement methods. 4) Longer rig run time (21 hr vs. 7 hr) produced thicker deposits for fuel with normal additive/contaminant treat rates, as expected. 5) Discrimination between additive/contaminant levels was demonstrated at both 21 hr and 7 hr run times.
- Seventy tests were conducted using fuels blended to a designed experimental plan. The fuels were blends of a base diesel fuel (clay-treated to remove additives) and combinations of eight different contaminants and/or fuel additives.
- Using the Variable Angle Spectroscopic Ellipsometer (VASE), pintle deposits as thin as 10 nanometers were measurable. Deposits of this thickness are not discernable to the eye.
- Statistical analysis of the VASE/deposit results showed:
    - There were no statistical outliers.
    - Regarding deposit by location on the injector pintle
        - No significant axial location differences
        - No significant radial location differences
    - Sodium increases deposit thickness
    - No significant corrosion inhibitor and cetane number improver differences
    - Detergent additive reduces deposit thickness in fuels without biodiesel

- Sodium increases deposit thickness in fuels without
  - Detergent additive
  - Glycerin
  - Mono-acid lubricity additive
- Conductivity additive increases deposit thickness in fuel without
  - Biodiesel
  - Glycerin
- Conductivity additive increases deposit thickness in fuel with mono-acid lubricity additive

- Statistical analysis of the results of the final six tests showed:
  - Based upon the estimated standard deviation (RMSE) and repeatability (r), there is no significant difference between deposit thickness results of

    5nm and 14nm, or

    10nm and 50nm, or

    15nm and 140nm.
  - This is a measure of the repeatability based on the 9 data points (3 repeats of 3 fuels). The deposits are transformed since the variability of deposits increase as deposits increase. So different levels of deposits will have a different magnitude of differences as you increase the deposits. This is an initial measure of test precision (repeatability) and more data is needed to really define this.

APPENDIX A

TEST RIG OPERATING DATA

Test Number	Average Rail Pressure (bar)	Standard Deviation Rail Pressure (bar)	Average Fuel Supply Temperature (°C)	Standard Deviation Fuel Supply Temperature (°C)	Average Fuel Inlet Temperature (°C)	Standard Deviation Fuel Inlet Temperature (°C)	Average Pump Drain Return Temperature (°C)	Standard Deviation Pump Drain Return Temperature (°C)	Average Fuel Rail Return Temperature (°C)	Standard Deviation Fuel Rail Return Temperature (°C)	Average Injector Return Temperature (°C)	Standard Deviation Injector Return Temperature (°C)	Average Injector Nozzle Nut Temperature 1 (°C)	Standard Deviation Injector Nozzle Nut Temperature 1 (°C)	Average Injector Nozzle Nut Temperature 2 (°C)	Standard Deviation Injector Nozzle Nut Temperature 2 (°C)	Overall Average Injector Nozzle Nut Temperature (°C)	Overall Standard Deviation Injector Nozzle Nut Temperature (°C)	Average Pump Speed (RPM)	Standard Deviation Pump Speed (RPM)	Fuel Weight Test Start (g)	Fuel Weight Test End (g)	Cumulative Fuel Injected (g)
CL18_2520-MT01	1800.0	0.56	29.35	0.26	30.00	0.19	53.77	0.66	135.0	0.35	115.7	2.90	200.0	0.38	200.0	0.39	200.0	0.36	1750.0	0.30	4373.6	2249.6	2124.0
CL18_2521-MT02	1800.0	0.50	29.40	0.25	30.00	0.19	53.32	0.42	134.9	0.33	116.6	2.94	204.5	0.62	195.5	0.57	200.0	0.35	1750.0	0.30	4426.6	2299.2	2127.4
CL18_2527-MT03	1800.0	0.52	29.65	0.26	30.00	0.20	52.74	0.24	134.5	0.16	128.2	0.91	189.1	0.48	210.9	0.49	200.0	0.36	1750.0	0.31	4400.2	2303.8	2096.4
CL18_2528-MT04	1800.0	0.80	29.66	0.23	30.00	0.16	52.43	0.40	133.4	0.26	105.0	3.00	197.0	0.33	203.0	0.35	200.0	0.31	1750.0	0.31	4529.4	2390.6	2138.8
CL18_2529-MT05	1800.0	0.63	29.52	0.21	30.00	0.16	52.67	0.39	133.9	0.51	130.4	1.61	200.5	0.43	199.5	0.34	200.0	0.33	1750.0	0.32	4518.6	2428.8	2089.8
CL18_2544-MT06	1800.0	0.77	29.39	0.21	29.99	0.17	53.56	0.33	134.8	0.26	130.5	1.67	204.5	0.33	195.5	0.42	200.0	0.30	1750.0	0.31	4392.4	2297.0	2095.4
CL18_2549-MT07	1800.0	0.74	29.42	0.22	30.00	0.17	53.45	0.23	133.8	0.32	117.4	2.52	198.2	0.62	201.8	0.59	200.0	0.49	1750.0	0.30	4487.4	2378.8	2108.6
CL18_2551-MT08	1800.0	0.74	29.45	0.21	30.00	0.17	53.90	0.27	134.5	0.22	109.1	2.12	194.8	0.64	205.1	0.71	200.0	0.61	1750.0	0.31	4602.6	2489.2	2113.4
CL18_2552-MT09	1800.0	0.93	29.51	0.17	30.00	0.12	53.58	0.32	133.8	0.29	101.4	3.22	195.4	0.41	204.7	0.51	200.0	0.36	1750.0	0.30	4424.6	2315.8	2108.8
CL18_2571-MT10	1800.0	0.79	29.72	0.16	30.00	0.14	53.04	0.40	134.0	0.17	111.9	1.51	197.2	1.18	202.7	1.20	199.9	1.18	1750.0	0.30	4500.6	2378.8	2121.8
CL18_2572-MT11	1800.0	1.65	29.49	0.21	30.00	0.17	53.00	0.35	133.6	0.25	105.9	3.02	196.6	0.52	203.4	0.61	200.0	0.50	1750.0	0.30	4427.4	2220.8	2206.6
CL18_2573-MT12	1800.0	0.50	29.54	0.16	30.00	0.13	52.65	0.37	134.4	0.19	129.2	1.50	196.8	0.50	203.2	0.55	200.0	0.29	1750.0	0.30	3939.2	1851.6	2087.6
CL18_2588-MT13	1800.0	0.92	29.60	0.22	30.00	0.15	53.08	0.26	133.6	0.27	110.8	3.75	201.9	0.49	198.1	0.46	200.0	0.45	1750.0	0.30	4149.6	2063.8	2085.8
CL18_2605-MT14	1800.0	0.74	29.79	0.18	30.00	0.15	51.99	0.20	133.9	0.22	128.8	3.43	207.5	0.96	192.4	0.70	200.0	0.65	1750.0	0.31	4023.2	1939.4	2083.8
CL18_2606-MT15	1800.0	0.84	29.70	0.22	30.00	0.16	52.07	0.28	133.4	0.32	110.2	4.71	194.8	1.34	205.0	1.30	199.9	1.27	1750.0	0.31	4134.0	2058.2	2075.8
CL18_2624-MT16	1800.0	2.56	29.64	0.24	30.00	0.16	52.38	0.19	133.8	0.24	116.0	4.75	199.4	0.63	200.6	0.63	200.0	0.54	1750.0	0.31	4229.6	2097.0	2132.6
CL18_2625-MT17	1800.0	0.63	29.49	0.21	30.00	0.14	52.67	0.22	134.1	0.25	116.2	4.74	197.3	1.39	202.5	1.44	199.9	1.38	1750.0	0.30	4022.4	1901.8	2120.6
CL18_2638-MT18	1800.0	0.57	29.54	0.19	30.00	0.15	50.99	0.20	133.6	0.23	115.4	4.21	191.9	0.73	208.1	0.80	200.0	0.68	1750.0	0.30	4088.0	1962.0	2126.0
CL18_2647-MT19	1800.0	0.70	29.61	0.24	30.00	0.15	53.74	0.42	134.4	0.41	117.0	6.05	197.3	1.03	202.6	0.93	200.0	0.96	1750.0	0.30	4107.8	2005.8	2102.0
CL18_2648-MT20	1800.0	0.82	29.61	0.23	30.00	0.14	52.14	0.29	133.7	0.43	127.8	4.45	192.1	1.13	206.4	1.19	199.3	1.14	1750.0	0.31	4106.8	2007.8	2099.0
CL18_2649-MT21	1800.0	0.78	29.66	0.23	30.00	0.14	52.92	0.18	134.2	0.31	118.3	6.93	196.3	1.55	203.4	1.57	199.8	1.50	1750.0	0.31	4078.2	2001.0	2077.2
CL18_2650-MT22	1800.0	3.81	29.44	0.21	30.00	0.14	52.89	0.49	133.8	0.40	120.5	5.08	207.0	0.74	192.9	0.64	200.0	0.63	1750.0	0.31	3994.4	1914.8	2079.6
CL18_2685-MT23	1799.8	3.33	30.40	1.92	30.88	1.71	54.09	1.84	135.3	1.23	128.2	7.65	193.5	4.20	200.6	4.18	197.0	4.16	1750.0	0.31	4136.4	1928.2	2208.2
CL18_2686-MT24	1799.9	1.96	29.48	0.21	30.00	0.14	52.48	0.26	134.3	0.28	120.5	5.24	204.8	2.15	194.7	1.90	199.8	1.99	1750.0	0.30	4106.4	1998.2	2108.2
CL18_2690-MT25	1799.9	1.40	29.57	0.22	30.00	0.15	52.75	0.26	134.1	0.35	108.4	4.67	193.8	2.25	205.9	2.07	199.8	2.13	1750.0	0.31	4093.6	1953.4	2140.2
CL18_2691-MT26	1800.0	1.00	29.66	0.23	30.00	0.16	50.77	0.16	133.5	0.22	108.5	3.68	203.3	0.84	196.6	0.77	200.0	0.77	1750.0	0.31	4164.8	2088.2	2076.6
CL18_2703-MT27	1800.0	1.10	29.47	0.22	30.00	0.13	52.33	0.20	134.5	0.32	129.6	3.54	196.0	1.74	197.3	1.73	196.6	1.72	1750.0	0.30	4063.8	1917.8	2146.0
CL18_2704-MT28	1800.0	1.76	29.45	0.20	30.00	0.13	53.11	0.20	134.5	0.33	119.2	5.18	195.8	0.61	204.1	0.70	200.0	0.61	1750.0	0.31	4065.0	1917.8	2147.2
CL18_2705-MT29	1800.0	1.80	29.56	0.19	30.00	0.14	52.18	0.18	134.3	0.32	126.8	3.75	200.1	1.43	199.6	0.99	199.8	1.11	1750.0	0.31	4070.2	1953.0	2117.2
CL18_2714-MT30	1800.0	1.14	29.60	0.22	30.00	0.15	52.05	0.36	133.5	0.34	107.1	4.15	193.5	0.51	206.6	0.61	200.0	0.47	1750.0	0.30	4108.8	1985.4	2123.4
CL18_2724-MT31	1800.0	1.04	29.63	0.24	30.00	0.18	52.49	0.38	133.8	0.36	106.4	4.42	201.8	2.06	197.8	1.99	199.8	2.02	1750.0	0.31	4151.8	2066.4	2085.4
CL18_2725-MT32	1800.0	0.76	29.53	0.21	30.00	0.14	53.16	0.29	134.2	0.32	120.2	4.22	196.2	0.66	203.7	0.74	200.0	0.67	1750.0	0.31	4068.2	1955.0	2113.2
CL18_2726-MT33	1800.0	0.98	29.56	0.23	30.00	0.14	52.69	0.29	134.1	0.37	118.1	5.50	191.3	0.49	208.7	0.56	200.0	0.40	1750.0	0.32	4159.2	2058.0	2101.2
CL18_2737-MT34	1800.0	0.69	29.70	0.19	30.00	0.13	52.62	0.17	133.8	0.28	119.2	4.31	198.6	1.10	201.2	1.10	199.9	1.09	1750.0	0.32	4082.6	1968.8	2113.8
CL18_2750-MT35	1800.0	0.67	29.57	0.25	30.00	0.17	52.24	0.31	134.3	0.34	129.2	3.44	204.3	1.81	192.9	1.41	198.6	1.57	1750.0	0.31	4156.6	2019.8	2136.8
CL18_2751-MT36	1800.0	0.63	29.59	0.21	30.00	0.14	52.87	0.49	134.1	0.37	112.7	3.71	193.7	1.34	206.1	1.44	199.9	1.32	1750.0	0.32	4096.8	2007.4	2089.4
CL18_2752-MT37	1800.0	0.71	29.57	0.21	30.00	0.14	53.25	0.33	134.3	0.34	117.2	4.21	197.7	1.72	202.1	1.86	199.9	1.77	1750.0	0.32	4039.0	1892.2	2146.8
CL18_2753-MT38	1800.0	0.56	29.51	0.21	30.00	0.14	52.87	0.26	134.6	0.40	130.8	3.76	199.1	2.27	195.6	1.21	197.4	1.70	1750.0	0.29	4085.4	1999.0	2086.4
CL18_2799-MT39	1800.0	0.74	29.63	0.20	30.00	0.14	52.12	0.35	133.4	0.32	110.4	3.93	194.8	0.92	205.1	0.90	200.0	0.87	1750.0	0.31	4195.0	2096.2	2098.8
CL18_2800-MT40	1800.0	0.69	29.69	0.19	30.00	0.15	52.41	0.29	133.2	0.28	112.1	3.91	199.3	1.06	200.6	1.17	199.9	1.10	1750.0	0.31	4157.2	2049.6	2107.6
CL18_2801-MT41	1800.0	0.71	29.65	0.21	30.00	0.14	52.41	0.24	133.3	0.33	118.2	3.25	203.4	0.83	196.6	0.75	200.0	0.77	1750.0	0.32	4204.2	2116.6	2087.6
CL18_2802-MT42	1800.0	0.71	29.57	0.21	30.00	0.14	53.47	0.36	134.2	0.33	116.1	3.27	201.5	1.90	198.1	1.82	199.8	1.85	1750.0	0.32	3851.4	1708.6	2142.8
CL18_2835-MT43	1800.0	0.75	29.53	0.22	30.00	0.14	52.67	0.25	133.8	0.29	112.2	3.33	203.5	1.10	196.4	1.07	199.9	1.07	1750.0	0.32	4157.0	2040.8	2116.2
CL18_2836-MT44	1799.9	0.60	29.55	0.23	30.00	0.14	52.60	0.20	134.2	0.35	124.2	5.21	201.7	1.39	198.1	1.21	199.9	1.07	1750.0	0.32	4093.0	1983.8	2109.2
CL18_2837-MT45	1800.0	0.67	29.67	0.21	30.00	0.14	50.94	0.51	132.7	0.43	109.4	4.74	197.5	0.61	202.5	0.60	200.0	0.59	1750.0	0.32	4152.0	2032.8	2119.2
CL18_2838-MT46	1799.9	0.79	29.63	0.44	29.97	0.38	50.92	0.47	133.0	0.40	113.1	5.38	198.7	1.88	201.0	1.77	199.9	1.81	1750.0	0.30	4268.0	2117.0	2151.0
CL18_2883-MT47	1799.9	0.78	29.62	0.21	30.00	0.17	55.02	3.86	134.4	1.37	110.5	5.04	191.9	0.79	208.1	0.80	200.0	0.54	1750.0	0.31	4207.0	2087.8	2119.2
CL18_2884-MT48	1800.0	0.78	29.51	0.22	30.00	0.17	52.97	0.50	134.1	0.43	119.0	5.23	199.2	2.11	200.3	2.06	199.8	2.08	1750.0	0.31	4145.0	2018.4	2126.6
CL18_2885-MT49	1800.0	0.70	29.69	0.17	30.00	0.15	50.02	0.34	133.3	0.34	112.3	4.23	198.2	1.12	201.7	1.27	199.9	1.18	1750.0	0.31	4072.4	1971.2	2101.2
CL18_2886-MT50	1800.0	0.92	29.47	0.26	30.00	0.16	53.03	0.26	134.8	0.43	130.2	3.69	202.1	1.53	197.6	0.90	199.8	1.16	1750.0	0.30	4137.2	2009.8	2127.4
CL18_2910-MT51	1800.0	0.85	29.86	0.19	30.00	0.16	53.04	0.33	134.1	0.32	119.9	4.41	194.4	0.83	205.5	0.72	200.0	0.68	1750.0	0.31	4097.2	1945.0	2152.2
CL18_2911-MT52	1800.0	0.55	29.88	0.21	30.00	0.15	51.62	0.20	133.6	0.25	105.1	3.45	200.4	0.78	199.5	0.71	200.0	0.74	1750.0	0.31	4165.0	2048.2	2116.8
CL18_2912-MT53	1800.0	0.54	29.86	0.18	30.01	0.15	51.71	0.23	133.2	0.27	104.1	5.39	196.0	0.62	204.0	0.65	200.0	0.53	1750.0	0.31	4045.4	1929.2	2116.2
CL18_2915-MT54	1800.0	0.74	29.64	0.20	30.00	0.16	53.10	0.37	134.9	0.44	130.8	3.70	209.2	1.81	188.9	2.00	199.0	1.89	1750.0	0.31	4164.0	2046.6	2117.4
CL18_2927-MT55	1800.0	0.60	29.54	0.23	30.01	0.17	53.00	0.47	133.9	0.36	107.5	3.47	197.4	1.24	202.5	1.15	199.9	1.17	1750.0	0.30	4172.6	2064.0	2108.6
CL18_2928-MT56	1800.0	0.62	29.57	0.22	30.00	0.17	53.84	0.32	134.6	0.30	121.5	5.85	195.6	1.11	204.3	1.09	200.0	1.01	1750.0	0.30	4160.8	2056.0	2104.8
CL18_2929-MT57	1800.0	0.55	29.67	0.17	30.00	0.15	52.98	0.27	133.6	0.19	111.4	2.30	206.9	0.78	193.1	0.63	200.0	0.64	1750.0	0.3	4116.6	1997.6	2119.0
CL18_2930-MT58	1800.0	0.60	29.48	0.20	30.00	0.15	52.86	0.28	134.7	0.33	128.6	2.78	203.4	1.39	196.4	0.93	199.9	1.07	1750.0	0.3	4084.2	2012.0	2072.2
CL18_2951-MT59	1800.0	0.60	29.55	0.20	30.00	0.16	53.05	0.32	134.3	0.30	114.0	5.23	196.6	0.78	203.3	0.84	200.0	0.79	1750.0	0.3	4164.0	2013.4	2150.6
CL18_2952-MT60	1800.0	0.65	29.52	0.23	30.00	0.15	53.21	0.44	133.9	0.50	116.7	5.02	190.1	1.05	209.9	1.06	200.0	0.92	1750.0	0.3	4120.4	2020.2	2100.2
CL18_2953-MT61	1800.0	0.91	29.70	0.22	30.00	0.16	49.86	0.21	133.4	0.35	127.6	3.46	195.9	1.80	203.8	1.28	199.9	1.42	1750.0	0.3	3916.0	1834.4	2081.6
CL18_2954-MT62	1800.0	0.63	29.86	0.52	30.11	0.47	53.02	0.53	134.0	0.48	121.1	3.25	199.4	1.15	200.5	0.84	199.9	0.96	1750.0	0.3	4175.0	2029.6	2145.4
CL18_2971-MT63	1800.0	0.59	29.71	0.22	30.00	0.17	53.26	0.31	134.0	0.33	116.1	3.99	199.2	1.64	200.5	1.66	199.8	1.64	1750.0	0.3	4106.6	2014.8	2091.8
CL18_2972-MT64	1800.0	0.52	29.71	0.23	30.00	0.16	52.67	0.34	133.4	0.39	113.6	3.58	201.0	1.05	198.9	1.05	199.9	1.04	1750.0	0.3	4231.6	2094.0	2137.6
CL19_3475-MT65	1800.0	0.63	30.10	0.17	30.00	0.14	50.53	0.22	132.5	0.17	106.1	2.59	198.4	0.59	201.6	0.63	200.0	0.60	1750.0	0.3	4059.0	1952.8	2106.2
CL19_3500-MT66	1800.0	0.57	30.06	0.17	30.00	0.14	51.03	0.22	132.7	0.20	106.4	2.00	196.2	0.43	203.8	0.48	200.0	0.42	1750.0	0.3	3993.6	1897.2	2096.4
CL19_3501-MT67	1800.0	0.57	30.03	0.18	30.00	0.14	51.62	0.20	133.0	0.21	117.2	3.01	190.3	0.52	209.7	0.56	200.0	0.38	1750.0	0.3	4118.0	2030.4	2087.6
CL19_3518-MT68	1800.0	0.61	30.07	0.17	30.00	0.14	51.84	0.22	133.1	0.24	104.5	3.29	202.3	0.56	197.7	0.53	200.0	0.53	1750.0	0.3	4120.6	2006.6	2114.0
CL19_3560-MT69	1800.0	0.64	30.16	0.16	30.00	0.12	52.45	0.33	133.3	0.17	126.2	0.77	189.8	0.31	210.2	0.32	200.0	0.18	1750.0	0.3	4068.6	1915.2	2153.4
CL19_3561-MT70	1800.0	0.55	30.37	0.22	30.00	0.13	52.03	0.26	132.8	0.31	100.5	3.20	199.6	0.59	200.4	0.59	200.0	0.58	1750.0	0.3	4033.8	1894.6	2139.2

APPENDIX B

MATRIX TESTS – FUEL BLEND MATRIX AND PINTLE CODES

Matrix		Factors (Additives)								
Test No.	Pattern	Biodiesel	Sodium	Glycerin	Corrosion Inibitor	Lubricity Additive	Injector Sticking Additive	Cetane Number Improver	Conductivity Additive	Number of Additives
1	−+−−−+−−	No	Yes	No	No	No	Yes	No	No	2
2	−−−+−+−+	No	No	No	Yes	No	Yes	No	Yes	3
3	−++++++−	No	Yes	Yes	Yes	Yes	Yes	Yes	No	6
4	+−−+−−++	Yes	No	No	Yes	No	No	Yes	Yes	4
5	++−−+++−	Yes	Yes	No	No	Yes	Yes	Yes	No	5
6	−+−++−++	No	Yes	No	Yes	Yes	No	Yes	Yes	5
7	+−−+−+−−	Yes	No	No	Yes	No	Yes	No	No	3
8	−+−−++++	No	Yes	No	No	Yes	Yes	Yes	Yes	5
9	++++++++	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	8
10	−++−+−+−	No	Yes	Yes	No	Yes	No	Yes	No	4
11	+−−−−−−−	Yes	No	No	No	No	No	No	No	1
12	−−++−−−−	No	No	Yes	Yes	No	No	No	No	2
13	+−+−+++−	Yes	No	Yes	No	Yes	Yes	Yes	No	5
14	−+++−−+−	No	Yes	Yes	Yes	No	No	Yes	No	4
15	++−+−++−	Yes	Yes	No	Yes	No	Yes	Yes	No	5
16	−++++−−+	No	Yes	Yes	Yes	Yes	No	No	Yes	5
17	−−+−+−−−	No	No	Yes	No	Yes	No	No	No	2
18	++−+−−−+	Yes	Yes	No	Yes	No	No	No	Yes	4
19	−−−++++−	No	No	No	Yes	Yes	Yes	Yes	No	4
20	+−+++−+−	Yes	No	Yes	Yes	Yes	No	Yes	No	5
21	−−+−−+−−	No	No	Yes	No	No	Yes	No	No	2
22	++++−+−−	Yes	Yes	Yes	Yes	No	Yes	No	No	5
23	−−++−+++	No	No	Yes	Yes	No	Yes	Yes	Yes	5
24	−+−−−−++	No	Yes	No	No	No	No	Yes	Yes	3
25	+−−++−−−	Yes	No	No	Yes	Yes	No	No	No	3
26	−−−+−−+−	No	No	No	Yes	No	No	Yes	No	2
27	−+++−+−+	No	Yes	Yes	Yes	No	Yes	No	Yes	5
28	+−−−−+++	Yes	No	No	No	No	Yes	Yes	Yes	4
29	−−−−−−−+	No	No	No	No	No	No	No	Yes	1
30	+++−+−++	Yes	Yes	Yes	No	Yes	No	Yes	Yes	6
31	−−+++−++	No	No	Yes	Yes	Yes	No	Yes	Yes	5
32	−+−+−+++	No	Yes	No	Yes	No	Yes	Yes	Yes	5
33	−+−+++−−	No	Yes	No	Yes	Yes	Yes	No	No	4
34	+−++−++−	Yes	No	Yes	Yes	No	Yes	Yes	No	5
35	−−−−+−+−	No	No	No	No	Yes	No	Yes	No	2
36	−++−++−+	No	Yes	Yes	No	Yes	Yes	No	Yes	5
37	−+−−+−−−	No	Yes	No	No	Yes	No	No	No	2
38	+−−−+−++	Yes	No	No	No	Yes	No	Yes	Yes	4
39	+−+−+−−+	Yes	No	Yes	No	Yes	No	No	Yes	4
40	+−+−−−+−	Yes	No	Yes	No	No	No	Yes	No	3
41	+++−−−−−	Yes	Yes	Yes	No	No	No	No	No	3
42	−−++++−−	No	No	Yes	Yes	Yes	Yes	No	No	4
43	++−−−−+−	Yes	Yes	No	No	No	No	Yes	No	3
44	−++−−−−+	No	Yes	Yes	No	No	No	No	Yes	3
45	++−−−+−+	Yes	Yes	No	No	No	Yes	No	Yes	4
46	++++−−++	Yes	Yes	Yes	Yes	No	No	Yes	Yes	6
47	+−++++−+	Yes	No	Yes	Yes	Yes	Yes	No	Yes	6
48	+++−−+++	Yes	Yes	Yes	No	No	Yes	Yes	Yes	6
49	++−+++−+	Yes	Yes	No	Yes	Yes	Yes	No	Yes	6
50	−−−++−−+	No	No	No	Yes	Yes	No	No	Yes	3
51	−−+−++++	No	No	Yes	No	Yes	Yes	Yes	Yes	5
52	−+−+−−−−	No	Yes	No	Yes	No	No	No	No	2
53	+++++−−−	Yes	Yes	Yes	Yes	Yes	No	No	No	5
54	−−−−++−+	No	No	No	No	Yes	Yes	No	Yes	3
55	+++−++−−	Yes	Yes	Yes	No	Yes	Yes	No	No	5
56	−−−−−++−	No	No	No	No	No	Yes	Yes	No	2
57	+−−−++−−	Yes	No	No	No	Yes	Yes	No	No	3
58	−−+−−−++	No	No	Yes	No	No	No	Yes	Yes	3
59	−++−−++−	No	Yes	Yes	No	No	Yes	Yes	No	4
60	+−−+++++	Yes	No	No	Yes	Yes	Yes	Yes	Yes	6
61	++−−+−−+	Yes	Yes	No	No	Yes	No	No	Yes	4
62	+−++−−−+	Yes	No	Yes	Yes	No	No	No	Yes	4
63	+−+−−+−+	Yes	No	Yes	No	No	Yes	No	Yes	4
64	++−++−+−	Yes	Yes	No	Yes	Yes	No	Yes	No	5
65	−+++−−+−	No	Yes	Yes	Yes	No	No	Yes	No	4
66	−−+++−++	No	No	Yes	Yes	Yes	No	Yes	Yes	5
67	++−++−+−	Yes	Yes	No	Yes	Yes	No	Yes	No	5
68	++−++−+−	Yes	Yes	No	Yes	Yes	No	Yes	No	5
69	−−+++−++	No	No	Yes	Yes	Yes	No	Yes	Yes	5
70	−+++−−+−	No	Yes	Yes	Yes	No	No	Yes	No	4

Injector and Pintle Identification for Rig Matrix Tests

CRC Run #	SwRI Run #	SwRI Fuel #	SwRI Test #	Injector Serial Number	Test Date	Pintle Code
1	MT01	CL18-2520	CL18_2520-MT01	1792KL25F54	6/14/2018	21
2	MT02	CL18-2521	CL18_2521-MT02	1689KL25F64	6/15/2018	22
3	MT03	CL18-2527	CL18_2527-MT03	1798KL25F64	6/20/2018	23
4	MT04	CL18-2528	CL18_2528-MT04	1679KL25F64	6/21/2018	24
5	MT05	CL18-2529	CL18_2529-MT05	1645KL25F64	6/22/2018	25
6	MT06	CL18-2544	CL18_2544-MT06	1665KL25F54	6/27/2018	26
7	MT07	CL18-2549	CL18_2549-MT07	1593KL25F44	6/28/2018	27
8	MT08	CL18-2551	CL18_2551-MT08	1701KL25F64	6/29/2018	28
9	MT09	CL18-2552	CL18_2552-MT09	1660KL25F44	6/30/2018	29
10	MT10	CL18-2571	CL18_2571-MT10	1671KL25F54	7/4/2018	30
11	MT11	CL18-2572	CL18_2572-MT11	1644KL25F44	7/5/2018	31
12	MT12	CL18-2573	CL18_2573-MT12	1793KL25F64	7/6/2018	32
13	MT13	CL18-2588	CL18_2588-MT13	1974KL25F44	7/7/2018	33
14	MT14	CL18-2605	CL18_2605-MT14	1736KL25F64	7/9/2018	34
15	MT15	CL18-2606	CL18_2606-MT15	1687KL25F44	7/10/2018	35
16	MT16	CL18-2624	CL18_2624-MT16	1742KL25F64	7/11/2018	36
17	MT17	CL18-2625	CL18_2625-MT17	1693KL25F44	7/14/2018	37
18	MT18	CL18-2638	CL18_2638-MT18	1605KL25F44	7/15/2018	38
19	MT19	CL18-2647	CL18_2647-MT19	1766KL25F64	7/18/2018	39
20	MT20	CL18-2648	CL18_2648-MT20	0719JL20F54	7/19/2018	40
21	MT21	CL18-2649	CL18_2649-MT21	1725KL25F64	7/20/2018	41
22	MT22	CL18-2650	CL18_2650-MT22	1810KL25F64	7/21/2018	42
23	MT23	CL18-2685	CL18_2685-MT23	1730KL25F44	7/23/2018	43
24	MT24	CL18-2686	CL18_2686-MT24	1789KL25F54	7/24/2018	44
25	MT25	CL18-2690	CL18_2690-MT25	1809KL25F64	7/25/2018	45
26	MT26	CL18-2691	CL18_2691-MT26	1962KL25F44	7/28/2018	46
27	MT27	CL18-2703	CL18_2703-MT27	1710KL25F44	7/29/2018	47
28	MT28	CL18-2704	CL18_2704-MT28	1739KL25F64	7/30/2018	48
29	MT29	CL18-2705	CL18_2705-MT29	1985KL25F64	7/31/2018	49
30	MT30	CL18-2714	CL18_2714-MT30	1776KL25F44	8/1/2018	50
31	MT31	CL18-2724	CL18_2724-MT31	1963KL25F54	8/6/2018	51
32	MT32	CL18-2725	CL18_2725-MT32	1716KL25F54	8/7/2018	52
33	MT33	CL18-2726	CL18_2726-MT33	1788KL25F44	8/8/2018	53
34	MT34	CL18-2737	CL18_2737-MT34	1699KL25F44	8/10/2018	54
35	MT35	CL18-2750	CL18_2750-MT35	1987KL25F54	8/13/2018	55
36	MT36	CL18-2751	CL18_2751-MT36	1785KL25F54	8/14/2018	56
37	MT37	CL18-2752	CL18_2752-MT37	0721JL20F54	8/15/2018	57
38	MT38	CL18-2753	CL18_2753-MT38	1365KL25F44	8/16/2018	58
39	MT39	CL18-2799	CL18_2799-MT39	1830KL25F64	8/20/2018	59
40	MT40	CL18-2800	CL18_2800-MT40	1961KL25F64	8/21/2018	60

