CRC Report No. E-103

EVALUATION OF N₂O MEASUREMENT INSTRUMENTS WITH LIGHT-DUTY VEHICLES

September 2014



COORDINATING RESEARCH COUNCIL, INC. 5755 NORTH POINT PARKWAY SUITE 265 · ALPHARETTA, GA 30022

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FINAL REPORT

SwRI[®] Project No. 03.19027

CRC Project No. E-103

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FOREWORD

This report covers testing conducted by the Department of Engine and Vehicle R&D of Southwest Research Institute[®] (SwRI[®]) for the Coordinating Research Council (CRC). The test program, authorized by CRC Contract No. E-103, began in February 2013 and concluded in December of 2013. Vehicle testing was conducted from September 10, 2013 to November 11, 2013. The project was based on SwRI Proposal 03-67204 to CRC. The overall program was identified within SwRI as Project 03.19027. The project was monitored by Dr. Christopher J. Tennant of CRC. The SwRI Project Manager was Mr. Kevin A. Whitney, and the project leader was Mr. Gene Jimenez. Ms. Janet P. Buckingham of SwRI conducted the statistical analyses for the emissions results. Mr. Robert Vara, Laboratory Supervisor, was responsible for the emissions testing.

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 - o Horiba Instruments
 - o MKS Instruments
 - o Sensor Inc.

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LIST OF ABBREVIATIONS

ANOVA	Analysis of Variance
ASTM	American Society for Testing and Materials
BSNO _X	Brake-Specific NO _x
BSN ₂ O	Brake-Specific Nitrous Oxide
CAI	California Analytical
CARB	California Air Resources Board
CFR	Code of Federal Regulations
CH4	Methane
СО	Carbon Monoxide
CO ₂	Carbon Dioxide
COV	Coefficient of Variation
CRC	Coordinating Research Council
CVS	Constant Volume Sampling
ECD	Electron Capture Detector
EMA	Truck and Engine Manufacturers Association
EMTC	Emissions Measurement and Testing Committee
EO	Engine-out
EPA	U.S. Environmental Protection Agency
FID	Flame Ionization Detector
FTIR	Fourier Transform Infrared Spectroscopy
FTP	Federal Test Procedure
GC-ECD	Gas Chromatograph Instrument with Electron Capture Detector
GHG	Greenhouse Gas
H ₂ O	Water
IR	Infrared
LEV III	Low Emissions Vehicle Regulation
NH3	Ammonia
N ₂ O	Nitrous Oxide
NOx	Oxides of Nitrogen
QCL	Quantum Cascade Laser
RMC-SET	Ramped Modal Cycle Supplemental Emission Test
SwRI	Southwest Research Institute
SD	Standard Deviation
TDL	Tunable Diode Laser
THC	Total Hydrocarbons
ТР	Tailpipe

EXECUTIVE SUMMARY

This report documents a test program run at Southwest Research Institute[®] (SwRI[®]) on behalf of the Coordinating Research Council (CRC). The program objective was to examine a variety of commercially-available instruments for the laboratory measurement of nitrous oxide (N₂O) on light-duty vehicles.

In recent years, the U.S. Environmental Protection Agency (EPA) has promulgated greenhouse gas (GHG) regulations for various industry segments. As part of these regulations, EPA has introduced standards for nitrous oxide (N₂O) for the first time. The standards given in these regulations will require the measurement of N₂O at relatively low levels, in some cases well below 1 ppm. Four different instrument technologies capable of sampling dilute bag exhaust samples (see Table ES-1) were compared in this study to results obtained on a benchmark instrument. The benchmark instrument used as a reference for N₂O levels during this program was a gas chromatograph instrument which incorporated an electron capture detector (GC-ECD). Due to a combination of high resolution and lack of interference from other gases, the GC-ECD is considered the historical benchmark for N₂O measurements.

Company	Instrument
MKS	MKS FTIR (MG2030 MultiGas Analyzer)
Horiba	Horiba QCL-1100 (MEXA-1100QL-N ₂ O)
Sensors	Sensors (SEMTECH-LASAR)
CAI	CAI (700 Series FTIR)

 TABLE ES-1.
 N₂O INSTRUMENTS EVALUATED

This program was conducted following the completion of two phases. The first phase consisted of bench evaluation of seven instruments to characterize instrument performance and to verify compliance with the requirements of 40 CFR (Code of Federal Regulations) Part 1065. The second phase involved an on-engine evaluation, wherein the various instruments were used in parallel during a sequence of heavy-duty emissions test runs, on a test engine representative of post-2010 production on-highway heavy-duty technology. These first two phases were performed on behalf of the Truck and Engine Manufacturer's Association (EMA). The learning's from these two phases were used in this CRC-funded light-duty program.

The instruments were evaluated using diluted bagged exhaust samples generated from two light-duty vehicles operating over the chassis dynamometer portion of the Federal Test Procedure (FTP). The two vehicles were a Nissan Altima (NALT) and a Toyota Camry (TCAM), which were selected from the CRC-owned fleet used to conduct the EPAct/V2/E-89¹ Gasoline Light-Duty Exhaust Fuel Effects Test Program. The original plan was to test each vehicle over seven cold-start FTPs, however additional tests were performed due to issues during the bag read procedure while testing the Toyota Camry. Additional tests were also performed on the Nissan Altima due increasing CO and NO_X emissions during testing. This may have been due to catalytic converter sulfur poisoning, however the exact reason was not determined. A total of

¹ Whitney, K.A, "EPAct/V2/E89 Gasoline Light-Duty Exhaust Fuel Effects Test Program", 2010 SwRI Final Report 03-19027 XII

ten tests were performed on each vehicle. The Toyota Camry was tested first followed by the Nissan Altima.

During the first phase of the heavy-duty program each instrument was evaluated for interference gases to show compliance with Part 1065.375. This requires that the total interference at test conditions must be less than 0.5 ppm of N_2O . Additional and more stringent interference checks were not performed on the instruments for this light-duty program since it was beyond the work scope of this program. Additionally, SwRI was not informed on how and which instruments used compensation algorithms for accurate measurement.

Each instrument was compared to the GC-ECD reference. During test operations, the GC-ECD was used to read each bag twice. The first reading was taken as soon as the bags were transported to the laboratory that housed all the bag instruments. The second reading was taken after all other bag instruments had read the bags, in order to provide a bracketing reading to insure that the sample was not somehow compromised during the reading process. The GC-ECD reference value for final calculations was taken as the average of these two readings.

The results summarized below are averages of the multiple tests that were performed on each vehicle. The instruments proved to be highly variable compared the GC-ECD with some results deviating from the GC-ECD reference. However, the averages of the various tests showed better comparison over the FTP with the average results within plus or minus 9% of the GC-ECD.

The results of the program show that all of the instruments examined proved to be capable of performing N_2O measurements. The name of each instrument has been blinded in the results section to protect the reputation of each instrument manufacturer at the request of CRC.

While testing the Toyota Camry, Instrument #1 generated averaged results about 9% above the reference for FTP Composite. Tests with the Nissan Altima generated averaged results about 1% below the reference for FTP Composite. Overall measurement for both vehicles was about 4% above the reference mean.

While testing the Toyota Camry, Instrument #2 generated averaged results about 5% below the reference for FTP Composite. Tests with the Nissan Altima generated averaged results about 5% below the reference for FTP Composite. Overall measurement for both vehicles was about 5% below the reference mean.

While testing the Toyota Camry, Instrument #3 generated averaged results about 1% above the reference for FTP Composite. Tests with the Nissan Altima generated averaged results about 4% above the reference for FTP Composite. Overall measurement for both vehicles was about 3% above the reference mean.

While testing the Toyota Camry, Instrument #4 generated averaged results about 3% below the reference for FTP Composite. Tests with the Nissan Altima generated averaged results about 8% above the reference for FTP Composite. Overall measurement for both vehicles was about 2% above the reference mean.

It should be noted that some of the instruments used in this program were not designed with an automated zero, span and bag sampling sequence. For those instruments which had an automated process, due to the time limitation to read a bag on all instruments, it was chosen not to use their automated sequence. A significant amount of manipulation was required by a technician to perform the required tasks for accurate bag sample measurements. Additional effort would be required by the instrument providers to make the instruments and their processes more robust for users to integrate an instrument into a test cell for high production light-duty testing. A particular note should be made to the extended sample read time some of the instruments needed. If a test lab were to install this type of instrument, this additional time required would significantly reduce testing throughput. Test labs would need to make changes to test procedures to accommodate these extended sample read times. The results from this study, shown in Table ES-2 show that some techniques are available for the laboratory measurement of N₂O, with some instruments showing more variability than others. These values are a summary of Tables 6 through 9 and 14 through 17 from Section 5 of this report. The values in Table ES-2 labeled Ration of Means Versus Reference Mean were calculated using Equation 1 below.

Equation 1.

 $\label{eq:Ratio} \begin{array}{l} \mbox{Ratio of Means Versus Reference Mean} = (Mean \ N_2O \ of \ Instrument \ - \ Mean \ N_2O \ of \ GC\ ECD) \ / \ (Mean \ N_2O \ of \ GC\ ECD) \ * \ 100 \end{array}$

		Ratio of Means			
		V	ersus Refe	erence Mea	n
Vehicle		#1	#2	#3	#4
	Phase 1	-0.4%	-5.6%	2.4%	-1.0%
Toyota Camry	Phase 2	28.1%	12.2%	3.9%	-10.3%
Tests	Phase 3	18.2%	-13.3%	3.4%	-3.9%
	Composite FTP	9.2%	-4.9%	3.9%	-3.3%
	Phase 1	6.0%	-1.0%	2.3%	3.3%
Nissan Altima	Phase 2	-4.4%	-9.9%	3.6%	21.8%
Tests	Phase 3	-22.8%	-13.8%	9.4%	0.2%
	Composite FTP	-0.9%	-5.2%	3.6%	8.0%

TABLE ES-2. SUMMARY OF OVERALL N2O PERCENT DIFFERENCE FROMREFERENCE BY INSTRUMENT

The variability of the instruments is relatively high compared to the reference. A comparison of all instrument percent differences with respect to the GC-ECD within each Camry test shows a best agreement of 7% and worst agreement of 81%. The Altima showed a best agreement of 12% and worst agreement of 51% within each Altima test. Details of this analysis are given in Section 5.3. However, given the low N₂O emission rate average of 2.5 mg/mi for these two vehicles, the worst case agreement of 81% gives a spread of 0.5 mg/mi to 4.5 mg/mi. This is still less than the current 10 mg/mi N₂O standard. A review of late model vehicles with direct injection technology shows similar or lower N₂O emission rates. Nevertheless, the observed variability of the

instruments would make it difficult to accurately measure N_2O levels from vehicles closer to the N_2O standard.

Statistical Analysis Conclusions

- In Phases 1, 2, 3 and the Composite, the N_2O results for Instrument #1 and Instrument #2 were generally the most different from the N_2O results of the GC-ECD.
- Statistically (based on Section 6 analyses), there does not appear to be a bias in N₂O measurements for Instrument #1, Instrument #2, Instrument #3, and Instrument #4 compared to the GC-ECD.
- In choosing which instruments produced N_2O measurements closest to the GC-ECD, Instrument #3 and Instrument #4, statistically (based on Section 6 analyses), both showed no bias and had the smallest standard deviations of the N_2O differences over the three phases and the composite.

1.0 INTRODUCTION

This report documents a test program run at Southwest Research Institute (SwRI) on behalf of the Coordinating Research Council (CRC). The program objective was to examine a variety of commercially available instruments for the laboratory measurement of nitrous oxide (N_2O) on light-duty vehicles.

In recent years, EPA has promulgated greenhouse gas (GHG) regulations for various industry segments. As part of these regulations, EPA has introduced standards for N_2O for the first time. The standards given in these regulations will require the measurement of N_2O at relatively low levels, in some cases well below 1 ppm. Four different instruments capable of sampling dilute bag exhaust samples were evaluated in this program as given in the Table 1 below. The benchmark instrument used as a reference for N_2O levels during this program was a gas chromatograph instrument which incorporated an electron capture detector (GC-ECD). Due to a combination of high resolution and lack of interference from other gases, the GC-ECD is considered the historical benchmark for N_2O measurements.

