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Comparative Assessment of Different Ultra-Low NO_x Measurement Instruments for Heavy-Duty Diesel Engines

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**Comparative Assessment of Different Ultra-Low NO_x Measurement Instruments for
Heavy-Duty Diesel Engines**

Diego Mejia

**Thesis Submitted
to the Benjamin M. Statler College of
Engineering and Mineral Resources
at West Virginia University**

**In partial fulfilment of the requirements for the degree of
Master of Science in
Mechanical Engineering**

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Morgantown, West Virginia

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ABSTRACT

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Diego Mejia

Constant Volume Sampling (CVS) systems are an approved method for emission testing as stated in CFR Title 40 Part 1065 Engine Emission Testing Program. For future near zero emission vehicles, the emission measurement equipment must verify the results with the same accuracy as the limits in the past. The most critical values are the limitations for THC, NO_x and particulate matter.

The objective of this study was aimed at identifying challenges associated with measuring system-out emissions at proposed ultra-low NO_x (ULNO_x) levels - 0.02 (g/bhp-hr) and system robustness. The study compared a variety of existing instrument technologies for addressing the question of suitability of these instruments in satisfying the measurement accuracy standards at ULNO_x levels. In addition to the conventional automotive grade instrument (MEXA-ONE) an MKS MultiGas 2030HS and two other standalone low ppm NO_x instruments used in continuous emissions monitoring systems (CEMS), were also included (Brandgaus 7705 and Ecophysics CLD64). This study addressed linearity, drift, cycle-by-cycle performance, low concentration performance, and signal noise at various concentrations.

The study showed that the Ecophysics CLD64 outperformed the conventional MEXA-ONE during low concentration steady state ambient NO_x conditions (<7 ppb) while the Brandgaus 7705 and MKS MultiGas 2030HS reached their detection limits at 0.02 and 0.5 ppm respectively. The study also showed that NO₂ has negative effects on CLD analyzers regardless of photomultiplier tubes or solid-state photodiode detector technology. In summary, the study compared such analyzers in various conditions and addressed their respective uses in future ULNO_x environments.

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1 Introduction

Air quality improvement and the fight against global warming are the two targets that stand behind the limitations of pollutants from any source now and in the future. Upcoming legislation brings tremendous changes in the field of emission and air quality as well as for the certification authorities with a great challenge for emission measurement. With near zero requirements, ultra-low NO_x (ULNO_x) levels - 0.02 (g/bhp-hr), it is almost impossible to determine such low emission levels with adequate accuracy; a need for system improvement and robustness is required [1].

Emission measurement for engine certification process are widely performed via three main sampling methods, namely – i) Raw Measurement, ii) Bag Measurement, and iii) Constant Volume Sampling (CVS) Measurement. Some of the inherent characteristics of these three sampling methods that pose different levels of risk from low to high, when measurement of NO_x at near zero concentration levels, are listed as following:

Raw Measurement

- Interference effects from higher H₂O concentration, CO/CO₂ quench effects
- Challenging to meet drift requirements when measuring at low levels
- Signal stabilization and repeatability in analyzer response at low concentration range
- Necessity of high-speed and high-resolved exhaust flow measurement
- Possible lag in NO₂ response leading, and time alignment issues in unpredictable fashion

Bag Measurement

- Non-heated sections in the bagging system cooling down the sample stream
- Using a non-weighted sample fill rate, may be over sampling dilution air in areas where engine activity is low or null.
- The effect of bag materials towards HC outgassing, permeation and variability from bag to bag
- Necessity to use separate bags for cold and hot start phases when measuring pollutant concentrations at very low levels.

CVS Measurement

- In applications such as diesel engine-based plug in hybrid electric vehicles, the continuity in carbon flow is not consistent, which could challenge the accuracy of carbon balance calculations in such instances
- Requiring better accountability of water lost in the sampling system
- Need for tighter control in the uncertainty of tunnel flow, tunnel wall temperature and sampling plane humidity
- At very low concentration levels, the tunnel residence time of certain aerosol constituents due to hang up effects would affect the sampling accuracy [2].

When comparing different sampling conditions and techniques, CVS method is an accepted, as a standard reference method when comparing different sampling conditions and techniques. CVS systems exist since 1972 [3]. For future almost zero emission vehicles, the Exhaust Emission Measurement equipment must verify the results with the same accuracy as the limits in the past. The most critical values are the limitations for THC, NO_x and particulate matter, where the detection limits of the measurement instruments require new concepts and some adaptations. The main challenge is not the range or the accuracy of the analyzers but more the minimal difference between two comparable values are measured (ambient and exhaust bag concentration), where the difference is very small.

In the present scenario a wide variety of instrument technologies utilizing different physical measurement principles are available. In this work, a CVS emissions analyzer suite MEXA-ONE from Horiba Instruments was utilized, MKS MultiGas 2030HS, Ecophysics CLD64 and Brandgaus 7705 for the low concentration measurements of NO_x. From an instrument principle perspective, the analyzer from Brandgaus traditionally is used in continuous monitoring systems (CEMS) for gas turbines or stack measurement, while the Ecophysics is used in the automotive industry [4]. However, due to the solid-state detection capability of the Brandgaus 7705 which eliminates the use of photomultiplier tubes and thermoelectric chillers, this study found interest in evaluating this device for its suitability for low concentration NO_x measurement, especially at sub-50ppm levels.