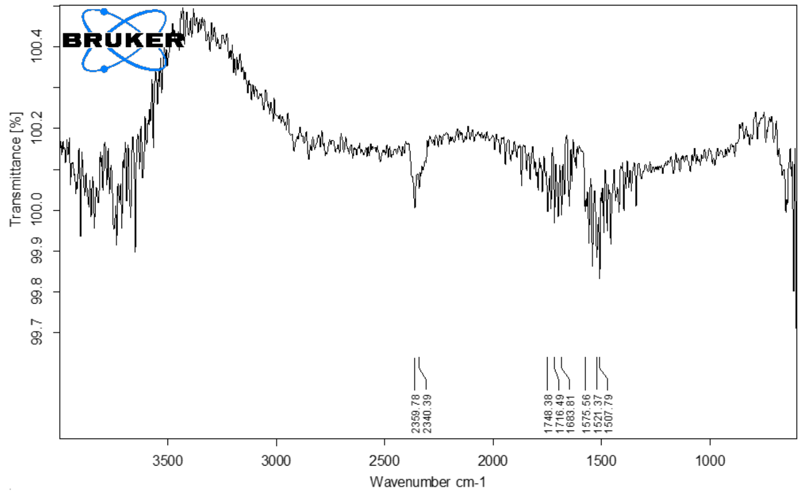
Injector and Pintle Identification for Rig Matrix Tests cont'd

CRC Run #	SwRI Run #	SwRI Fuel #	SwRI Test #	Injector Serial Number	Test Date	Pintle Code
41	MT41	CL18-2801	CL18_2801-MT41	1599KL25F44	8/22/2018	61
42	MT42	CL18-2802	CL18_2802-MT42	1827KL25F54	8/23/2018	62
43	MT43	CL18-2835	CL18_2835-MT43	1767KL25F44	8/27/2018	63
44	MT44	CL18-2836	CL18_2836-MT44	1969KL25F54	8/28/2018	64
45	MT45	CL18-2837	CL18_2837-MT45	1633KL25F64	8/29/2018	65
46	MT46	CL18-2838	CL18_2838-MT46	1986KL25F44	8/30/2018	66
47	MT47	CL18-2883	CL18_2883-MT47	1805KL25F64	9/4/2018	67
48	MT48	CL18-2884	CL18_2884-MT48	1639KL25F44	9/5/2018	68
49	MT49	CL18-2885	CL18_2885-MT49	1512KL25F44	9/6/2018	69
50	MT50	CL18-2886	CL18_2886-MT50	1751KL25F64	9/7/2018	70
51	MT51	CL18-2910	CL18_2910-MT51	1653KL25F44	9/10/2018	71
52	MT52	CL18-2911	CL18_2911-MT52	1954KL25F54	9/11/2018	72
53	MT53	CL18-2912	CL18_2912-MT53	1800KL25F64	9/12/2018	73
54	MT54	CL18-2915	CL18_2915-MT54	1784KL25F64	9/13/2018	74
55	MT55	CL18-2927	CL18_2927-MT55	1885KL25F44	9/18/2018	75
56	MT56	CL18-2928	CL18_2928-MT56	1356KL25F44	9/19/2018	76
57	MT57	CL18-2929	CL18_2929-MT57	1829KL25F54	9/20/2018	77
58	MT58	CL18-2930	CL18_2930-MT58	2899LL14F64	9/21/2018	78
59	MT59	CL18-2951	CL18_2951-MT59	1702KL25F44	9/24/2018	79
60	MT60	CL18-2952	CL18_2952-MT60	1839KL25F54	9/25/2018	80
61	MT61	CL18-2953	CL18_2953-MT61	0714JL20F44	9/26/2018	81
62	MT62	CL18-2954	CL18_2954-MT62	1607KL25F64	9/27/2018	82
63	MT63	CL18-2971	CL18_2971-MT63	1956KL25F44	9/30/2018	83
64	MT64	CL18-2972	CL18_2972-MT64	1993BL06F44	10/3/2018	84
65	MT65	CL19-3475	CL19_3475-MT65	1790KL25F64	2/1/2019	85
66	MT66	CL19-3500	CL19_3500-MT66	1595KL25F64	2/3/2019	86
67	MT67	CL19-3501	CL19_3501-MT67	1756KL25F54	2/6/2019	87
68	MT68	CL19-3518	CL19_3518-MT68	1622KL25F44	2/7/2019	88
69	MT69	CL19-3560	CL19_3560-MT69	3651LL14F64	2/19/2019	89
70	MT70	CL19-3561	CL19_3561-MT70	1753KL25F54	2/20/2019	90

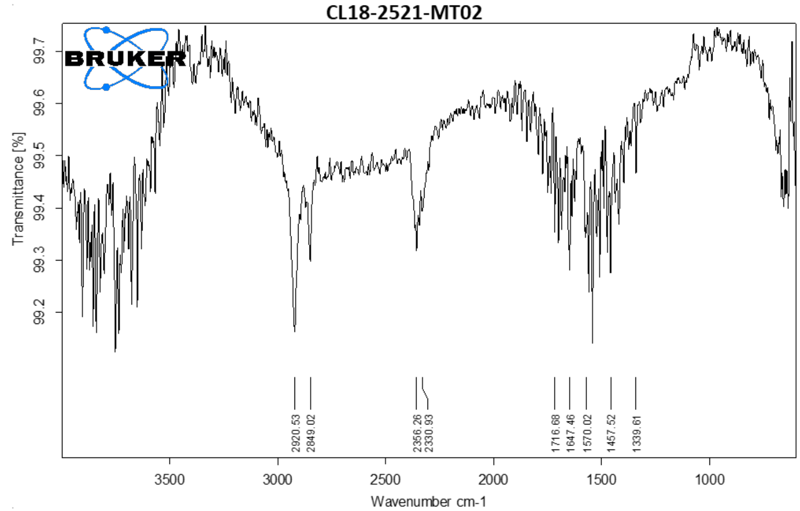
APPENDIX C

FTIR SPECTRA OF MATRIX TEST PINTLE DEPOSITS

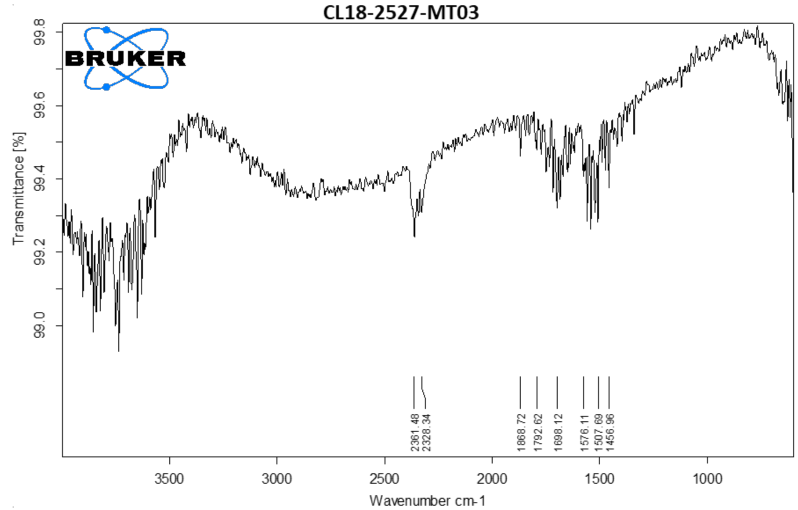
CL18-2520-MT01



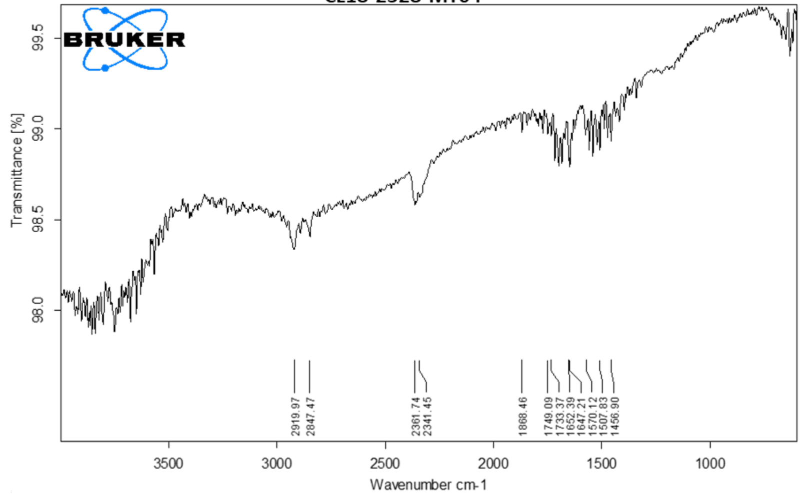
CL18-2521-MT02



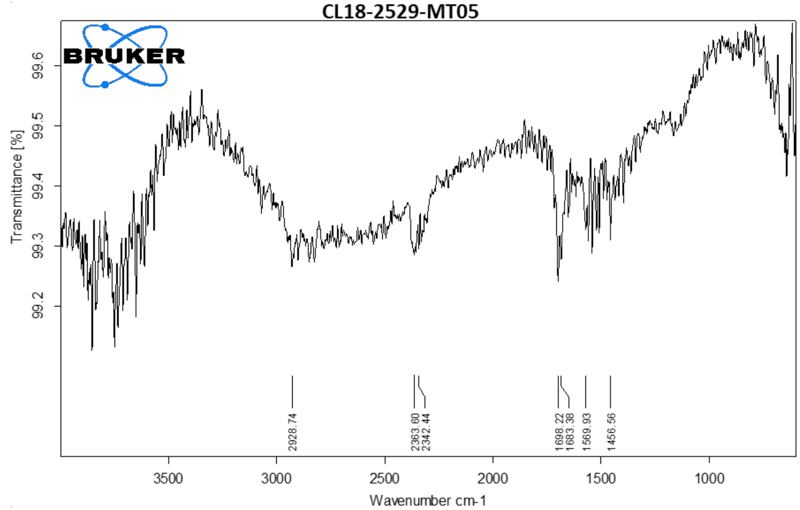
CL18-2527-MT03



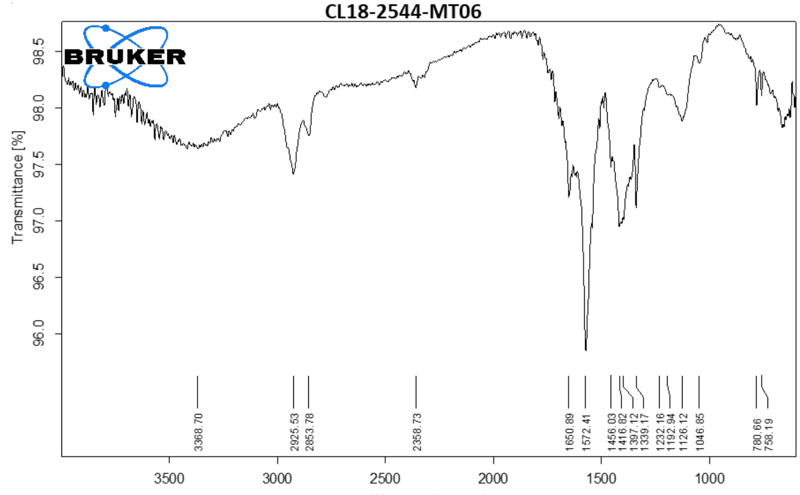
CL18-2528-MT04



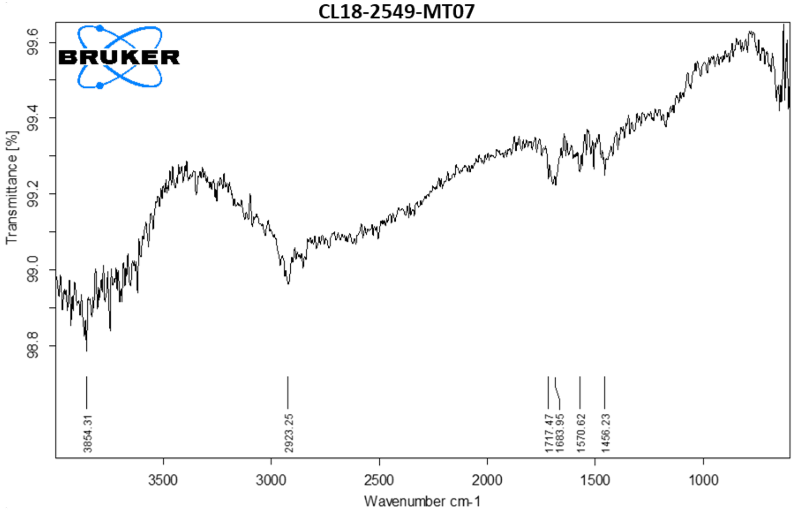
CL18-2529-MT05



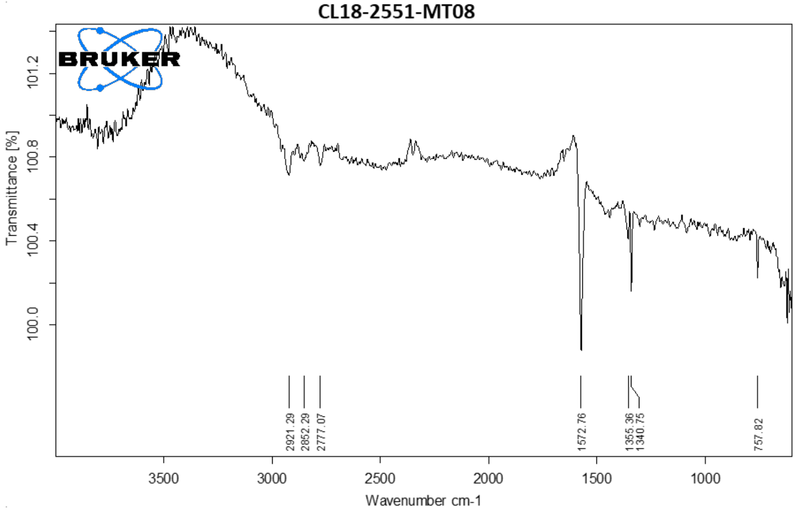
CL18-2544-MT06



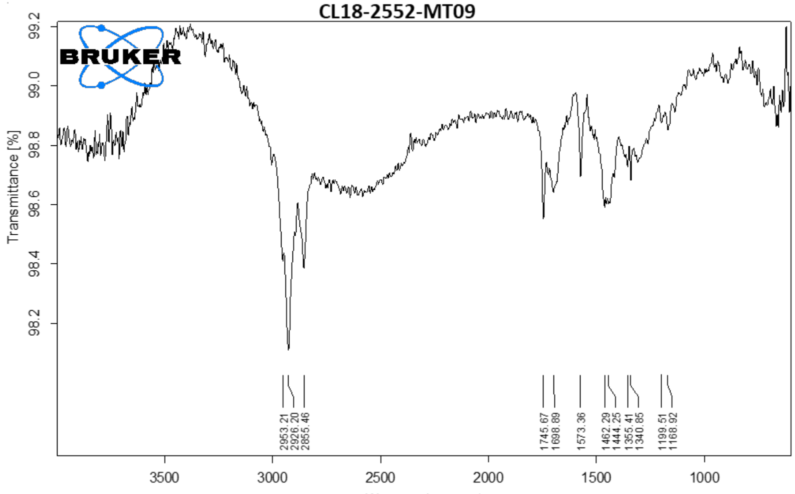
CL18-2549-MT07



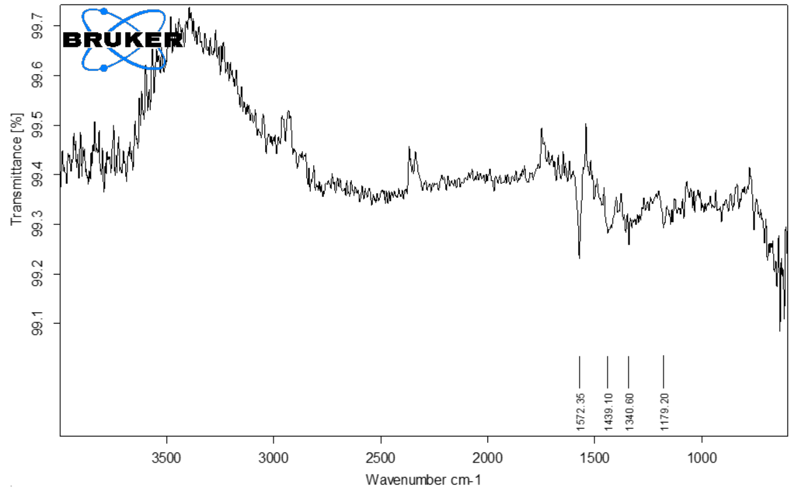
CL18-2551-MT08



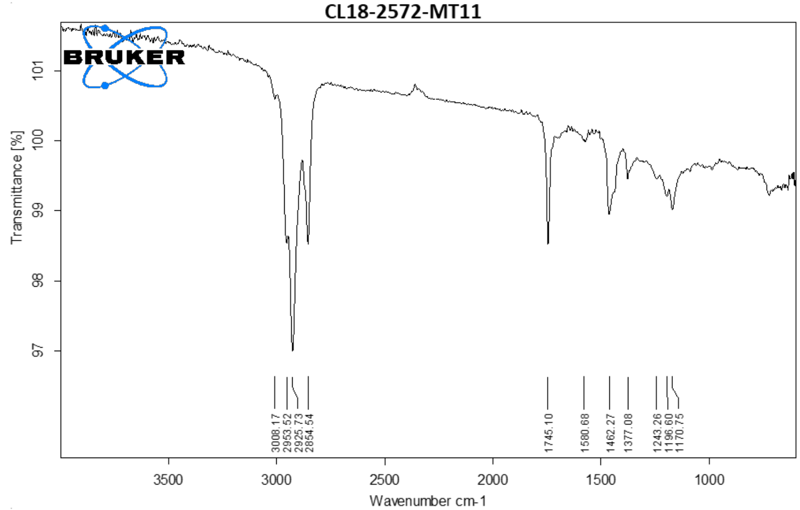
CL18-2552-MT09



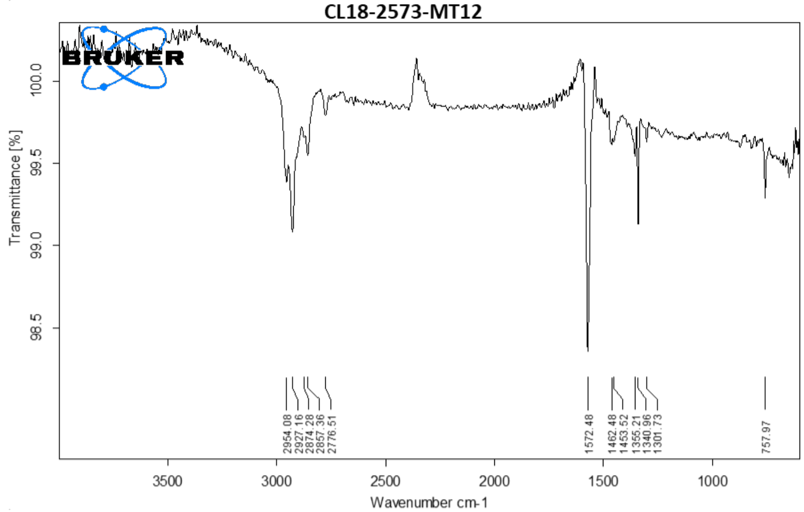
CL18-2571-MT10

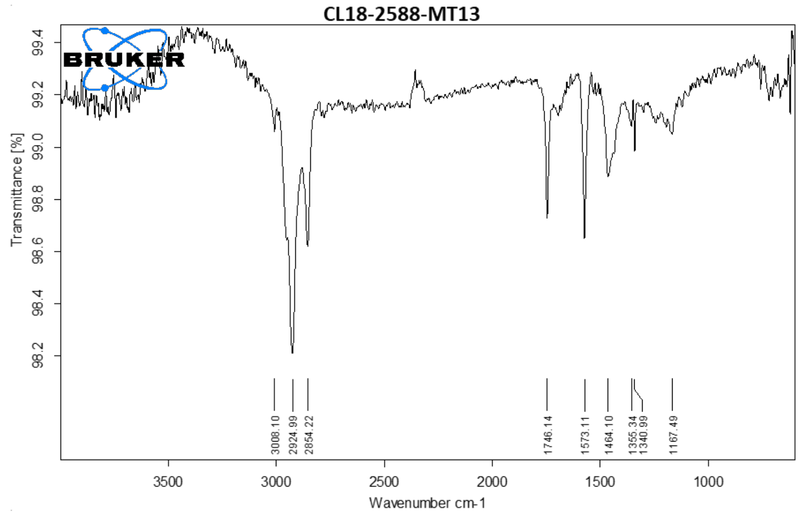


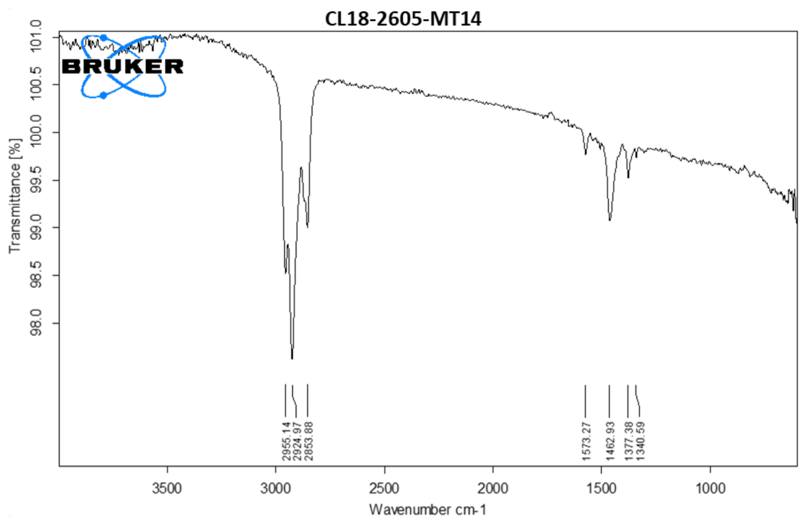
CL18-2572-MT11

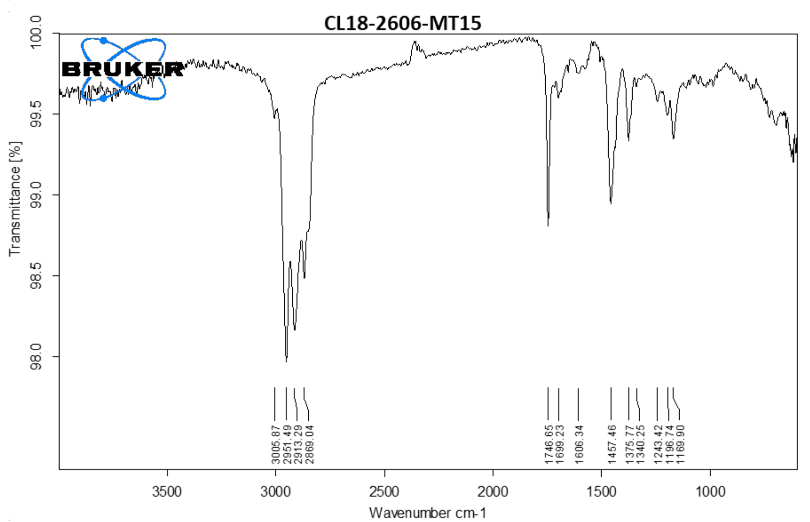


CL18-2573-MT12

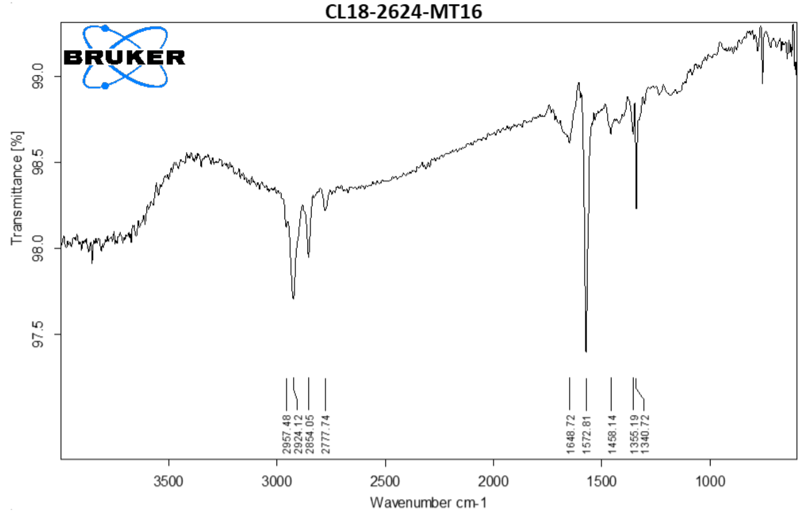



CL18-2588-MT13
BRUKER
Transmittance [%]
99.4
99.2
99.0
98.8
98.6
98.4
98.2
3008.10
2924.99
2854.22
1746.14
1573.11
1464.10
1355.34
1340.99
1167.49
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

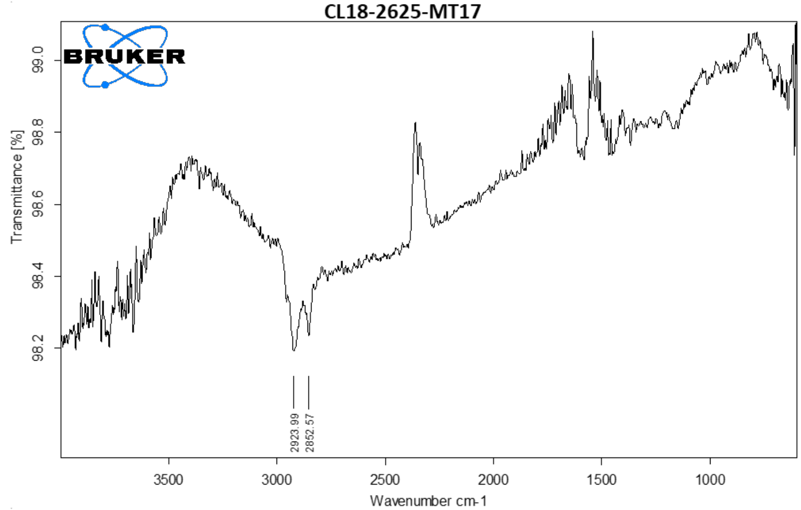

CL18-2605-MT14
BRUKER
Transmittance [%]
101.0
100.5
100.0
99.5
99.0
98.5
98.0
2955.14
2924.97
2853.88
1573.27
1462.93
1377.38
1340.59
3500
3000
2500
2000
1500
1000
Wavenumber cm-1


CL18-2606-MT15
BRUKER
Transmittance [%]
100.0
99.5
99.0
98.5
98.0
3005.87
2951.49
2913.29
2869.04
1746.65
1699.23
1606.34
1457.46
1375.77
1340.25
1243.42
1196.74
1169.90
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