Company	Instrument
MKS	MKS FTIR (MG2030 MultiGas Analyzer)
Horiba	Horiba QCL-1100 (MEXA-1100QL-N ₂ O)
Sensors	Sensors (SEMTECH-LASAR)
CAI	CAI (700 Series FTIR)

TABLE 1. N2O INSTRUMENTS EVALUATED

The program was conducted following the completion of two phases funded by the Truck and Engine Manufacturer's Association (EMA). The first phase consisted of bench evaluation of seven instruments to characterize instrument performance and to verify compliance with the requirements of 40 CFR Part 1065. The second phase involved an on-engine evaluation, wherein the various instruments were used in parallel during a sequence of heavy-duty emissions test runs, on a test engine representative of post-2010 production on-highway heavy-duty technology. The learnings from these two phases were used in this CRC-funded light-duty program.

The benchmark used as a reference measurement for N_2O levels was a gas chromatograph analyzer which incorporated a GC-ECD. Because of a combination of high resolution and lack of interference response from other gases common in gasoline exhaust, the GC-ECD serves as a good reference for other methods of N_2O detection, with a proven track record of accuracy. However, the GC-ECD instrument is also a complicated piece of laboratory equipment, and it is only suitable for batch samples of diluted gaseous emissions which are stored in a sample bag for evaluation of post test measurement.

2.0 TEST VEHICLE, TEST FUEL, AND TEST PROCEDURES

This section of the report describes the test vehicles, measurement, and sampling systems used during the program, with the exception of the N_2O instruments themselves. Those instruments are described in Section 3 of the report.

2.1 Test Vehicles

The two test vehicles used in this program were chosen from the EPAct/V2/E-89 Gasoline Light-Duty Exhaust Fuel Effects Test Program. Raw exhaust concentrations of N₂O were measured with a Fourier Transform Infrared Spectroscopy (FTIR) during Phase 1 of the EPAct Program. Both vehicles produce consistently measurable peak concentrations of N₂O in raw exhaust on the order of 3 ppm during Bag 1 and consistently measurable N₂O concentrations of less than 1 ppm in Bags 2 and 3. Based on these results, SwRI recommended using the Nissan Altima and the Toyota Camry for this study. Vehicle information is shown in Table 2. This program used the same vehicle chassis dynamometer settings as the EPAct/V2/E-89 program and CRC E-98 program. The vehicles were tested with "as-is" crankcase lubricants following the completion of CRC Project E-98. The crankcase lubricant had approximately 2,300 miles.

TABLE 2.	TEST VEHICLES
----------	----------------------

Make	Model Year	Brand	Model	Vehicle Name	Engine	Engine Family	T2 Bin	Starting Odometer
Toyota	2008	Toyota	Camry	TCAM	2.4L I4	8TYXV02.4BEA	5	12,515
Nissan	2008	Nissan	Altima	NALT	2.5L I4	8NSXV02.5G5A	5	14,117

2.2 Test Fuel

The test fuel for this program was a California Air Resources Board (CARB) Low Emissions Vehicle Regulation (LEV III) certification gasoline provided by SwRI. The fuel was obtained as part of a single batch from Haltermann Solutions, and was coded SwRI EM-8491-F. This same batch of fuel was used for all testing during this program. The fuel properties are given in Appendix A. It was agreed upon by SwRI and CRC that this fuel should be used as it was representative of a new emissions certification fuel.

2.3 Test Procedures

Each vehicle was to be tested over seven (7) cold-start FTPs. As will be explained in Section 5, a total of ten (10) tests were conducted on each vehicle. It was expected that both vehicles would be tested in parallel, however due to the large amount of time required to read each bag/phase on the five instruments, this was not possible. Therefore, the Toyota Camry was tested first followed by the Nissan Altima. The same driver used during the CRC E-98 program was used for this program.

2.4 Vehicle Conditioning

Prior to testing, the vehicles underwent a fuel change to flush out any remaining fuel in the tank and the test fuel was installed. Each vehicle was then conditioned with a cold-start FTP cycle. An example job request for testing is given in Appendix B.

2.5 Chassis Dynamometer

All tests were conducted using a Horiba 48-inch single-roll electric chassis dynamometer. The dynamometer electrically simulates inertia weights up to 12,000 lb over the FTP, and provides programmable road load simulation of up to 150 hp continuous at 65 mph. This program used the same chassis dynamometer settings as the EPAct/V2/E-89 and E-98 programs. They were originally derived from target road load coefficients as reported in EPA's on-line Test Car List Data Files. The dynamometer Set Coefficients are given in the Table 3.

					Ta	rget Coeffi	cients	:	Road Load		
Model Voor	Maka	Model	Namo	ETW,	A, lbs	B,	C,	A,	B, lbs/mpb	C,	Hp @ 50
Tear	wiake	WIGUEI	Name	105	105	ius/mpn	ibs/mpn	105	ius/mpn	ibs/mpn	шрп
2008	Toyota	Camry	TCAM	3625	29.16	0.1659	0.01844	10.110	-0.14630	0.019592	11.1
2008	Nissan	Altima	NALT	3500	47.47	-04531	0.02414	19.710	-0.30660	0.021358	11.4

 TABLE 3. DYNAMOMETER SET COEFFICIENTS

2.6 Emissions Measurements

The primary focus of the program was on N_2O measurements. Therefore, regulated emissions measurements were made only to insure representative vehicle operation, and as needed to perform N_2O emission mass calculations in accordance with 40 CFR Part 86. Gaseous emissions were determined in a manner consistent with EPA protocols for light-duty emission testing as given in the CFR, Title 40, Part 86. A constant volume sampler was used to collect proportional dilute exhaust in Kynar[®] bags for analysis of carbon monoxide (CO), carbon dioxide (CO₂), total hydrocarbons (THC), methane (CH₄), and oxides of nitrogen (NO_X).

2.7 Bag Sampling Systems

In order to support the considerable number of bag measurements for each instrument, it was necessary to increase the bag fill rate at the test cell beyond what is typically used for testing. Also, in order to supply sufficient sample gas to all instruments, and to allow some margin for instrument issues, large volume bags were procured for this program.

The sample and background bags for this program were all constructed using 4 mil thick Kynar[®] and were pre-baked by the bag manufacturer. The bags incorporated Teflon[®] sampling loops for proper distribution and mixing of sample gases, as well as proper bag evacuation. The bags were designed to hold about 110 liters of sample at an 80 percent fill. An example of the bags used is shown in Figure 1.



FIGURE 1. N₂O PROGRAM SAMPLE BAG

3.0 N₂O INSTRUMENT DESCRIPTIONS

This section of the report describes the measurement instruments that were evaluated and tested. All instruments were designed to comply with all of the relevant requirements for N_2O measurement instruments given in 40 CFR 1065. The individual instruments evaluated are described briefly below, along with details related to test cell installation, instrument operations, and sampling system details. A summary of the instruments evaluated is given below in Table 4.

Company	Instrument
MKS	MKS FTIR (MG2030 MultiGas Analyzer)
Horiba	Horiba QCL-1100 (MEXA-1100QL-N ₂ O)
Sensors	Sensors (SEMTECH-LASAR)
CAI	CAI (700 Series FTIR)

TABLE 4. SUMMARY OF N₂O INSTRUMENTS

3.1 MKS FTIR (MG2030 MultiGas Analyzer)

The instrument supplied by MKS for this program was the 2030 FTIR. This instrument is distinct from the FTIR instruments typically used for development work in that it does not employ a liquid nitrogen cooled detector. Rather the instrument operates the detector near room temperature, and therefore the infrastructure involved with handling liquid nitrogen (N₂) is avoided. The instrument is shown in Figure 2. The unit as configured also reported data for CO, CO_2 , H_2O , and CH_4 .

The MKS instrument is a 19" rack mount unit which is designed to be incorporated into a larger analytical bench system. The 2030 does incorporate an internal sample pump. For the purposes of this program, MKS supplied the instrument with a special sample connection box, shown in Figure 3, to allow for zero-span-purge actions, and Part 1065 leak checks. This sample connection box is not usually provided with the instrument; however it was necessary to allow for independent operation of the instrument, which was a program requirement. For this program, all of these functions were executed manually by an operator.

For bag measurements, the instrument was set into a bag mode, wherein data were reported as a single data point which was the average of 30 seconds of measurement. Zero and span calibrations were run at the start of each test day (shift), as well as the Part 1065 leak check. For all subsequent tests, zero and span data were generated pre-test and a post-test by flowing the appropriate gases and recording data. However, no further zero-span adjustment was made following the initial daily calibration.



FIGURE 2. MKS 2030 FTIR INSTRUMENT (SHOWN IN BAG LABORATORY)



FIGURE 3. ZERO-SPAN LEAK CHECK BOX FOR MKS 2030

In bag mode a single data file was generated for each test consisting of pre-read zerospan data, the background bag read, the sample bag read, and the post-read zero-span data. The span value used for dilute bag measurements was nominally 1 ppm. Leak checks were performed using a decay of vacuum method that was performed manually at the start of each shift, and processed via a template provided by MKS.

3.2 Horiba QCL-1100 (MEXA-1100QL-N₂O)

Horiba supplied a Quantum Cascade Laser (QCL) instrument for this program. This is an infrared (IR) instrument that uses a QCL as a source to examine a narrow range of the IR band at a very high resolution. The instrument was a QCL-1100 (model 1100QL), which is designed only as an N_2O instrument. Figure 4 shows the Horiba QCL-1100 instrument. Figure 5 shows the Horiba computer setup.



FIGURE 4. HORIBA QCL-1100 INSTRUMENT



FIGURE 5. HORIBA COMPUTER SETUP

The unit was configured to report data for a high and low range of N_2O , but only the low range (10 ppm) was used for this program. A nominal span concentration of 1 ppm was used for the bag measurement. Data was collected at 1 Hz and exported to a flash drive. Adjustments of the zero and span were performed at the start of each test day (shift), as well as the Part 1065 leak check. For all subsequent tests, zero and span data were generated pre-test and post-test by flowing the appropriate gases and recording data. However, no further zero-span adjustment was made following the initial daily procedures.

A single data file was generated for each test consisting of pre-read zero-span data, the background bag read, the sample bag read, and the post-read zero-span data. Leak checks were performed by the span overflow method using Horiba's automated leak check procedure and a span overflow attachment that they provided. For bag testing, the instrument host computer was used to log a continuous data file during bag read, including pre-test zero-span, sample and background bag readings, and the post-test zero-span data. The bag data files were manually post-processed to provide 30-second averaged concentrations for subsequent final data processing.

3.3 Sensors (SEMTECH-LASAR)

Sensors Inc. provided the LASAR instrument for the program. The LASAR is a mid-IR instrument that uses a special tunable diode laser (TDL) as a source, and incorporates a number of techniques in its detection chamber to increase resolution and effective pathlength. The LASAR operates under a high vacuum, which is maintained from a location near the sample probe though the detector assembly. As a result, a heated sampling line is not utilized because the vacuum conditions prevent condensation. The unit as configured, also reported CH_4 and ammonia (NH₃) values. The LASAR instruments are shown in Figure 6.



FIGURE 6. SENSORS LASAR AS SET UP FOR DILUTE BAG MEASUREMENT

Continuous data files were recorded for each test which included all zero-span data (pretest and post-test), as well as test data (either cycle traces or bag reads), and background bag data (if needed). The files were then post-processed and time aligned to the base data from the test cell host. Bag measurement data were recorded at 1 Hz and a nominal span concentration of 1ppm was used.

3.4 CAI (700 Series FTIR)

California Analytical (CAI) supplied the 700 Series FTIR. This instrument was a non-LN₂ cooled FTIR analyzer. The detector itself ran at 50°C, but the sample train did not otherwise incorporate any heating. The instrument, sampling system, and host laptop were supplied in an instrument rack, and are shown in Figure 7. The instrument as supplied reported data for N₂O, CO, CO₂, and water (H₂O).