The study addressed the factors influencing the uncertainty in measuring NO_x at near zero levels with major focus on ambient background NO_x concentrations. The study used the analyzers in question with a proposed 0.02 (g/bhp-hr) engine to compare instrument performance but due to hardware issues the engine and after-treatment were not able to achieve such levels. The following factors were studied by performing individual tests that could discern the merits and demerits of utilizing such improvements and conclude their efficacy.

- Variability in background concentration
- CVS sampling system conditions
- System integrity verification
- Low concentration instrument performance

Further, a comparison of such analyzers is performed to address the question if these instrumentations are applicable for future engine certification testing or whether a need for technological improvements is necessary to guarantee that OEMs have the capabilities to certify at such proposed 0.02 (g/bhp-hr) NO_x limits.

1.1 Objective

The objective of the study was aimed at identifying challenges in measuring system-out emissions at proposed ultra-low NO_x (ULNO_x) levels - 0.02 (g/bhp-hr) and system robustness. The study compared a variety of existing instrument technologies for addressing the question of suitability of these instruments in meeting the measurement accuracy standards at ULNO_x levels. In addition to the conventional automotive grade instrument (MEXA-ONE), two other standalone low ppm NO_x instruments used in continuous emissions monitoring systems (CEMS), were also included (Brandgaus 7705 and Ecophysics CLD64). To understand the effect on CVS measurement performance of each analyzer, a series of steady state and engine tests were performed with varying CVS conditions such as flow rate, temperature, and humidity.

2 Background

With ever increasing vehicles on the road and population growth rates not seeing a decrease in the near future, our need for fossil fuels are in high demand. The impact of burning fossil fuels has inherent health risks that legislation has tried to mitigate resulting in more stringent vehicle emission standards.

2.1 History

Although trends show that emissions per vehicle have decreased the concern for cleaner air and the impacts associated with climate change have not [5]. As a result, legislation has steered towards cleaner emissions and more stringent guidelines to address ambient air quality. The following is an illustration of the evolution in emission regulation and compliance standards for Light-Duty Vehicles (LDV) and Heavy-Duty Vehicles (HDV).

Figure 1: Chronological history of EPA and CARB regulatory actions [6]

In the decades following the enactment of the Clean Air Act (CAA) was initially enacted in 1963, regulators from the U.S. Environmental Protection Agency (EPA) and California Air Resources Board (CARB) have developed comprehensive and rigorous certification and compliance programs [6]. Since the implementation of In-use Compliance, major strides have been made to ensure that both LDE's and HDE's comply with regulations during the certification process and after.

The automotive industry over the last few years is described as a major source of toxic emissions into the atmosphere. It explains the rationale behind most countries signing up for both the Kyoto and Paris agreement and its implementations worldwide [7].

The drivetrain technology of a diesel engine offers the advantage of low CO₂ emissions due to its efficient combustion method. As a by-product of this optimized combustion, exhaust gases such as nitrogen oxides (NO_x) are produced, which then must be neutralized in complex exhaust gas after-treatment processes to a legally prescribed level. The two most prevalent nitrogen oxides (NO_x) are nitrogen dioxide (NO₂) and nitric oxide (NO). Air quality control studies have shown the NO₂ exposure can intensify responses to allergens in allergic asthmatics. In addition, several epidemiological studies have demonstrated associations between NO₂ exposure and premature death, cardiopulmonary effects, and decreased lung function growth in children, respiratory symptoms, emergency room visits for asthma, and intensified allergic responses [7].

The EPA regulates NO_x and the most prevalent form of NO_x in the atmosphere is NO₂. The bulk NO_x emitted is in the form of NO and are oxidized in the atmosphere to NO₂ within a short time. Approximately 10-20% of NO_x from diesel engines are emitted as NO₂, which is five times more toxic than NO. NO and NO₂ are collectively called as NO_x [8].

The following figure illustrates the progressive movement towards tighter control on NO_x and PM.

Figure 2: Reduction in emission limits for NO_x and PM in (g/bhp-hr) [9]

A further complicating factor is that exhaust gas after-treatment processes are highly temperature-dependent, which is why they are becoming more and more challenging as combustion efficiency increases, resulting in a decrease in exhaust gas temperature for NO_x control [7]. The major pathways for NO_x formation can be explained by three different mechanisms: Thermal NO_x, Fuel NO_x, and Prompt NO_x [10].

2.2 NO_x Formation

Thermal NO_x is produced when nitrogen reacts with excess oxygen at higher temperatures greater than 1800 K in the combustion process as shown in the following graph [8].

Figure 3: The effects on NO_x concentration via Diesel combustion temperatures [8]

NO_x formation mainly depends on the temperature of burnt gas, the residence time of the burnt gas at high temperature and the amount of excess oxygen and turbulence in the combustion process [10]. As described in the Zeldovich Mechanism, thermal NO_x has two main reactions that produce it. NO formed in the flame zone can be rapidly converted to NO₂ via,

an additional reaction is shown necessary at near stoichiometric and fuel rich mixture is,

inclusion of hydroxyl (OH) in the above equation as an extension of thermal NO_x was proposed by Lavoie et al. [11]. With the inclusion of hydroxyl, NO can be produced in the flame zone and is converted to NO₂ through,

in addition, subsequently, conversion of this NO₂ to NO occurs via the reaction.