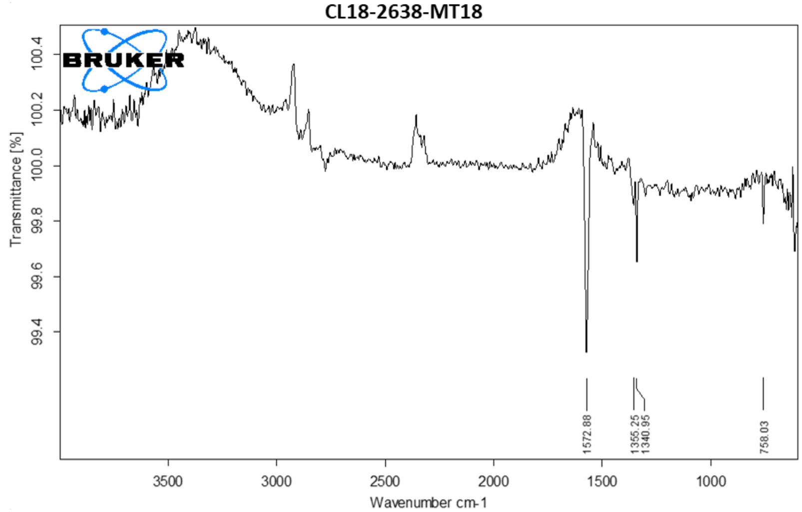
CL18-2624-MT16



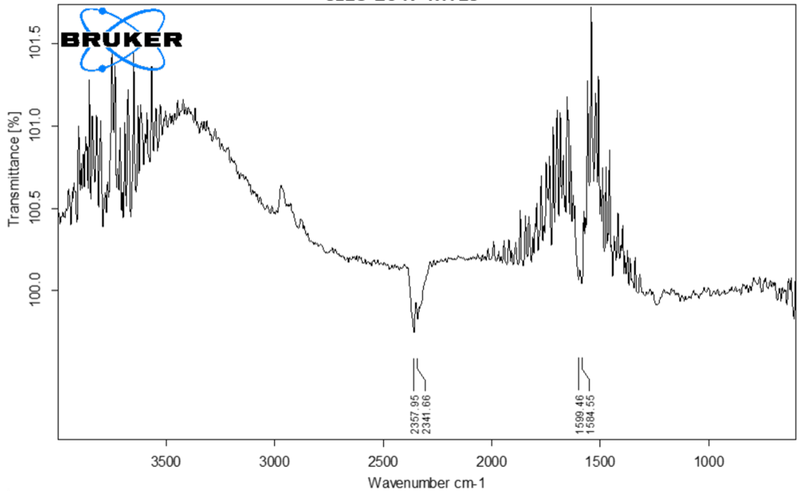
CL18-2625-MT17



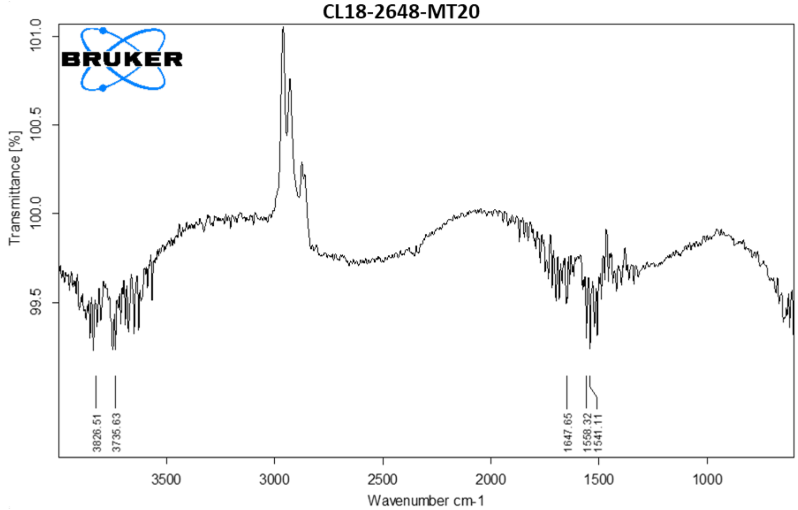
CL18-2638-MT18



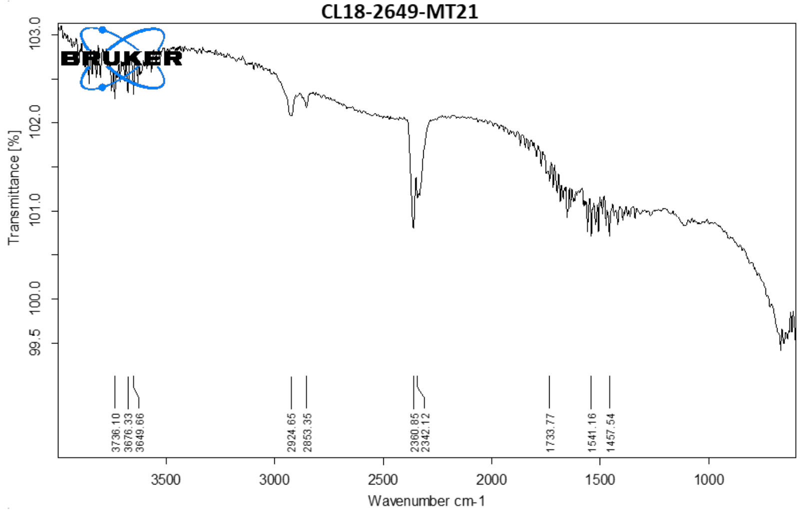
CL18-2647-MT19



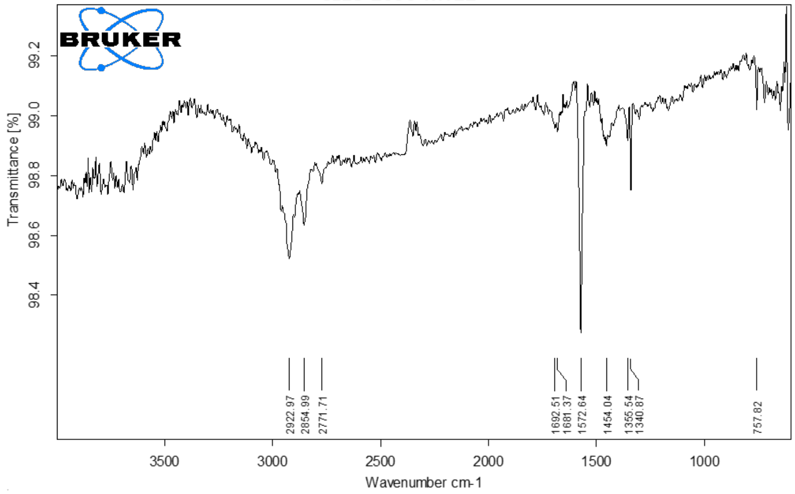
CL18-2648-MT20



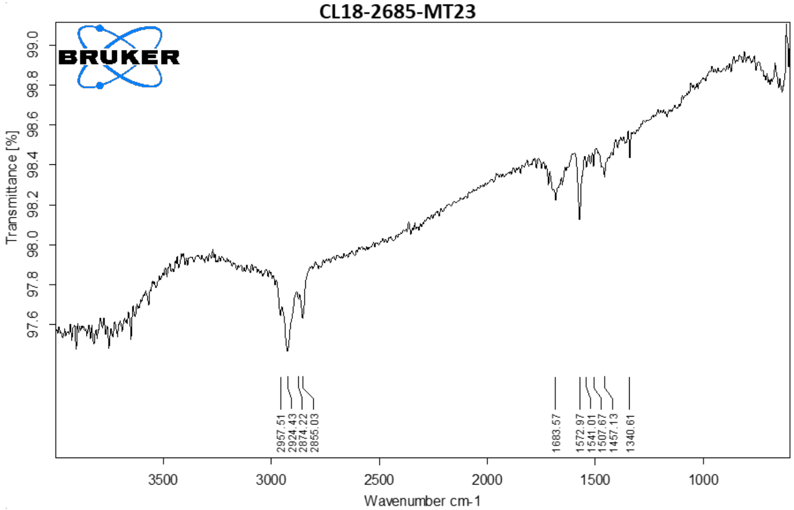
CL18-2649-MT21



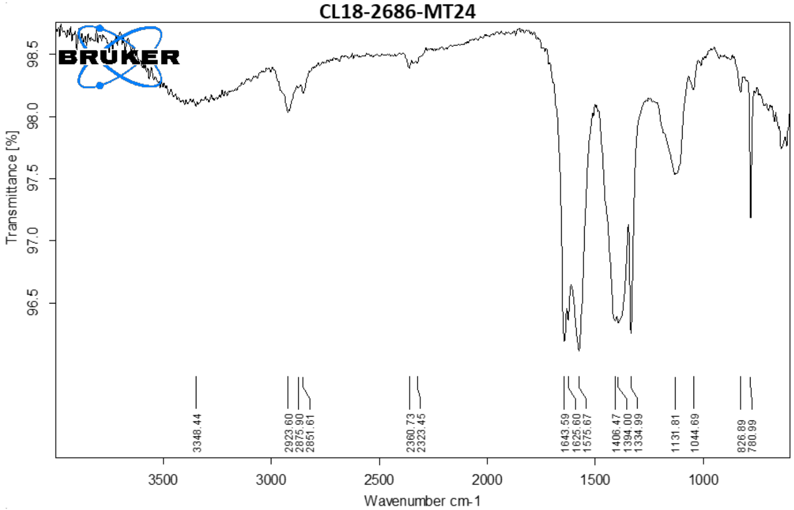
CL18-2650-MT22



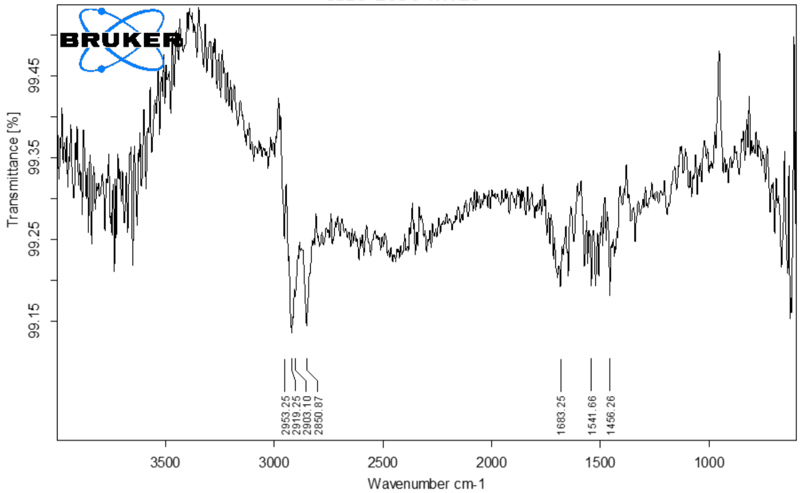
CL18-2685-MT23



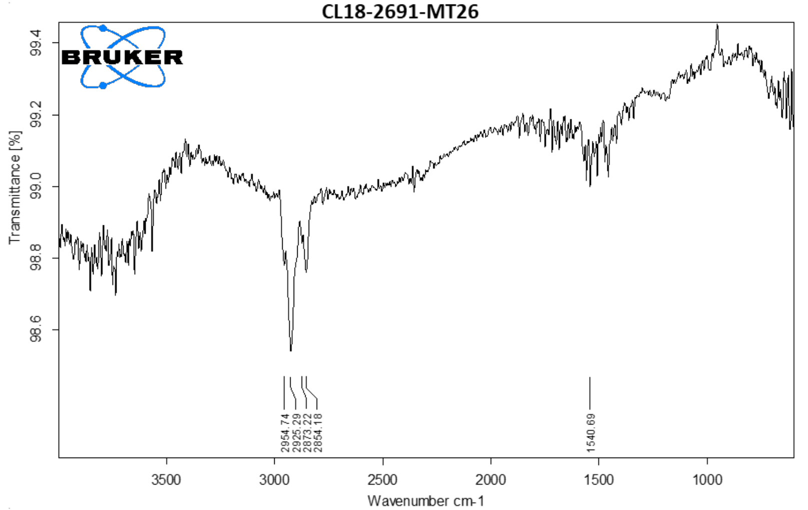
CL18-2686-MT24



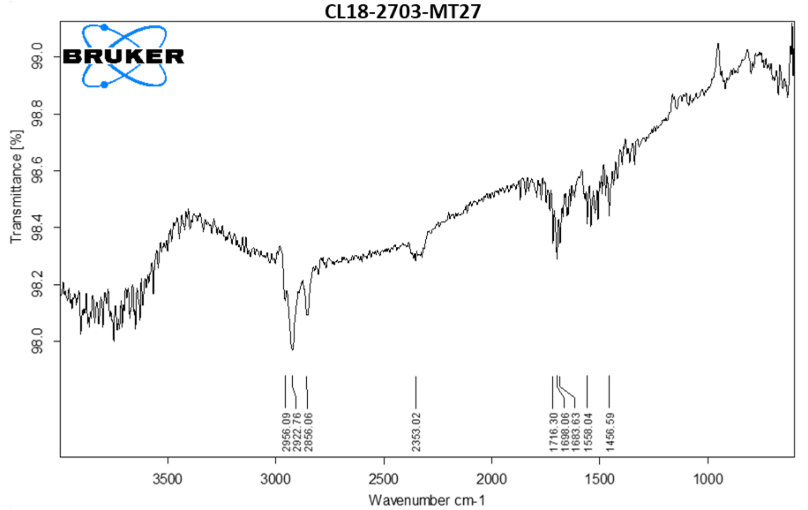
CL18-2690-MT25



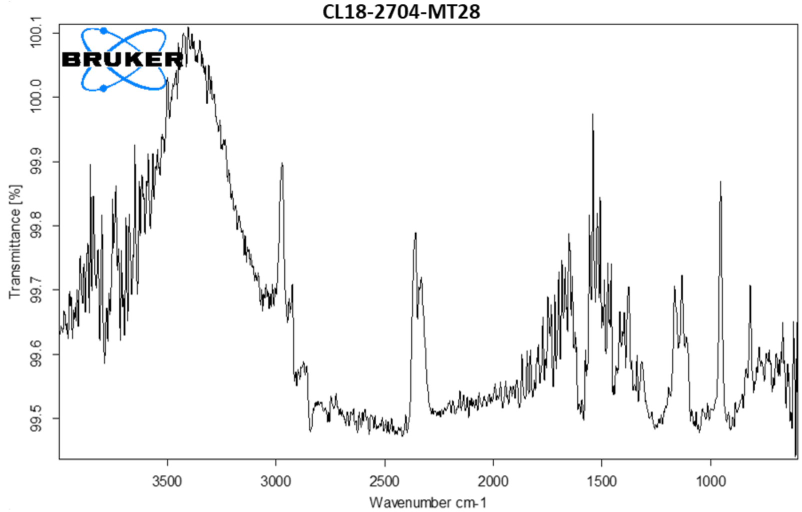
CL18-2691-MT26



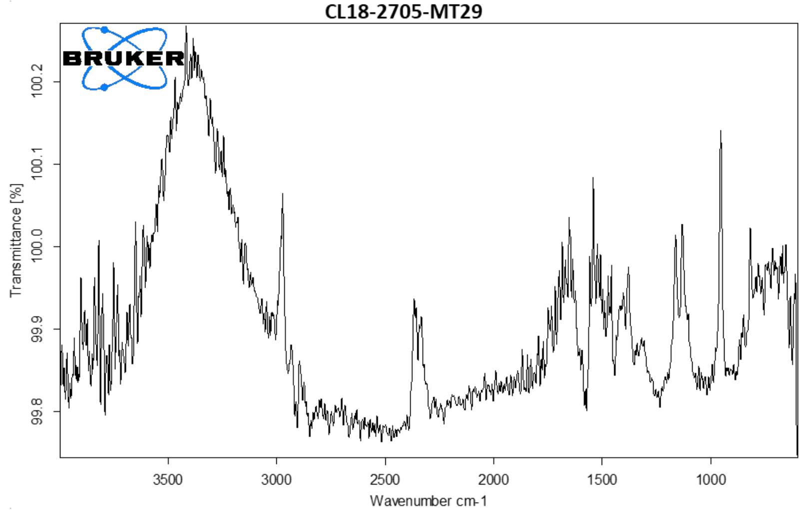
CL18-2703-MT27



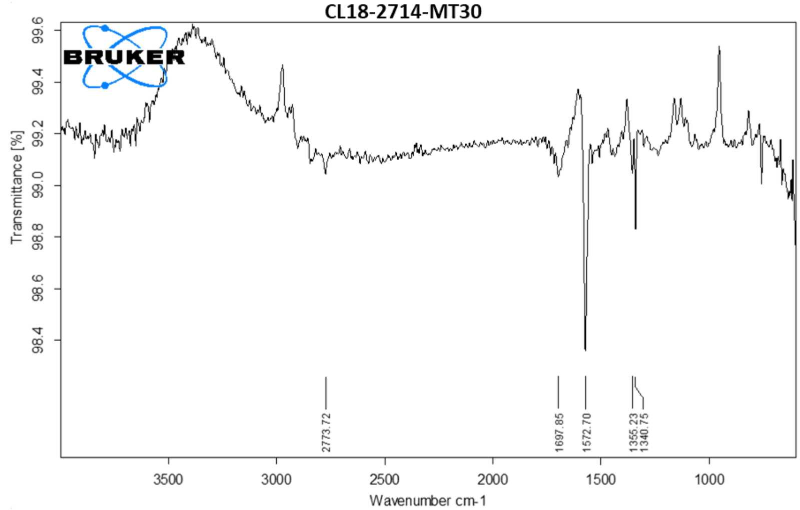
CL18-2704-MT28

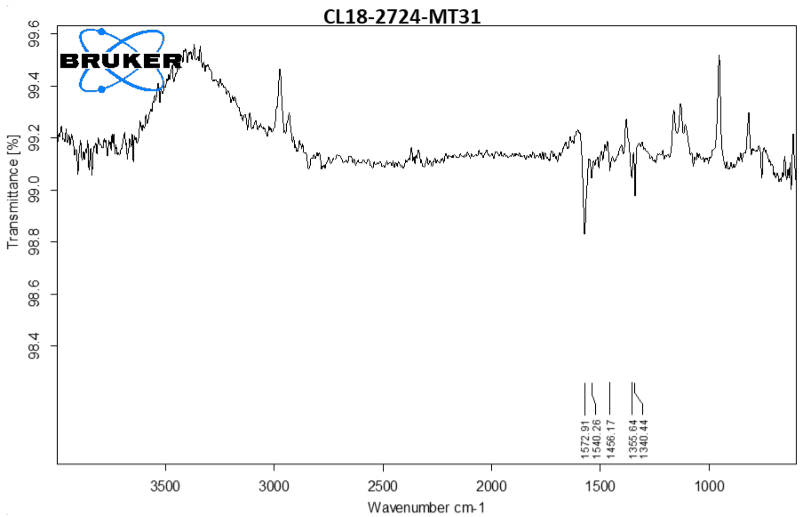


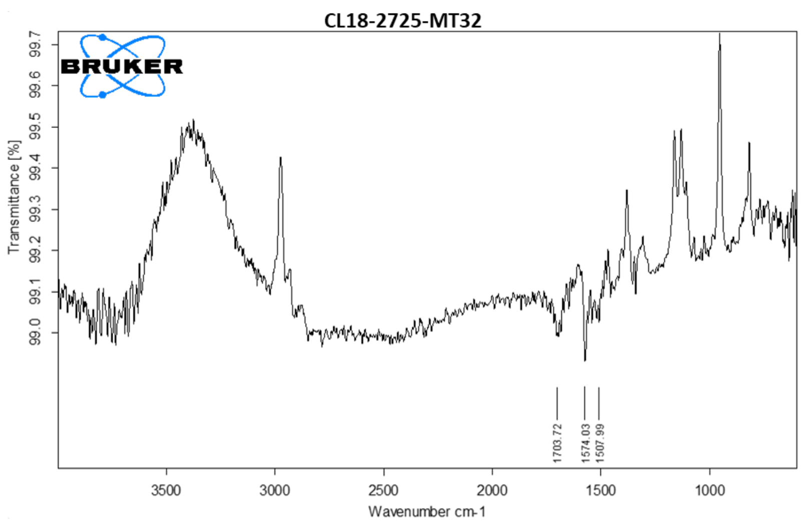
CL18-2705-MT29

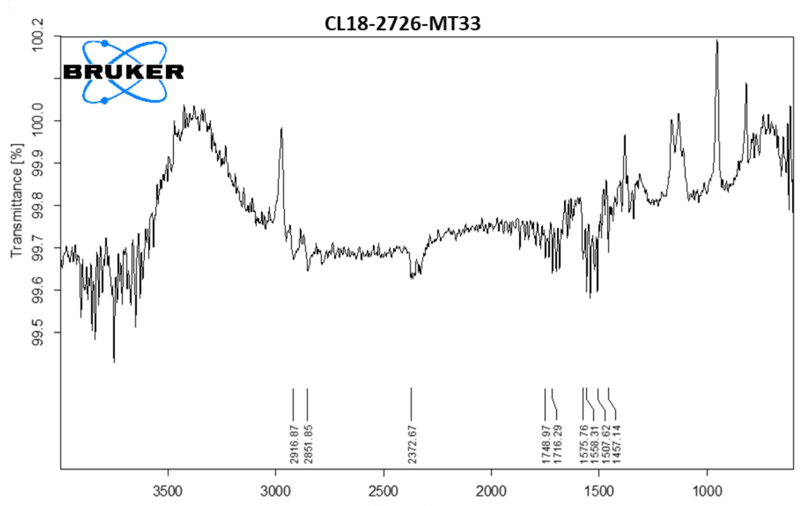


CL18-2714-MT30

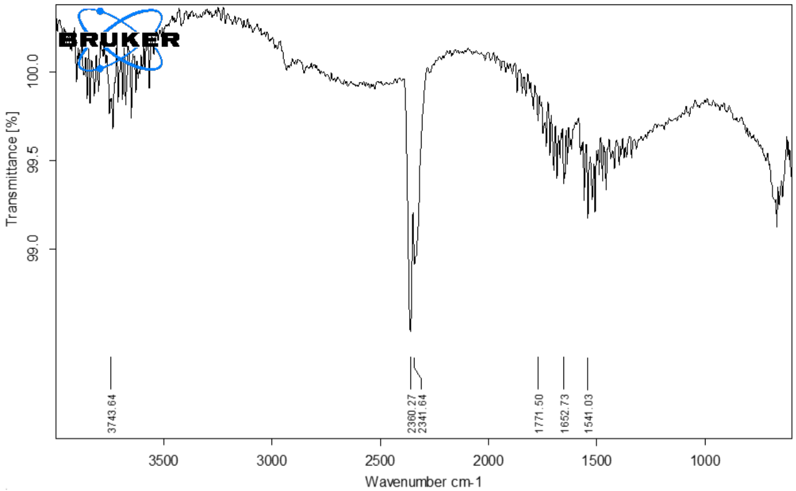



CL18-2724-MT31
BRUKER
Transmittance [%]
99.6
99.4
99.2
99.0
98.8
98.6
98.4
1572.91
1540.26
1456.17
1355.64
1340.44
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

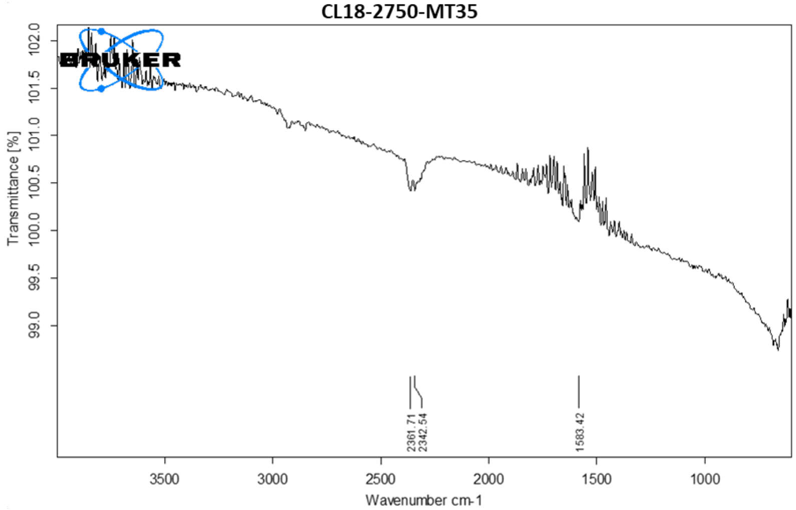

CL18-2725-MT32
BRUKER
Transmittance [%]
99.7
99.6
99.5
99.4
99.3
99.2
99.1
99.0
1703.72
1574.03
1507.99
3500
3000
2500
2000
1500
1000
Wavenumber cm-1


CL18-2726-MT33
BRUKER
Transmittance [%]
100.2
100.0
99.9
99.8
99.7
99.6
99.5
2916.87
2851.85
2372.67
1748.97
1716.29
1575.76
1558.31
1507.62
1457.14
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