FIGURE 7. CAI 700 SERIES FTIR BAG ANALYZER AND SAMPLING SYSTEM

The CAI FTIR did not report continuous data; each data point was created by taking 32 scans of the sample. These scans were then analyzed to provide a single set of readings for the measured gases. Each 32-scan run required about 110 seconds to complete. During any read process, several initial runs were taken in order to be sure the data were stable, and that all gas from any previous measurement had cleared the sample cell. In order to fully stabilize, a total of six runs were taken for each measurement. Due to the length of time involved for each test, the pre-test zero span data for a given test was also utilized as the post-test zero-span data for the previous run (except for on the final test of a given day). Zero-span calibrations were conducted only at the start of a given test day, along with the leak check.

Data for all the test runs were recorded on the instrument host computer, using the software provided with the instrument. A log file was saved with the measurement results for all of the 32-scan runs in a given measurement sequence, with one data point reported for each run. These included zero-span sample bag reads and background bag reads. For the final test of a given day, the post-test zero-span was also included in the log file. These log files were post-processed to give the final concentration readings. A nominal 1 ppm span was used for the bag measurements.

3.5 Reference Instrument – GC-ECD (Gas Chromatograph with Electron Capture Detector)

The reference instrument for this study was the GC-ECD instrument. The instrument has historically been considered a "gold-standard" for N_2O measurement due to the fact that it is capable of detecting very low levels of N_2O and is essentially interference free due to the detection method. The GC-ECD instrument is shown in Figure 8. The instrument is actually built into an Agilent greenhouse gas analyzer which also can measure CO_2 using an electron capture detector (ECD), and CH_4 using a flame ionization detector (FID).



FIGURE 8. GC-ECD REFERENCE INSTRUMENT

Span standards were run at the start of a shift and at the end of a shift. For Part 1065 measurements, these bracketing standards were used to perform quantification and the Part 1065 drift calculations. There was no zero value for this instrument, given the peak area integration used to generate values. Drift corrected values were calculated using both the pre-test and posttest standard values, while the uncorrected values were calculated using only the pre-test standard values. In practice, very little movement was observed between the start of shift and end of shift standards. Any baseline (zero) shift was accounted for by the integration process, therefore there was no distinct zero process that generated a value. Therefore, for this program, the uncorrected values using only the pre-test standard were applied.

During test operations, the GC-ECD was used to read each bag twice. The first reading was taken as soon as the bags were transported to the laboratory that housed all the bag instruments. The second reading was taken after all other bag instruments had read the bags, in order to provide a bracketing reading to insure that the sample was not somehow compromised during the reading process. The reference value for final calculations was taken as the average of these two readings. In practice, the two readings generally were within 2-3 ppb of each other cases. This QA measure was done to insure that all bag instruments saw the same stable sample. The GC-ECD instrument was also used for the naming and checking of the span bottles used during this program.

4.0 INSTRUMENT STABILIZATION CRITERIA

This section of the report describes the process of determining the stabilization period for each instrument. Initial stabilization criteria checks were performed on each instrument prior to the start of the program. Given that the instruments had varying stabilization periods, the read times during testing had to allow for sufficient time to meet established stabilization criteria. The post processing of all test data with these established stabilization criteria were used to determine when a reading would be used as the test results. The MKS and CAI instruments used similar stabilization criteria, while Sensors and Horiba instruments had different stabilization criteria. A bag read procedure consisted of a procedure given in the Table 5.

1	Pre-Zero
2	Pre-Span
3	Sample Bag
4	Ambient Bag
5	Post-Zero
6	Post-Span

TABLE 5. BAG READ PROCEDURE

In order to enforce a similar calibration and sampling sequence for all analyzers, manufacturer recommended automated sequences, where available, were not used in all cases. Although SwRI is confident that the calibration and sampling sequence used for this study is robust, comparison of this sequence to those used in more typical applications was outside the scope of this program. Therefore, it is possible that analyzer performance in this study may not be representative of performance realized utilizing manufacturer recommended practices. Since the purpose of this study is to determine if commercially available analyzers are capable of measuring at the low levels necessary to demonstrate compliance and not to compare individual analyzer performance, enforcing a common calibration and sampling sequence was deemed an acceptable compromise in order to facilitate a workable and efficient test program.

The MKS and CAI instruments both provided a single data point after an instrument defined number of scans were performed during a bag read procedure. The reading was considered stable when the average of three points was within 0.3% of full scale. A 1 ppm concentration was considered full scale for all instruments. An example of the MKS and CAI bag read is shown in Figures 9 and 10, respectively. The red dots show when a stabilization period has been met and the larger green dots show when the data point was taken and used as a test data point. For the CAI instrument each zero, span or bag read took approximately 12 minutes to complete. Due to the long wait time of the CAI instrument to produce a reading, the post bag read zero and span was only performed once between bag reads. Therefore, the pre-zero and pre-span values were used as the previous bags post-zero and post-span values. This reduced the bag read procedure time from what would have been 72 minutes down to 48 minutes. The MKS instrument took approximately six minutes to complete each zero, span or bag read. The entire bag read procedure took about 36 minutes to complete.







FIGURE 10. CAI STABILIZATION EXAMPLE

The Sensors and Horiba instruments each had a continuous output measurement at 1 hertz. Each zero, span or bag read took approximately 80 seconds to complete. The entire bag read procedure took about 480 seconds to complete. A reading was considered stable when an average of three 10-second points was within 0.3% of full scale. An example of a bag read is shown in Figure 11.



FIGURE 11. SENSORS STABILIZATION EXAMPLE

5.0. TEST RESULTS

5.1 Toyota Camry Test Sequence

The Toyota Camry was run over a total of ten FTP tests. The original test matrix had each vehicle conducting seven FTP tests; however due to several N_2O bag measurement issues on individual instruments while testing the Camry, three additional tests were performed. Also, one test (Test Number 6) was voided due to a test cell issue and was not included in the results. Figures 12 through 15 illustrate N_2O emission levels in mg/mile for Phases 1-3 of the FTP and the Composite FTP, for all instruments, including the reference GC-ECD. The error bars represent one standard deviation for ten tests. A detailed summary table of individual test results for N_2O , as well as the difference or delta from the reference value for each instrument is given in Tables 6 through 9. A statistical analysis of the results for each instrument is given in Section 6.0. The GC-ECD reference value was generally in the middle of the various instrument results.



FIGURE 12. TOYOTA CAMRY AVERAGE N₂O EMISSIONS FOR ALL INSTRUMENTS – FTP PHASE 1



FIGURE 13. TOYOTA CAMRY AVERAGE N₂O EMISSIONS FOR ALL INSTRUMENTS – FTP PHASE 2







FIGURE 15. TOYOTA CAMRY AVERAGE N₂O EMISSIONS FOR ALL INSTRUMENTS – FTP COMPOSITE

TABLE 6. FTP PHASE 1 N2O RESULTS, MG/MI AND PERCENT FROMREFERENCE – TOYOTA CAMRY

	Instrument									
TEST		#1	#2		#3		#4		GC-ECD Ref	
	mg/mi	% from Ref	mg/mi	% from Ref	mg/mi	% from Ref	mg/mi	% from Ref	mg/mi	
TCAM-Test 1	1.42	-63.9%	3.36	-14.6%	4.71	19.7%	4.11	4.5%	3.93	
TCAM-Test 2	4.50	3.7%	4.95	14.1%	4.75	9.5%	4.32	-0.6%	4.34	
TCAM-Test 3	4.81	2.0%	3.41	-27.6%	4.25	-9.7%	4.88	3.7%	4.71	
TCAM-Test 4	5.47	0.4%	4.13	-24.3%	na	na	5.31	-2.7%	5.45	
TCAM-Test 5	4.62	-13.1%	6.28	18.1%	4.84	-8.9%	4.84	-8.9%	5.32	
TCAM-Test 7	4.42	-3.1%	3.49	-23.5%	4.81	5.4%	4.41	-3.2%	4.56	
TCAM-Test 8	5.00	-0.8%	5.23	3.8%	5.56	10.3%	4.89	-3.0%	5.04	
TCAM-Test 9	5.73	-0.9%	4.64	-19.8%	5.72	-1.0%	5.49	-5.0%	5.78	
TCAM-Test 10	7.03	54.8%	5.31	17.0%	4.64	2.3%	4.78	5.4%	4.54	
TCAM-Test 11	6.60	7.6%	6.20	1.2%	6.13	0.1%	6.24	1.9%	6.13	
Avg	4.96	-1.3%	4.70	-5.6%	5.05	3.1%	4.93	-0.8%	4.98	
STDev	1.528		1.092		0.612		0.627		0.687	
COV	30.8%		23.2%		12.1%		12.7%		13.8%	
Difference to Ref	-0.021		-0.281		0.119]	-0.052]		
Ratio of Means Versus Reference Mean	-0.4%		-5.6%		2.4%		-1.0%			

TABLE 7. FTP PHASE 2 N2O RESULTS, MG/MI AND PERCENT FROMREFERENCE – TOYOTA CAMRY

	Instrument									
TEST		#1		#2		#3		#4	GC-ECD Ref	
	mg/mi	% from Ref	mg/mi	% from Ref	mg/mi	% from Ref	mg/mi	% from Ref	mg/mi	
TCAM-Test 1	0.72	54.7%	0.00	-100.0%	0.84	81.9%	0.22	-52.2%	0.46	
TCAM-Test 2	0.32	-41.0%	0.00	-100.0%	0.13	-77.2%	0.35	-36.5%	0.55	
TCAM-Test 3	0.65	-32.9%	1.20	24.0%	1.18	22.1%	0.69	-28.3%	0.97	
TCAM-Test 4	0.01	-97.0%	0.88	93.0%	0.48	0.06	0.22	-50.9%	0.45	
TCAM-Test 5	0.56	-21.9%	1.24	71.2%	0.87	19.8%	0.53	-26.3%	0.72	
TCAM-Test 7	0.61	20.5%	0.00	-100.0%	0.69	35.2%	0.62	22.0%	0.51	
TCAM-Test 8	0.50	-14.7%	0.35	-40.4%	0.28	-52.1%	0.70	19.8%	0.58	
TCAM-Test 9	0.62	18.7%	1.54	194.9%	0.19	-64.0%	0.35	-33.4%	0.52	
TCAM-Test 10	1.91	373.4%	1.05	159.6%	0.65	60.6%	0.67	67.0%	0.40	
TCAM-Test 11	1.22	210.6%	0.00	-100.0%	0.49	23.6%	0.63	60.7%	0.39	
Avg	0.71	47.0%	0.62	10.2%	0.58	5.6%	0.50	-5.8%	0.56	
STDev	0.520		0.616		0.333		0.194		0.173	
COV	72.9%		98.7%		57.6%		39.0%		31.1%	
Difference to Ref	0.156		0.068		0.022		-0.057			
Ratio of Means Versus Reference Mean	28.1%		12.2%]	3.9%		-10.3%			

TABLE 8. FTP PHASE 3 N2O RESULTS, MG/MI AND PERCENT FROMREFERENCE – TOYOTA CAMRY

Instrument									
TEST		#1		#2	#3		#4		GC-ECD Ref
	mg/mi	% from Ref	mg/mi	% from Ref	mg/mi	% from Ref	mg/mi	% from Ref	mg/mi
TCAM-Test 1	1.54	-17.9%	1.32	-29.3%	2.30	22.9%	1.63	-12.9%	1.87
TCAM-Test 2	2.43	16.4%	2.55	22.1%	2.17	4.1%	1.94	-7.3%	2.09
TCAM-Test 3	2.24	-0.3%	1.39	-38.3%	na	na	2.31	2.6%	2.25
TCAM-Test 4	2.53	33.8%	1.81	-4.4%	1.50	-0.21	1.78	-6.1%	1.89
TCAM-Test 5	2.00	60.1%	0.33	-73.3%	1.24	-1.1%	1.16	-7.1%	1.25
TCAM-Test 7	1.62	43.2%	0.39	-65.6%	1.45	27.7%	1.10	-2.6%	1.13
TCAM-Test 8	1.32	42.2%	0.75	-19.1%	1.11	20.0%	0.83	-10.4%	0.93
TCAM-Test 9	3.46	18.1%	3.68	25.8%	2.90	-0.9%	2.89	-1.1%	2.93
TCAM-Test 10	1.86	29.8%	2.20	53.5%	1.67	16.4%	1.34	-6.5%	1.44
TCAM-Test 11	2.17	1.8%	1.10	-48.6%	1.86	-12.6%	2.22	4.2%	2.13
Avg	2.12	22.7%	1.55	-17.7%	1.80	6.2%	1.72	-4.7%	1.79
STDev	0.612		1.043		0.573		0.638		0.607
COV	28.9%		67.2%		31.8%		37.1%		33.9%
Difference to Ref	0.327		-0.238		0.061		-0.070		
Ratio of Means Versus Reference Mean	18.2%		-13.3%]	3.4%]	-3.9%		