This reaction continues until all the NO₂ produced is quenched by mixing with cooler fluid formation rate of thermal NO is slow and is considered unimportant below 1800 K [8].

Unfortunately, the diesel engine's great potential to deliver high thermal efficiency with low fuel consumption is coupled with a low exhaust temperature that affects exhaust After-treatment efficiency. Since the efficiency of all catalysts is highly dependent on temperature, these effects will be more relevant in the near future due to the use of Exhaust Gas Recirculation (EGR) and cooler combustion temperatures for NO_x reduction [7]. As the reduction of NO_x continues, the need for updated robust measurement equipment and testing procedures. This will ensure that the proper accounting of emission species is relevant for future certification.

2.3 Measurement Techniques

The U.S. Environmental Protection Agency permits coordinated and effective governmental action to assure the protection of the environment by abating and controlling pollution on a systematic basis EPA reinforces efforts among other Federal agencies with respect to the impact of their operations on the environment [12]. In turn, OEMs must comply with legislation and submit emissions of their products in order to gain certification and participate in the Heavy-Duty Market. OEMs are required to test their engines and submit all necessary documentation and emissions data. This requires OEMs to use several approved measurement techniques. The following are some measurement techniques approved by the regulatory agencies [12].

2.3.1 Raw Measurement

Raw Measurement is the measurement technique of sampling the flue gas directly from the source i.e. diesel engine. This continuous measurement technique sees higher concentrations since the exhaust gas from the diesel engine is not diluted before measurement. This since the exhaust gas is at higher temperatures the systems analyzing the flue gas needs to be heated in order to prevent water condensation and so change the mass and concentrations of the gas species. In this method, time alignment is critical for accurate calculations of the integrated over time data for total emissions during a test [13]. Mahadevan et al. found that the delay in analyzer response due to the time taken for transport of the sample gases could cause deformation of the signal due to mixing and diffusion during the transport. They also stated that some error is introduced and so they developed a deconvolution algorithm that corrected for time delay and signal deformation. Brian Mace et al also stated that NO_x emissions from SCR equipped engines tend to accumulate in short duration peaks once the catalyst is hot, making time alignment with exhaust flow very critical for accurate mass calculation [14].

2.3.2 Bag Measurement

Dilute bag method represents an integrated sample for the exhaust species over the duration of a test. This method continuously samples the diluted exhaust and fills the bag at a continuous rate and after the test is completed, the concentrations are integrated over the duration of the test and results in a total emissions value. This method eliminates the need for fast response and high-resolution analyzers since the analyzers have no need of capturing transient spikes in the species concentration [15]. Satoshi et al. found that residual HC could have a negative effect on measurement accuracy and suggest that the bags should be purged sufficiently after every measurement to avoid influences from residual HC. This in turn has led to improvement methods such as using separate bags for Cold Start vs Hot Start FTPs and heated bags for decreasing hang-up effects. E. Schiefer et al. also found that long residence time in the bag, solubility, permeability and diffusion of dissolved components can cause significant effects and discussed the negative effects of bagging material vs temperature and gas species [16].

2.3.3 Constant Volume Sampler

The working principles of a CVS measurement system is as follows. All the flow from the vehicles' exhaust and/or engines' exhaust is introduced into the CVS and is diluted with ambient

air. A blower draws the diluted exhaust gas through the system and the total volume of the diluted exhaust is determined by integrating the constant flow rate through the CVS system. A small portion of the diluted exhaust is collected into a sample bag during a test mode/phase [15]. The ambient air used as a diluent, is also simultaneously sampled, and collected into an ambient bag for compensation of the background concentrations of the pollutants. The bag samples are introduced to the gas analyzers after sampling period is completed [15]. The following is a generalized schematic of a CVS measurement system. Some of the disadvantages to the CVS system include but are not limited to, temperatures, leak proofing, background sampling, adsorption, desorption, and condensation, as addressed in Section 2.5.

Figure 4: Illustration of a Constant Volume Sampler system and its various components for vehicle emissions testing [15]

2.4 NO_x Measurement Technologies

The Code of Federal Regulation Title 40 Part 1065 states which analyzer technologies are acceptable for vehicle/engine certification with certain criterion such as response time drift, etc. [12]. Additionally, with the push for ULNO_x these analyzers need to perform at a higher level of accuracy and precision. Continuous measurements from diluted exhaust stream pose measurement challenges due to further dilution of certain species that are already low concentrations in exhaust gas. This can result in low signal to noise ratios and high measurement uncertainties for these species [13].