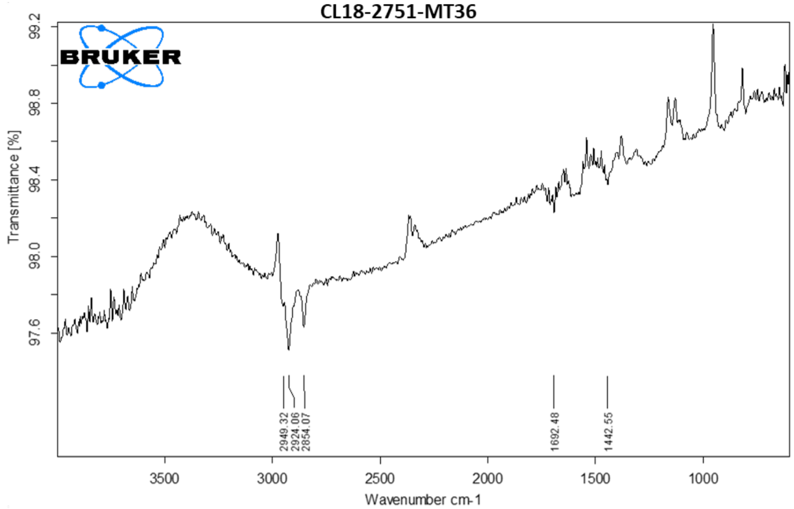
CL18-2737-MT34



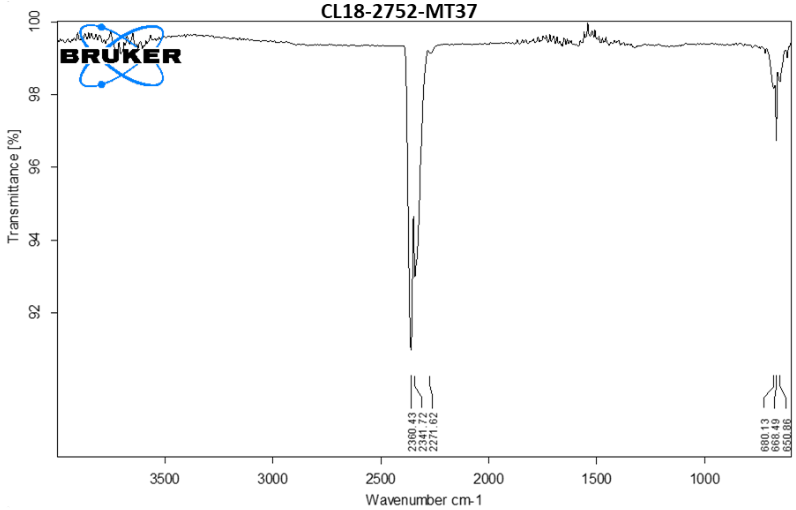
CL18-2750-MT35



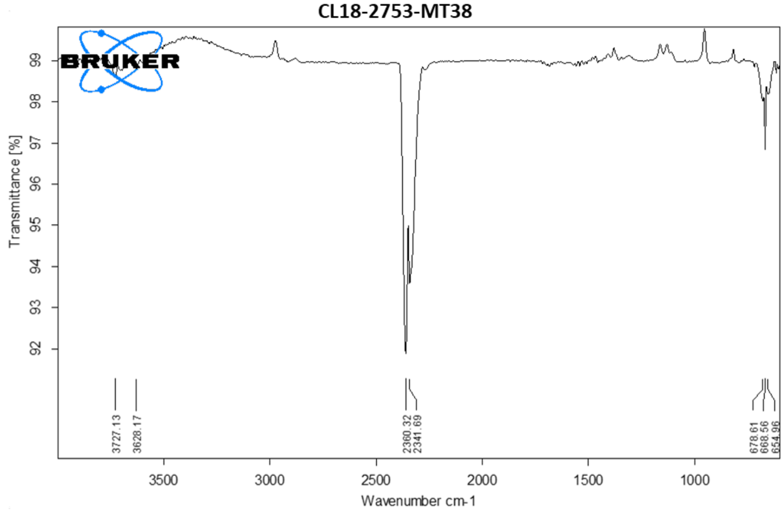
CL18-2751-MT36



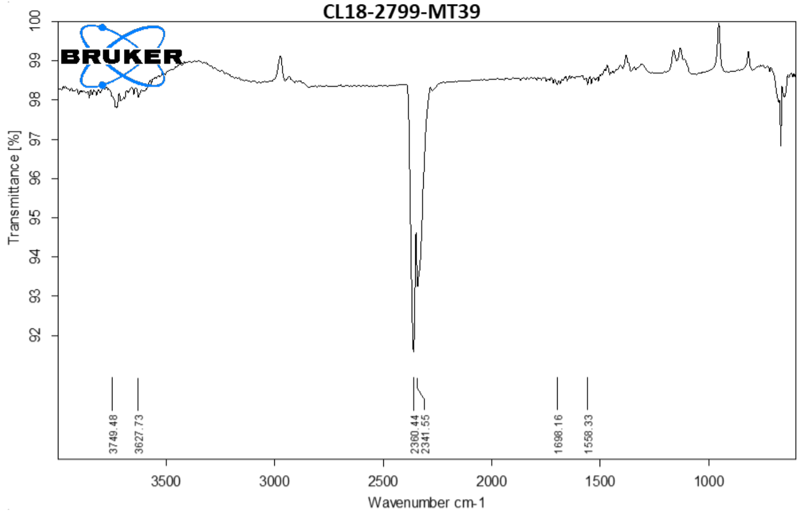
CL18-2752-MT37



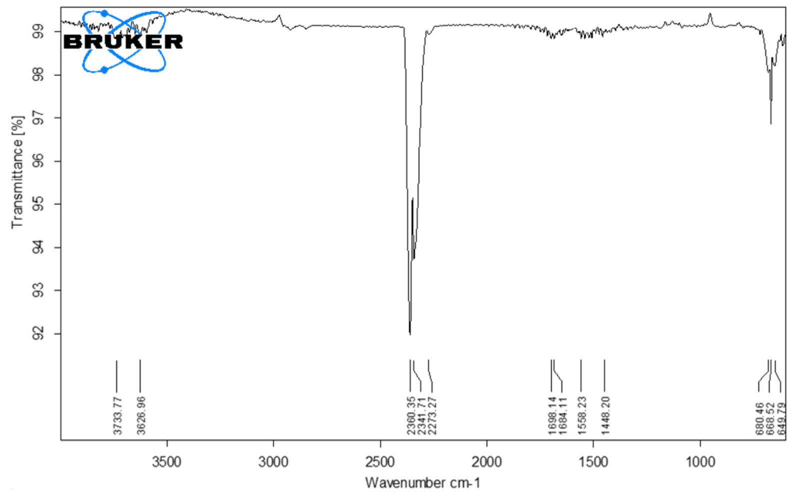
CL18-2753-MT38



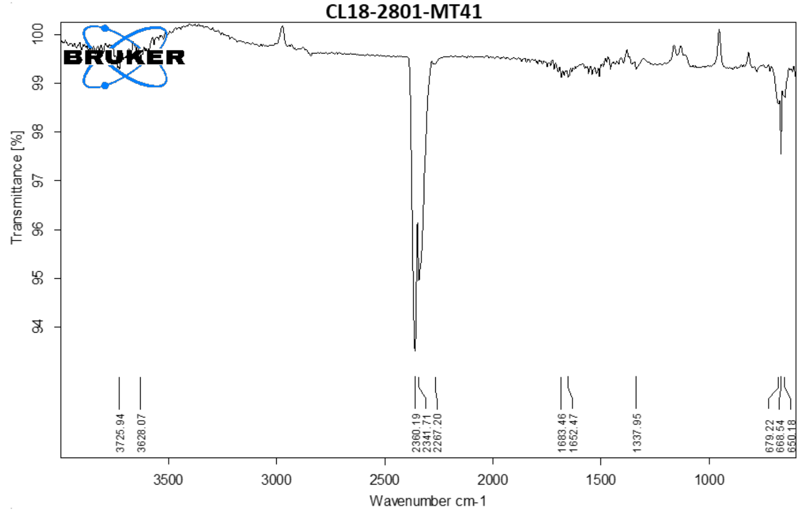
CL18-2799-MT39



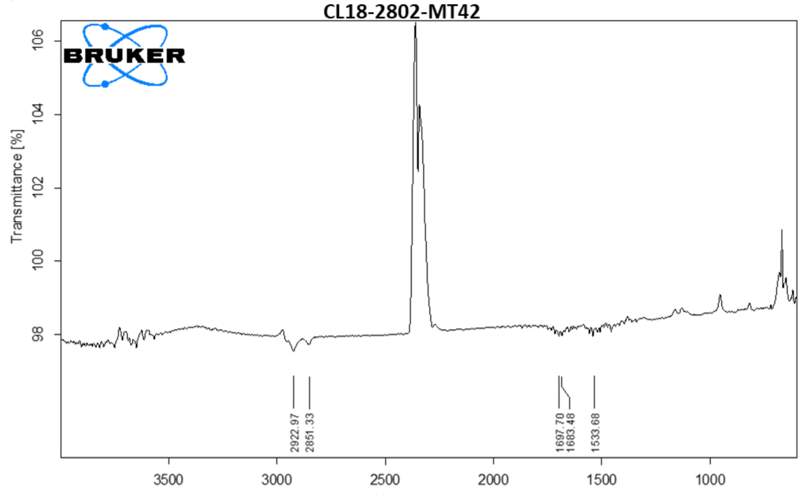
CL18-2800-MT40



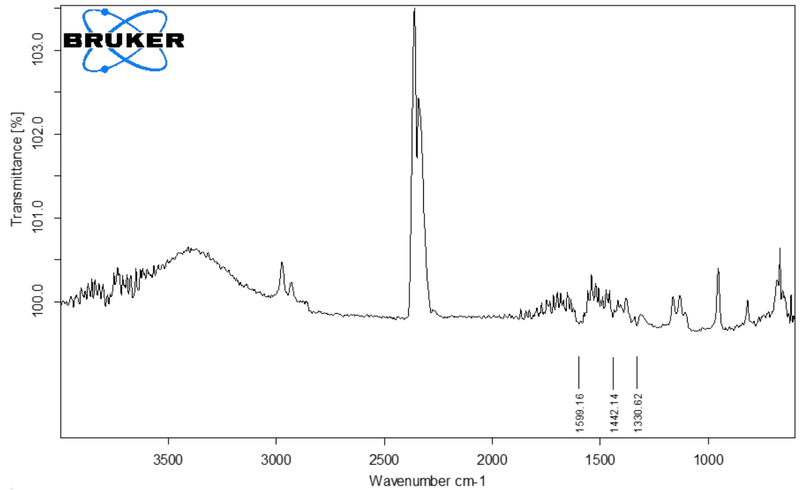
CL18-2801-MT41



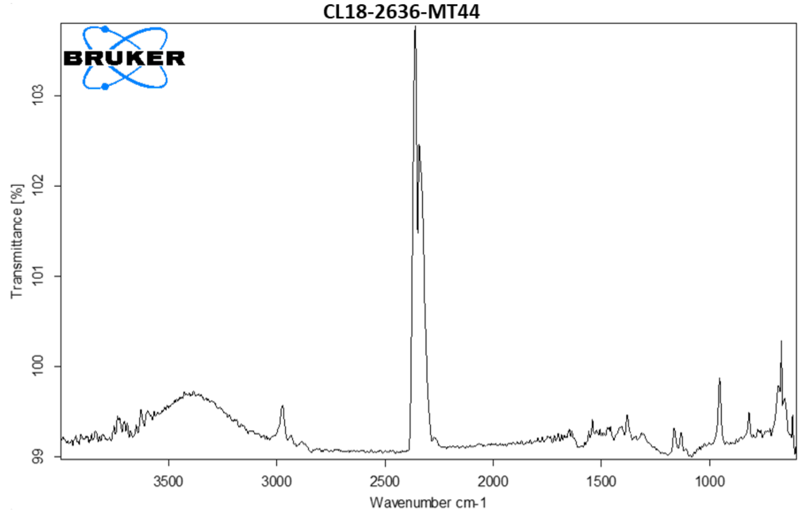
CL18-2802-MT42



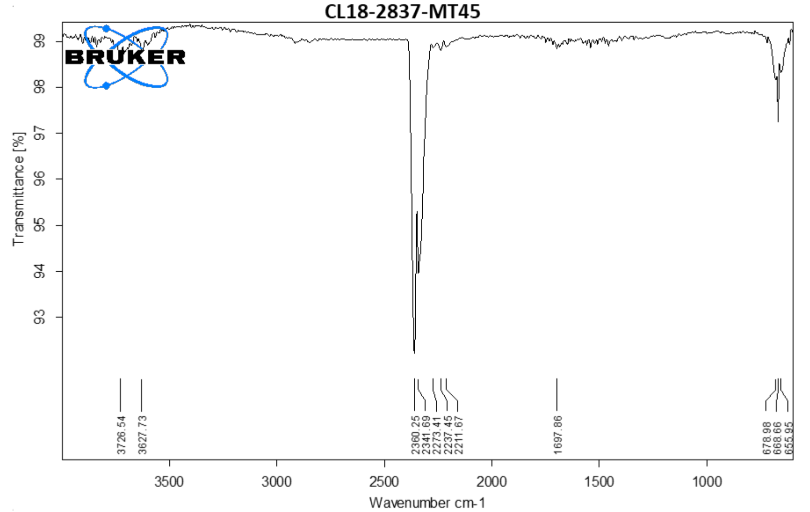
CL18-2835-MT43



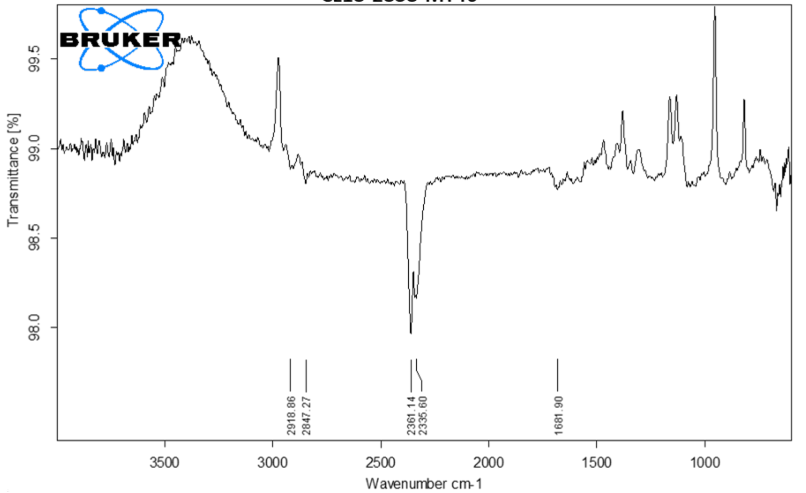
CL18-2636-MT44



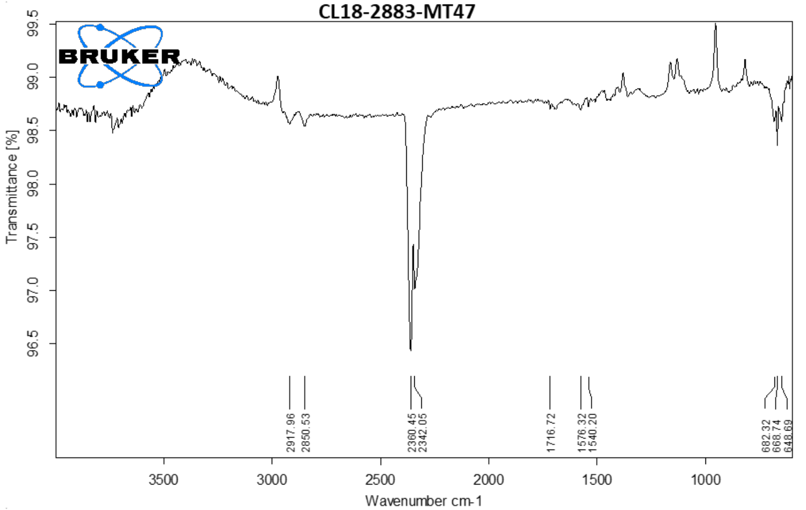
CL18-2837-MT45



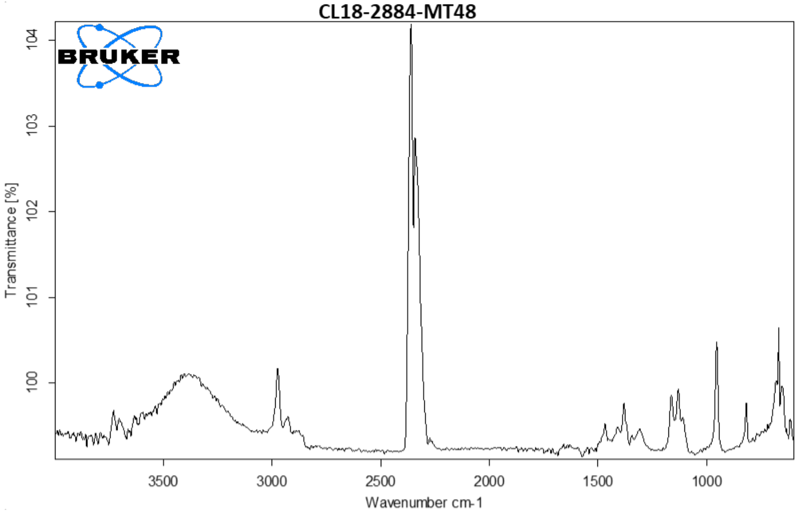
CL18-2838-MT46

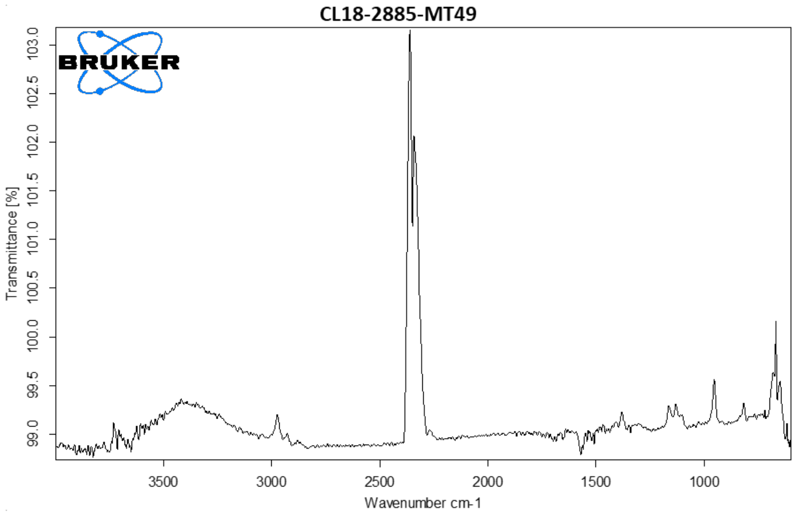


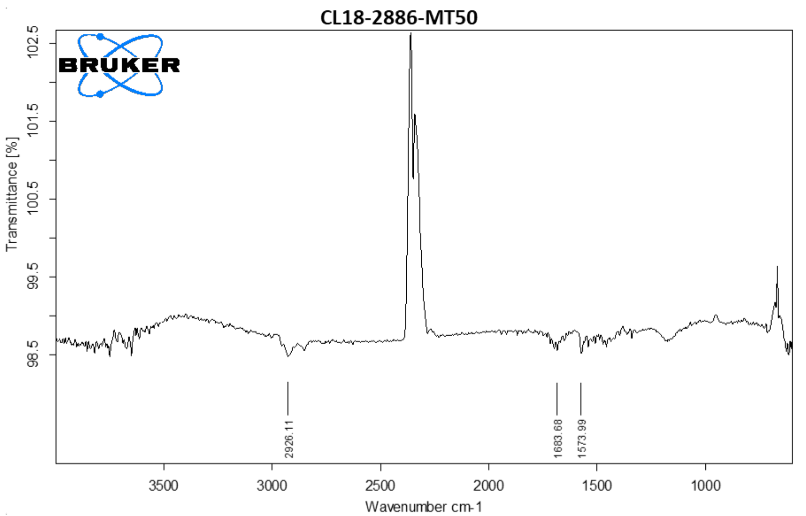
CL18-2883-MT47

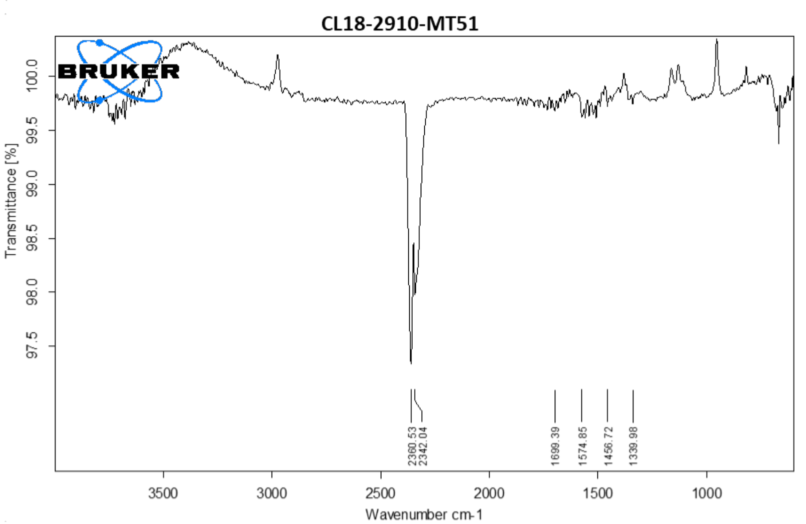


CL18-2884-MT48

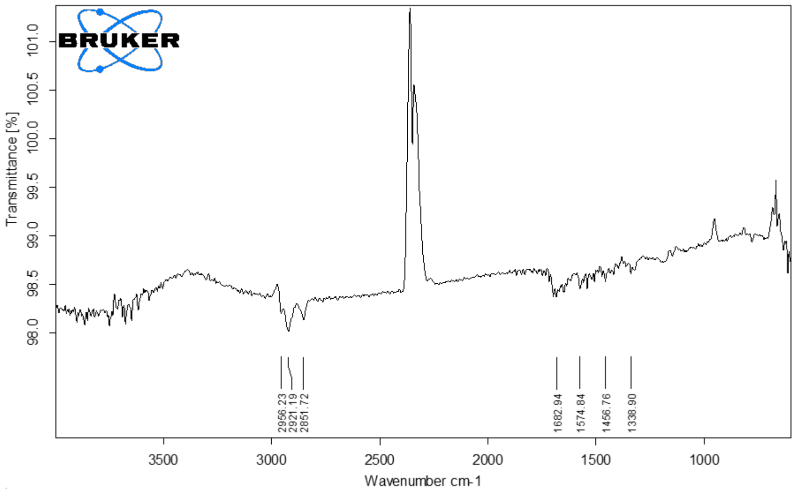



CL18-2885-MT49
Transmittance [%]
Wavenumber cm-1

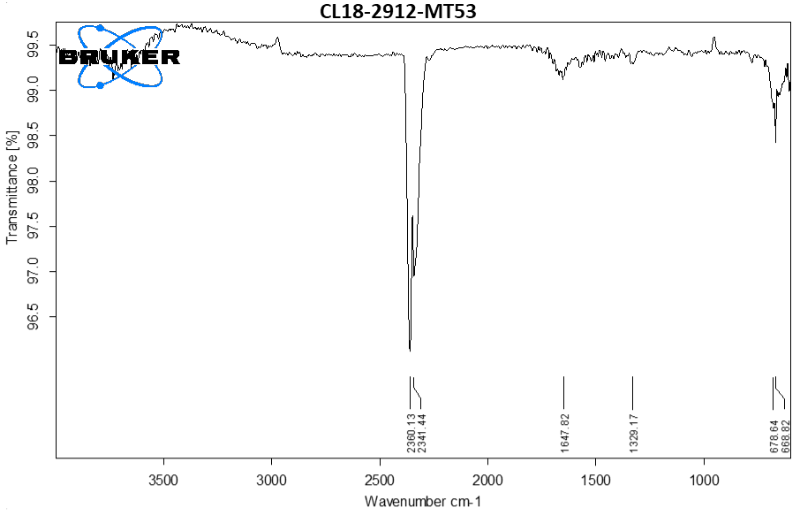

CL18-2886-MT50
Transmittance [%]
Wavenumber cm-1
2926.11
1683.68
1573.99


CL18-2910-MT51
Transmittance [%]
Wavenumber cm-1
2360.53
2342.04
1699.39
1574.85
1456.72
1339.98

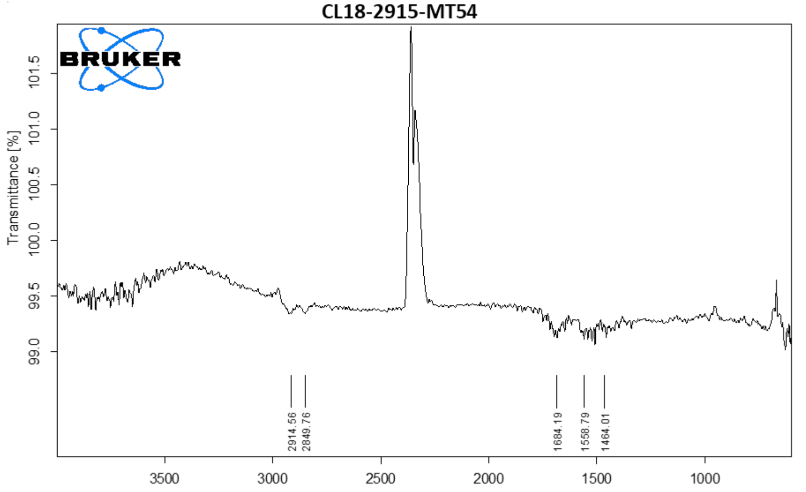
CL18-2911-MT52

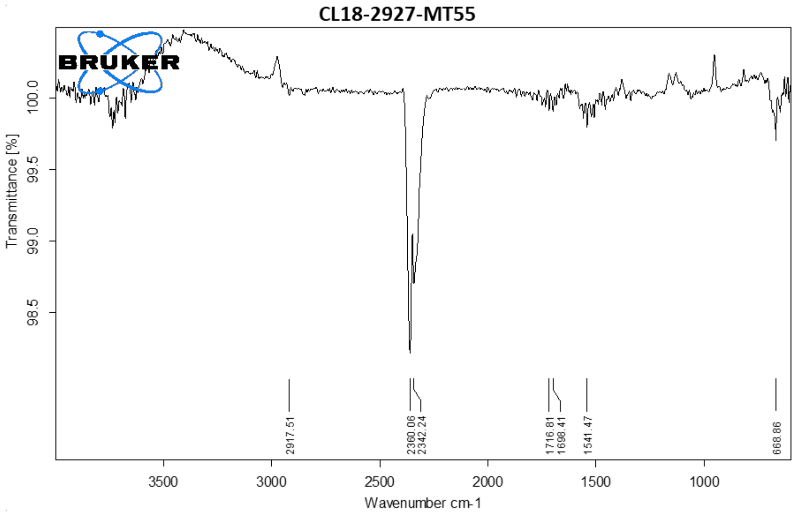


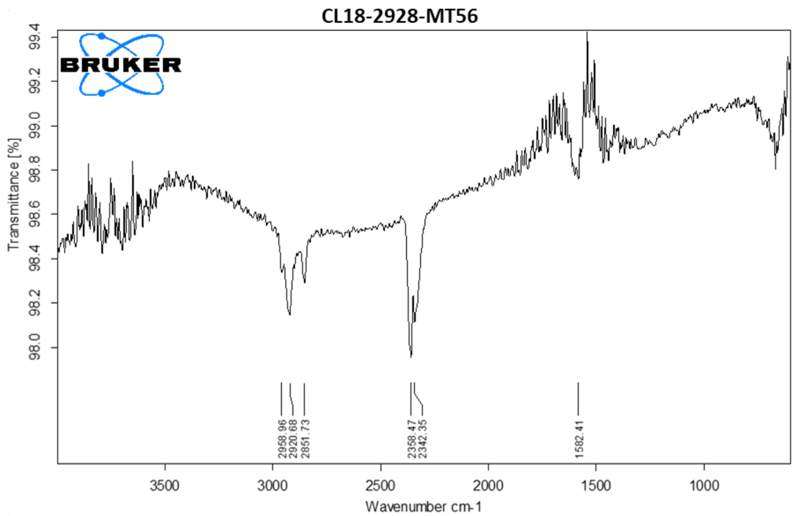
CL18-2912-MT53

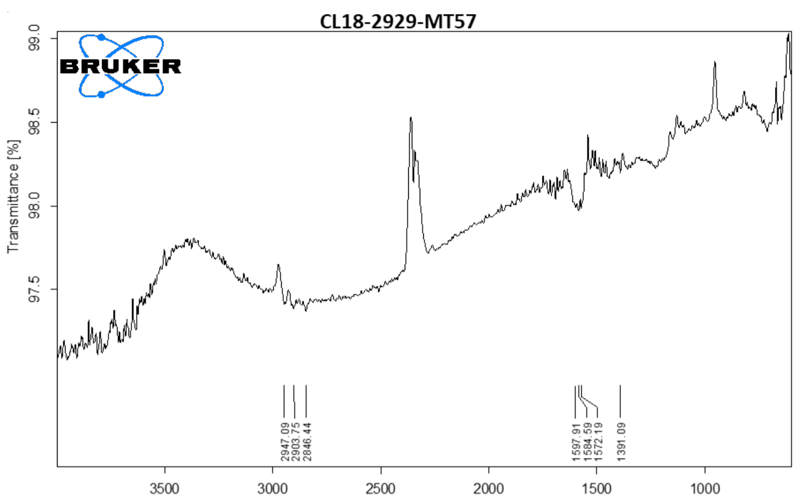


CL18-2915-MT54

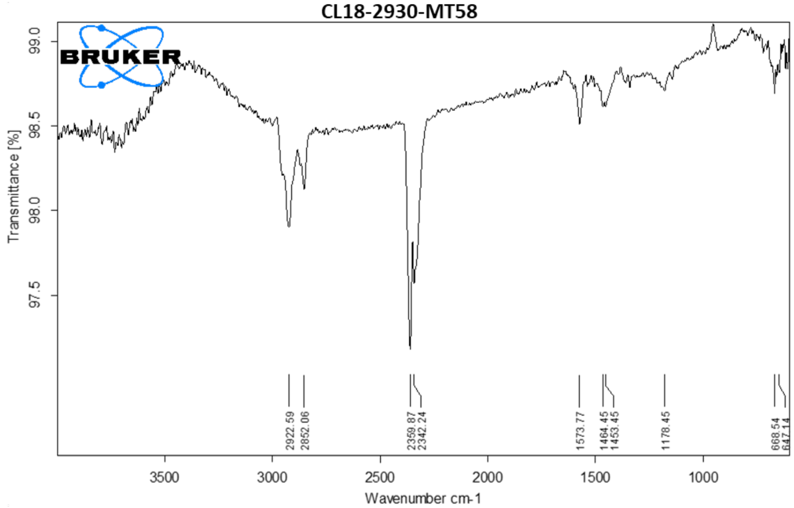



CL18-2927-MT55
BRUKER
Transmittance [%]
100.0
99.5
99.0
98.5
2917.51
2360.06
2342.24
1716.81
1698.41
1541.47
668.86
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

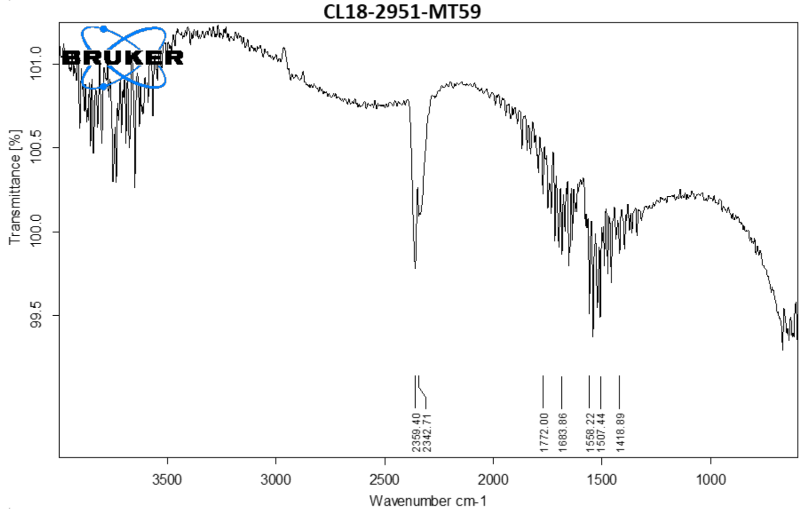

CL18-2928-MT56
BRUKER
Transmittance [%]
99.4
99.2
99.0
98.8
98.6
98.4
98.2
98.0
2958.96
2920.68
2851.73
2358.47
2342.35
1582.41
3500
3000
2500
2000
1500
1000
Wavenumber cm-1


CL18-2929-MT57
BRUKER
Transmittance [%]
99.0
98.5
98.0
97.5
2947.09
2903.75
2846.44
1597.91
1584.59
1572.19
1391.09
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

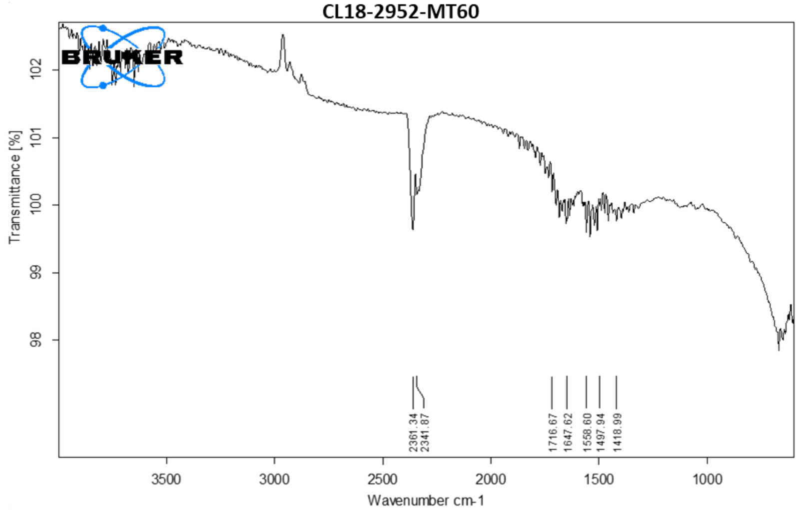
CL18-2930-MT58



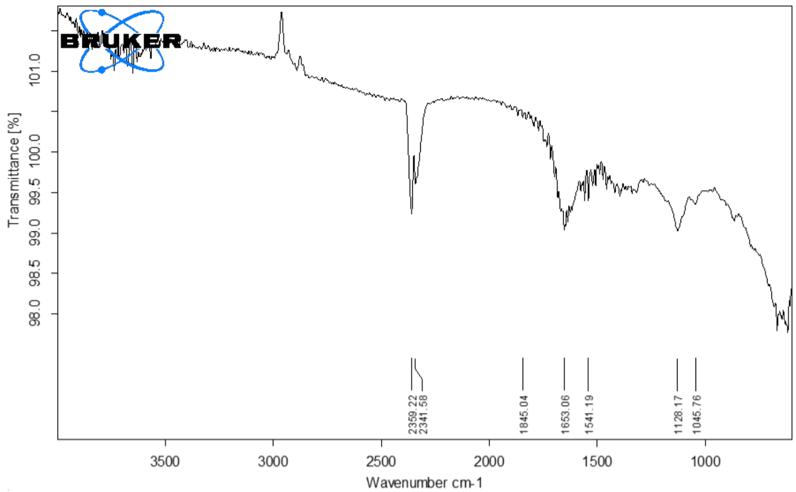
CL18-2951-MT59



CL18-2952-MT60



CL18-2953-MT61



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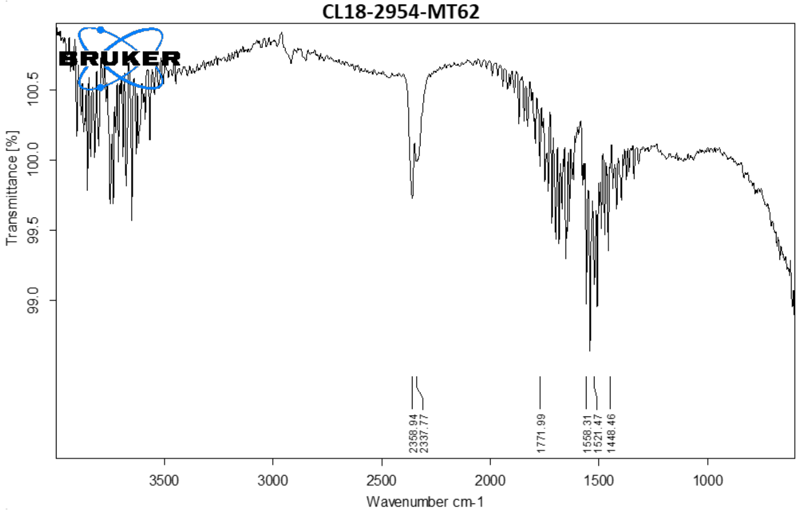
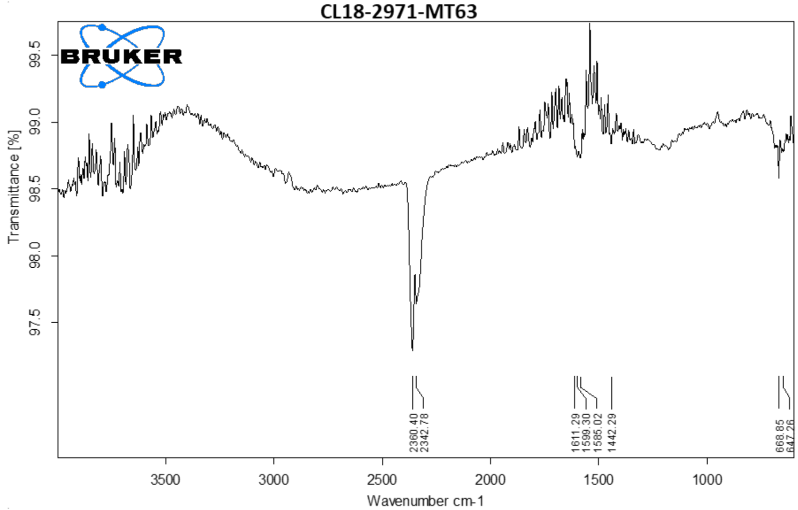
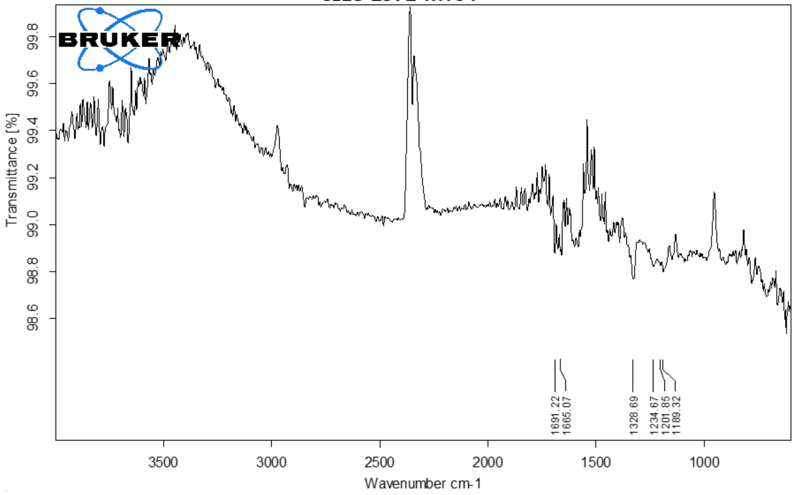