TABLE 9. FTP COMPOSITE N2O RESULTS, MG/MI AND PERCENT FROMREFERENCE – TOYOTA CAMRY

TEST		#1	#2		#3		#4		GC-ECD Ref
	mg/mi	% from Ref	mg/mi	% from Ref	mg/mi	% from Ref	mg/mi	% from Ref	mg/mi
TCAM-Test 1	1.09	-30.8%	1.07	-32.4%	2.05	30.1%	1.42	-9.8%	1.58
TCAM-Test 2	1.77	0.6%	1.73	-1.7%	1.65	-6.3%	1.61	-8.6%	1.76
TCAM-Test 3	1.95	-7.0%	1.71	-18.5%	na	na	2.01	-4.2%	2.10
TCAM-Test 4	1.85	-2.4%	1.81	-4.3%	na	na	1.71	-9.6%	1.89
TCAM-Test 5	1.81	-1.1%	2.04	11.7%	1.80	-1.6%	1.60	-12.1%	1.82
TCAM-Test 7	1.68	10.5%	0.83	-45.3%	1.75	15.1%	1.54	1.3%	1.52
TCAM-Test 8	1.66	3.5%	1.47	-8.2%	1.61	0.1%	1.61	0.1%	1.60
TCAM-Test 9	2.46	8.1%	2.77	21.8%	2.08	-8.4%	2.12	-7.0%	2.27
TCAM-Test 10	2.96	91.4%	2.25	45.6%	1.76	13.7%	1.71	10.7%	1.55
TCAM-Test 11	2.60	26.0%	1.59	-22.9%	2.04	-1.2%	2.24	8.3%	2.06
Avg	1.98	9.9%	1.73	-5.4%	1.84	5.2%	1.76	-3.1%	1.82
STDev	0.543		0.556		0.189		0.270		0.263
COV	27.4%		32.2%		10.3%		15.3%		14.5%
Difference to Ref	0.166		-0.089		0.071		-0.060		
Ratio of Means Versus Reference Mean	9.2%		-4.9%		3.9%		-3.3%		

The Toyota Camry's average N_2O level for the Composite FTP was 1.82 mg/mi, as determined by the GC-ECD reference instrument. The composite FTP results show that all four of the instruments on average fell within $\pm 10\%$ of the GC-ECD reference values.

There are a few missing data values for one instrument due to an issue that was discovered during post-processing. This occurred twice on Instrument #3 during Test 3 of Phase 3 sample bag read and during Test 4 of Phase 1 sample bag read. As mentioned earlier, two additional tests were conducted to compensate for these measurement errors.

After the first three days of testing were completed, it was observed that Instrument #1 was producing N₂O measurements for sample bags that were up to 70% lower than the other instruments. Background bags and zero/span measurements agreed well with other instruments; it seemed that the issue was an interferent rather than a sampling problem or instrument malfunction. The previous heavy-duty program had accurately measured low N₂O concentrations with this instrument, but the heavy-duty engines involved in the previous program produced much lower concentrations of CO than observed in these tests. For this reason, the instrument provider was asked to investigate their quantification method, especially their compensation for CO interference. The instrument provider discovered that there were a few reference spectra that were causing the CO compensation to negatively bias the reported N₂O concentration. They provided a new quantification method that ignored these errant reference spectra. This new quantification method was used to reprocess the previously collected data from the first three days of testing. It was also used for the remainder of the program. All data reported were from the corrected quantification method.
Due to the very low N_2O concentration emitted in Phase 2 and Phase 3, the measured sample and background bag concentrations were very similar. Out of the ten tests conducted on the Toyota Camry, there were nine cases where either Phase 2 or Phase 3 background concentrations were higher than sample concentrations. However, using the dilution factor to calculate the net concentration, most of these cases resulted in a positive net concentration. If the difference between the two concentrations is large enough, the dilution factor will not compensate for the difference. Instrument #2 calculated a negative net concentration during Phase 2 on four tests which resulted in zero N_2O mass. These zero mass results increased the instruments' variability when compared to the GC-ECD. Instrument #2 was the only analyzer which calculated a mass of zero for an individual test phase.

Another way to examine the variability of a given instrument is to look at the variation of the difference, or delta, between the individual readings for that instrument and the corresponding readings for the reference. This can help to remove the test article itself from the comparison. For Phases 1, 2, 3 and Composite FTP, these deltas are shown in Tables 10 through Table 13, respectively. In each case, the table shows the individual deltas, as well as the mean and standard deviation of the deltas over the data set. The standard deviation is also shown as a percentage of the reference mean for the cycle, as a means of scaling the variation. Note that this evaluation does not necessarily indicate good agreement with the reference, but rather it tracks the stability of that instrument in comparison to the stability of the reference.

Reviewing the Delta tables for the Composite FTP, results show that the instrument that tracked the reference value the best was Instrument #4 at 7.9%. It was followed by Instrument #3 at 12.0% and Instrument #2 at 24.9%. Instrument #1 demonstrated higher levels of variation in the delta at 28.0%. This is an indication that the instrument had a higher degree of variability run-to-run than the other instruments.

TEST		Instru	iments	
IESI	#1	#2	#3	#4
TCAM-Test 1	-2.51	-0.57	0.77	0.18
TCAM-Test 2	0.16	0.61	0.41	-0.03
TCAM-Test 3	0.09	-1.30	-0.46	0.17
TCAM-Test 4	0.02	-1.32	na	-0.15
TCAM-Test 5	-0.70	0.96	-0.47	-0.48
TCAM-Test 7	-0.14	-1.07	0.25	-0.15
TCAM-Test 8	-0.04	0.19	0.52	-0.15
TCAM-Test 9	-0.05	-1.15	-0.06	-0.29
TCAM-Test 10	2.49	0.77	0.10	0.24
TCAM-Test 11	0.47	0.07	0.00	0.11
Avg Delta from Ref	-0.021	-0.281	0.119	-0.052
STDev of the Deltas	1.214	0.905	0.421	0.231
Stdev-Deltas over Ref Mean	24.4%	18.2%	8.5%	4.6%

TABLE 10. TOYOTA CAMRY PHASE 1 FTP - ANALYSIS OF DELTAS FROMREFERENCE

TEST		Instrur	nents	
IESI	#1	#2	#3	#4
TCAM-Test 1	0.25	-0.46	0.38	-0.24
TCAM-Test 2	-0.23	-0.55	-0.42	-0.20
TCAM-Test 3	-0.32	0.23	0.21	-0.27
TCAM-Test 4	-0.44	0.42	0.03	-0.23
TCAM-Test 5	-0.16	0.52	0.14	-0.19
TCAM-Test 7	0.10	-0.51	0.18	0.11
TCAM-Test 8	-0.09	-0.24	-0.30	0.12
TCAM-Test 9	0.10	1.01	-0.33	-0.17
TCAM-Test 10	1.51	0.64	0.24	0.27
TCAM-Test 11	0.83	-0.39	0.09	0.24
Avg Delta from Ref	0.156	0.068	0.022	-0.057
STDev of the Deltas	0.594	0.566	0.277	0.215
Stdev-Deltas over Ref Mean	106.8%	101.7%	49.7%	38.7%

TABLE 11. TOYOTA CAMRY PHASE 2 FTP - ANALYSIS OF DELTAS FROMREFERENCE

TABLE 12. TOYOTA CAMRY PHASE 3 FTP - ANALYSIS OF DELTAS FROM
REFERENCE

TEST	Instruments							
IESI	#1	#2	#3	#4				
TCAM-Test 1	-0.34	-0.55	0.43	-0.24				
TCAM-Test 2	0.34	0.46	0.09	-0.15				
TCAM-Test 3	-0.01	-0.86	na	0.06				
TCAM-Test 4	0.64	-0.08	-0.39	-0.11				
TCAM-Test 5	0.75	-0.92	-0.01	-0.09				
TCAM-Test 7	0.49	-0.74	0.31	-0.03				
TCAM-Test 8	0.39	-0.18	0.19	-0.10				
TCAM-Test 9	0.53	0.76	-0.03	-0.03				
TCAM-Test 10	0.43	0.77	0.24	-0.09				
TCAM-Test 11	0.04	-1.04	-0.27	0.09				
Avg Delta from Ref	0.327	-0.238	0.061	-0.070				
STDev of the Deltas	0.332	0.696	0.267	0.097				
Stdev-Deltas over Ref Mean	18.5%	38.8%	15.4%	5.4%				

TEST		Instru	ments	
IESI	#1	#2	#3	#4
TCAM-Test 1	-0.49	-0.51	0.48	-0.15
TCAM-Test 2	0.01	-0.03	-0.11	-0.15
TCAM-Test 3	-0.15	-0.39	na	-0.09
TCAM-Test 4	-0.05	-0.08	na	-0.18
TCAM-Test 5	-0.02	0.21	-0.03	-0.22
TCAM-Test 7	0.16	-0.69	0.23	0.02
TCAM-Test 8	0.06	-0.13	0.00	0.00
TCAM-Test 9	0.19	0.50	-0.19	-0.16
TCAM-Test 10	1.41	0.70	0.21	0.17
TCAM-Test 11	0.54	-0.47	-0.02	0.17
Avg Delta from Ref	0.166	-0.089	0.071	-0.060
STDev of the Deltas	0.509	0.452	0.219	0.143
Stdev-Deltas over Ref Mean	28.0%	24.9%	12.3%	7.9%

TABLE 13. TOYOTA CAMRY COMPOSITE FTP - ANALYSIS OF DELTAS FROMREFERENCE

5.2 Nissan Altima Test Sequence

The Nissan Altima was tested following the completion of testing for the Toyota Camry. A total of ten tests were conducted with this vehicle, due to an increasing trend in emissions. The initial three tests showed repeatable results; however Tests 4 through Tests 6 showed a considerable increase in N₂O, NO_X and CO concentrations, mainly in Phase 1 of the FTP. A sulfur purge procedure was performed on the vehicle in an effort to return the N₂O levels to those seen in the initial tests. A day after the sulfur purge, the vehicle was preconditioned with an FTP cycle, and a cold-start FTP cycle was performed to evaluate exhaust emissions. N₂O levels were not measured for this check out test; however the regulated emissions results showed a decrease in NO_X and CO emissions. These findings were discussed with CRC and testing continued. Three additional tests were performed in an effort to decrease the variability of the test data. The three additional tests also showed increasing trends in N₂O. The fuel used for this program was a CARB LEV III certification gasoline with a sulfur level of 9 ppm. A fuel sample was taken from the vehicle's fuel rail and analyzed for sulfur level. The results showed a sulfur level of 12.4 ppm. It is unclear why the NO_X, N₂O, and CO emissions were trending upward, as there were no diagnostic codes present during the tests. The upward trending N₂O levels are shown in Figure 16.

Figures 17 through 20 illustrate N_2O emission levels in mg/mile for Phases 1-3 of the FTP and the Composite FTP for each instrument, including the reference GC-ECD. The error bars represent one standard deviation. A detailed summary table of individual test results for N_2O , as well as the difference or delta from the reference value for each instrument, is given in Tables 14 through 17. A statistical analysis of the results for individual instruments is given in Section 6.0. The GC-ECD reference value was generally in the middle of the various instruments in terms of N_2O emissions.