2.4.1 CLD Technology

The CLD technology was developed in the Ford Research Laboratory in the early 1970's. The principle behind CLD is a reaction between NO and O₃ (ozone) where nitrogen dioxide (NO₂) at an excited state is created by the specific reaction and the product emits light at a known frequency and the photons emitted are detected by a photo multiplier tube (PMT). The output is a voltage, which is calibrated to be proportional to NO concentration. Therefore, mixing a gas with an excess of ozone allows counting photons as a measure of NO concentration [17]. Engine exhaust contains both NO and NO₂ furthermore, NO converts to NO₂ in atmospheric conditions on a time scale of minutes. Therefore, it is conventional practice to measure the sum of NO and NO₂ as NO_x. For a CLD to measure NO_x it must first convert the NO₂ to NO this done by passing the gas through a heated converter these converters are typically carbon-molybdenum, molybdenum, carbon, gold, ferrous sulfate, or even stainless steel [17]. The problem is to find a combination of materials and operating temperature that gives high conversion of NO₂ to NO but does not convert anything else specifically NH₃ to NO. Conversely, NO_x can be under-read if the converter causes reactions that remove NO_x. All CLD analyzers must have an NO₂ reduction catalyst, and all such catalysts are likely to have some degree of NH₃ storage, or activity toward NO_x NH₃ reaction. This chemical reaction can be consistently reproduced due to the high degree of linearity in a wide measurement range. The following is an illustration of such technology,

Figure 5: Components and systems within the Chemiluminescence Technology [18]

ozone is produced by an ozone generator and a vacuum pump allows samples to be pulled into the reaction chamber. The light-producing reaction is very rapid so careful sample handling is important in a very rapid response instrument [18].

2.4.2 MKS MultiGas 2030HS Technology

The discovery of infrared light dates back to the 19th century. MKS MultiGas 2030HS spectrometers (Fourier Transform Infrared Spectrometer) are widely used in organic synthesis, polymer science, petrochemical engineering, pharmaceutical industry and food analysis [19]. The infrared light wave's energy is absorbed by the molecular bonds causing vibrational and rotational motions resulting in excitation allowing measurable energy absorbed to be proportional to the number of molecules. Since different molecules with different combination of atoms produce their unique spectra, infrared spectroscopy can be used to qualitatively identify substances. In addition, the intensity of the peaks in the spectrum is proportional to the amount of substance present, enabling its application for quantitative analysis [19]. Based on IR light absorption energy (IR radiation), the pattern and intensity of the spectrum provides all the information about gas type and concentration. Potential concerns in MKS MultiGas 2030HS analysis include interference from gases not included in the analysis set. Since no reference spectrum is provided, the software cannot correct for such errors.

2.5 CVS System Measurement Improvements

Accurately measuring Ultra Low NO_x (ULNO_x) in a Constant Volume Sampling System (CVS) has become a major focus of research once more since the proposed regulation is towards a 0.02 (g/bhp-hr) NO_x limit. Such low concentrations bring unwanted measurement uncertainties and so modifications are needed to quantify measurement inaccuracies using the technology at hand [20]. One modification needed is a background ambient air dilution filter, an activated carbon filter.

2.5.1 Background Variability Improvement: Carbon Filter

Activated Carbon is carbon treated with oxygen to produce millions of micro cracks or pores between the carbon atoms to increase the surface area. Depending on the carbon in use and the type of filter, aggregate surface area is in the range of 2000 m²/g. This represents a surface area roughly equivalent to about four football fields [20]. The main principle of which the filtration of gas molecules takes place is the concept of adsorption. Adsorption can be physical or chemical where physical adsorption is by diffusion (Brownian Movement) using Van Der Waals' forces and

the latter is a chemical adsorption (chemisorption) in which the two substances (gases and filter media) react and the resultant chemical is trapped on the filter material because of the covalent bonds formed [20]. Activated carbon filtering for emissions measurement systems is a way of cleaning dilution ambient air. Edward et al. discovered that such dilution air filters could remove 54% of ambient air NO_x . This same study concluded that these filters were also effective in removing ambient air Non-Methane Hydrocarbons (NMHC) by 72%, though no significant effect on removing Methane, CO, or CO_2 . For super ultra-low emitting vehicles (SULEV), non-methane organic gases (NMOG) in the dilution air can lead to “negative” gaseous emissions [21]. They also concluded that the “negative” results (systematic error) were apparently eliminated from the implementation of the dilution air filter. The following tables illustrate the effectiveness of the implementation of the carbon filter.

Table 1: Effectiveness of filter for Methane and NMHC removal [21]

	CH₄ In (ppm)	THC In (ppm)	NMHC In (ppm)	CH₄ Out (ppm)	THC Out (ppm)	NMHC Out (ppm)	% NMHC Removed
1	2.897	4.367	1.041	2.899	3.601	0.273	74%
2	2.911	4.444	1.102	2.912	3.630	0.287	74%
3	2.903	4.447	1.114	2.900	3.611	0.282	75%
4	3.006	4.641	1.190	2.977	3.756	0.338	72%
5	2.940	4.511	1.136	2.926	3.687	0.328	71%
6	2.907	4.427	1.090	2.884	3.659	0.348	68%
Avg.	2.927	4.473	1.112	2.916	3.657	0.309	72%

Table 2: NO_x removal using dilution air filter [21]

	NO_x In (ppm)	NO_x Out (ppm)	% Removed
1	0.402	0.185	54%
2	0.415	0.191	54%
3	0.423	0.196	54%
4	0.417	0.197	53%
5	0.395	0.185	53%
6	0.384	0.180	53%
Avg.	0.406	0.189	53%

The weakness of the CVS used in this study is that it had high variability when measuring NMHC for phases 2 and 3 of the FTP in which the NMHC levels were near zero. However, with the addition of the dilution air filter, there was significantly less variability in the phase 2 NMHC results and no negative results were reported. Jacob Swanson et al. also used a Donaldson dilution air filter and demonstrated that cleaner dilution air was necessary to eliminate negative emissions readings. These negative values are indicative of the detection limits with increase in measurement errors reporting a 50% decrease in trace gases [21].