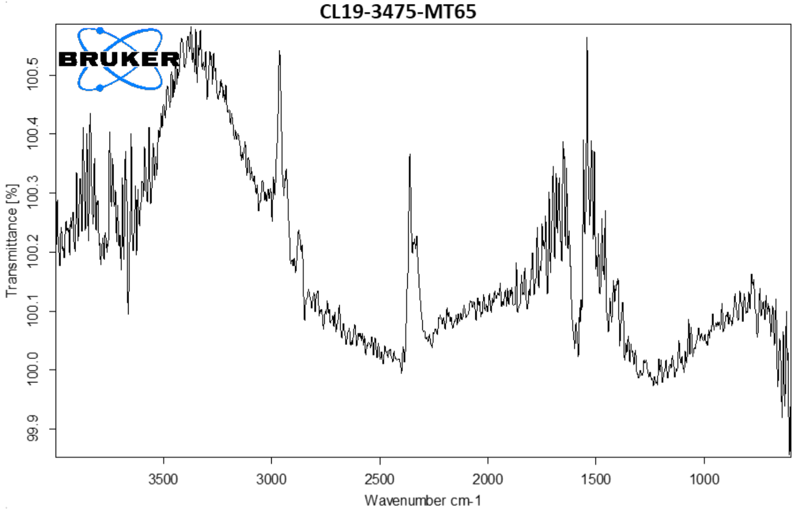
CL18-2971-MT63



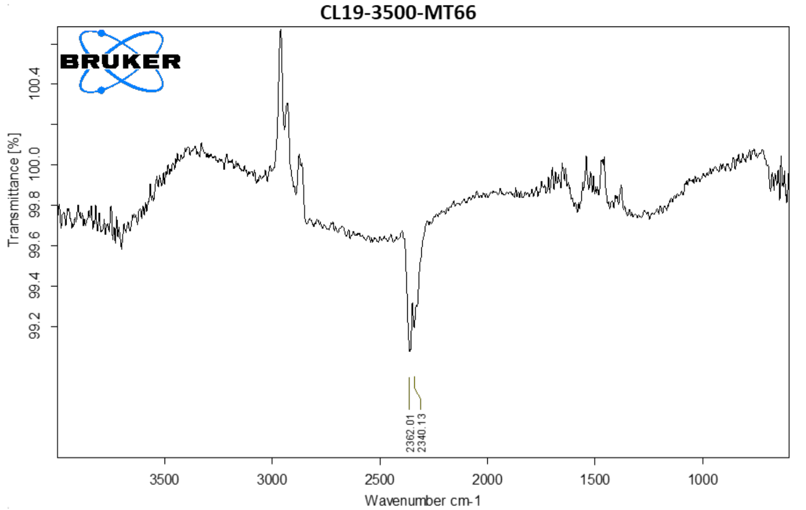
CL18-2972-MT64



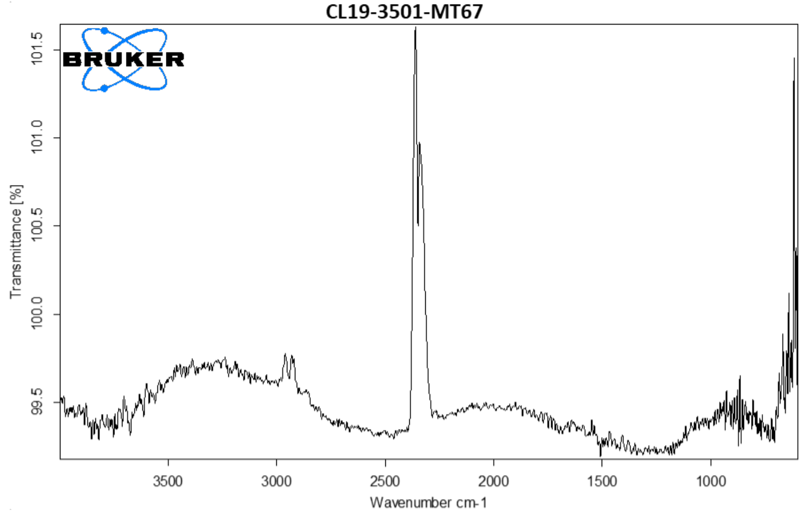
CL19-3475-MT65



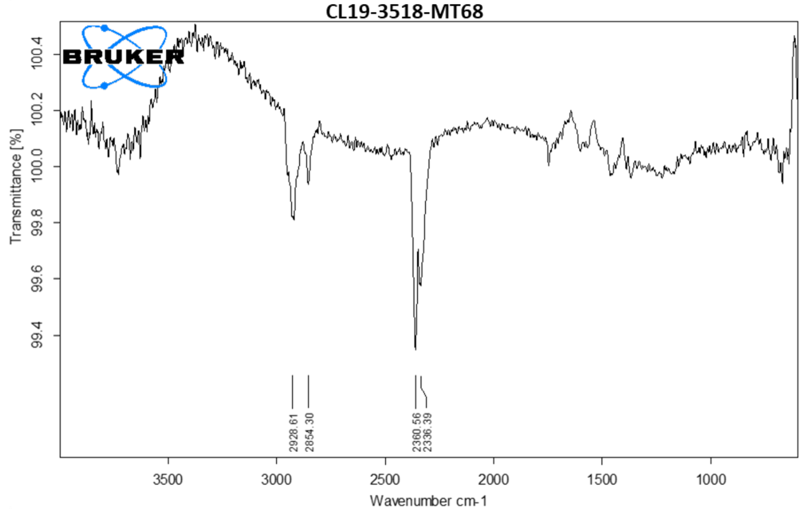
CL19-3500-MT66



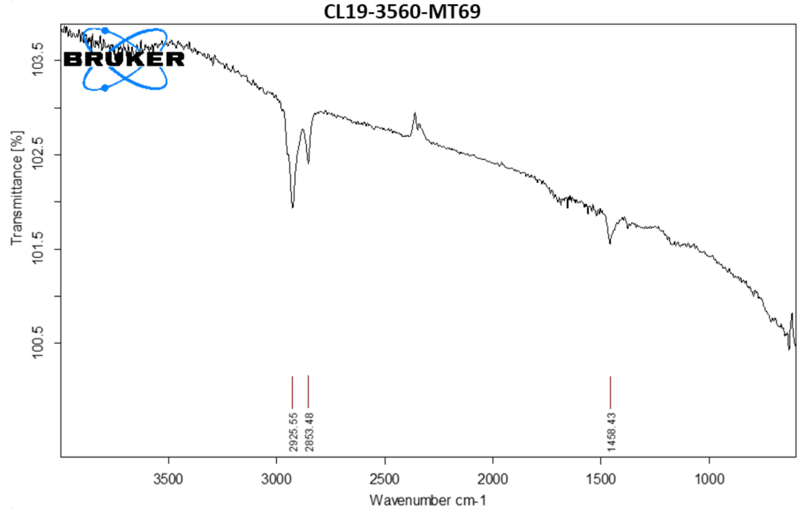
CL19-3501-MT67

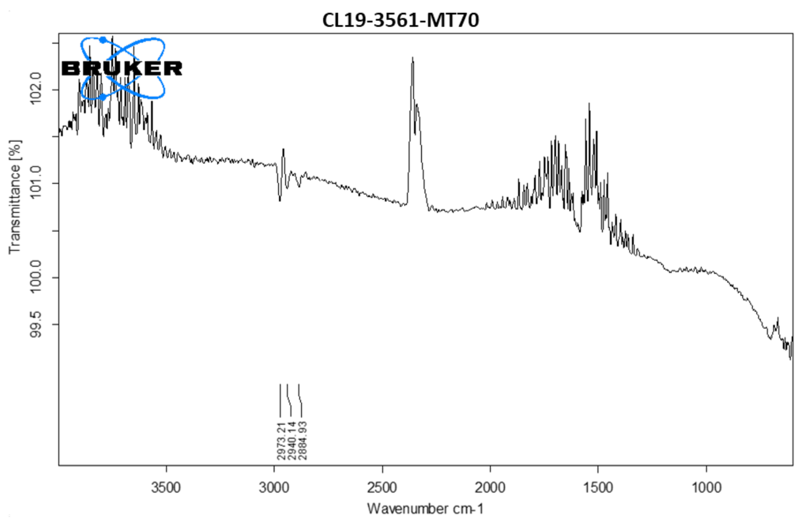


CL19-3518-MT68



CL19-3560-MT69





CL19-3561-MT70
BRUKER
Transmittance [%]
102.0
101.0
100.0
99.5
2973.21
2940.14
2884.93
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

APPENDIX D

INJECTOR PINTLE PHOTOGRAPHS

On the following two pages are the combined photographs of all the pintles used in the matrix program. Each photograph contains ten (10) pintles from the matrix program, in numerical order, arranged around the untested, reference pintle.

With the centrally place reference pintle in each picture, it is obvious that the matrix pintles are used. What is not apparent is any obvious relationship between their appearance and their associated results in the matrix program.

MT 01 – 10 **REFERENCE**

MT 11 - 20

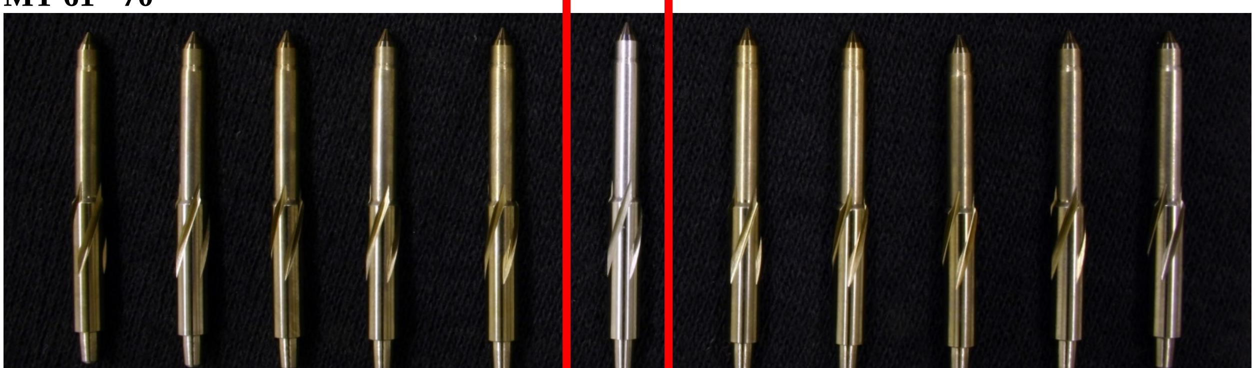
MT 21 - 30

MT 31 - 40

MT 41 – 50 **REFERENCE**

MT 51 - 60

MT 61 - 70



APPENDIX E

Statistical Analyses Conducted by Chevron

Fuel Research Using the Internal Diesel Injector Deposit (IDID) Rig (CRC Project No. DP-04-17)

Matrix Analysis

Jo Martinez

Staff Statistician, Chevron

Dec. 4, 2018

Conclusions

Deposit by Location on Pintle

- No significant axial location differences
- No significant radial location differences

Deposit (average of 84 measurements)

- Sodium increases deposit thickness
- No significant Corrosion Inhibitor and Cetane Number Improver differences
- Detergent additive reduces deposit thickness in fuels without biodiesel
- Sodium increases deposit thickness in fuels without
  - Detergent additive
  - Mono acid lubricity additive
- Sodium increases deposit thickness more significantly in fuels without glycerin than with glycerin
- Conductivity additive increases deposit thickness in fuels without
  - Biodiesel
  - Glycerin
- Conductivity additive increases deposit thickness in fuels with mono acid lubricity additive

Summary of Interaction Effects

Without Detergent Additive	With Detergent Additive
- Sodium	- Sodium
Without Biodiesel	With Biodiesel
- Detergent Additive	- Detergent Additive
- Conductivity Additive	- Conductivity Additive
Without Glycerin	With Glycerin
- Sodium (significant)	- Sodium (marginal)
- Conductivity Additive	- Conductivity Additive
Without Mono Acid Lubricity Additive	With Mono Acid Lubricity Additive
- Sodium	- Sodium
- Conductivity Additive	- Conductivity Additive

- Interaction effects color legend:
  - Green (reduces deposit thickness)
  - Red (increases deposit thickness)
  - Black (differences are not statistically significant, neutral)

Matrix Design

- **Fractional Factorial Design:** $2^{8-2} = 64$ tests

- **Factors (Levels):**
  - Biodiesel (No, Yes)
  - Sodium (No, Yes)
  - Glycerin (No, Yes)
  - Corrosion Inhibitor (No, Yes)
  - Mono Acid Lubricity Additive (No, Yes)
  - Detergent Additive (No, Yes)
  - Cetane Number Improver (No, Yes)
  - Conductivity Additive (No, Yes)

- **Response:** Deposit Thickness, nm

- **Objective:** Determine factors affecting Deposit Thickness

Deposit Thickness Data

- Repeated Measurements per matrix test
  - Axial Location: 21
  - Radial Location: 4
  - Total measurements per test: 84

- Analyses performed on the following deposit thickness responses:
  - Deposit (Average of all 84 measurements per test)
  - Ri, i=1 to 4 (Average of 21 measurements per radial location)
  - Aj, j=1 to 21 (Average of 4 measurements per axial location)
  - Slope (Slope of the estimated linear equation from A1 to A21)
  - Deposit_Axial (Average of 4 radial measurements per axial location)
    - To determine differences in axial location
  - Deposit_Radial (Average of 21 axial measurements per radial location)
    - To determine differences in radial location

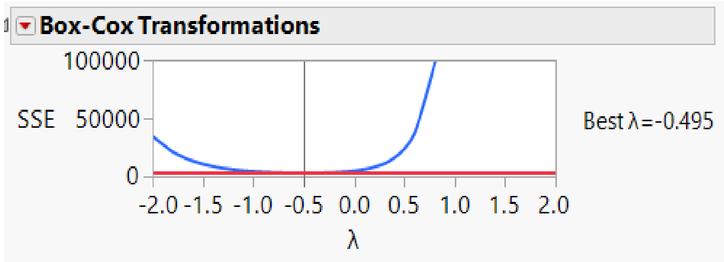
Analysis of Variance (ANOVA)

- Modeled 64 deposit thickness data
- **Inverse square root** transformation was applied to the deposit thickness data
- Regressed **transformed deposit thickness data** on:
  - Main effects (8)
  - Two-factor interaction effects (28)

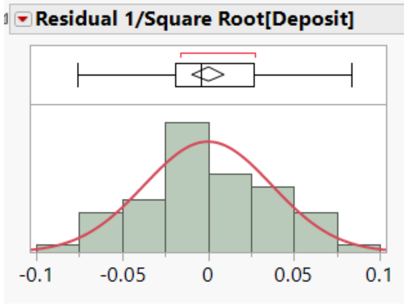
Transformation of Deposit Thickness

- Since ANOVA is based on the assumption that the model residuals (difference between actual and model predicted values) come from a Normal distribution, often times a transformation is needed to ensure that this assumption is not violated.

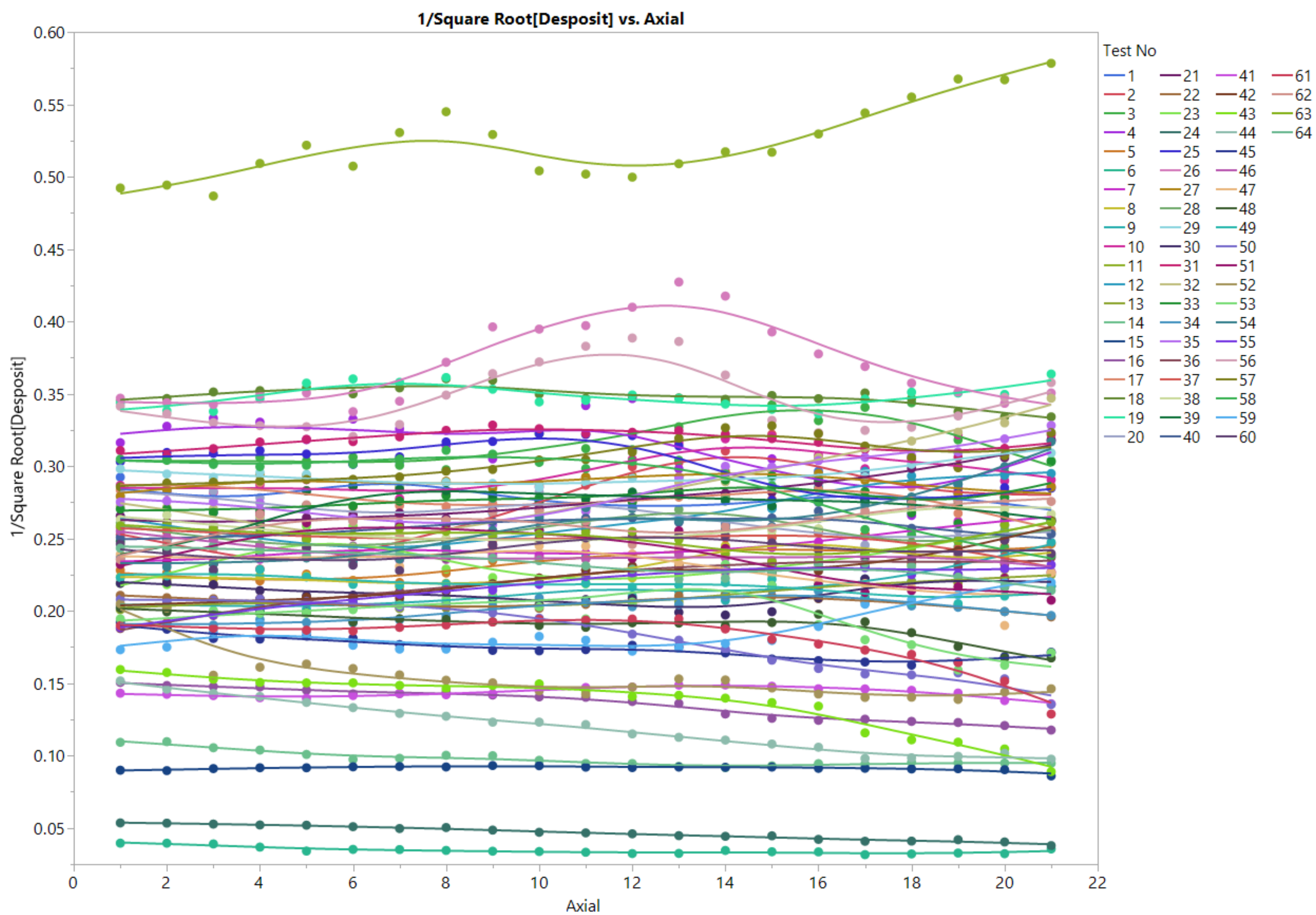
- The Box-Cox analysis curve suggests that an inverse square root (λ = -0.5) is the best transformation to use.



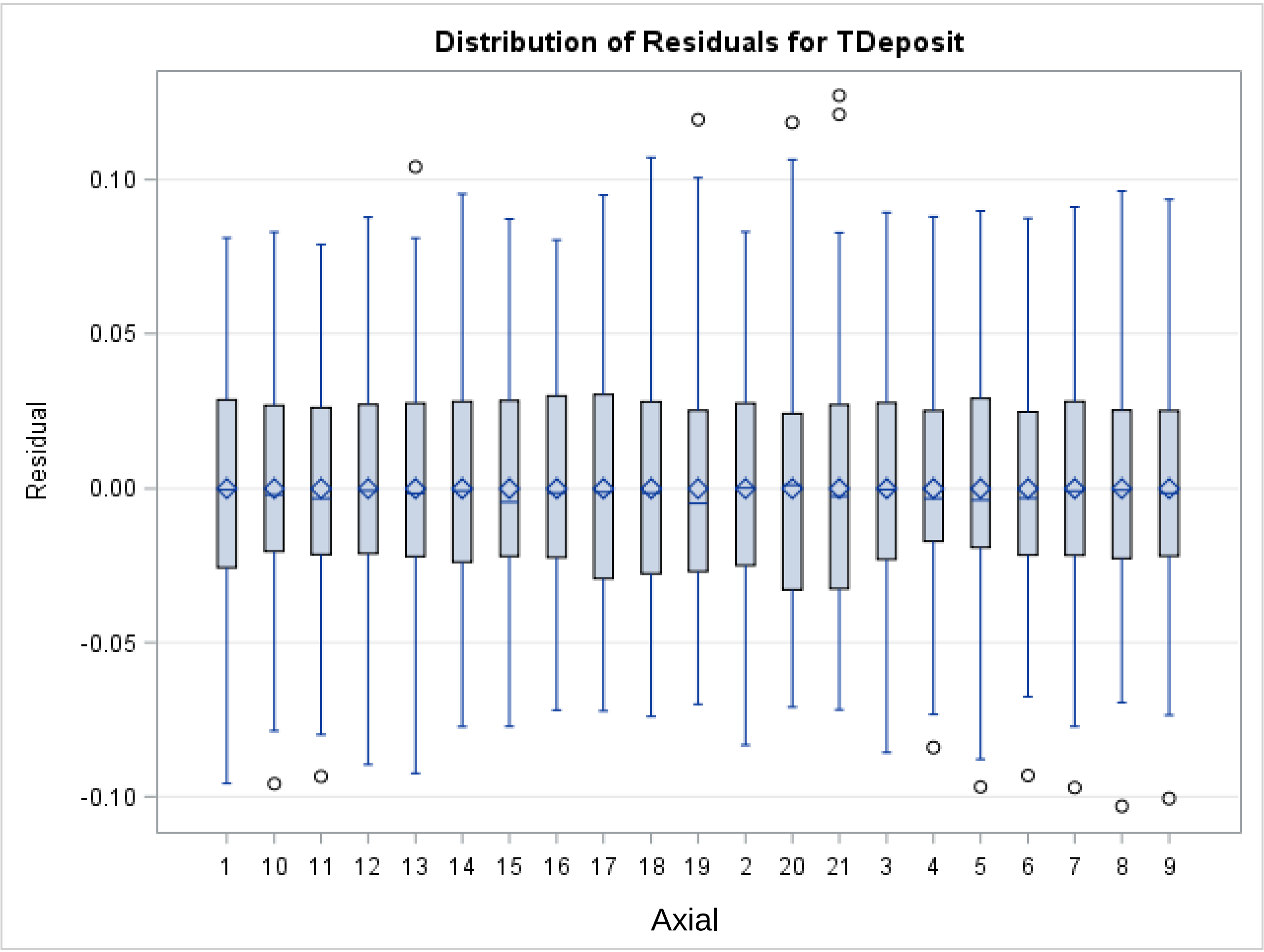
- Histogram of residuals from the inverse square root model suggests that the assumption of Normal distribution is achieved.



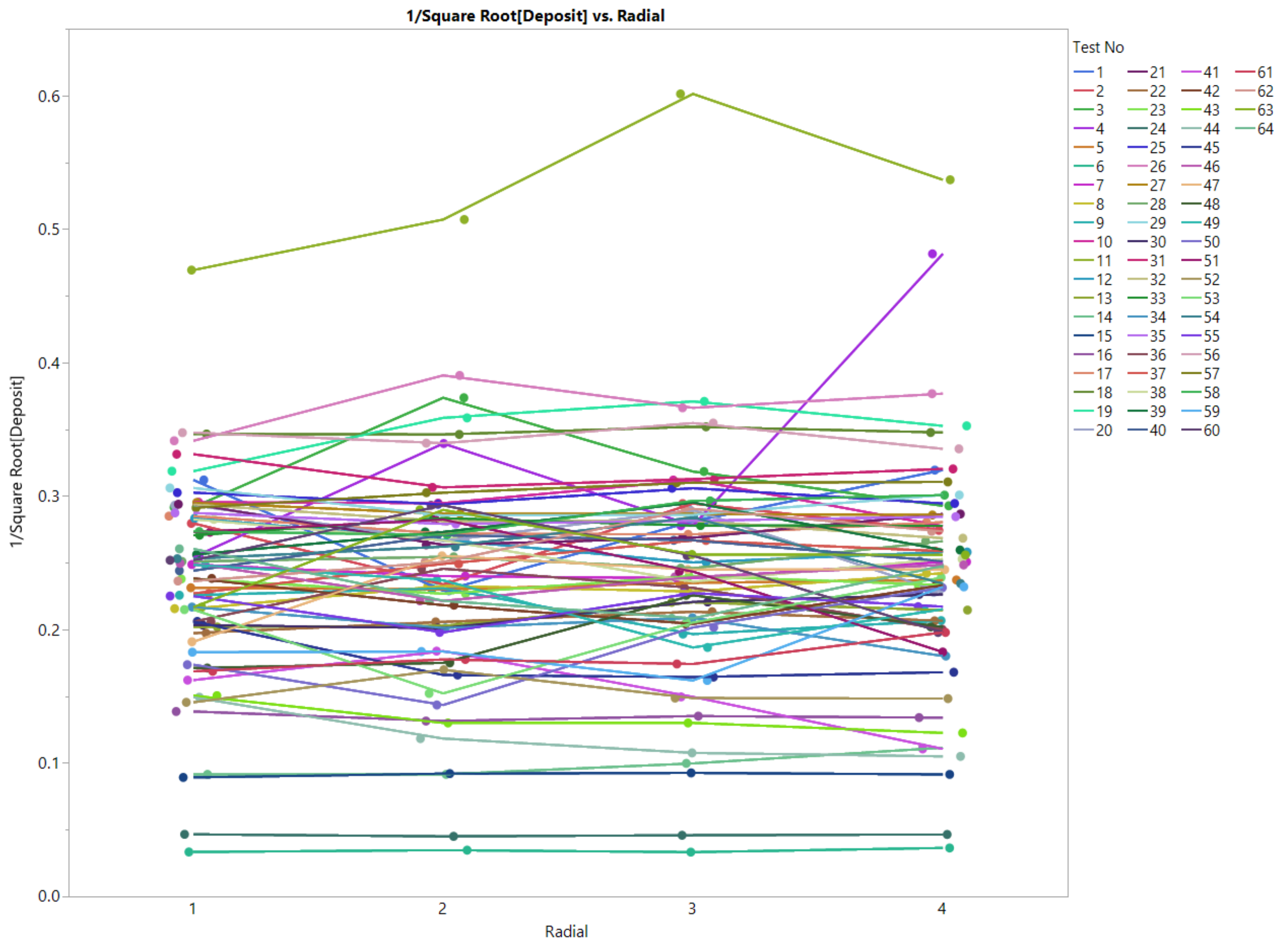
Deposit by Axial Location



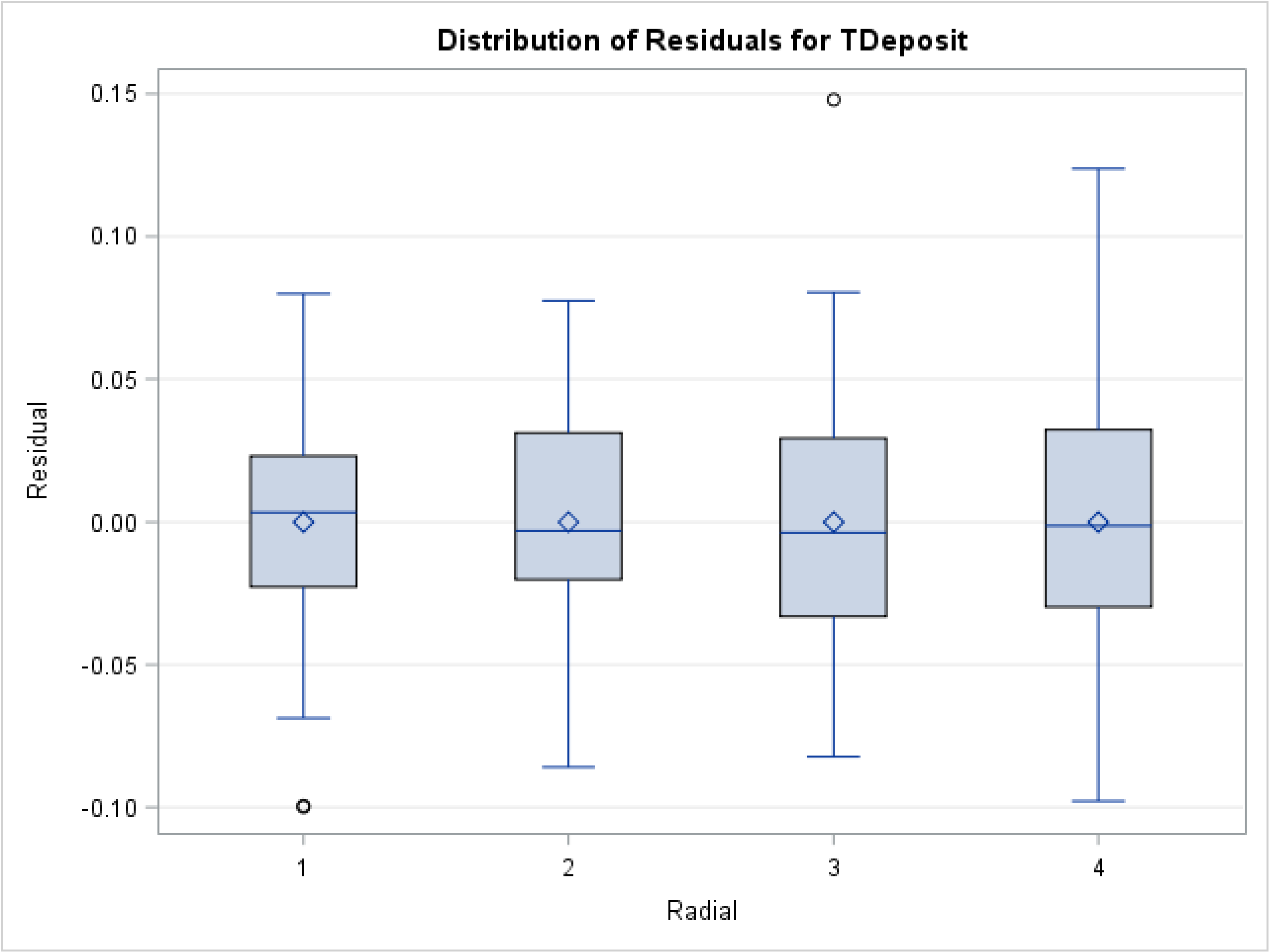
No significant Axial Location differences



Deposit by Radial Location



No significant Radial Location differences



ANOVA Results

- There is convergence of ANOVA results among deposit thickness responses so the results for Deposit (average of 84 measurements) is presented in detail in the following slides.