FIGURE 16. INCREASING N2O TREND – NISSAN ALTIMA



FIGURE 17. NISSAN ALTIMA AVERAGE N₂O EMISSIONS FOR ALL INSTRUMENTS – FTP PHASE 1



FIGURE 18. NISSAN ALTIMA AVERAGE N₂O EMISSIONS FOR ALL INSTRUMENTS – FTP PHASE 2



FIGURE 19. NISSAN ALTIMA AVERAGE N₂O EMISSIONS FOR ALL INSTRUMENTS – FTP PHASE 3



FIGURE 20. NISSAN ALTIMA AVERAGE N₂O EMISSIONS FOR ALL INSTRUMENTS – FTP COMPOSITE

					Instru	ment			
TEST		#1		#2		#3		#4	GC-ECD Ref
	mg/mi	% from Ref	mg/mi	% from Ref	mg/mi	% from Ref	mg/mi	% from Ref	mg/mi
NALT-Test 1	5.7	3.2%	4.4	-19.5%	5.3	-4.4%	5.8	5.3%	5.5
NALT-Test 2	8.2	5.4%	7.2	-7.4%	8.1	3.7%	8.1	4.0%	7.8
NALT-Test 3	9.1	9.3%	7.3	-12.2%	8.7	4.0%	8.5	1.3%	8.3
NALT-Test 4	11.5	8.5%	11.1	4.6%	10.8	1.8%	10.9	3.1%	10.6
NALT-Test 5	11.9	3.8%	11.7	1.9%	11.8	3.0%	11.9	4.1%	11.4
NALT-Test 6	12.9	9.9%	13.3	13.4%	11.8	0.7%	12.1	3.2%	11.7
NALT-Test 7	7.1	0.0%	8.3	17.2%	7.2	0.8%	7.7	7.7%	7.1
NALT-Test 8	7.8	-4.0%	8.3	2.2%	8.5	4.3%	8.3	1.4%	8.2
NALT-Test 9	9.6	7.1%	7.9	-11.8%	9.4	4.5%	9.2	2.3%	9.0
NALT-Test 10	9.7	13.1%	7.8	-9.2%	8.8	2.3%	8.8	2.0%	8.6
Avg	9.359	0.056	8.743	-0.021	9.029	0.021	9.121	0.034	8.828
STDev	2,249		2.565		2.034		1.975		1.941
COV	24.0%		29.3%		22.5%		21.7%		22.0%
Difference to Ref	0.531		-0.085		0.201		0.293		
Patio of Moone Vorsus Potoroneo Moon	6 0%	1	-1 0%		2 30/		3 30/		

TABLE 14. FTP PHASE 1 N2O RESULTS, MG/MI AND PERCENT FROMREFERENCE – NISSAN ALTIMA

TABLE 15. FTP PHASE 2 N2O RESULTS, MG/MI AND PERCENT FROMREFERENCE – NISSAN ALTIMA

	Instrument								
TEST		#1		#2		#3		#4	GC-ECD Ref
	mg/mi	% from Ref	mg/mi	% from Ref	mg/mi	% from Ref	mg/mi	% from Ref	mg/mi
NALT-Test 1	0.48	14.8%	0.00	-100.0%	0.28	-33.7%	1.39	230.9%	0.42
NALT-Test 2	0.00	-100.0%	1.58	224.7%	1.40	188.1%	0.71	45.5%	0.49
NALT-Test 3	0.58	-53.7%	1.55	23.2%	0.78	-38.1%	1.62	28.5%	1.26
NALT-Test 4	2.49	17.6%	1.20	-43.4%	2.26	0.07	3.00	41.4%	2.12
NALT-Test 5	1.74	-19.5%	2.51	16.1%	2.49	15.3%	3.39	57.1%	2.16
NALT-Test 6	2.68	-32.4%	2.71	-31.7%	3.93	-0.9%	3.82	-3.6%	3.96
NALT-Test 7	0.82	36.9%	1.27	111.4%	0.91	51.3%	0.45	-26.0%	0.60
NALT-Test 8	1.59	79.1%	0.06	-93.5%	0.19	-78.9%	1.38	56.0%	0.89
NALT-Test 9	2.52	17.8%	1.80	-15.6%	2.37	11.1%	2.09	-2.3%	2.14
NALT-Test 10	3.01	14.9%	2.32	-11.3%	2.64	1.0%	2.45	-6.6%	2.62
Avg	1.59	-2.5%	1.50	8.0%	1.73	12.2%	2.03	42.1%	1.67
STDev	1.067		0.926		1.208		1.128		1.141
COV	67.1%		61.8%		70.0%		55.6%		68.5%
Difference to Ref	-0.074]	-0.165]	0.061		0.363		
Ratio of Means Versus Reference Mean	-4.4%		-9.9%]	3.6%		21.8%		

TABLE 16. FTP PHASE 3 N2O RESULTS, MG/MI AND PERCENT FROMREFERENCE – NISSAN ALTIMA

	Instrument								
TEST		#1		#2		#3		#4	GC-ECD Ref
	mg/mi	% from Ref	mg/mi	% from Ref	mg/mi	% from Ref	mg/mi	% from Ref	mg/mi
NALT-Test 1	0.46	-34.2%	1.59	126.8%	1.07	51.8%	0.85	21.1%	0.70
NALT-Test 2	1.06	2.2%	1.99	92.0%	1.39	33.8%	1.26	21.2%	1.04
NALT-Test 3	0.42	-65.2%	0.53	-56.2%	1.39	15.3%	1.03	-14.4%	1.20
NALT-Test 4	1.37	-18.2%	2.17	29.8%	1.78	0.07	1.64	-1.8%	1.67
NALT-Test 5	1.83	-23.0%	1.43	-39.9%	2.30	-3.4%	2.31	-2.7%	2.38
NALT-Test 6	1.98	-17.6%	1.55	-35.6%	2.58	7.2%	2.58	7.5%	2.40
NALT-Test 7	0.95	-6.0%	0.35	-65.6%	1.11	9.7%	0.77	-24.6%	1.01
NALT-Test 8	0.99	-18.3%	0.71	-41.7%	1.10	-8.9%	1.53	26.0%	1.21
NALT-Test 9	1.16	-31.5%	0.94	-44.8%	1.91	12.5%	1.62	-4.9%	1.70
NALT-Test 10	1.96	-20.4%	2.35	-4.6%	2.64	7.2%	2.22	-9.6%	2.46
Avg	1.22	-23.2%	1.36	-4.0%	1.73	13.2%	1.58	1.8%	1.58
STDev	0.566		0.702		0.610		0.630		0.647
COV	46.5%		51.6%		35.3%		39.9%		41.0%
Difference to Ref	-0.360		-0.218		0.148]	0.003		
Ratio of Means Versus Reference Mean	-22.8%		-13.8%		9.4%		0.2%		

TABLE 17. FTP COMPOSITE N2O RESULTS, MG/MI AND PERCENT FROM
REFERENCE – NISSAN ALTIMA

	Instrument								
TEST		#1		#2		#3		#4	GC-ECD Ref
	mg/mi	% from Ref	mg/mi	% from Ref	mg/mi	% from Ref	mg/mi	% from Ref	mg/mi
NALT-Test 1	1.56	0.2%	1.36	-12.5%	1.54	-1.4%	2.16	38.5%	1.56
NALT-Test 2	2.01	-7.2%	2.87	32.7%	2.79	29.0%	2.41	11.1%	2.16
NALT-Test 3	2.31	-14.8%	2.47	-9.1%	2.59	-4.7%	2.88	5.9%	2.72
NALT-Test 4	4.05	7.9%	3.51	-6.4%	3.90	0.04	4.27	13.7%	3.75
NALT-Test 5	3.86	-6.7%	4.11	-0.8%	4.36	5.3%	4.86	17.3%	4.14
NALT-Test 6	4.61	-10.5%	4.59	-10.8%	5.19	0.9%	5.20	1.0%	5.15
NALT-Test 7	2.17	4.7%	2.49	20.1%	2.27	9.5%	2.04	-1.7%	2.08
NALT-Test 8	2.72	9.4%	1.96	-21.3%	2.17	-12.8%	2.85	14.8%	2.49
NALT-Test 9	3.62	5.3%	2.84	-17.5%	3.71	7.7%	3.44	-0.1%	3.44
NALT-Test 10	4.11	7.8%	3.47	-9.1%	3.92	2.7%	3.70	-3.1%	3.82
Avg	3.10	-0.4%	2.97	-3.5%	3.24	4.0%	3.38	9.7%	3.13
STDev	1.066		0.975		1.144		1.113		1.112
COV	34.4%		32.9%		35.3%		32.9%		35.5%
Difference to Ref	-0.027		-0.163]	0.114		0.250		
Ratio of Means Versus Reference Mean	-0.9%		-5.2%		3.6%		8.0%		

For the Nissan Altima, the average N_2O level on the Composite FTP was 3.13 mg/mi, as determined by the GC-ECD reference instrument. The Nissan Altima showed higher variability from test-to-test with a COV of 35.5% due to the increasing emissions trend mentioned earlier.

The composite FTP results show that all four instruments on average fell within $\pm 10\%$ of the GC-ECD reference value.

Analysis of the individual instrument deltas from the GC-ECD reference on a test-by-test basis for Phases 1, 2, 3 and Composite FTP are shown in Tables 18 through 21, respectively. As noted previously, this evaluation does not necessarily indicate good agreement with the reference, but rather it tracks the stability of that instrument in comparison to the stability of the reference.

тест		Instr	uments	
IESI	#1	#2	#3	#4
NALT-Test 1	0.18	-1.08	-0.24	0.29
NALT-Test 2	0.42	-0.58	0.29	0.31
NALT-Test 3	0.78	-1.02	0.33	0.11
NALT-Test 4	0.90	0.48	0.19	0.33
NALT-Test 5	0.43	0.21	0.34	0.46
NALT-Test 6	1.16	1.57	0.08	0.37
NALT-Test 7	0.00	1.22	0.05	0.54
NALT-Test 8	-0.33	0.18	0.35	0.12
NALT-Test 9	0.64	-1.06	0.41	0.21
NALT-Test 10	1.12	-0.79	0.20	0.17
Avg Delta from Ref	0.531	-0.085	0.201	0.293
STDev of the Deltas	0.486	0.972	0.195	0.144
Stdev-Deltas over Ref Mean	5.5%	11.0%	2.2%	1.6%

TABLE 18. ANALYSIS OF PHASE 1 FTP DELTAS FROM REFERENCE FOR
NISSAN ALTIMA

TABLE 19. ANALYSIS OF PHASE 2 FTP DELTAS FROM REFERENCE FOR
NISSAN ALTIMA

TECT		Instru	iments	
	#1	#2	#3	#4
NALT-Test 1	0.06	-0.42	-0.14	0.97
NALT-Test 2	-0.49	1.09	0.92	0.22
NALT-Test 3	-0.67	0.29	-0.48	0.36
NALT-Test 4	0.37	-0.92	0.14	0.88
NALT-Test 5	-0.42	0.35	0.33	1.23
NALT-Test 6	-1.29	-1.26	-0.04	-0.14
NALT-Test 7	0.22	0.67	0.31	-0.16
NALT-Test 8	0.70	-0.83	-0.70	0.50
NALT-Test 9	0.38	-0.33	0.24	-0.05
NALT-Test 10	0.39	-0.29	0.03	-0.17
Avg Delta from Ref	-0.074	-0.165	0.061	0.363
STDev of the Deltas	0.619	0.750	0.450	0.517
Stdev-Deltas over Ref Mean	37.2%	45.1%	27.0%	31.0%

TABLE 20. ANALYSIS OF PHASE 3 FTP DELTAS FROM REFERENCE FORNISSAN ALTIMA

TEST		Instru	ments	
IESI	#1	#2	#3	#4
NALT-Test 1	-0.24	0.89	0.36	0.15
NALT-Test 2	0.02	0.95	0.35	0.22
NALT-Test 3	-0.78	-0.68	0.18	-0.17
NALT-Test 4	-0.30	0.50	0.11	-0.03
NALT-Test 5	-0.55	-0.95	-0.08	-0.06
NALT-Test 6	-0.42	-0.86	0.17	0.18
NALT-Test 7	-0.06	-0.67	0.10	-0.25
NALT-Test 8	-0.22	-0.50	-0.11	0.32
NALT-Test 9	-0.54	-0.76	0.21	-0.08
NALT-Test 10	-0.50	-0.11	0.18	-0.24
Avg Delta from Ref	-0.360	-0.218	0.148	0.003
STDev of the Deltas	0.246	0.734	0.155	0.201
Stdev-Deltas over Ref Mean	15.6%	46.5%	9.8%	12.7%

TEST	Instruments					
IESI	#1	#2	#3	#4		
NALT-Test 1	0.00	-0.19	-0.02	0.60		
NALT-Test 2	-0.16	0.71	0.63	0.24		
NALT-Test 3	-0.40	-0.25	-0.13	0.16		
NALT-Test 4	0.30	-0.24	0.15	0.51		
NALT-Test 5	-0.28	-0.04	0.22	0.72		
NALT-Test 6	-0.54	-0.56	0.05	0.05		
NALT-Test 7	0.10	0.42	0.20	-0.04		
NALT-Test 8	0.23	-0.53	-0.32	0.37		
NALT-Test 9	0.18	-0.60	0.27	0.00		
NALT-Test 10	0.30	-0.35	0.10	-0.12		
Avg Delta from Ref	-0.027	-0.163	0.114	0.250		
STDev of the Deltas	0.302	0.427	0.253	0.289		
Stdev-Deltas over Ref Mean	9.6%	13.6%	8.1%	9.2%		

TABLE 21. ANALYSIS OF FTP COMPOSITE DELTAS FROM REFERENCE FOR NISSAN ALTIMA

The Composite FTP results show that the instrument that tracked the reference value best was Instrument #3 at 8.1%. It was followed by Instrument #4 at 9.2%, and Instrument #1 at 9.6%. Instrument #2 demonstrated higher levels of variation in the delta at 13.6%. This is an indication that the instrument had a higher degree of variability run-to-run than the other instruments.