2.5.2 Sampling Condition Improvement

Water condensation elimination in The Constant Volume Sampling System (CVS) has always been of concern and a challenge to implement. The Code of Federal Regulation (CFR) provides some guidance for establishing a dew point safety factor for sample lines. Amendments to the CFR state, “The temperature of the sample lines shall be more than 5 °F (3 °C) above the maximum dew point of the sample [12].” The water vapor present in the sampling system originates from three sources: the dilution air, the combusted fuel, and the ambient air ingested in the vehicle's engine [22]. If the sampling system is not above dew point, a thermodynamic of condensation will occur and as air cools, its saturation vapor pressure decreases, i.e., the maximum amount of water vapor that the air can hold decreases so the mass of the flue gas changes and the concentration of the species increases giving rise to measurement error [23]. Without enough dilution and heating, condensation on the surfaces can absorb soluble compounds such as such as NO₂, alcohols and Aldehydes that change the sampling mixtures characteristics as well as mass concentrations introducing errors that cannot be calculated [22]. These compounds left unanalyzed, result in non-representative emissions and fuel economy measurements. As stated, water condensation in the bag sampling system such as pumps, filters, sampling lines, etc., will increase the emissions measurements due to the change in total mass when the removal of water vapor occurs. The measurement detects higher concentrations of the species measured. The following illustrates the effect of heated lines on the measured and predicted T_{dew}.

Figure 6: The effects of heated sample lines versus dew point temperature and modeled dew point temperature [22]

In the no heating condition, the sample lines and ambient air were at room temperature which shows that when no heat is applied, the measured dew point temperature was considerably lower than the predicted dew point when heating is applied [22]. This indicates a mass difference where water condensed and was lost in the sampled exhaust before reaching the sample bags in turn affecting the mass calculation. Heating the entire system allows significantly lower dilution ratios to be used and reduces system hydrocarbon contamination. This type of enhancement requires very careful operation and maintenance to ensure that there are no areas (cold spots) within the system not being heated which could cause condensation of the exhaust sample [24]. Cold spots along the CVS system leads to water condensation as exhaust gases dissolve and are adsorbed, the CVS tunnel has to be monitored and maintained at specific temperatures where condensation will not be possible [25]. Since the raw exhaust contains 10-14%, the dilution factor of the raw exhaust plays a significant role. Therefore, a need to balance the dilution factor (ratio exhaust gas flow and dilution air flow) such that there is no water condensation along the sampling set up at any time of the test [25]. However, care must be taken to ensure that there is no other significant source of error coming from the elevated temperature [19].

The benefits of both the heated CVS system and the implementation of the Activated Carbon Filter minimizes error propagation by the reduction of ambient concentrations to nearly zero such that

the DF error becomes negligible and the elimination of water condensation in the system as a whole thus allowing for accurate concentration measurements [24].

3 Methodology

3.1 Laboratory

West Virginia University's Center for Alternative Fuels, Engines and Emission (CAFEE) acquired a 13-liter diesel engine for ULNO_x testing. The experimentation for this study took place in the Vehicle Emission and Testing Laboratory (VETL), which housed a full-size Constant Volume Sampler (CVS) System. The engine test cell is comprised of a dynamometer for load and motoring control and several instrumentations for temperature and fueling control. The engine after-treatment consisted of a DOC, DPF, SCR, and ASC configuration and had NO_x emission certification 0.2 (g/bhp-hr). All procedures prescribed in the Code of Federal Regulations (40 CFR Part 1065) during testing were implemented.

3.1.1 CVS Tunnel Set-up

The Constant Volume Sampler used in this study consisted of a Full Dilution Tunnel, an Air Handler System, Sample Plane, Variable Speed Blower, a Bagging System, Gas Bottles, and several Analyzers described herein. The CVS system had modifications for this study in order to reduce uncertainties and error propagation during ULNO_x measurement. Some of which were the addition of a Dilution Air Filtration System, Tunnel Heating Jacket Control, and Proportional Sampling Control. The following is an illustration of the CVS system used in this study.

Figure 7: Constant Volume Sampling System at West Virginia University, schematic of equipment, analyzers, improvements (red), and location of systems [2]

As stated in the Section 2.5.1 the Dilution Air Filtration system introduced the hypothesis that such an implementation would reduce ambient NO_x and THC concentration introduced in the intake. The Tunnel Heating Jacket addressed the hypothesis of Cold Spots in the Tunnel Mixing Plane before the Sample Plane and the Proportional Bagging Control served as an addition to the improvements made but is not part of the scope of this paper. These improvements were considered for the benefit they added to measurement accuracy and the ability to minimize as many uncertainties as possible. Verification testing for each improvement for this study were conducted and are further discussed in Section 3.5.