1/sqrt transformation	Deposit	R1	R2	R3	R4	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10	A11	A12	A13	A14	A15	A16	A17	A18	A19	A20	A21	SlopeT
Source	Prob > F	Prob > F	Prob > F	Prob > F	Prob > F	Prob > F	Prob > F	Prob > F	Prob > F	Prob > F	Prob > F	Prob > F	Prob > F	Prob > F	Prob > F	Prob > F	Prob > F	Prob > F	Prob > F	Prob > F	Prob > F	Prob > F	Prob > F	Prob > F	Prob > F	Prob > F	Prob > F
Biodiesel	0.91	0.71	0.96	0.97	0.90	0.92	0.98	0.95	0.98	0.90	0.91	0.90	0.89	0.91	0.99	1.00	0.87	0.66	0.70	0.75	0.73	0.70	0.70	0.70	0.64	0.54	0.16
Sodium	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.11
Glycerin	0.19	0.22	0.28	0.33	0.08	0.11	0.11	0.19	0.27	0.30	0.22	0.19	0.20	0.22	0.20	0.18	0.15	0.17	0.18	0.19	0.20	0.29	0.30	0.24	0.13	0.15	0.93
Corrosion Inibitor	0.83	0.83	0.94	0.63	0.89	0.91	0.98	1.00	0.92	0.82	0.85	0.78	0.84	0.94	0.94	0.93	0.89	0.78	0.83	0.87	0.70	0.68	0.67	0.60	0.63	0.81	0.43
Mono Acid Lubricity Additive	0.93	0.82	0.65	0.91	0.63	0.82	0.86	0.99	0.88	0.85	0.91	0.99	0.96	0.89	0.83	0.83	0.95	0.85	0.81	0.84	0.95	0.83	0.90	0.98	0.86	0.98	0.89
Detergent Additive	0.63	0.53	0.36	0.72	0.89	0.78	0.72	0.81	0.85	0.90	0.95	0.94	0.98	0.98	0.76	0.61	0.67	0.54	0.48	0.40	0.38	0.37	0.36	0.35	0.19	0.09	0.00
Cetane Number Improver	0.42	0.36	0.75	0.34	0.42	0.45	0.44	0.51	0.48	0.40	0.33	0.27	0.32	0.44	0.46	0.47	0.47	0.49	0.52	0.50	0.42	0.40	0.37	0.43	0.41	0.43	0.90
Conductivity Additive	0.13	0.09	0.20	0.16	0.23	0.19	0.20	0.23	0.25	0.22	0.23	0.21	0.21	0.17	0.15	0.20	0.16	0.10	0.09	0.10	0.08	0.07	0.08	0.09	0.09	0.11	0.10
Biodiesel*Sodium	0.83	0.28	0.68	0.98	0.94	0.82	0.86	0.72	0.82	0.91	0.86	0.77	0.76	0.72	0.76	0.66	0.61	0.55	0.68	0.81	0.93	0.90	0.86	0.99	0.95	0.90	0.71
Biodiesel*Glycerin	0.43	0.20	0.25	1.00	0.43	0.43	0.37	0.31	0.23	0.25	0.29	0.34	0.41	0.46	0.43	0.49	0.52	0.56	0.54	0.54	0.56	0.55	0.51	0.51	0.50	0.65	0.35
Biodiesel*Corrosion Inibitor	0.87	0.51	0.87	0.92	0.73	0.80	0.78	0.64	0.62	0.68	0.73	0.84	0.89	0.85	0.73	0.69	0.85	0.94	0.95	0.93	0.94	0.88	0.85	0.96	0.97	0.97	0.28
Biodiesel*Mono Acid Lubricity Additive	0.76	0.68	0.44	0.52	0.75	0.88	0.88	0.72	0.60	0.62	0.62	0.64	0.73	0.82	0.80	0.87	0.94	0.97	0.81	0.78	0.76	0.71	0.78	0.81	0.82	0.82	0.87
Biodiesel*Detergent Additive	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.12
Biodiesel*Cetane Number Improver	0.16	0.35	0.09	0.13	0.29	0.38	0.34	0.26	0.14	0.10	0.13	0.15	0.12	0.12	0.14	0.18	0.17	0.10	0.10	0.17	0.24	0.18	0.17	0.18	0.22	0.16	0.57
Biodiesel*Conductivity Additive	0.05	0.13	0.02	0.20	0.02	0.04	0.03	0.06	0.07	0.06	0.05	0.09	0.11	0.09	0.08	0.06	0.06	0.08	0.09	0.10	0.08	0.05	0.05	0.05	0.06	0.06	0.83
Sodium*Glycerin	0.08	0.15	0.08	0.07	0.05	0.14	0.13	0.09	0.12	0.17	0.14	0.12	0.12	0.12	0.09	0.05	0.05	0.06	0.05	0.06	0.11	0.09	0.07	0.05	0.04	0.05	0.16
Sodium*Corrosion Inibitor	0.24	0.19	0.18	0.37	0.53	0.24	0.22	0.26	0.26	0.29	0.32	0.27	0.29	0.31	0.37	0.36	0.38	0.26	0.22	0.25	0.30	0.22	0.16	0.24	0.16	0.14	0.47
Sodium*Mono Acid Lubricity Additive	0.05	0.15	0.05	0.10	0.02	0.16	0.14	0.11	0.12	0.14	0.08	0.07	0.08	0.07	0.06	0.04	0.04	0.05	0.03	0.02	0.03	0.04	0.05	0.05	0.04	0.03	0.07
Sodium*Detergent Additive	0.00	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.19
Sodium*Cetane Number Improver	0.43	0.20	0.26	0.65	0.59	0.29	0.30	0.30	0.27	0.26	0.23	0.26	0.30	0.35	0.31	0.32	0.30	0.30	0.35	0.47	0.64	0.91	0.97	0.93	0.91	0.96	0.02
Sodium*Conductivity Additive	0.43	0.31	0.54	0.54	0.84	0.56	0.54	0.44	0.51	0.58	0.77	0.69	0.54	0.49	0.55	0.46	0.47	0.46	0.51	0.52	0.39	0.25	0.25	0.31	0.25	0.21	0.16
Glycerin*Corrosion Inibitor	0.69	0.52	0.93	0.69	0.82	0.73	0.75	0.78	0.82	0.73	0.80	0.91	0.88	0.79	0.77	0.79	0.88	0.75	0.66	0.66	0.64	0.59	0.52	0.52	0.52	0.47	0.33
Glycerin*Mono Acid Lubricity Additive	0.19	0.15	0.22	0.21	0.19	0.25	0.24	0.28	0.27	0.26	0.19	0.16	0.18	0.18	0.17	0.12	0.12	0.11	0.13	0.15	0.21	0.27	0.26	0.18	0.21	0.21	0.64
Glycerin*Detergent Additive	0.84	0.41	0.81	0.73	0.73	0.78	0.92	0.98	0.89	0.93	1.00	1.00	0.91	0.85	0.84	0.88	0.77	0.73	0.69	0.67	0.71	0.83	0.94	0.91	0.81	0.72	0.53
Glycerin*Cetane Number Improver	0.12	0.08	0.26	0.08	0.21	0.08	0.07	0.08	0.08	0.09	0.06	0.06	0.09	0.15	0.14	0.15	0.22	0.19	0.20	0.16	0.15	0.16	0.16	0.12	0.14	0.24	0.42
Glycerin*Conductivity Additive	0.07	0.16	0.08	0.05	0.15	0.06	0.05	0.08	0.04	0.02	0.02	0.02	0.03	0.05	0.06	0.06	0.09	0.09	0.13	0.20	0.16	0.16	0.15	0.14	0.14	0.16	0.15
Corrosion Inibitor*Mono Acid Lubricity Additive	0.51	0.74	0.52	0.54	0.53	0.93	0.85	0.85	0.71	0.79	0.77	0.85	0.87	0.83	0.72	0.61	0.51	0.51	0.37	0.27	0.22	0.20	0.22	0.24	0.23	0.29	0.01
Corrosion Inibitor*Detergent Additive	0.75	0.77	0.44	0.71	0.61	0.85	0.86	0.84	0.87	0.81	0.73	0.76	0.86	0.93	0.96	0.96	0.94	0.85	0.68	0.57	0.58	0.53	0.46	0.47	0.71	0.74	0.33
Corrosion Inibitor*Cetane Number Improver	0.41	0.43	0.22	0.42	0.52	0.60	0.62	0.58	0.53	0.46	0.37	0.40	0.50	0.49	0.47	0.43	0.44	0.54	0.59	0.51	0.38	0.33	0.28	0.25	0.23	0.30	0.24
Corrosion Inibitor*Conductivity Additive	0.11	0.11	0.21	0.13	0.05	0.20	0.16	0.12	0.13	0.14	0.11	0.13	0.17	0.19	0.16	0.11	0.14	0.16	0.15	0.10	0.07	0.09	0.09	0.06	0.04	0.05	0.16
Mono Acid Lubricity Additive*Detergent Additive	0.43	0.84	0.07	0.48	0.62	0.58	0.53	0.60	0.41	0.40	0.48	0.51	0.41	0.40	0.38	0.35	0.48	0.51	0.44	0.38	0.40	0.41	0.45	0.53	0.41	0.28	0.56
Mono Acid Lubricity Additive*Cetane Number Improver	0.10	0.03	0.06	0.14	0.49	0.09	0.08	0.14	0.13	0.13	0.10	0.12	0.18	0.25	0.26	0.24	0.32	0.25	0.18	0.12	0.09	0.07	0.04	0.03	0.03	0.05	0.17
Mono Acid Lubricity Additive*Conductivity Additive	0.07	0.07	0.17	0.10	0.04	0.07	0.05	0.03	0.05	0.07	0.05	0.07	0.11	0.12	0.10	0.10	0.07	0.09	0.06	0.05	0.07	0.10	0.10	0.12	0.09	0.08	0.85
Detergent Additive*Cetane Number Improver	0.77	0.90	0.62	0.53	0.87	0.72	0.73	0.84	0.58	0.51	0.71	0.76	0.69	0.69	0.79	0.86	0.99	0.85	0.81	0.94	0.97	0.70	0.63	0.78	0.74	0.93	0.70
Detergent Additive*Conductivity Additive	0.41	0.29	0.16	0.32	0.85	0.38	0.36	0.41	0.40	0.52	0.61	0.57	0.54	0.48	0.48	0.39	0.38	0.29	0.29	0.30	0.34	0.38	0.44	0.44	0.41	0.33	0.60
Cetane Number Improver*Conductivity Additive	0.72	0.57	0.88	0.86	0.46	0.66	0.64	0.74	0.75	0.71	0.68	0.66	0.75	0.94	0.99	0.95	0.92	0.85	0.84	0.76	0.66	0.67	0.69	0.69	0.49	0.45	0.65

1/sqrt(Deposit) ANOVA

Summary of Fit

RSquare	0.772485
RSquare Adj	0.469132
Root Mean Square Error	0.05673
Mean of Response	0.238183
Observations (or Sum Wgts)	64

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	36	0.29503343	0.008195	2.5465
Error	27	0.08689421	0.003218	**Prob > F**
C. Total	63	0.38192764		0.0069*

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Biodiesel	1	1	0.00004403	0.0137	0.9077
Sodium	1	1	0.09079904	28.2133	<.0001*
Glycerin	1	1	0.00581604	1.8072	0.1900
Corrosion Inibitor	1	1	0.00015942	0.0495	0.8255
Mono Acid Lubricity Additive	1	1	0.00002739	0.0085	0.9272
Detergent Additive	1	1	0.00075574	0.2348	0.6319
Cetane Number Improver	1	1	0.00216136	0.6716	0.4197
Conductivity Additive	1	1	0.00800700	2.4880	0.1264
Biodiesel*Sodium	1	1	0.00015484	0.0481	0.8280
Biodiesel*Glycerin	1	1	0.00203290	0.6317	0.4337
Biodiesel*Corrosion Inibitor	1	1	0.00009186	0.0285	0.8671

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Biodiesel*Mono Acid Lubricity Additive	1	1	0.00031815	0.0989	0.7556
Biodiesel*Detergent Additive	1	1	0.03582981	11.1331	0.0025*
Biodiesel*Cetane Number Improver	1	1	0.00679794	2.1123	0.1576
Biodiesel*Conductivity Additive	1	1	0.01300661	4.0414	0.0545
Sodium*Glycerin	1	1	0.01072300	3.3319	0.0790
Sodium*Corrosion Inibitor	1	1	0.00473697	1.4719	0.2356
Sodium*Mono Acid Lubricity Additive	1	1	0.01318476	4.0968	0.0530
Sodium*Detergent Additive	1	1	0.03055602	9.4944	0.0047*
Sodium*Cetane Number Improver	1	1	0.00205073	0.6372	0.4317
Sodium*Conductivity Additive	1	1	0.00210925	0.6554	0.4253
Glycerin*Corrosion Inibitor	1	1	0.00053856	0.1673	0.6857
Glycerin*Mono Acid Lubricity Additive	1	1	0.00589092	1.8304	0.1873
Glycerin*Detergent Additive	1	1	0.00013314	0.0414	0.8403
Glycerin*Cetane Number Improver	1	1	0.00847800	2.6343	0.1162
Glycerin*Conductivity Additive	1	1	0.01149384	3.5714	0.0696
Corrosion Inibitor*Mono Acid Lubricity Additive	1	1	0.00144530	0.4491	0.5085
Corrosion Inibitor*Detergent Additive	1	1	0.00033868	0.1052	0.7481
Corrosion Inibitor*Cetane Number Improver	1	1	0.00228323	0.7095	0.4070
Corrosion Inibitor*Conductivity Additive	1	1	0.00902543	2.8044	0.1056
Mono Acid Lubricity Additive*Detergent Additive	1	1	0.00202680	0.6298	0.4344
Mono Acid Lubricity Additive*Cetane Number Improver	1	1	0.00931451	2.8942	0.1004
Mono Acid Lubricity Additive*Conductivity Additive	1	1	0.01176895	3.6569	0.0665
Detergent Additive*Cetane Number Improver	1	1	0.00027133	0.0843	0.7738
Detergent Additive*Conductivity Additive	1	1	0.00223084	0.6932	0.4124
Cetane Number Improver*Conductivity Additive	1	1	0.00043105	0.1339	0.7172

1/sqrt(Deposit) ANOVA Results

- Significant effects (p-value≤0.05)
  - Sodium
  - Biodiesel*Detergent Additive
  - Sodium*Detergent Additive

- Marginal effects (0.05<p-value≤0.10)
  - Biodiesel*Conductivity Additive
  - Sodium*Glycerin
  - Sodium*Mono Acid Lubricity Additive
  - Glycerin*Conductivity Additive
  - Mono Acid Lubricity Additive*Conductivity Additive

- Not statistically significant effects (p-value>0.10)
  - Corrosion Inhibitor
  - Cetane Number Improver

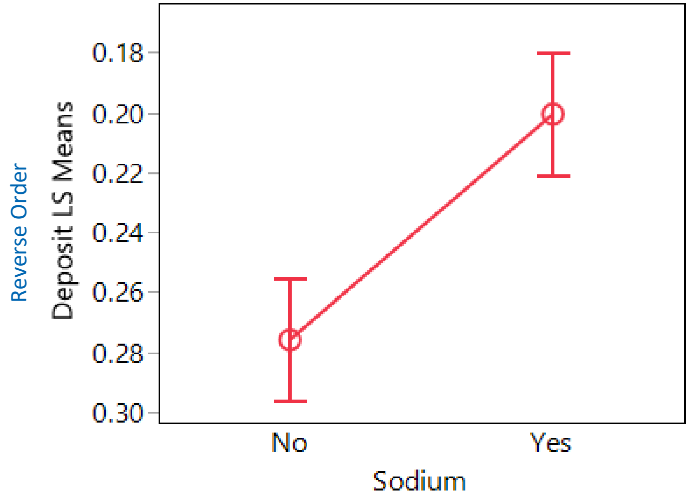
*Note: **p-value** is the probability of getting something more extreme than your result, when there is no effect in the population*

- Not statistically significant effects (p-value>0.10)
  - Biodiesel*Sodium
  - Biodiesel*Glycerin
  - Biodiesel*Corrosion Inhibitor
  - Biodiesel*Mono Acid Lubricity Additive
  - Biodiesel*Cetane Number Improver
  - Sodium*Corrosion Inhibitor
  - Sodium*Cetane Number Improver
  - Sodium*Conductivity Additive
  - Glycerin*Corrosion Inhibitor
  - Glycerin*Mono Acid Lubricity Additive
  - Glycerin*Detergent Additive
  - Glycerin*Cetane Number Improver
  - Corrosion Inhibitor*Mono Acid Lubricity Additive
  - Corrosion Inhibitor*Detergent Additive
  - Corrosion Inhibitor*Cetane Number Improver
  - Corrosion Inhibitor*Conductivity Additive
  - Mono Acid Lubricity Additive*Detergent Additive
  - Mono Acid Lubricity Additive*Cetane Number Improver
  - Detergent Additive*Cetane Number Improver
  - Detergent Additive*Conductivity Additive
  - Cetane Number Improver*Conductivity Additive

Sodium Effect on 1/sqrt(Deposit)

- Sodium effect on deposit thickness is statistically significant
  - Sodium significantly increases deposit thickness

1/sqrt(Deposit) LS Means with 95% Confidence Intervals

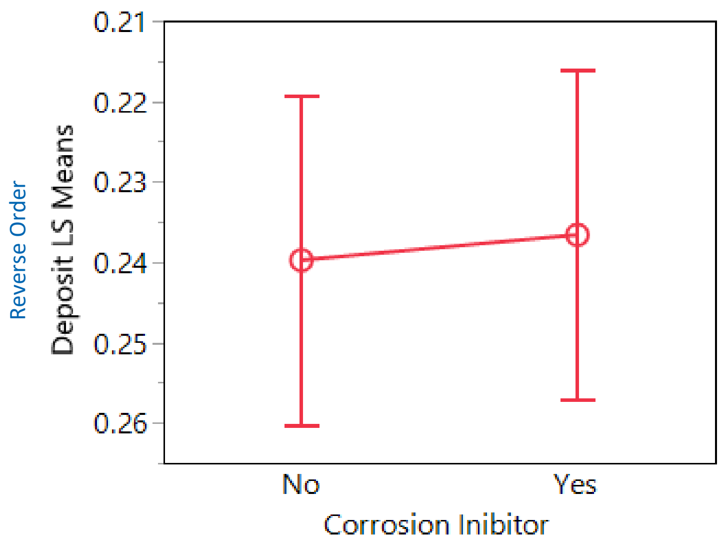


Sodium	1/sqrt(Deposit) LSMean	Deposit LSMean
No	0.2758	13.14
Yes	0.2005	24.87

Corrosion Inhibitor Effect on 1/sqrt(Deposit)

- Corrosion Inhibitor effect on deposit thickness is not statistically significant
  - Presence or absence of corrosion inhibitor is not statistically different

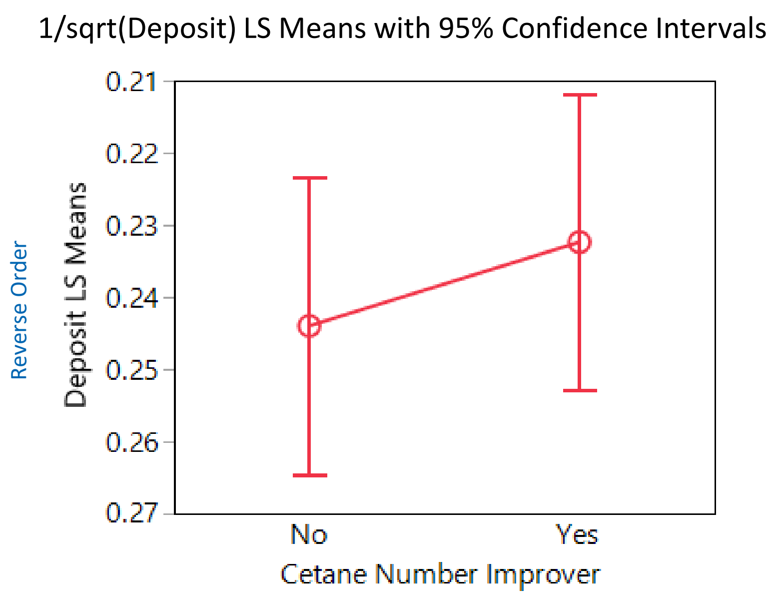
1/sqrt(Deposit) LS Means with 95% Confidence Intervals



Corrosion Inhibitor	1/sqrt(Deposit) LSMean	Deposit LSMean
No	0.2398	17.39
Yes	0.2366	17.86

Cetane Number Improver Effect on 1/sqrt(Deposit)

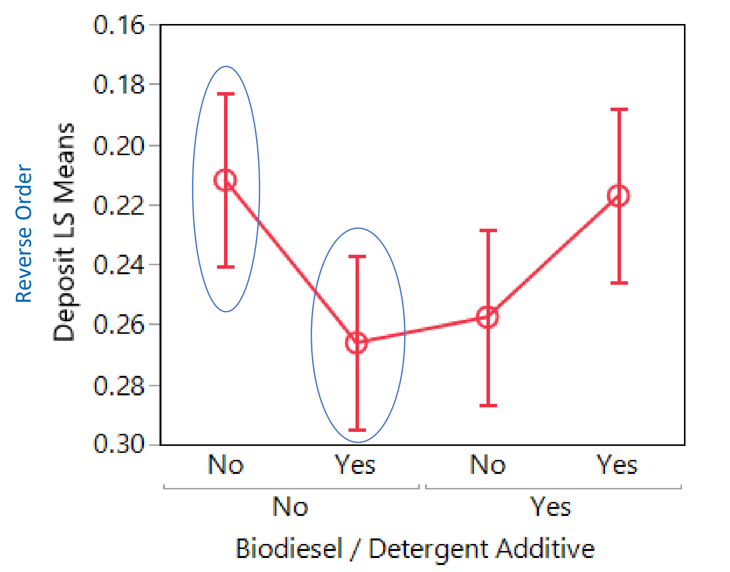
- Cetane Number Improver effect on deposit thickness is not statistically significant
  - Presence or absence of cetane number improver is not statistically different



Cetane Number Improver	1/sqrt(Deposit) LSMean	Deposit LSMean
No	0.2440	16.80
Yes	0.2324	18.52

Biodiesel-Detergent Additive Effect on 1/sqrt(Deposit)

- Biodiesel-Detergent Additive interaction effect is statistically significant
  - Without biodiesel, presence of detergent additive has significantly lower deposit thickness than absence of detergent additive
  - With biodiesel, presence or absence of detergent additive is not statistically different



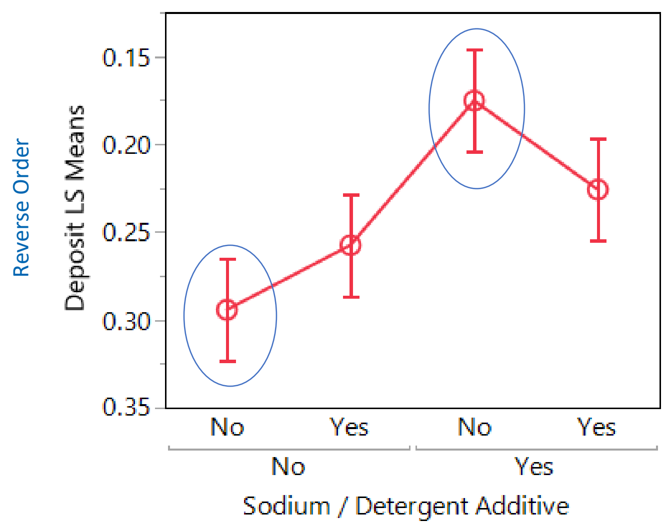
Biodiesel, Detergent Additive	1/sqrt(Deposit) LSMean	Deposit LSMean
No,No	0.2119	22.27
No,Yes	0.2661	14.12
Yes,No	0.2576	15.07
Yes,Yes	0.2171	21.21

Level	- Level	Difference	p-Value
No,Yes	No,No	0.0542	0.0539
No,Yes	Yes,Yes	0.0490	0.0930
Yes,No	No,No	0.0457	0.1288
Yes,No	Yes,Yes	0.0404	0.2069
No,Yes	Yes,No	0.0085	0.9736
Yes,Yes	No,No	0.0052	0.9937

Sodium-Detergent Additive Effect on 1/sqrt(Deposit)

- Sodium-Detergent Additive interaction effect is statistically significant
  - Without detergent additive, presence of sodium has significantly higher deposit thickness than absence of sodium
  - With detergent additive, presence or absence of sodium is not statistically different

1/sqrt(Deposit) LS Means with 95% Confidence Intervals

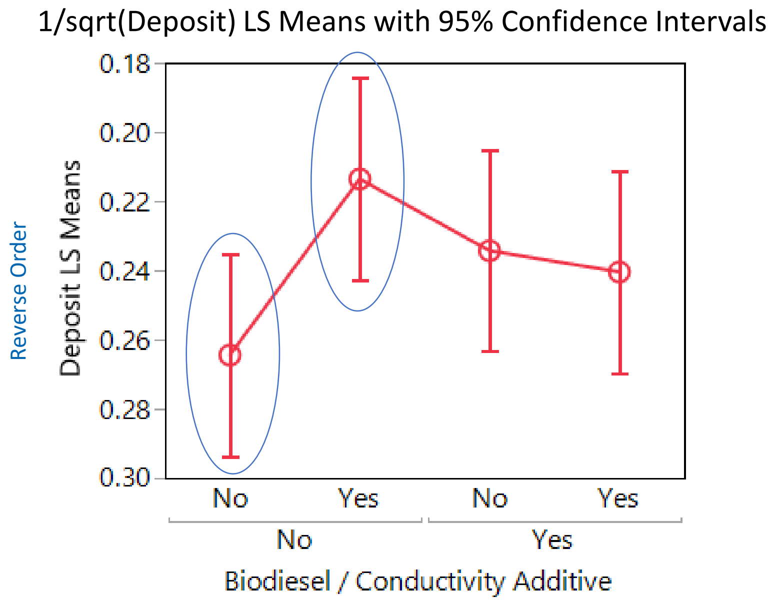


Sodium, Detergent Additive	1/sqrt(Deposit) LSMean	Deposit LSMean
No,No	0.2943	11.55
Yes,No	0.1752	32.57
No,Yes	0.2574	15.09
Yes,Yes	0.2258	19.61

Level	- Level	Difference	p-Value
No,No	Yes,No	0.1190	<.0001*
No,Yes	Yes,No	0.0822	0.0018*
No,No	Yes,Yes	0.0685	0.0103*
Yes,Yes	Yes,No	0.0506	0.0790
No,No	No,Yes	0.0368	0.2790
No,Yes	Yes,Yes	0.0316	0.4080

Biodiesel-Conductivity Additive Effect on 1/sqrt(Deposit)

- Biodiesel-Conductivity Additive interaction effect is marginally significant
  - Without biodiesel, presence of conductivity additive has marginally higher deposit thickness than absence of conductivity additive
  - With biodiesel, presence or absence of conductivity additive is not statistically different

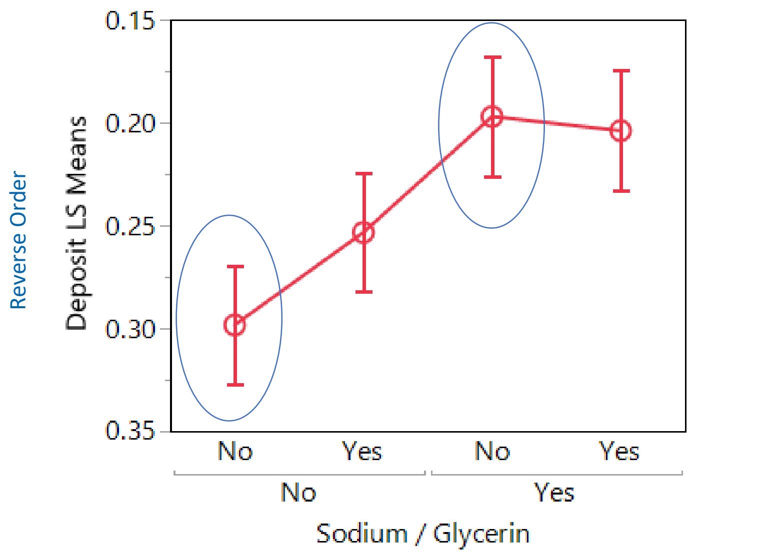


Biodiesel, Conductivity Additive	1/sqrt(Deposit) LSMean	Deposit LSMean
No,No	0.2645	14.30
No,Yes	0.2136	21.92
Yes,No	0.2343	18.22
Yes,Yes	0.2404	17.30