While testing the Nissan Altima, Instrument #2 calculated a negative net concentration during Tests 1 of Phase 2 of the FTP. Similar to the situation with the Toyota Camry, the background concentration was larger than the sample concentration which resulted in a negative net concentration and thus a zero mass for that phase. This increased the instruments' calculated variability when compared to the GC-ECD.

5.3 Overall Summary of Results

A summary of the average difference in percent from the reference for each instrument and each test run is given in Table 22. The table shows each instrument and its percent difference from the Reference versus the Reference mean. These values are a summary of Tables 6 through 9 and 14 through 17 from Section 5 of this report.

		Ratio of Means					
		V	ersus Refe	erence Mea	n		
Vehicle		#1 #2 #3 #4					
	Phase 1	-0.4%	-5.6%	2.4%	-1.0%		
Toyota Camry	Phase 2	28.1%	12.2%	3.9%	-10.3%		
Tests	Phase 3	18.2%	-13.3%	3.4%	-3.9%		
	Composite FTP	9.2%	-4.9%	3.9%	-3.3%		
	Phase 1	6.0%	-1.0%	2.3%	3.3%		
Nissan Altima	Phase 2	-4.4%	-9.9%	3.6%	21.8%		
Tests	Phase 3	-22.8%	-13.8%	9.4%	0.2%		
	Composite FTP	-0.9%	-5.2%	3.6%	8.0%		

TABLE 22. SUMMARY OF OVERALL N2O PERCENT DIFFERENCE FROMREFERENCE BY INSTRUMENT

The instrument variability can also be examined by determining the spread of each instrument compared to the GC-ECD reference. Tables 23 and 24 show the spread by determining the standard deviation of the delta for each instrument. A plus and minus one standard deviation from the average delta is then calculated. By dividing these values by the reference mean, an upper and lower percentage is determined. This shows the data spread of each instrument. Also given in the table is a best, worst, and average agreement value across all ten tests for a given vehicle. This is determined by finding the difference in the maximum and minimum percent difference with respect to the GC-ECD reference for each instrument across a single test. The best agreement and worst agreement and average is then determined across all ten tests. This eliminates the vehicle variability from the results. These values are shown in each table for both the Camry and Altima.

The variability of the instruments is relatively high compared to the reference. A comparison of all instrument percent differences with respect to the GC-ECD within each Camry test shows a best agreement of 7% and worst agreement of 81%. The Altima showed a best agreement of 12% and worst agreement of 51% within each Altima test. However, given the low N₂O emission rate average of 2.5 mg/mi for these two vehicles, the worst case agreement of 81% gives a spread of 0.5 mg/mi to 4.5 mg/mi. This is still less than the current 10 mg/mi N₂O standard. A review of late model vehicles with direct injection technology shows similar or lower N₂O emission rates. Nevertheless, these instruments would have trouble accurately measuring N₂O levels from vehicles closer to the N₂O standard.

TABLE 23. SUMMARY OF INSTRUMENT VARIBILITY FORTOYOTA CAMRY TESTS

		Instrument					
		#1		#2	#3		#4
		mg/mi		mg/mi	mg/n	ni	mg/mi
	Avg Delta from Ref	0.17		-0.09	0.07	7	-0.06
	Stdev of Deltas	0.51		0.45	0.22	2	0.14
Toyota Camry	Avg Delta from Ref + 1Stdev	0.68		0.36	0.29)	0.08
	Avg Delta from Ref - 1Stdev	-0.34		-0.54 -0.15		5	-0.20
	Avg Delta over Ref Mean (Upper)	37.2%		20.0%	15.9%	V ₀	4.6%
	Avg Delta over Ref Mean	-18.9%		-29.8%	-8.2%	6	-11.1%
Tests	(Lower)						
	Camry: Comparison of all instrument	nt % diff w.r.	.t. G	C-ECD but	t within e	each v	vehicle
	test (removes vehicle variability)						
	Post Worst Aug agroomont	Best		Wor	st		Avg
	across all 10 tests	Agreemen	nt	Agreer	nent	Di	fference
	across an 10 tests	7.1%		80.8	%		34.9%

TABLE 24. SUMMARY OF INSTRUMENT VARIBILITY FORNISSAN ALTIMA TESTS

		Instrument					
		#1		#2	#3		#4
		mg/mi		mg/mi	mg/n	ni	mg/mi
	Avg Delta from Ref	-0.03		-0.16	0.11		0.25
	Stdev of Deltas	0.30		0.43	0.25		0.29
	Avg Delta from Ref + 1Stdev	0.27		0.26	0.37	'	0.54
	Avg Delta from Ref - 1Stdev	-0.33		-0.59	-0.14	1	-0.04
Nissan	Avg Delta over Ref Mean (Upper)	8.8%		8.4%	11.7%	⁄0	17.2%
Altima	Avg Delta over Ref Mean	-10.5%	-	-18.9%	-4.4%	6	-1.3%
Tests	(Lower)						
	Altima: Comparison of all instrume	nt % diff w.r	.t. G	C-ECD bu	t within e	each v	vehicle
	test (removes vehicle variability)						
	Best Worst Avg agreement	Best		Wor	st		Avg
	across all 10 tests	Agreemen	nt	Agreer	nent	Di	fference
	across an 10 tests	11.9%		51.0	%		26.8%

6.0 STATISTICAL ANALYSIS

N₂O data were collected on transient FTP cycles using the following five instruments:

- Instrument #1
- Instrument #2
- Instrument #3
- Instrument #4
- GC-ECD (considered as the reference method)

The GC-ECD is the reference method by which the other four instruments were statistically compared. During the testing phase one FTP test was conducted for all five instruments simultaneously. FTP N₂O results were obtained for Phase 1, Phase 2, Phase 3 and the FTP Composite. A total of ten test days were completed on the Toyota Camry resulting in 200 N₂O measurements (5 instrument methods x 10 test days x 4 FTP phases). The same number of tests and test days were then completed on the Nissan Altima (200 N₂O measurements = 5 instruments x 10 test days x 4 FTP phases).

The primary focus of the analysis was to determine if there were any significant differences in the four instruments compared to the GC-ECD dilute bag reference method. Several analyses were conducted including graphical analyses, limits of agreement, and analysis of variance. Since the tests were not repeated for each vehicle and instrument within each test day, there is no information available to estimate the repeatability of the instruments. Each FTP phase was analyzed separately.

6.1 N₂O Test Results

 N_2O test results for the Nissan Altima and the Toyota Camry are plotted in Figures 21 through 28 for each of the three FTP phases and composite, respectively. These plots represent the between-day variability of the N_2O measurements. Note that for Phases 1, 2, 3 and the Composite, the N_2O results for Instruments #1 and #2 are generally the most different from the N_2O results of the GC-ECD. Also, in Phase 1 the Nissan Altima generally produced higher N_2O than the Toyota Camry. Also note that the plots depict the day-to-day variability for the five instruments.



FIGURE 21. N₂O TESTS FOR ALTIMA OVER 10 TEST DAYS BY INSTRUMENT - PHASE 1



FIGURE 22. N₂O TESTS FOR CAMRY OVER 10 TEST DAYS BY INSTRUMENT - PHASE 1



FIGURE 23. N_2O TESTS FOR ALTIMA OVER 10 TEST DAYS BY INSTRUMENT - PHASE 2



FIGURE 24. $N_{2}O$ TESTS FOR CAMRY OVER 10 TEST DAYS BY INSTRUMENT - PHASE 2



FIGURE 25. N₂O TESTS FOR ALTIMA OVER 10 TEST DAYS BY INSTRUMENT - PHASE 3



FIGURE 26. N₂O TESTS FOR CAMRY OVER 10 TEST DAYS BY INSTRUMENT - PHASE 3



FIGURE 27. N₂O TESTS FOR ALTIMA OVER 10 TEST DAYS BY INSTRUMENT - COMPOSITE



FIGURE 28. N₂O TESTS FOR CAMRY OVER 10 TEST DAYS BY INSTRUMENT - COMPOSITE

6.2 Limits of Agreement

The first analysis in comparing the measurement analyzers involved a very simple approach called the "limits of agreement" first published by J. Bland and Douglas Altman². This approach examined the paired N₂O differences between two measurement analyzers across the ten test days on each of the two test vehicles. Five different instruments were tested with the GC-ECD analyzer considered as the 'reference'. Since we tested five instruments, we assessed the paired differences using only two methods at a time resulting in four analyses. These analyses examined bias and variability between two methods by computing the difference in the paired N₂O measurements and the average value of the paired N₂O values. Data from the two vehicles were combined for each comparison. The steps in the limits of agreement analysis are as follows:

- Calculate the difference in N₂O from the paired data for two instruments (test instrument vs. GC-ECD reference)
- Plot the N₂O difference vs. N₂O average for each data pair
- Calculate the average and standard deviation of the differences
- Compute 95% limits of agreement on the average differences defined by:

$Average_{Difference} \pm 1.96 Standard Deviation_{Difference}$

• If 95% of the N₂O differences lie between the limits, then measurement methods are in agreement. If the measurement methods are comparable, the differences should be small, centered around 0 and show no systematic variation with the average of the measurement pairs.

The plot of N_2O difference against the N_2O mean for each data pair allows one to investigate any possible relationship between the measurement error and the "true" N_2O value. Since the true value is not known, the mean of the two measurements is the best estimate available. It would be incorrect to plot the difference against either the 'test instrument' or the GC-ECD reference N_2O value separately because the difference would be related to each value.

Table 25 lists the overall average and standard deviation for the 20 N_2O measurements by instrument type and phase (2 vehicles x 10 test days).

 ² Bland, J.M. and Altman, D.G., "Statistical Methods for Assessing Agreement Between Two Methods of Clinical Measurement," *The Lancet*, February 1986, pp. 307-310.
 SwRI Final Report 03.19027
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Instrument	Phase	N	N ₂ O Average,	N ₂ O Standard	$N_2O COV,$
	1	20	7 1502	2 0214	/0
	1	20	/.1595	2.9314	40.95
Instrument #1	2	20	1.1520	0.9330	80.99
	3	20	1.6678	0.7364	44.15
	Composite	20	2.5428	1.0040	39.48
	1	20	6.7218	2.8257	42.04
Instrument #2	2	20	1.0622	0.8877	83.57
Instrument #2	3	20	1.4562	0.8709	59.81
	Composite	20	2.3471	1.0008	42.67
	1	19	7.1426	2.5313	35.44
Instrument #2	2	20	1.1521	1.0440	90.62
Instrument #5	3	19	1.7616	0.5772	32.77
	Composite	18	2.6208	1.1054	42.18
	1	20	7.0247	2.5804	36.73
Instrument #4	2	20	1.2638	1.1118	87.97
Instrument #4	3	20	1.6506	0.6212	37.63
	Composite	20	2.5681	1.1465	44.64
	1	20	6.9044	2.4298	35.19
CCECD	2	20	1.1108	0.9768	87.94
UC-EUD	3	20	1.6844	0.6207	36.85
	Composite	20	2.4732	1.0359	41.89

TABLE 25. N₂O DESCRIPTIVE STATISTICS BY INSTRUMENT AND PHASE

6.2.1 Comparison of Instrument #1 and GC-ECD

Figures 29 through 36 represent GC-ECD instrument N_2O results and Instrument #1 N_2O results using the limits of agreement plots.