3.1.2 Engine Test Cell

The Engine Test Cell consisted of a General Electric Dynamometer for speed and load control (1), an After-treatment system that housed a DOC-DPF-SCR-ASC configuration for emission reduction (2), a 13-liter Diesel Engine with VGT-EGR hardware with US EPA 2017 certification (3), CVS Tunnel for emission measurement (4), and a Test Cell Control Room (5). The following is an illustration of the Engine Test Cell used during this study.

Figure 8: West Virginia University CAFE Engine Test Cell for ULNO_x Study

3.1.3 DAQ System

The DAQ system for this study was simplistic in design and due to time constraints, had some modifications using a previous set-up. The data acquisition software used is an in-house developed tool called SCIMITAR that allows ease of DAQ, analyzer, and sensor integration. One DAQ system used was a data logging device developed by ICP DAS USA INC. This hardware was a type of analog to digital converter (ADC) that allowed for thermocouples and relays to be integrated for temperature control, valves used for span/zero gas, and heaters used for water condensation mitigation. The following figure illustrates the prototype configuration of the DAQ System used in this study.

Figure 9: DAQ system (1) with Brandgaus 7705 (3) and Ecophysics CLD64 (2) analyzers

Some challenges in exhaust gas sampling is measuring the flue gas without changing its composition. To this end, sample lines need to be maintained at 190°C . This temperature is high enough to avoid most wall adsorption of NH_3 and diesel HC, yet low enough to avoid oxidation in the sample lines. It is widely recognized that NH_3 , NO_2 and other gases are adsorbed on surfaces in the sampling system. Furthermore, if the exhaust sample cools below the dew point temperature, water may condense, and several gases of interest will dissolve in the condensed water changing the flue gas composition [17]. John Hoard et al. indicated that at low temperatures NH_3 and NO_x could react on the gas line surfaces to form ammonium nitrate, a white powdery solid, changing the composition of the flue gas and having negative effects on measurement quality. Because of such literature, precautions such as the implementation of heated pumps, heated sample lines, and a heated filter were introduced to the CVS system. The following is a schematic of some analyzers and their respective sample lines taken from the Sampling Plane.

Figure 10: Schematic of analyzers used for study and location with respect to CVS Tunnel sampling point [2]

Another DAQ system used was a Lab Jack, which is used for the proportional bagging control. This hardware-controlled pumps, MFC's, and valves during sample bagging and measurement. As stated before, the Proportional Bagging implementation is not in the scope of this paper.

3.2 Analyzers

The following is a summary table of the analyzers used in this study and the specifications afforded.

Table 3: Summary Table of Analyzer Specifications with regards to measuring NO_x, N₂O, NO₂, NO [4, 19, 26, 27]

	MEXA-ONE	Ecophysics CLD64	Brandgaus 7705	MKS MultiGas 2030HS
Measurement Principle (ppm)	CLD	CLD	CLD	FTIR
Measurement Range NO_x	0-10	0.5-100	1-500	N/A
Measurement Range N₂O	N/A	N/A	N/A	0-26
Measurement Range NO₂	N/A	N/A	N/A	0-24
Measurement Range NO	N/A	N/A	N/A	0-149
Zero Noise	N/P	0.001	≤ 0.02	N/P
Dry/Wet Measurement	Dry	Dry	Dry	Wet
Limit of Detection	N/P	0.002 ppm	N/P	0.1 N ₂ O, 0.4 NO ₂ , 0.5 NO
Response Time	N/P	T ₉₀ <1 sec	T ₉₅ <15 sec	N/P
Converter Efficiency	N/P	>95%	<95%	N/A

*NOTE: N/P – Not Provided, N/A – Not Applicable

3.2.1 Ecophysics CLD64

Ecophysics is a leader in pollutant measurement systems. The company develops, manufactures and distributes sophisticated analyzers for NO, NO₂, and NO_x, an important contributor to global greenhouse warming and possible causes of increased levels of tropospheric ozone [26]. The Ecophysics CLD64 using the CLD principles and is used for NO_x measurement, specifically used in Continuous Emissions Monitoring (CEMS). The fast response and lag time is less than a second (<1 sec) with humidity tolerances of 5-95% and manufacturer's specifications allowing for ranges from 0.5 to 100 ppm make it an attractive analyzer. It has a zero-point noise limit of 0.001 ppm

and minimum detectable concentration of 0.002 ppm. NO₂ and total NO_x is measured by molybdenum. The modular layout and ozone generator and scrubber are integrated in the Ecophysics CLD64 and maintenance simply means annual replacement of filters and membranes. At certain sampling conditions, the Ecophysics CLD64 has attractive qualities for ULNO_x measurement.

3.2.2 Brandgaus 7705

The Brandgaus 7705 NO_x-O₂ Analyzer is designed specifically for use in low-NO_x CEMS and process control applications. Total NO_x is measured using the Chemiluminescence method and a high temperature NO₂ converter. Oxygen concentration is measured using a high-performance linear-output zirconium oxide cell [4].

Chemiluminescence technology has long been recognized as the optimal technological method or principle for NO_x detection and is recognized as the practical choice for ambient air quality monitoring to measure parts per billion (ppb) ambient concentrations. Delicate photomultiplier tubes and high voltage power supplies, thermally sensitive electronics, unreliable ozone generators, finicky NO₂ converters, and many other problematic components have plagued many implementations of this technology over the years [4]. While most chemical reactions occur in a small fraction of a second, the NO₂ to NO takes up to a day under normal atmospheric conditions. At elevated temperatures, the reaction between NO and NO₂ occurs very quickly, this is the basis for high temperature thermal conversion. Many analyzers use this type of thermal conversion, but the drawbacks are catalytic poisoning and unpredictable reactions, just to name a few.