Level	- Level	Difference	p-Value
No,No	No,Yes	0.0509	0.0765
No,No	Yes,No	0.0302	0.4490
Yes,Yes	No,Yes	0.0269	0.5472
No,No	Yes,Yes	0.0240	0.6333
Yes,No	No,Yes	0.0207	0.7321
Yes,Yes	Yes,No	0.0061	0.9898

Sodium-Glycerin Effect on 1/sqrt(Deposit)

- Sodium-Glycerin interaction effect is marginally significant
  - Without glycerin, presence of sodium has significantly higher deposit thickness than absence of sodium
  - With glycerin, presence of sodium has marginally higher deposit thickness than absence of sodium

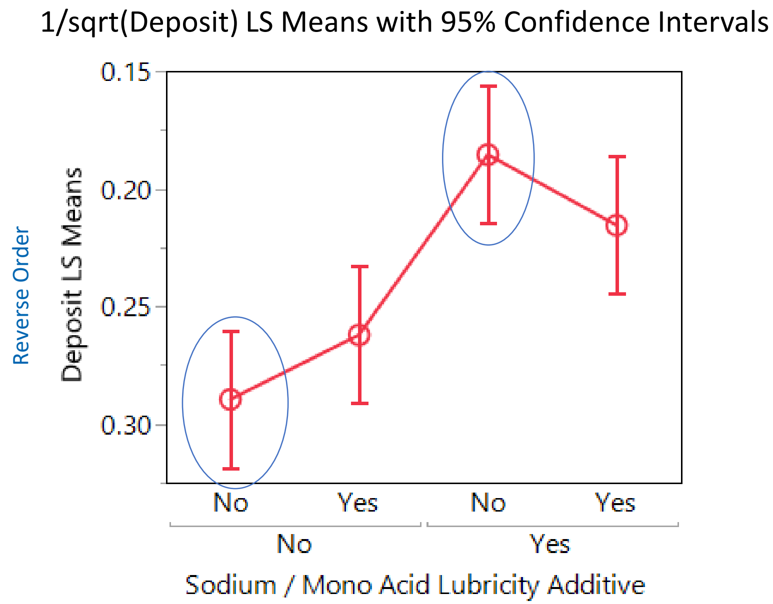


Sodium, Glycerin	1/sqrt(Deposit) LSMean	Deposit LSMean
No,No	0.2983	11.24
Yes,No	0.1971	25.74
No,Yes	0.2534	15.58
Yes,Yes	0.2039	24.05

Level	- Level	Difference	p-Value
No,No	Yes,No	0.1012	0.0002*
No,No	Yes,Yes	0.0944	0.0004*
No,Yes	Yes,No	0.0563	0.0430*
No,Yes	Yes,Yes	0.0494	0.0887
No,No	No,Yes	0.0450	0.1377
Yes,Yes	Yes,No	0.0068	0.9862

Sodium-Mono Acid Lubricity Additive Effect on 1/sqrt(Deposit)

- Sodium-Mono Acid Lubricity Additive interaction effect is marginally significant
  - Without mono acid lubricity additive, presence of sodium has significantly higher deposit thickness than absence of sodium
  - With mono acid lubricity additive, presence or absence of sodium is not statistically different

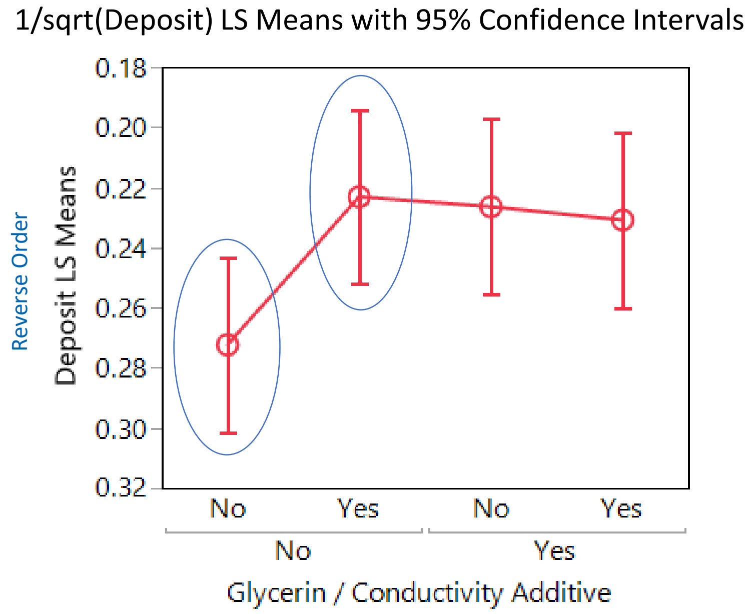


Sodium, Mono Acid Lubricity Additive	1/sqrt(Deposit) LSMean	Deposit LSMean
No,No	0.2895	11.93
Yes,No	0.1855	29.06
No,Yes	0.2622	14.55
Yes,Yes	0.2155	21.53

Level	- Level	Difference	p-Value
No,No	Yes,No	0.1040	0.0001*
No,Yes	Yes,No	0.0766	0.0037*
No,No	Yes,Yes	0.0740	0.0052*
No,Yes	Yes,Yes	0.0466	0.1174
Yes,Yes	Yes,No	0.0300	0.4534
No,No	No,Yes	0.0274	0.5307

Glycerin-Conductivity Additive Effect on 1/sqrt(Deposit)

- Glycerin-Conductivity Additive interaction effect is marginally significant
  - Without glycerin, presence of conductivity additive has marginally higher deposit thickness than absence of conductivity additive
  - With glycerin, presence or absence of conductivity additive is not statistically different



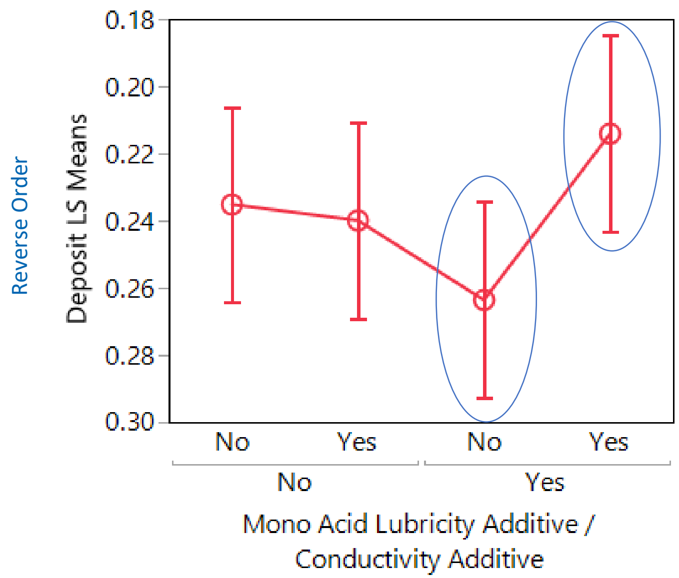
Glycerin, Conductivity Additive	1/sqrt(Deposit) LSMean	Deposit LSMean
No,No	0.2723	13.49
No,Yes	0.2231	20.09
Yes,No	0.2264	19.50
Yes,Yes	0.2309	18.76

Level	- Level	Difference	p-Value
No,No	No,Yes	0.0492	0.0912
No,No	Yes,No	0.0459	0.1263
No,No	Yes,Yes	0.0414	0.1899
Yes,Yes	No,Yes	0.0077	0.9801
Yes,Yes	Yes,No	0.0044	0.9961
Yes,No	No,Yes	0.0033	0.9984

Mono Acid Lubricity Additive-Conductivity Additive Effect on 1/sqrt(Deposit)

- Mono Acid Lubricity Additive-Conductivity Additive interaction effect is marginally significant
  - Without mono acid lubricity additive, presence or absence of conductivity additive is not statistically different
  - With mono acid lubricity additive, presence of conductivity additive has marginally higher deposit thickness than absence of conductivity additive

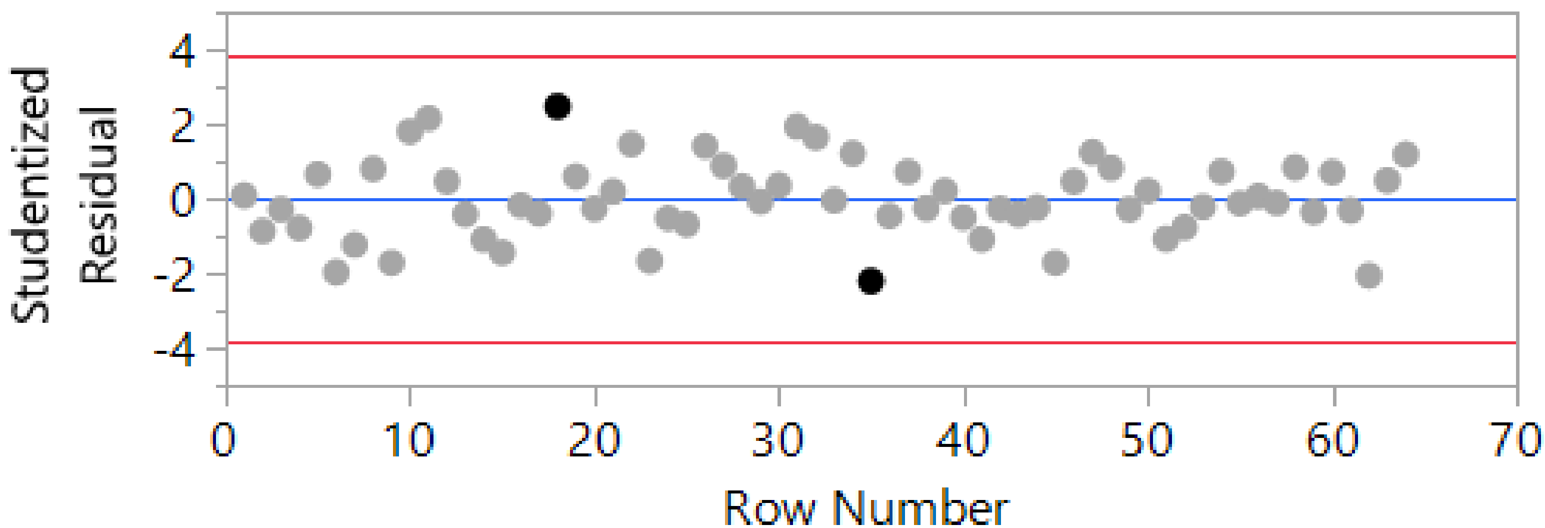
1/sqrt(Deposit) LS Means with 95% Confidence Intervals



Mono Acid Lubricity Additive, Conductivity Additive	1/sqrt(Deposit) LSMean	Deposit LSMean
No,No	0.2352	18.08
No,Yes	0.2399	17.37
Yes,No	0.2636	14.39
Yes,Yes	0.2141	21.82

Level	- Level	Difference	p-Value
Yes,No	Yes,Yes	0.0495	0.0883
Yes,No	No,No	0.0284	0.4998
No,Yes	Yes,Yes	0.0258	0.5788
Yes,No	No,Yes	0.0237	0.6440
No,No	Yes,Yes	0.0211	0.7219
No,Yes	No,No	0.0048	0.9952

No Statistical Outliers



- All residuals fall within the 95% Confidence Limits so no statistical outliers
- Test number 18 has the highest residual followed by test number 35

Estimate of Repeatability

- Root Mean Square Error (RMSE) - estimate of standard deviation

$$Test\_Repeatability = RMSE_{Model} * 1.96 * \sqrt{2}$$

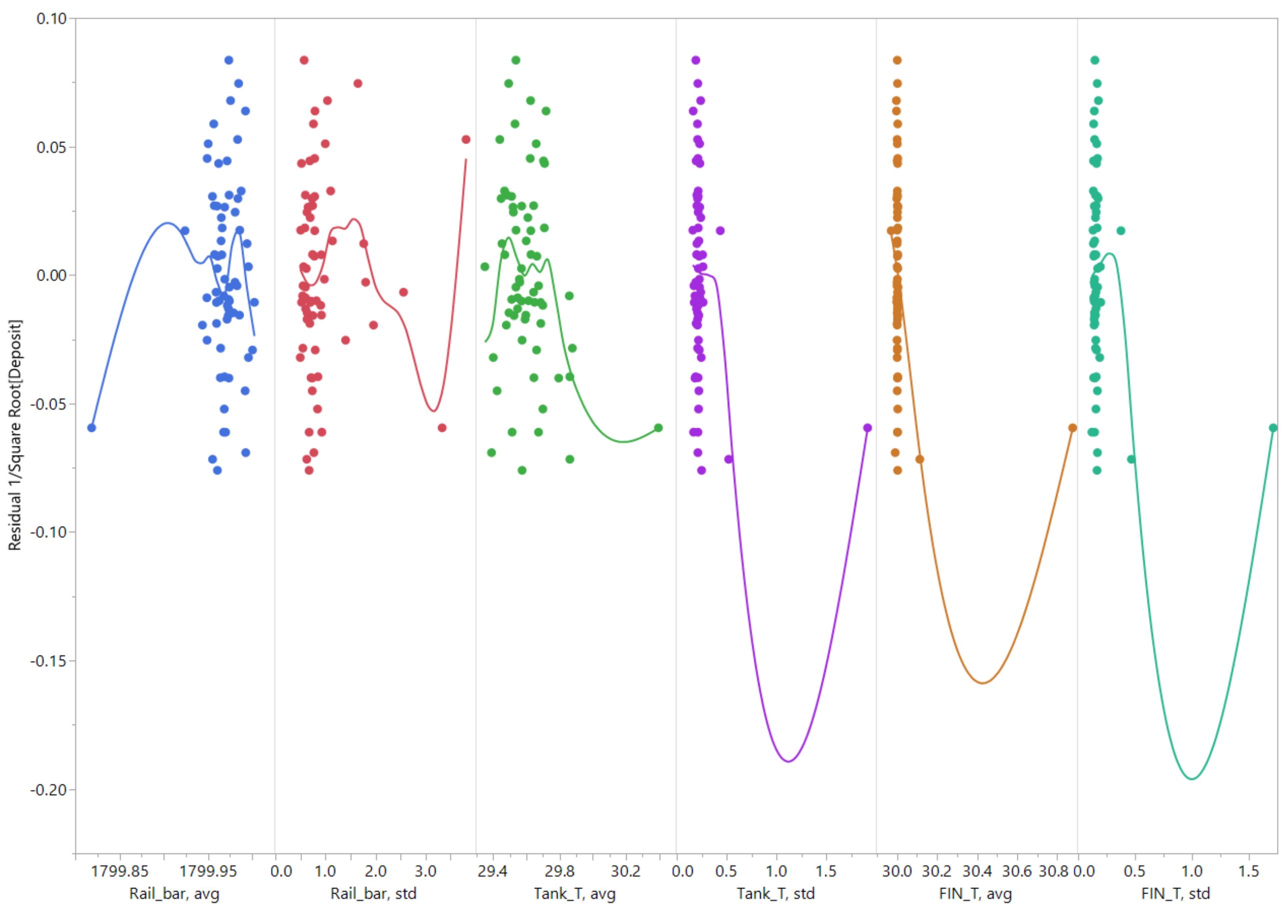
- $RMSE_{Model}$: Estimated standard deviation of results within a rig
- 1.96: 95% coverage based on a **Normal distribution** of residuals
- $\sqrt{2}$: Multiplier due to inference on 2 results

- 1/sqrt(Deposit) Model RMSE = 0.0567
- Repeatability, r = 0.1572
- Based upon the estimated standard deviation (RMSE) and repeatability (r), there is no significant difference between deposit thickness results of 10nm and 40nm. (A result of 10nm was arbitrarily chosen)

Appendix A

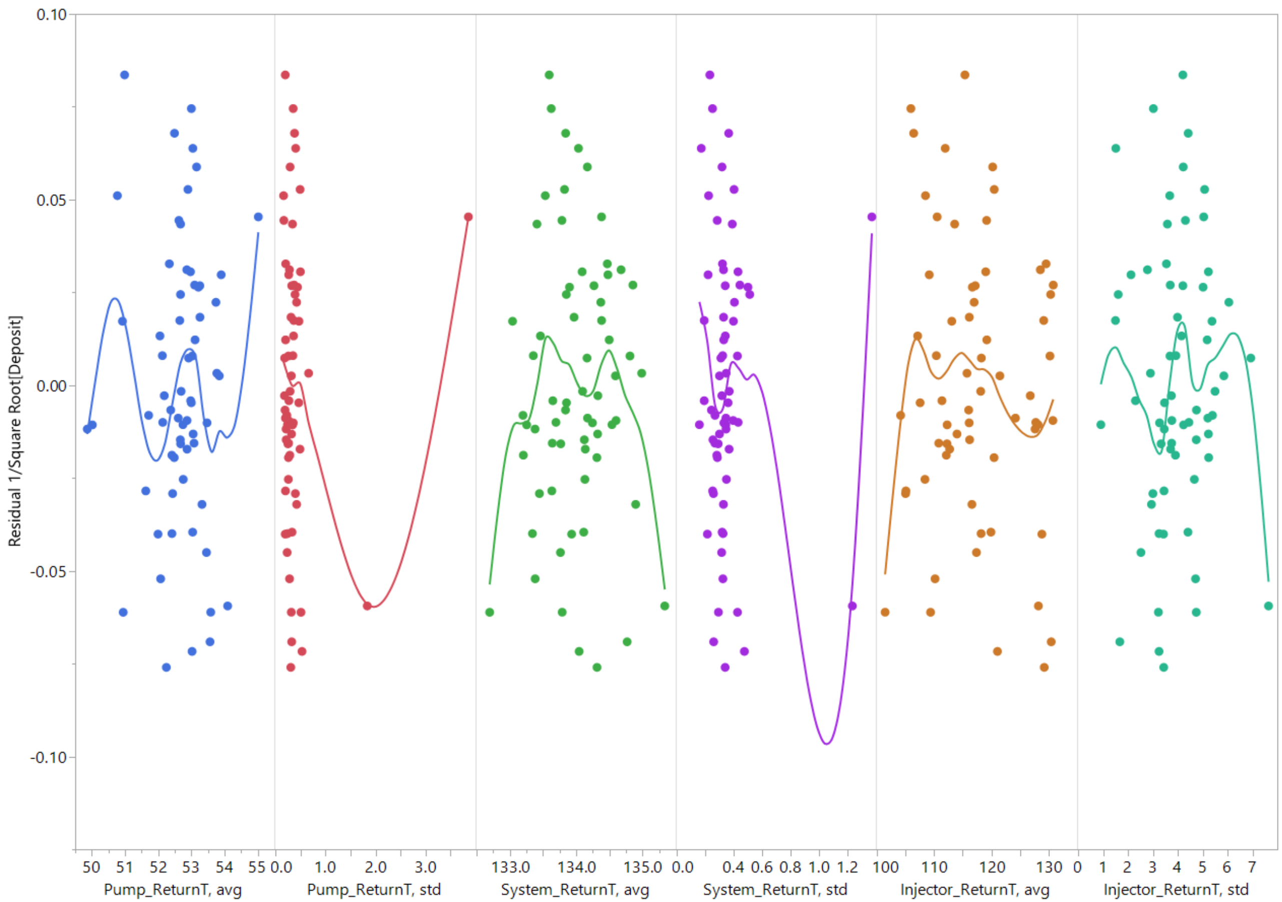
Residual Plots by Operational Parameters

Operational Parameters
Rail bar, Tank_T, FIN_T



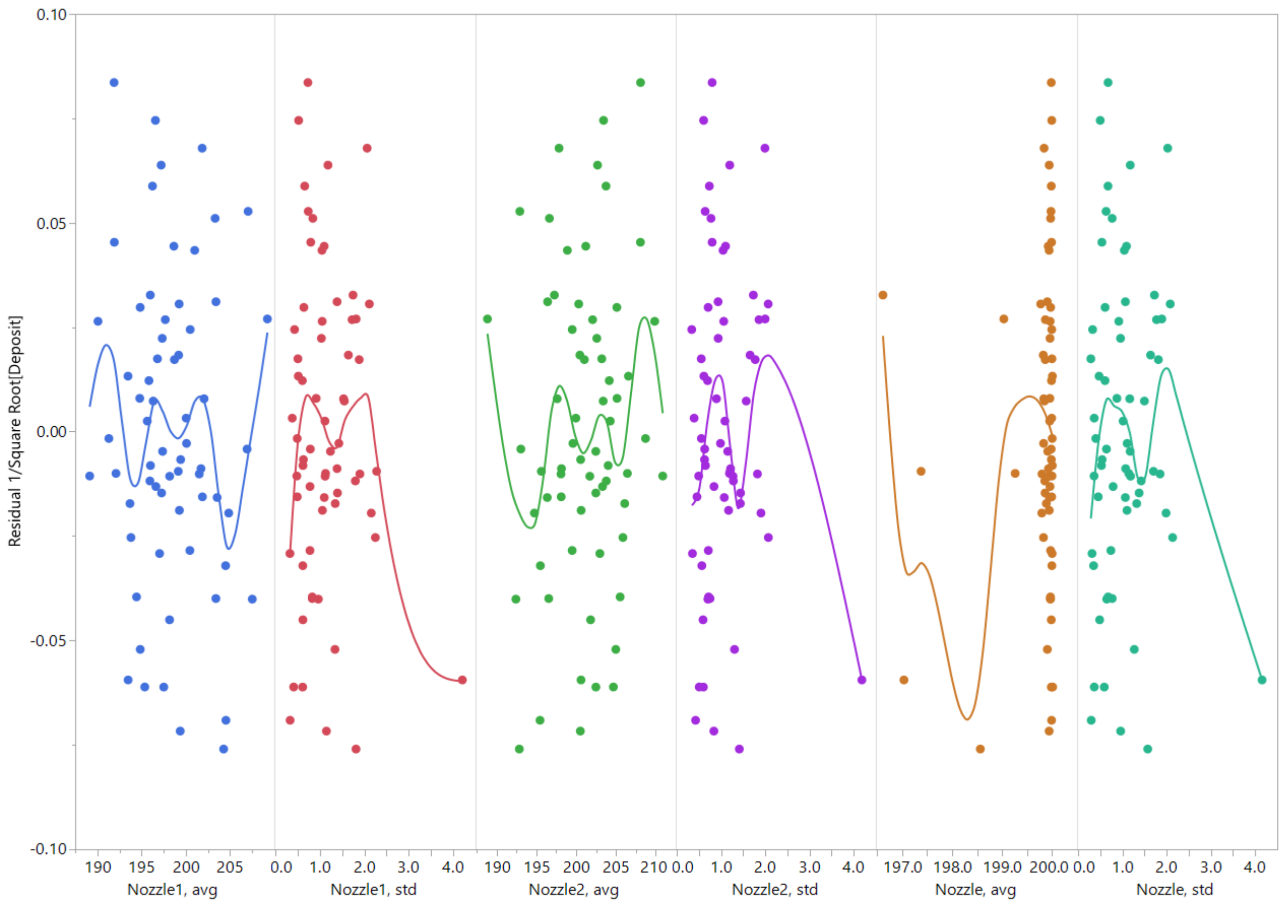
Test 23 seems to be different in terms of Rail bar, Tank_T and FIN_T

Operational Parameters
Pump, System, Injector



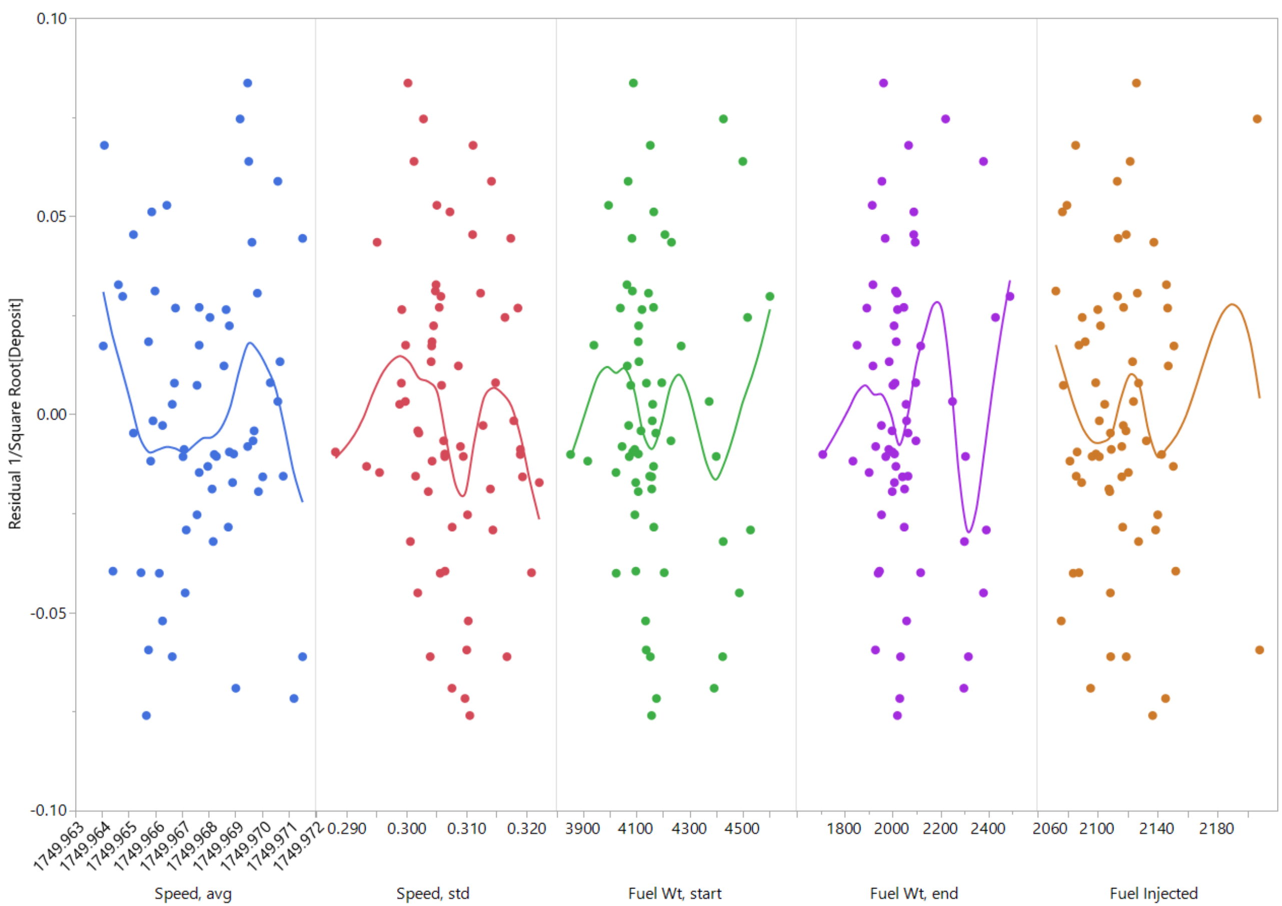
Tests 47 and 23 have higher Pump and System return std