Figures 29, 31, 33 and 35 illustrate N_2O measurements for the 20 test pairs of test data using Instrument #1 and the GC-ECD for Phases 1, 2, 3 and the Composite, respectively. A line is drawn on each plot which would indicate perfect agreement between measurements using the two instruments.

The statistics on the differences are listed in Table 26 and the resulting limits plots are shown in Figures 30, 32, 34 and 36 for Phase 1, Phase 2, Phase 3 and Composite, respectively. The Bland-Altman analysis 95% limits of agreement are also provided in Table 26 for each of the phases. Note that all but two test pairs for Phases 1 and 2 are within the limits, while all but one test pair for the Composite is within the limits. There does not appear to be a bias in Instrument #1 compared to the GC-ECD as can be seen in the ranges of the 95% limits of agreement.



FIGURE 29. N_2O INSTRUMENT #1 AND GC-ECD COMPARISON FOR PHASE 1







FIGURE 31. N₂O INSTRUMENT #1 AND GC-ECD COMPARISON FOR PHASE 2







FIGURE 33. N₂O INSTRUMENT #1 AND GC-ECD COMPARISON FOR PHASE 3







FIGURE 35. N₂O INSTRUMENT #1 AND GC-ECD COMPARISON FOR COMPOSITE





TABLE 26. DESCRIPTIVE STATISTICS ON N2O DIFFERENCE BETWEENINSTRUMENT #1 AND GC-ECD

Difference Statistics	Phase 1	Phase 2	Phase 3	Composite
Average	0.25492	0.04117	-0.01658	0.06963
Standard Deviation	0.94337	0.60238	0.45257	0.41944
Lower Limit	-1.59408	-1.13950	-0.90362	-0.75247
Upper Limit	2.10392	1.22184	0.87046	0.89173

6.2.2 Comparison of Instrument #2 and GC-ECD

Figures 37 through 33 represent GC-ECD instrument N_2O results and Instrument #2 N_2O results using the limits of agreement plots.

Figures 37, 39, 41 and 53 illustrate N_2O measurements for the 20 test pairs of test data using Instrument #2 and the GC-ECD for Phases 1, 2, 3 and the Composite, respectively. A line is drawn on each plot which would indicate perfect agreement between measurements using the two instruments.

The statistics on the differences are listed in Table 27 and the resulting limits plots are shown in Figures 38, 40, 42 and 54 for Phase 1, Phase 2, Phase 3 and Composite, respectively. The Bland-Altman analysis 95% limits of agreement are also provided in Table 27 for each of the phases. Note that none of the test pairs fell outside the 95% limits of agreement for any of the phases or the Composite. The Bland-Altman method would conclude that the instrument measurement methods are in agreement. There does not appear to be a bias in the Instrument #2 compared to the GC-ECD as can be seen in the ranges of the 95% limits of agreement.







FIGURE 38. N₂O DIFFERENCE IN INSTRUMENT #2 AND GC-ECD VS. AVERAGE N₂O FOR PHASE 1



FIGURE 39. N₂O INSTRUMENT #2 AND GC-ECD COMPARISON FOR PHASE 2



FIGURE 40. N₂O DIFFERENCE IN INSTRUMENT #2 AND GC-ECD VS. AVERAGE N₂O FOR PHASE 2







FIGURE 42. N₂O DIFFERENCE IN INSTRUMENT #2 AND GC-ECD VS. AVERAGE N₂O FOR PHASE 3







FIGURE 44. N₂O DIFFERENCE IN INSTRUMENT #2 AND GC-ECD VS. AVERAGE N₂O FOR COMPOSITE

TABLE 27.	DESCRIPTIVE STATISTICS ON N2O DIFFERENCE BETWEEN
	INSTRUMENT #2 AND GC-ECD

Difference Statistics	Phase 1	Phase 2	Phase 3	Composite
Average	-0.18266	-0.04859	-0.22825	-0.12606
Standard Deviation	0.91949	0.65770	0.69622	0.42990
Lower Limit	-1.98485	-1.33768	-1.59285	-0.96866
Upper Limit	1.61953	1.24051	1.13634	0.71654

6.2.3 Comparison of Instrument #3 and GC-ECD

Figures 45 through 52 represent GC-ECD instrument N_2O results and Instrument #3 N_2O results using the limits of agreement plots.

Figures 45, 47, 49 and 51 illustrate N_2O measurements for the 20 test pairs of test data using Instrument #3 and GC-ECD for Phases 1, 2, 3 and the Composite, respectively. A line is drawn on each plot which would indicate perfect agreement between measurements using the two instruments.

The statistics on the differences are listed in Table 28 and the resulting limits plots are shown in Figures 46, 48, 50 and 52 for Phase 1, Phase 2, Phase 3 and Composite, respectively. The Bland-Altman analysis 95% limits of agreement are also provided in Table 28 for each of the phases. Note that all but one test pair for Phases 1, 3 and the Composite are within the limits, while all but two test pairs for Phase 2 are within the limits. There does not appear to be a bias in Instrument #3 compared to the GC-ECD as can be seen in the ranges of the 95% limits of agreement.



FIGURE 45. N₂O INSTRUMENT #3 AND GC-ECD COMPARISON FOR PHASE 1



FIGURE 46. N₂O DIFFERENCE IN INSTRUMENT #3 AND GC-ECD VS. AVERAGE N₂O FOR PHASE 1







FIGURE 48. N₂O DIFFERENCE IN INSTRUMENT #3 AND GC-ECD VS. AVERAGE N₂O FOR PHASE 2



FIGURE 49. N₂O INSTRUMENT #3 AND GC-ECD COMPARISON FOR PHASE 3



FIGURE 50. N₂O DIFFERENCE IN INSTRUMENT #3 AND GC-ECD VS. AVERAGE N₂O FOR PHASE 3







FIGURE 52. N₂O DIFFERENCE IN INSTRUMENT #3 AND GC-ECD VS. AVERAGE N₂O FOR COMPOSITE

TABLE 28.	DESCRIPTIVE STATISTICS ON N₂O DIFFERENCE BETWEEN
	INSTRUMENT #3 AND GC-ECD

Difference Statistics	Phase 1	Phase 2	Phase 3	Composite
Average	0.16175	0.04131	0.10703	0.09469
Standard Deviation	0.31549	0.36413	0.21368	0.23240
Lower Limit	-0.45661	-0.67239	-0.31178	-0.30680
Upper Limit	0.78011	0.75500	0.52585	0.55018

6.2.4 Comparison of Instrument #4 and GC-ECD

Figures 53 through 60 represent GC-ECD instrument N_2O results and Instrument #4 N_2O results using the limits of agreement plots.

Figures 53, 55, 57 and 59 illustrate N_2O measurements for the 20 test pairs of test data using Instrument #4 and the GC-ECD for Phases 1, 2, 3 and the Composite, respectively. A line is drawn on each plot which would indicate perfect agreement between measurements using the two instruments.

The statistics on the differences are listed in Table 29 and the resulting limits plots are shown in Figures 54, 56, 58 and 60 for Phase 1, Phase 2, Phase 3 and Composite, respectively. The Bland-Altman analysis 95% limits of agreement are also provided in Table 29 or each of the phases. Note that all but one test pair for Phases 1, 2, 3 and Composite are within the limits. The Bland-Altman method would conclude that the instrument measurement methods are in agreement. There does not appear to be a bias in Instrument #4 compared to the GC-ECD as can be seen in the ranges of the 95% limits of agreement.



FIGURE 53. N₂O INSTRUMENT #4 AND GC-ECD COMPARISON FOR PHASE 1



FIGURE 54. N₂O DIFFERENCE IN INSTRUMENT #4 AND GC-ECD VS. AVERAGE N₂O FOR PHASE 1







FIGURE 56. N₂O DIFFERENCE IN INSTRUMENT #4 AND GC-ECD VS. AVERAGE N₂O FOR PHASE 2



FIGURE 57. N₂O INSTRUMENT #4 AND GC-ECD COMPARISON FOR PHASE 3


FIGURE 58. N₂O DIFFERENCE IN INSTRUMENT #4 AND GC-ECD VS. AVERAGE N₂O FOR PHASE 3







FIGURE 60. N₂O DIFFERENCE IN INSTRUMENT #4 AND GC-ECD VS. AVERAGE N₂O FOR COMPOSITE

TABLE 29.	DESCRIPTIVE STATISTICS ON N₂O DIFFERENCE BETWEEN
	INSTRUMENT #4 AND GC-ECD

Difference Statistics	Phase 1	Phase 2	Phase 3	Composite
Average	0.12025	0.15298	-0.03381	0.09489
Standard Deviation	0.25778	0.44163	0.15795	0.27296
Lower Limit	-0.38499	-0.71262	-0.34339	-0.44011
Upper Limit	0.62550	1.01859	0.27578	0.62990

6.3 Comparison of Average N₂O for Each Instrument to the GC-ECD

An analysis of variance (ANOVA) model was used to compare the average N_2O for each of the four tested instruments to the average N_2O for the GC-ECD instrument. The model contained the following factors:

- Vehicle [Levels: Altima and Camry]
- Test Day nested within Vehicle [Levels: 10 test days for each vehicle]
- Instrument [Levels: 5 instruments]

In this model it is assumed that there is no vehicle x test day x instrument interaction. Multiple-comparison techniques were used to compare the N₂O means across the instruments to determine statistical significance. Dunnett's multiple comparison procedure was used to assess the significance in the differences in the average N₂O from each of the four test instruments to the GC-ECD. All statistical tests were performed at the α =0.05 level of significance. In all analyses, the N₂O results were examined independently for each phase.

The results of the ANOVA for the N_2O Phase 1 are provided in Table 30. Note that statistically significant differences were observed between the two vehicles and across the test days for each vehicle. The N_2O Phase 1 results of Dunnett's comparison test against the GC-ECD instrument are displayed graphically in Figure 61. The x-axis represents the four instrument comparisons to the GC-ECD. The horizontal line within the shaded area is drawn at the GC-ECD mean N_2O value. The four vertical lines starting from the GC-ECD instrument line terminate at the means for each of the four instruments being compared to the GC-ECD. Thus, the lengths of the vertical lines represent the difference in the means for the GC-ECD vs. each of the four tested instruments. The horizontal shaded area indicates the upper and lower decision limits comparing the N_2O means for the four instruments against the mean N_2O for the GC-ECD instrument N_2O mean is significantly different from the GC-ECD instrument N_2O mean. As shown in Figure 61, none of the four instruments demonstrated differences compared to the GC-ECD instrument N_2O mean. As shown in Figure 61, none of the four instruments demonstrated differences compared to the GC-ECD instrument N_2O mean.

TABLE 30. ANOVA RESULTS FOR COMPARING N2O PHASE 1 TEST RESULTSACROSS INSTRUMENTS

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Vehicle	1	412.7916065	412.7916065	1159.11	<.0001
TestDay(Vehicle)	18	227.6819643	12.6489980	35.52	<.0001
Instrument	4	2.1996866	0.5499216	1.54	0.1981



FIGURE 61. PLOT OF N₂O PHASE 1 INSTRUMENT LSMEAN DIFFERENCES AGAINST THE GC-ECD INSTRUMENT

The results of the ANOVA for the N_2O Phase 2 are provided in Table 31. Note that statistically significant differences in average N_2O were observed between the two vehicles, and the test days within each vehicle. The N_2O Phase 2 results of the Dunnett's comparison test for the four instruments to the GC-ECD are graphically displayed in Figure 62. Note that the N_2O average for the GC-ECD for Phase 2 is lower than for Phase 1. However, the results are similar in that none of the four instruments demonstrated differences compared to the GC-ECD instrument for Phase 2.