Brandgaus 7705 uses a rugged solid-state photodiode to measure the light produced in the reaction. Instead of a PMT, this analyzer operates on standard circuit board voltages which eliminates the need for a high voltage power supply and does not require a thermoelectrically cooled housing, cutting on complexity and cost. In addition, the spectral response of the photodiode is much more closely matched to the Chemiluminescence reaction than a PMT, allowing for detection sensitivity and signal-to-noise ratios that are acceptable for lab grade equipment. Brandgaus 7705 is an analyzer that performs with dependable and stable measurements regardless of time, usage, or NO₂ concentration a drawback in some analyzers [4]. The Brandgaus 7705 has a measuring range of 1-500 ppm and zero noise of 0.02 ppm with zero calibration drift of +/-0.1 ppm.

3.2.3 MEXA-ONE

Through MEXA-ONE technology, HORIBA has attained a reputation for long-term support of its emission measurement systems. A result of continuous development, MEXA-ONE analyzes a wide, dynamic range of exhaust emission concentrations from engines running on a variety of fuel types. The system also supports the full range of sampling requirements for raw exhaust, dilute exhaust, EGR, and trace gas measurements [27]. This platform integrates several analyzer technologies into a single unit. Dual-CLD method detects NO_x and NO in the same time. MEXA-ONE can calculate NO_2 concentration through subtraction of the continuous concentration of NO from NO_x . This calculation is performed simultaneously with the NO_x and NO concentration measurements. The analyzer specifications indicate a NO/ NO_x range of 0-10 ppm and 0-10000 ppm [27].

3.2.4 MKS MultiGas 2030HS

The MKS MultiGas 2030 does not use the CLD principles instead uses infrared light (IR) from the Electromagnetic Spectrum. The MKS MultiGas 2030HS has minimal zero and calibration drift including minimal interference from water (up to 40%) or other gas components. The gas cell is heated to 191°C with automatic temperature and pressure compensation. It has a patented linearized MCT (Hg/Cd/Te) detector response which allows for peak analysis routines that keep resolution and frequency tolerances exceedingly tight [19]. Unlike the CLD analyzers, the MKS MultiGas 2030HS has an advantage of eliminating the need for calibration gases during routine operation. The MKS MultiGas 2030HS is stated to comply with t90 performance requirements and ensures instrument response through resolution diagnostics to maintain maximum accuracy. MKS MultiGas 2030HS indicates N_2O range of 0-26 ppm, NO range of 0-149 ppm, and NO_2 range 0-24 ppm with detection limits of 0.1, 0.5, and 0.4 ppm respectively. MKS MultiGas 2030HS spectroscopy operates by measuring the absorbance of a gas sample versus wavenumber (wavenumber is inversely proportional to wavelength) [19].

3.3 CVS Tunnel Material Improvements

Apart from the major modifications made, some minor material improvements were made for their chemical characteristics and quality of material. Kynar bags were introduced for their excellent chemical resistance, high heat resistance, excellent physical and mechanical properties, and mainly for their parts per billion-contamination quality unlike its predecessor Tedlar bags with parts per

million-contamination quality. Another improvement was the implementation of new Polytetrafluoroethylene (PTFE) tubing. This tubing is used for sample gas transport and has non-stick properties, temperature resistance up to 260°C, aging resistance, and its superior chemical resistivity quality. Another minor improvement was the use of Ultra High Purity (UHP) stainless steel tubing. This tubing has an electro polished internal surface, which theoretically decreases surface roughness and limits chemical adsorption to the internal surface which can decrease NO_x loss. Lastly, a Perma Pure Nafion Dryer was used for the Brandgaus 7705 and Ecophysics CLD64 analyzers. This dryer removes water vapor from the sample gas, which can decrease the H₂O interference for NO_x detection. Contamination by solid particulate components can be minimized using tubes with polished surfaces [16]. These claims by manufacturers are assumed reliable and no further investigation or testing were conducted for such specifications, as this was outside the scope of this study.

3.4 Testing Procedure

The CLD analyzers used in this study used the ‘dry’ measuring technique while the MKS MultiGas 2030HS uses a ‘wet’ measuring technique. The ‘dry’ samples remove the water from the sample gas and then use a correction factor to adjust for this process. The dry-wet correction of the sample gas is done with a multiplicative correction factor (K_{d-w}). The correction factor is based on gaseous dry-based concentrations of combustion products and the fuel properties assuming that neither condensation nor evaporation of water in the pipes takes place [28]. Condensation of water vapor and several other condensable semi-volatile components in the exhaust gas can take place when the temperatures of the pipes or after-treatment devices are below the dew point temperature of the exhaust gas. Thus, condensation during low ambient temperatures and engine cold start is inevitable [28].