Operational Parameters
Nozzle



Test 23 seems to be different in terms of Nozzle parameters

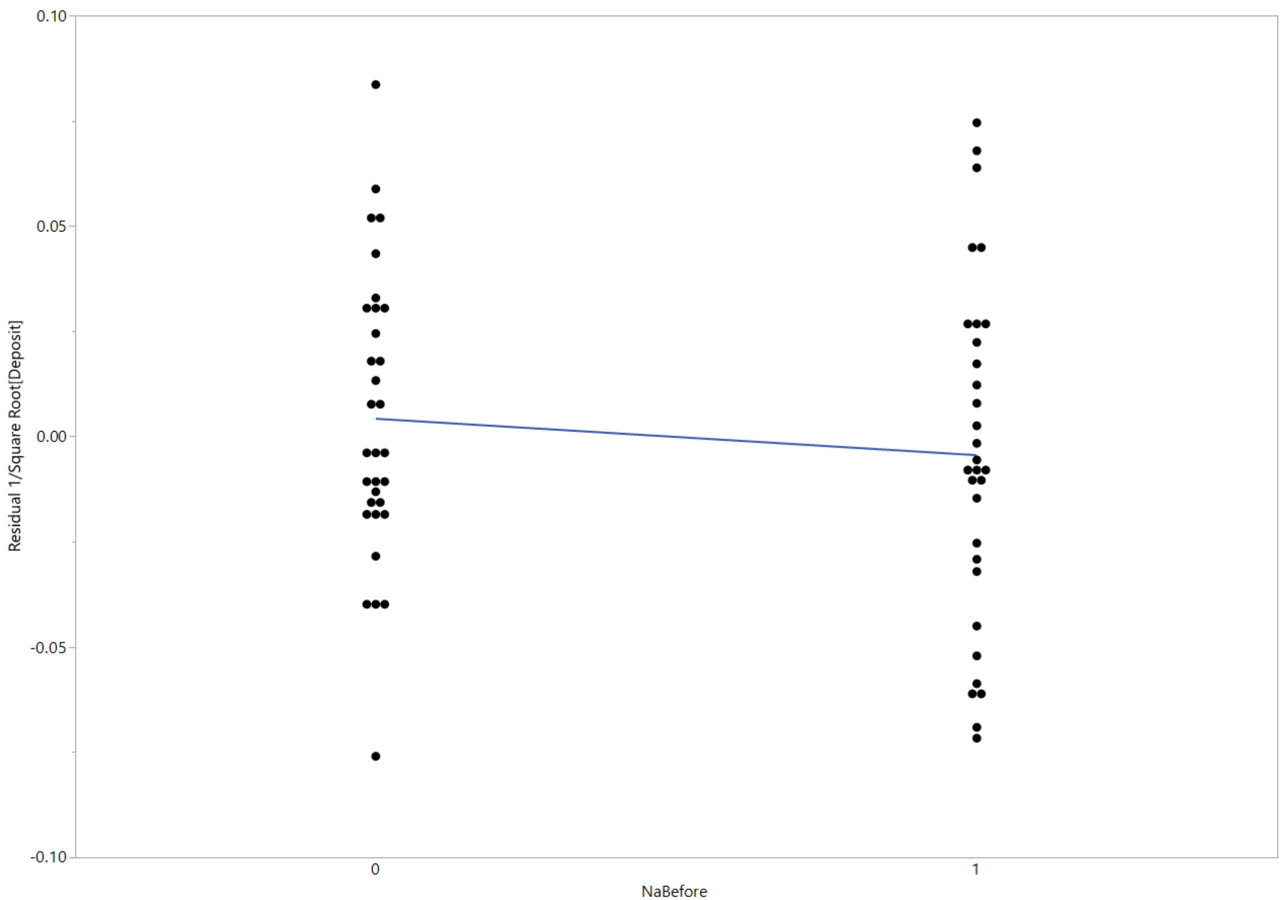
Operational Parameters
Speed, Fuel



No speed nor fuel parameter differences observed

Appendix B
Carry Over Effect

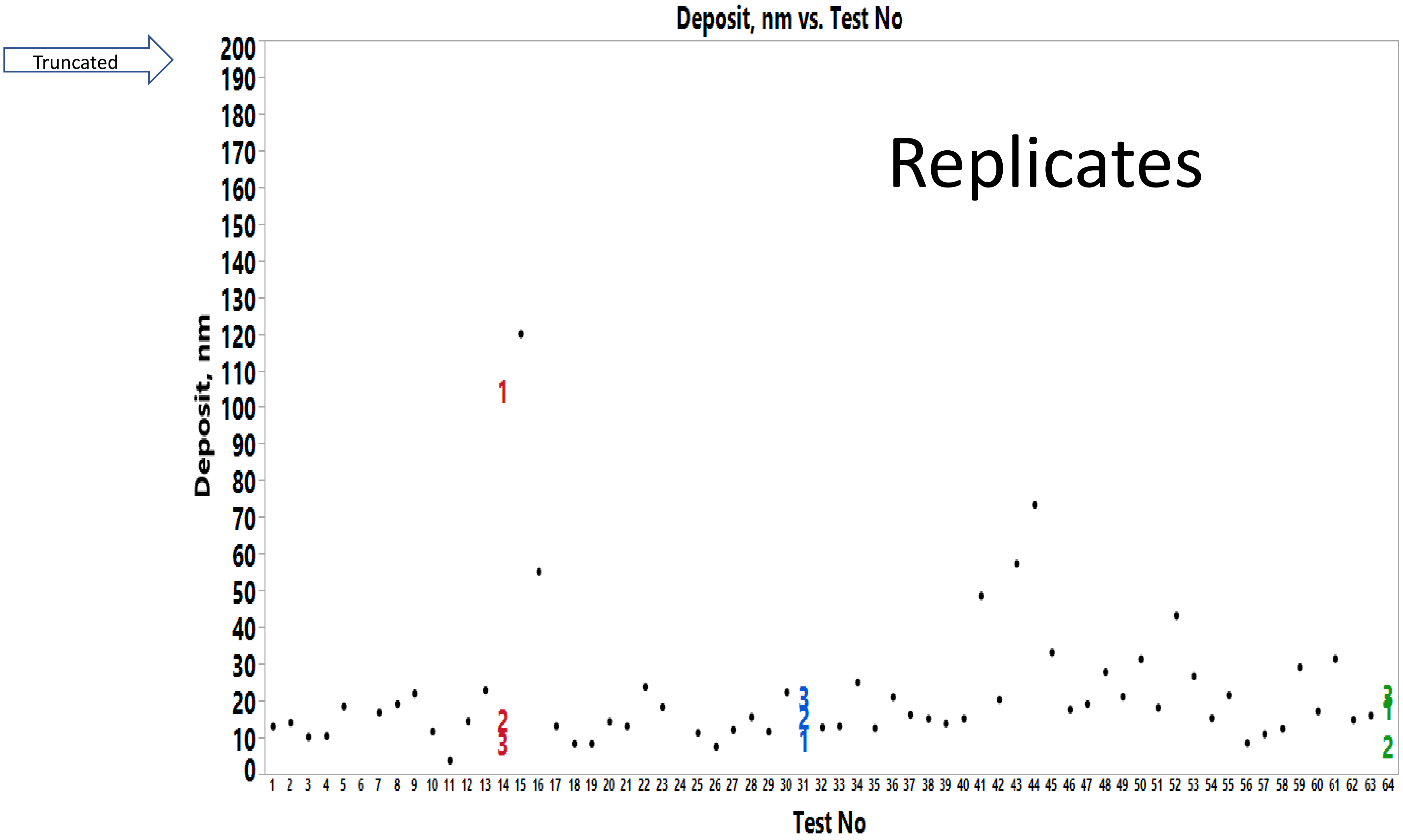
No significant carry over effect from Sodium



Fuel Research Using the Internal Diesel Injector Deposit (IDID) Rig (CRC Project No. DP-04-17)
Repeatability

Jo Martinez

Mar. 19, 2019



Truncated
Deposit, nm vs. Test No
Replicates
Deposit, nm
Test No
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64

Estimate of Standard Deviation

- RMSE from the ANOVA model with n=70

Summary of Fit

RSquare	0.676055
RSquare Adj	0.322661
Root Mean Square Error	0.06306
Mean of Response	0.241147
Observations (or Sum Wgts)	70

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	36	0.27386170	0.007607	1.9130
Error	33	0.13122599	0.003977	**Prob > F**
C. Total	69	0.40508769		0.0314*

Estimate of Repeatability

- Root Mean Square Error (RMSE) - estimate of standard deviation

$$Test\_Repeatability = RMSE_{Model} * 1.96 * \sqrt{2}$$

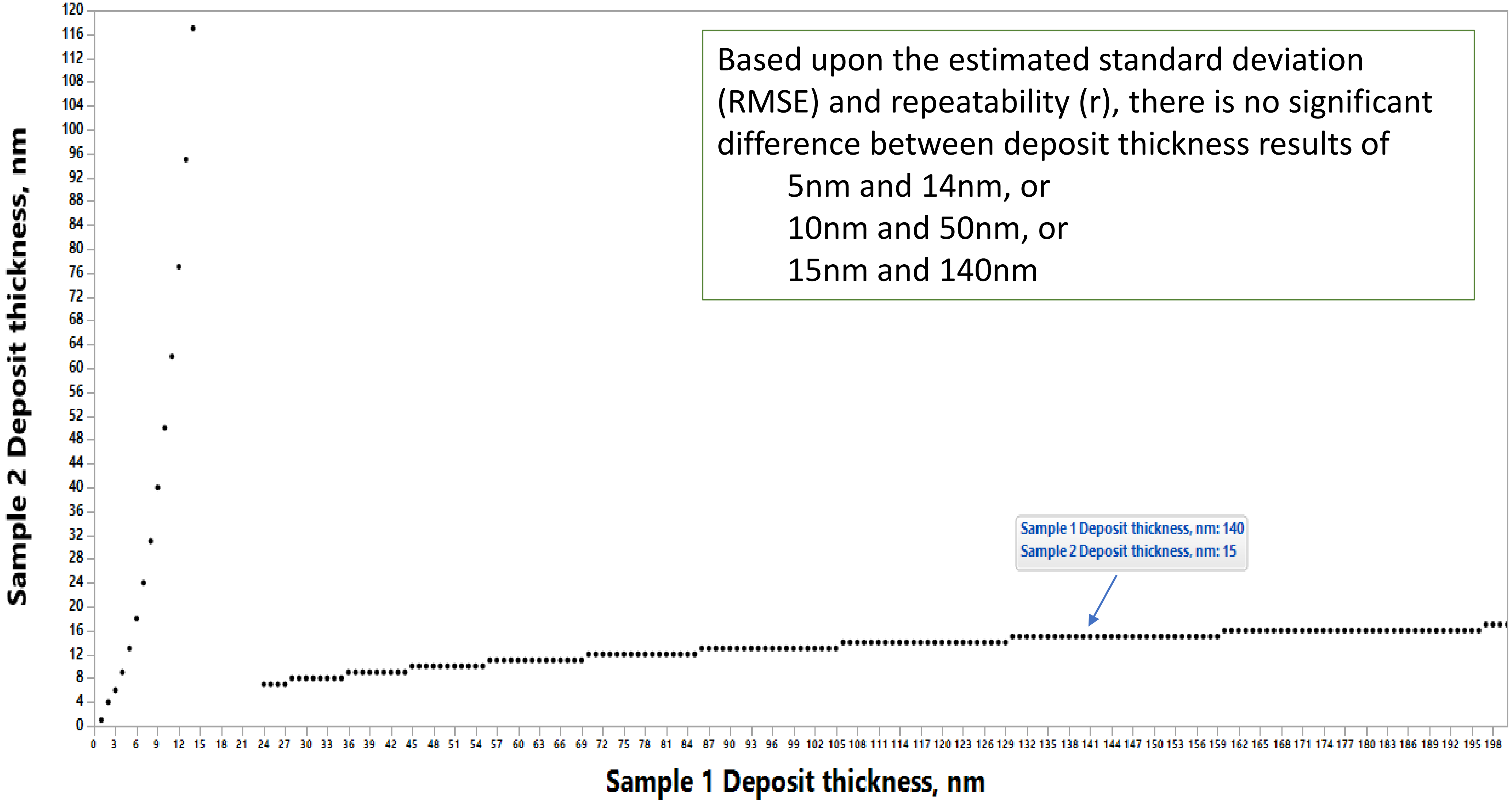
Estimated standard deviation of results within a rig

95% coverage based on a **Normal distribution** of residuals

Multiplier due to inference on 2 results

- 1/sqrt(Deposit) Model RMSE = 0.0631
- Repeatability, r = 0.1748

Repeatability



Based upon the estimated standard deviation (RMSE) and repeatability (r), there is no significant difference between deposit thickness results of

- 5nm and 14nm, or
- 10nm and 50nm, or
- 15nm and 140nm

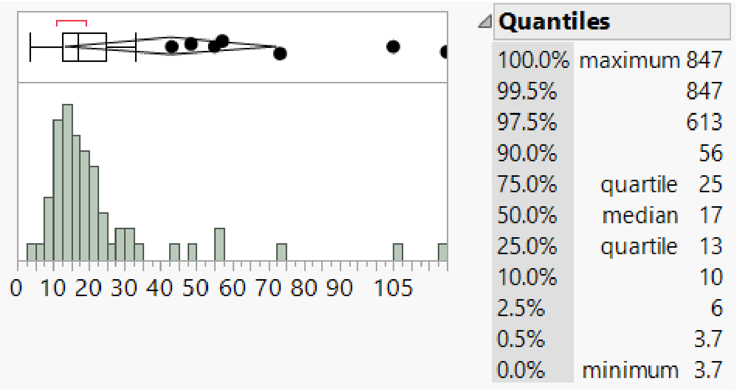
Appendix

Additional Testing Plan

Proposal for Additional Testing

<u>Objective</u>: To have a sense of repeatability of the test

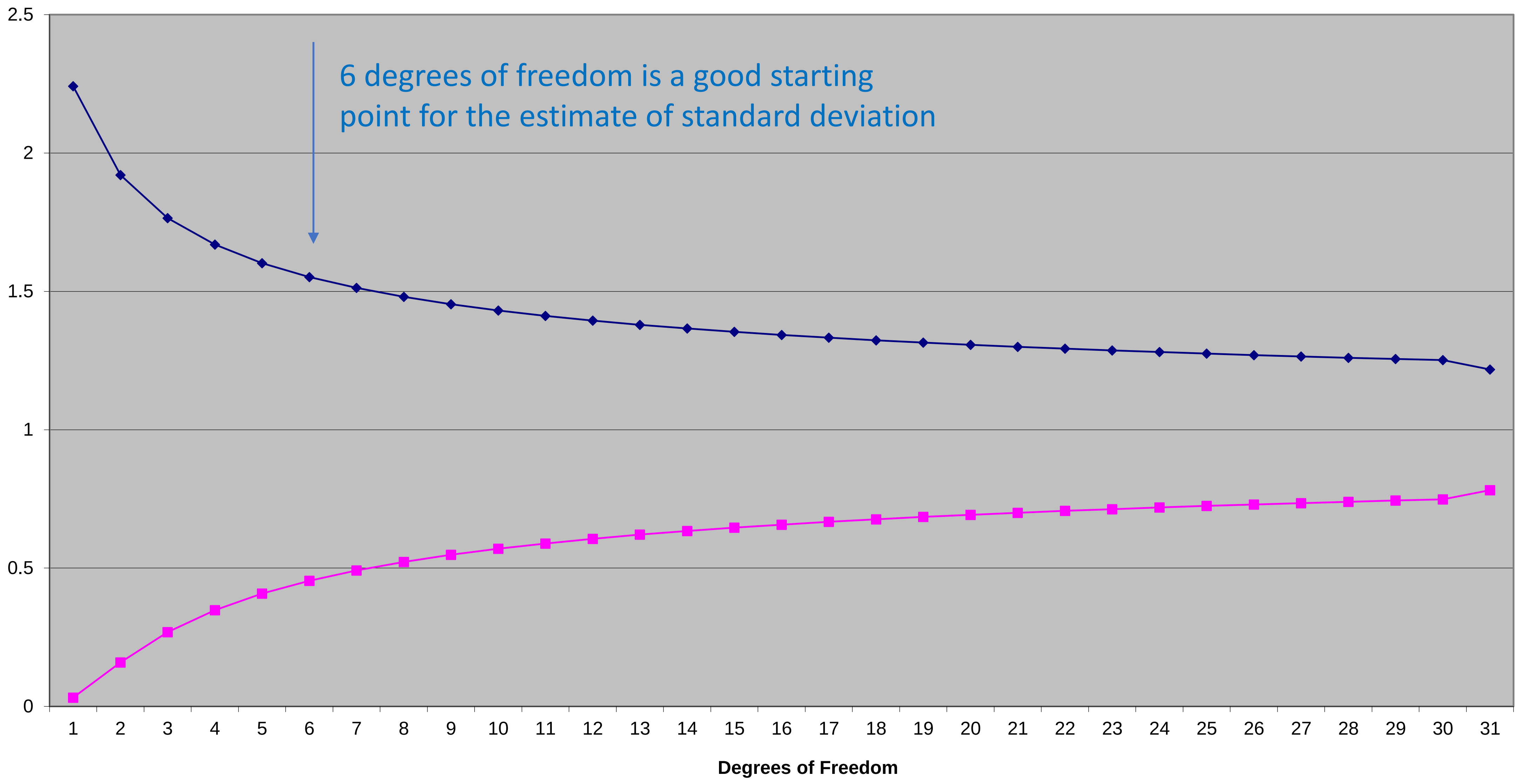
- 3 Fuels (tests no. 14, 31, 64)
    - Fuels chosen to span the range of deposits seen in the matrix
- 3 Replicates for each Fuel (1st replicate from the matrix)
- 6 error degrees of freedom to estimate standard deviation
- *Run 6 additional tests in designated run order*



Test No.	Matrix Result
31	10
64	19
14	105

Run Order	Test No.
1	14
2	31
3	64
4	64
5	31
6	14

Confidence Interval for Estimate of Standard Deviation



APPENDIX F

Rig Test Method

Test Method

Internal Diesel Injector Deposit (IDID) Test

[For Additional Information see Coordinating Research Council Report No. DP-04-17]

March 2019

Internal Diesel Injector Deposit (IDID) Test Method and Apparatus

1. Scope

This test method was designed to evaluate the relative internal diesel injector deposit (IDID) forming characteristics of compression ignition fuels and fuel/additive blends. The test is conducted under accelerated conditions and the results have not been shown to correlate to any specific period of normal engine operation. It is not applicable to evaluation of hardware effects, injection system design, or operating conditions. It is not specific to any high pressure common rail fuel injection system design. It is not applicable to recreation of injector nozzle hole deposits.

2. Summary of Test

Approximately 7-8 liters of test fuel are needed for this test. The apparatus is flushed with the test fuel prior to running the test. The test fuel flows through the injector apparatus at the prescribed flow rate, test duration and test temperature. At the conclusion of the test, the injector is removed and disassembled. The injector pintle is analyzed for deposits using an elipsometer.

3. Apparatus

a. **Injector Test Apparatus**

i. Hardware requirements:

Hartridge 2500 pump test stand or similar

Computerized Data Acquisition and Control System or similar

High Pressure Common Rail (HPCR) fuel injection pump capable of continuous operation at 1800 bar injection pressure

High Pressure Fuel Rail, compatible with 1800-bar pressure, with integrated pressure control valve and pressure transducer, GM 55496910 or equivalent

Injector heater block, as shown in Appendix, and 8 100W heater rods

Heat Sink Compound, manufactured by RS Supplies or similar Heat resistant tape, manufactured by RS Supplies or similar

6.35-mm round copper tab Type K thermocouples by RS Supplies or similar

Common Rail Diesel Fuel Injector and copper sealing washer, New Delphi Injector 28232248 or equivalent

Injector Driver with Variable Pulse Width Control Circuitry or ECM

Rail Pressure Controller with Variable Pulse Width Control Circuitry or ECM

ii. Test Rig Design:

A schematic diagram of the fuel delivery system layout is provided in Figure 1. The apparatus uses a high pressure common rail system, driven by a Hartridge 2500 pump test stand. The high pressure pump is operated at sufficient speed to generate the required pressure, typically 1750 rpm pump speed. Note the injection frequency and pump speed are decoupled, requiring a separate injector frequency generator.

The pump outlet is connected to a conventional rail, from which excess fuel is returned to the supply tank in the same way as on an operating vehicle. A fume extractor is used to ensure removal of any flammable vapors around the fuel tanks.

A high pressure pipe is connected from the rail to a single injector. The injection event is controlled by a variable width pulse to a custom peak and hold injector driver operating at a frequency of 12.5-Hz. The injection control as described is open loop, as there is not any feedback control on the injection quantity. Also connected to the fuel rail is a high pressure relief valve installed as a safety mechanism and set to vent 25% above the test operating pressure.

The injection pressure in the fuel rail is controlled by outlet metering using the rail pressure control valve and feedback from the rail pressure transducer. The rail pressure control valve is controlled by a variable width pulse operating at a frequency of 500-Hz. The Intake Control Valve (ICV) on the common rail pump is left disconnected so that the maximum rail pressure at each operating speed can be generated.

(An alternative approach may to be to use an ECM, appropriate control software, and dummy fuel injectors to mimic engine operation)

The single operating injector is clamped within a purpose made heater block. The heater block is subsequently bolted to a vessel that contains a cavity into which the fuel is injected, with a drain at the lowest point. The heater block contains a number of cartridge heater that simulate the combustion temperature present on an engine head. Eight 100 Watt cartridge heaters positioned around the heater block have been found to be sufficient.

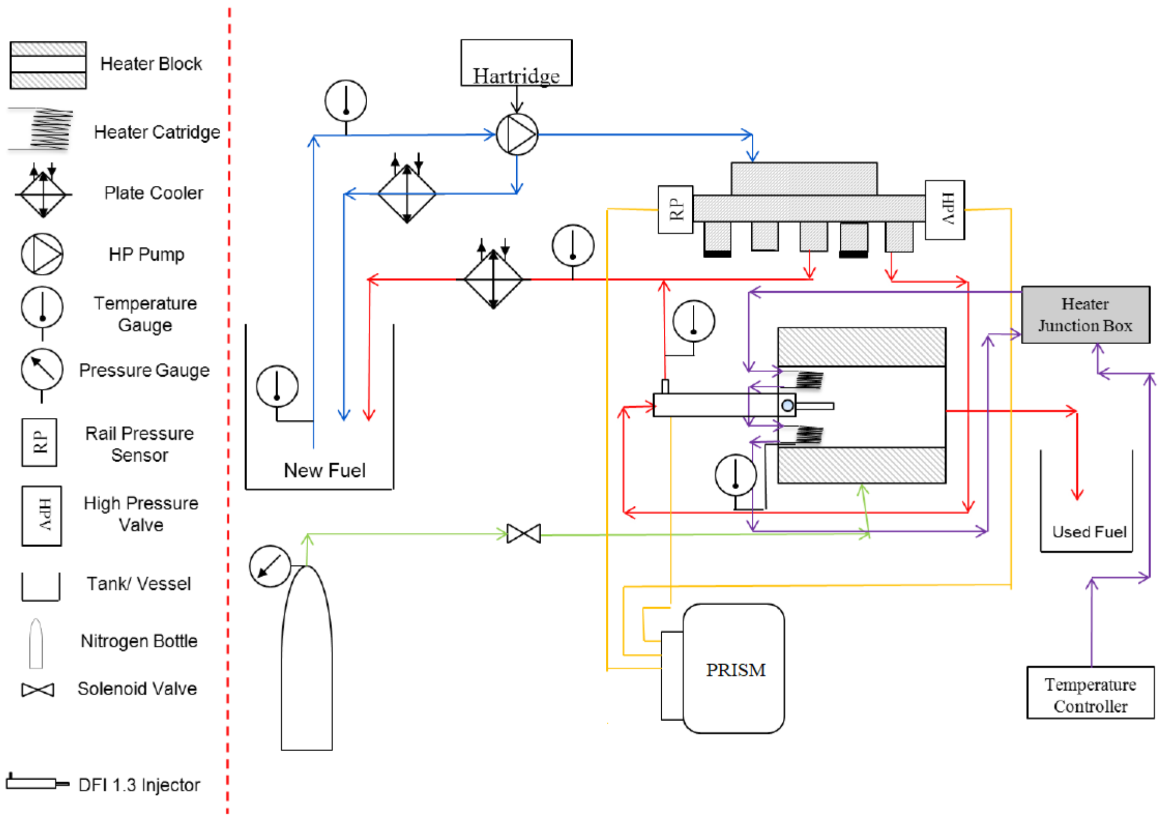


Figure 1. Test Rig Schematic Diagram

The injected fuel passes into the chamber attached to the heated block. This chamber is purged with nitrogen. Five second purges at 30 second intervals have been found to be sufficient. This purge process maintains an inert atmosphere within the test heater block and also serves to carry the injected fuel to a waste tank. The injected fuel is not returned to the main storage tank, as this fuel would normally be combusted on an operating engine. The main storage tank is mounted on a digital weighing scale to allow accurate real time measure of injected fuel flow rate throughout the test period.

The fuel return from the pump, rail and injector control valve (not injected fuel) passes through a heat exchanger which uses water plate coolers to cool down the fuel before returning it to the main storage tank. All tubing and pipework must be of sufficient diameter to prevent excessive back pressure. The materials used must be able to withstand the expected fuel temperatures, which can be up to 150ºC. Copper, zinc, or their alloys may not be used anywhere in the fuel system as this can have an effect on the deposit formed on the injector components.

Fuel filters are not used anywhere in the system. This is to facilitate easy cleaning. In addition, some metal carboxylate soaps are produced in the fuel tank and the resulting soap micelles may be removed by the fuel filter, resulting in filter plugging and inconsistent injector deposit results. As a result, great care must be taken to ensure cleanliness from hard particulates while storing, transporting and blending test fuel. Ideally, the fuel should be filtered prior to placement in the system.

The injector temperature is measured using surface mount thermocouples mounted on the injector capnut, as shown in Figure 2. The second back-up thermocouple mounted at the appropriate location, has the capability to halt operation should an over-temperature event occur. Experience has shown that a fuel passage within the injector can affect the fuel temperatures measured at the capnut. It was determined the two capnut thermocouples should be mounted 45° off the centerline of the electrical connector on the injector. A conventional thermocouple within the heater block was also utilized for control and as a safety shutdown.

Temperature and pressure measurements are taken at appropriate locations on the system and the output recorded using an appropriate data acquisition system. Ideally, this system should have the ability to shut down the test if the measured temperature or pressure exceeds certain predetermined values or if a fuel leak occurs.

Figure 2: Photograph Showing Location of Surface Mount Thermocouple on Injector

b. **Deposit Measurement (VASE)**

Deposits on the surface of the pintle are measured using a Variable Angle Spectroscopic Ellipsometer (VASE). In order to properly utilize the VASE a new, clean pintle was scanned to build the baseline reflectance model.

4. Test Fuel

Prepare at least 7 liters of test fuel. The test fuel will be blended within 2 days prior to testing. When specific fuel additives or contaminants are part of the test fuel blend, the base fuel should be additive/contaminant free.

5. Test Conditions

The test operating conditions are given in Table 1.

Table 1. Test Operating Conditions

Test Parameter	Value	Units
Fuel Supply Temperature	30	°C
Cap Nut Temperature	200	°C
Rail Pressure	1800	Bar
Pump Speed	1750	RPM
Run Time	7	Hours
Injection Frequency	12.5	Hertz
Injected Volume	5	gram/minute
Fuel volume placed in tank (with rinse)	7	Liters
Fuel volume placed in tank (without rinse)	5	Liters

6. Injector Apparatus Operating Procedure

a. Remove thermocouples from an old injector, or use two new thermocouples, and place on the new injector using heat sink compound which acts as a conducting agent. Use the heat resistant tape to secure the thermocouples in place.

b. Place a copper washer onto the injector nozzle, and clamp the injector into the pressurized chamber by securing the clamp plates and cap head bolts.

c. Connect the High Pressure Fuel Supply Pipe, Fuel Return Pipe and Electrical Connector to the injector.

d. Check that all heater elements are fully fixed into the heater block. A view of a typical assembled heater block and injector assembly is provided in Figure 3.

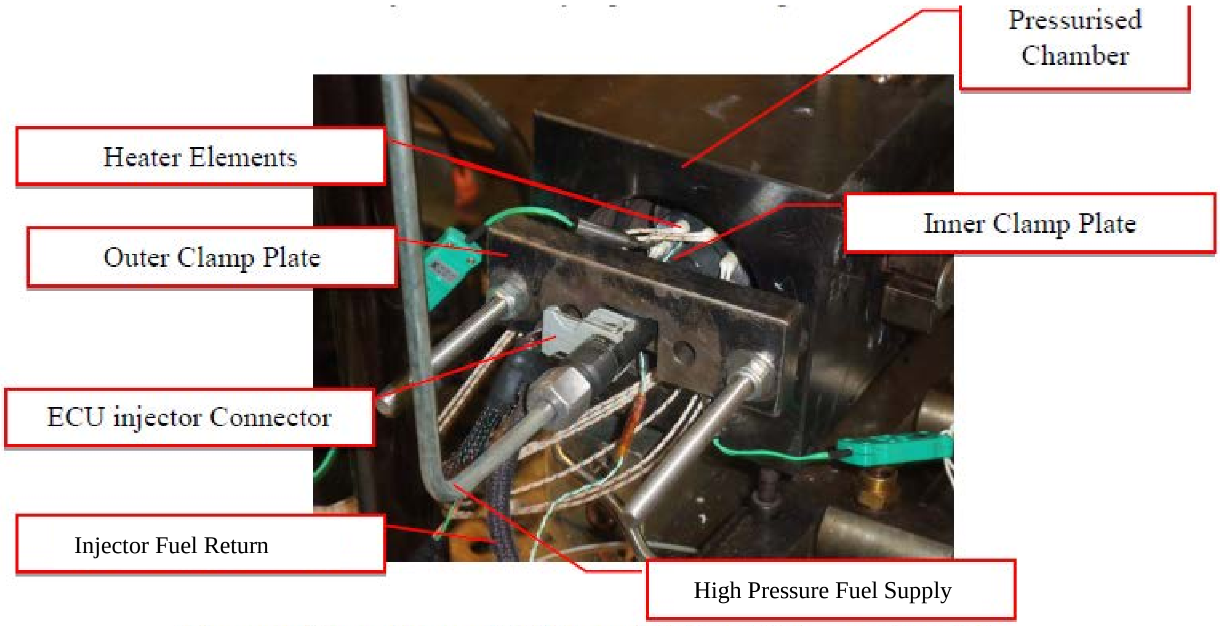


Figure 3: View of Assembled Heater Block and Injector Assembly

e. Blend sufficient fuel to allow rinse and subsequent testing. Typically 7L is found to be sufficient with a 2L rinse. Otherwise a separate fuel or solvent may be used for cleaning of the apparatus. Place the fuel in the storage tank and align the tank to position appropriately so that the feed and return pipe connections are in line.

f. The rinsing procedure will depend on the system design and the chemistry of the previous fuel used. Typically the control system should be programmed to slowly accelerate the rig to 500 RPM allow the existing fuel to be rinsed from the system and to fill with the new test fuel.

g. During this process, the rail and pump returns are temporarily fed into a separate container while the system is filled up with the new fuel batch. Approximately 2L of fuel is used to rinse the system into the separate container, leaving 5L in the storage tank. Following the cleaning procedure the return fuel pipe lines are replaced into the main fuel tank allowing the fuel to be recirculated for testing. Ensure the system is free of airlocks. After completion of the rinse, the rig speed is increased to the desired test speed.

h. Switch on the nitrogen purge system. Check that it is functional and that no leaks are occurring.

i. Switch on coolant for water plate cooler heat exchangers and return fuel coolers.

j. Slowly increase the pump speed. Ideally according to a predetermined ramp up procedure.

k. Set the required test temperature and cut-out temperature in case of malfunction on the heater controller.

l. Carefully check low pressure system for fuel leaks around the plate coolers or within the rig itself. Do not approach high pressure components.

m. Slight smoke may be seen from the heater block and is normal due to evaporation of fuel etc.

n. Smoke that persists for longer than 10 to 15 minutes may indicate a malfunction.

o. Turn on the vapor extractor for the rig and increase the rail pressure to 1800 bar.

p. Begin recording temperature and the other variables using appropriate data logging system.

q. The test apparatus should be carefully monitored for correct and safe operation regularly.

r. The injector pulse width may need be finely adjusted to ensure precise fuel flow after the system has reached operating temperature to ensure a fuel delivery of 5g/min has been achieved. Record mass difference in 5 minute or 10 minute intervals and work out fuel delivery using the mass difference and time frame. Keep doing this in the first hour until the correct pulse length is found to give a fuel delivery of 5g/min. Once complete let the test run normally for a period of 7 hours, keeping the pulse length unchanged from the 5g/min injection pulse length value.(open loop control of injection pulse width may require adjustment if flow deviates more than 5% from 5g/min)

s. The correct operation of the test stand should be monitored at regular intervals. In particular:

    i. Visually check for leaks, taking great care to avoid high pressure components

    ii. Ensure the fuel supply tank does not go below 0.5 litters

    iii. Record the fuel mass every hour for the entire duration of the test.

t. Log instrumented variables at 1Hz throughout test period.

7. Measurement of Deposits

Using Variable Angle Spectroscopic Ellipsometer (VASE) methodology, measure the deposit thickness in the desired region of the pintle. Example measurements are found in CRC Report No. DP-04-17.

8. Report

Report fuel blend information and measured deposit thickness results.