TABLE 31.	ANOVA RESULTS FOR COMPARING N ₂ O PHASE 2 TEST RESULTS	5
	ACROSS INSTRUMENTS	

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Vehicle	1	30.67819592	30.67819592	141.64	<.0001
TestDay(Vehicle)	18	46.69620338	2.59423352	11.98	<.0001
Instrument	4	0.44363315	0.11090829	0.51	0.7270



FIGURE 62. PLOT OF N₂O PHASE 2 INSTRUMENT LSMEAN DIFFERENCES AGAINST THE GC-ECD INSTRUMENT

The results of the ANOVA for the N_2O Phase 3 are provided in Table 32. Note that statistically significant differences in average N_2O were observed between the two vehicles and the test days within each vehicle. The N_2O Phase 3 results of the Dunnett's comparison test for the four instruments to the GC-ECD are graphically displayed in Figure 63. Note that the N_2O average for the GC-ECD for Phase 3 is also lower than for Phase 1. However, the results are similar in that none of the instruments demonstrated differences compared to the GC-ECD instrument for Phase 3.

TABLE 32.	ANOVA RESULTS FOR COMPARING N2O PHASE 3 TEST RESULTS
	ACROSS INSTRUMENTS

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Vehicle	1	2.41243712	2.41243712	16.82	< 0.0001
TestDay(Vehicle)	18	32.27555611	1.79308645	12.50	< 0.0001
Instrument	4	1.11977685	0.27994421	1.95	0.1107



FIGURE 63. PLOT OF N₂O PHASE 3 INSTRUMENT LSMEAN DIFFERENCES AGAINST THE GC-ECD INSTRUMENT

Lastly, the results of the ANOVA for the N_2O Composite are provided in Table 33. Note that statistically significant differences in average N_2O were observed between the two vehicles and the test days within each vehicle. The N_2O Composite results of the Dunnett's comparison test for the four instruments to the GC-ECD are graphically displayed in Figure 64. These results are similar to Phases 1, 2 and 3 in that none of the instruments demonstrated differences compared to the GC-ECD instrument for the Composite.

TABLE 33. ANOVA RESULTS FOR COMPARING N₂O COMPOSITE TEST RESULTS ACROSS INSTRUMENTS

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Vehicle	1	43.37019517	43.37019517	474.62	< 0.0001
TestDay(Vehicle)	18	53.78196590	2.98788699	32.70	< 0.0001
Instrument	4	0.66017345	0.16504336	1.81	0.1367



FIGURE 64. PLOT OF N₂O COMPOSITE INSTRUMENT LSMEAN DIFFERENCES AGAINST THE GC-ECD INSTRUMENT

In conclusion, for each of the Phases 1, 2, 3 and Composite, none of the instruments demonstrated statistically significant differences in the average N_2O when compared to the average N_2O of the GC-ECD.

Since it is not possible to estimate the repeatability of the instrument with respect to the N_2O measurements, a measure of the variation in the N_2O difference between the GC-ECD and the other four instruments from day-to-day across both vehicles can be assessed in the standard deviation of the differences as shown in Table 34. Note that none of the instruments had a significant bias when compared to the GC-ECD. In Table 34, the instruments with the smallest standard deviation in the N_2O differences were Instrument #3 and Instrument #4. In choosing which instruments produced N_2O measurements closest to the GC-ECD, Instrument #3 and Instrument #4 both showed no bias and had the smallest standard deviations of the N_2O differences over the three phases and the composite.

TABLE 34. STANDARD DEVIATION OF N2O PAIRED DIFFERENCE BETWEENTHE GC-ECD AND EACH OF THE FOUR TESTED INSTRUMENTS

Instrument	Phase 1	Phase 2	Phase 3	Composite
Instrument #1	0.94337	0.60238	0.45257	0.41944
Instrument #2	0.91949	0.65770	0.69622	0.42990
Instrument #3	0.31549	0.36413	0.21368	0.23240
Instrument #4	0.25778	0.44163	0.15795	0.27296

6.4 Conclusions

- In Phases 1, 2, 3 and the Composite, the N_2O results for Instruments #1 and #2 were generally the most different from the N_2O results of the GC-ECD.
- In Phase 1, the Altima generally produced higher N₂O than the Camry.
- There does not appear to be a bias in N_2O measurements for the Instruments #1 #4 compared to the GC-ECD.
- The Bland-Altman difference plot analyses indicate that none of the instruments have more than two test results outside the 95% limits of agreement.
- The ANOVA results showed statistically significant differences in average N_2O were observed between the two vehicles and the test days within each vehicle for Phases 1, 2, 3 and the Composite. None of the four instruments demonstrated differences in average N_2O compared to the GC-ECD instrument.
- In choosing which analyzers produced N₂O measurements closest to the GC-ECD, Instruments #3 and #4 both showed no bias and had the smallest standard deviations of the N₂O differences over the three phases and the composite.

APPENDIX A

FUEL PROPERTIES



Product Information

FAX: (281) 457-1469

Johann Haltermann Ltd.

PRODUCT:	CARB LEV III E10 Certification Fuel	Batch No.:	AI1921GP01
	Regular Octane	-	MTS
PRODUCT CODE:	<u>HF0892</u>	Tank No.:	52

Date: 11/7/2012

TEST	METHOD	UNITS	SPECIFICATIONS		NS	RESULTS
			MIN	TARGET	MAX	
Distillation - IBP	ASTM D86	°F				107
5%		۴F			(0 	131
10%		۴F	130		150	137
20%		۴F				144
30%		°F			10	150
40%		°F				170
50%		۴F	205		215	214
60%		۴F				238
70%		۴F				260
80%		۴F				287
90%		۴F	310		320	316
95%		۴F				328
Distillation - EP		۴F			390	352
Recovery		vol %		Report		97.6
Residue		vol %			2.0	1.0
Loss		vol %		Report		1.4
Gravity @ 60° F	ASTM D4052	°API		Report		57.3
Specific Gravity	ASTM D4052	-		Report		0.7496
Reid Vapor Pressure	ASTM D5191	psi	6.9		7.2	7.2
Carbon	ASTM D5291	wt%		Report		82.88
Hydrogen	ASTM D5291	wt%		Report		13.65
Hydrogen/Carbon ratio	ASTM D5291	mole/mole		Report		1.963
Oxygen	ASTM D4815	wt %	3.3		3.7	3.6
Ethanol content	ASTM D4815	vol %	9.8		10.2	9.8
MTBE content	ASTM D4815	vol %			0.05	None detected
Sulfur	ASTM D5453	ppm wt	8		11	9
Phosphorus	ASTM D3231	g/gal			0.005	None detected
Lead	ASTM D3237	g/gal			0.01	None detected
Composition, aromatics	ASTM D5580	vol %	19.5		22.5	20.9
Composition, olefins	ASTM D6550	vol %	4.0		6.0	4.9
Multisubstituted Alkyl Aromatics	ASTM D5769	vol %	13		15	14
Benzene	ASTM D5580	vol %	0.6		0.8	0.6
Oxidation Stability	ASTM D525	minutes	1000			1000+
Copper Corrosion	ASTM D130				1	1a
Existent gum, washed	ASTM D381	mg/100mls			3.0	<0.5
Existent gum, unwashed	ASTM D381	mg/100mis		Report		8.4
Research Octane Number	ASTM D2699			Report		92.3
Motor Octane Number	ASTM D2700			Report		83.4
R+M/2	D2699/2700		87.0		88.4	87.8
Sensitivity	D2699/2700		7.5			8.9
Net Heat of Combustion	ASTM D240	BTU/lb		Report		18027
Deposit Control Additive	Calculated	ptb active		75		75

APPROVED BY:

John Dum

APPENDIX B

TEST REQUESTS FOR VEHICLE CONDITIONING AND TESTING

Driver Test Sheet CRC E-103 Testing 03.19027.01.001

Date:	Vehicle: Nissan Altima: EPA-NALT
Test #	:E103-NALT-T5 Fuel #:GA-8491-F
	Dyno RTM: Perform 30 min. Dyno warm-up against Loss No. 1932.
	Enter Record No.: and Loss Record No.:
	Dyno RTM: Perform parasitic friction curve against Loss No. 1932.
	(Save this record - Do Not make it the current record). Enter Record
	No and Loss Record No
	Dyno RTM: Select "Road Load Simulation".
	Dyno RTM: Select "Vehicle Database". Select " EPA-NALT
	Dyno RTM : Select "Set Up" and select "Aug Braking off
	Dyno RTM: Select "Host Mode".
	Check oil sump temperature and record : should be $72 \pm 3^{\circ}F$
	Install vehicle on chassis dyno. Align vehicle using laser level.
	Tie down vehicle. Adjust tie down straps at 150 to 200 lbs/ft.
	Connect RMT to vehicle.
	Record front tire pressures; (Veh. Spec = $32psi$).
	LR: RR:
	Record vehicle odometer:
	Connect DBK 70 cable to vehicle OBDII connector.
	Verify correct bags installed at CVS.
	PC Host: Open DBK 70 PidPro. Select "Connect". Select "Load config file".
	Select "Obdcan-EPA". Select "Display current channel values".
	Dyno RTM: Enter test number in comment box on "Road Load Simulation" screen.
	MEXA: Turn off blower.
	Dyno RTM: Enter Record No and Loss Record No
	MEXA: Select "Online".
	Verify that humidity is between 9.9 and 11.4 on the Multi Signal Chart
	If not, notify Supervisor or Project Leader

Driver Test Sheet CRC E-103 Testing 03.19027.01.001

Date: _____ Vehicle: Nissan Altima: EPA-NALT

Test #: E103-NALT-T5

Fuel #:GA-8491-F

- **CDTCS**: Select "Run". Select "Test Schedule". Select "Emissions TestEPA"
- □ **CDTCS**: Select "File". Select "Open Answer File. Select file

"EPA-NALT

- **CDTCS**: Select "File". Select "ID/Preferences" and make correct entries
- □ **CDTCS**: Select "Test Options"
 - □ Select "Measure Emissions"
 - □ Select "Bags"
 - □ Select "Clean" Bagline
 - Select Shift Schedule
 - □ Select "EPA-75"
 - □ Turn on Dilution Heat
 - \Box Shift 1: Auto
 - \Box Shift 2: Auto
 - □ Shift 3: Auto
 - Select CVS flow rates:
 - □ Select "Do Cert Z/S/Z" in "Zero Span Options"
 - □ Bag 1: **320 cfm**
 - □ Bag 2: **320 cfm**
 - □ Bag 3: **320 cfm**
- □ **CDTCS**: Select "Vehicle Data" and make correct entries.
- □ CDTCS: Select "Fuel Table". EM-8491-F Fuel
- □ **CDTCS**: Select "Dyno Data" and verify coeff. with RTM values:
 - □ a=19.71 lb
 - □ **b=-0.3066 lb/mph**
 - □ c=0.021358 lb/mph2/

Driver Test Sheet CRC E-103 Testing 03.19027.01.001

Date: _____ Vehicle: Nissan Altima: EPA-NALT

Test #: E103-NALT-T5

Fuel #:GA-8491-F

- □ **CDTCS**: Select "File". Select "Save Answer File". Select "OK" Select "Overwrite" EPA file.
- D CDTCS: Record Horiba Run No._____.
- □ **CDTCS**: Select "File". Select "Run Test"
- Dyno RTM: Select "Start Test" when CDTCS is ready to start test
 Verify green dyno light in test cell is on.
- □ Start of Test. Turn vehicle Traction Control (T/C) to OFF
- Dev PC Host: DBK70 PidPro: Select "Disconnect"
- D MEXA: Take MEXA offline.

BAG 1 Start: 1, 2, 3	1: Good Start	2: Hesitate Start	3: Restart
BAG 3 Start: 1, 2, 3	1: Good Start	2: Hesitate Start	3: Restart

- CDTCS: Run these reports: "Bag Data," "Zero/Span Data", and "1 HZ Data", then select "Print".
- PC Host: Rename vertical reports in "Results on Workstation" folder, then copy reports to both "Results on PC Host" folder and "EPA" folder
- Disconnect vehicle and push off dyno into designated soak space
- □ Connect battery charger and set for 2 amp trickle charge

Lead Technician's Signature: ______
Driver's Signature _____