The concentrations measured on a dry basis (C_{dry}) are converted to a wet basis (C_{wet}) with the dry-wet conversion factor (K_{d-w}) as shown in Equation (6).

$$C_{wet} = K_{d-w} \times C_{dry} \quad (6)$$

Roberto Varella et al. conducted several experiments to compare portable emissions measurement systems (PEMS) with laboratory grade equipment. They indicated that NO_x concentration from the PEMS analyzers were within 5% for the mean levels of 20 ppm or higher, but the differences

increased to 15% at 7 ppm and 30% at 1 ppm. They observed that a difference between ‘wet’ and ‘dry’ measurement techniques is greater during Cold-Start, which the dry-wet correction does not take into account [29]. In addition to these findings, the condensation effect as technologies such as stop-start, hybridization, and improvements in engine efficiency become more common, a need to investigate lower exhaust temperatures and its effects.

3.5 Improvement Verification

3.5.1 Tunnel Heating

As literature suggests, maintaining temperature above the flue gas dew point is critical for accurate emission measurement as discussed in Section 2.5.2. The engine exhaust is diluted with ambient air and goes through a mixing chamber where the dilution air and exhaust gas have ample time to become a homogenous mixture. A heating jacket that contains flowing water, which acts as a heat exchanger, allows for the flue gas temperature to remain above dew point. The following is a schematic of the system set-up with the various thermocouples and their respective locations.

Figure 11: Schematic of thermocouple locations on the Tunnel Heating Jacket [2]

The Tunnel Heating Jacket allows a uniform distribution of heat across the mixing plane in order to avoid any cold spots. A Vaisala's RH sensor and Temperature Probe measure the

humidity and temperature at the sample plane. The Vaisala's RH sensor and Temperature Probe have accuracies of 0.8 %RH and 0.1°C respectively [30].

3.5.2 SF₆ Injection

During Propane Checks, or leak checks of the CVS system, the system is cold and not running and so verifying that the system maintains its integrity during testing was in question. SF₆ was used during engine running and motoring operation to see if the dynamics of the CVS system changed as parts vibrated and heated up.

Table 4: SF₆ gas injection during transient operation for verification of the CVS system during operation [2]

Test ID	Test Type	Engine Start	Tunnel	Injection Location	% Error in Recovery SF ₆
H0003-001-509	FTP	Warm	Heated	Tunnel Mixing Plane	1.72 %
H0003-001-510	FTP	Warm	Heated	Tunnel Mixing Plane	1.77 %
H0003-001-511	Motoring	NA	Not heated	Post EATS	0.33 %
H0003-001-512	Motoring	NA	Not heated	Post EATS	0.99 %
H0003-001-513	FTP	Cold	Not Heated	Post EATS	1.02 %
H0003-001-514	FTP	Warm	Not Heated	Post EATS	2.04 %
H0003-001-515	FTP	Warm	Heated	Post EATS	-0.45 %
H0003-001-516	FTP	Warm	Heated	Post EATS	-1.41 %
H0003-001-517	RMC	Warm	Heated	Post EATS	0.96 %
H0003-001-518	RMC	Warm	Not heated	Post EATS	0.97 %

As shown in the table the system maintained its integrity during SF₆ injection seen in the ‘% Error recovery’ column. The table also indicates that heated and non-heated tunnel makes no difference in recovery for SF₆ gas. The SF₆ gas was introduced in the Tunnel via an injection port and a mass flow controller (MFC) was used to measure how much mass was introduced into the Tunnel. The MFC was a Sierra instrument with an up to date 5-point NIST calibration and an accuracy of +/- 1% of full scale [31]. This dynamic transient leak check or recovery verification can become the standard for future regulations due to the nature of components expanding and contracting during thermal cycling.

3.5.3 Carbon Filter: Background Investigation

Quantifying the variability in background ambient air concentrations while performing emission measurement testing is unpredictable and difficult to accurately measure. Thus, a background measurement procedure was created in order to measure background concentrations across different days ranging from a fully operating day in the testing laboratory facility to a weekend day with minimal to no activity. The following figures are a representation of Day 1 testing of an operational day in the laboratory facility.

Figure 12: Continuous Measurement of Ambient NO_x Concentration vial CLD Analyzers: MEXA-ONE, Brandgaus 7705, Ecophysics CLD64

Table 5: Average and Standard Deviation of Continuous NO_x measurement for Day 1

	Average	Standard Deviation
MEXA-ONE	0.0062	0.0198
Brandgaus 7705	-0.0086	0.0426
Ecophysics CLD64	0.0069	0.0078
MKS MultiGas 2030HS	-0.061	0.8293

In Day 1 measurement data, as shown in Figure 12, we can see the continuous measurement of NO_x. The MKS MultiGas 2030HS data is not included since the detection limit is 0.5 ppm for NO. At these levels, the signal noise of this instrument outputted data that was unusable and no significant analysis can be conducted. The study showed that the Ecophysics CLD64 outperformed the conventional MEXA-ONE during low concentration steady state ambient NO_x conditions (<0.007 ppm) while the Brandgaus 7705 and MKS MultiGas 2030HS reached their detection limits at 0.02 and 0.5 ppm respectively. The data indicates that a continuous background measurement of NO_x is not adequate if using a Brandgaus 7705 instrument for CVS emissions testing where the ambient concentrations are (<0.01 ppm). The negative average as shown in Table 5, would induce errors when calculating the integrated or accumulated NO_x concentration. The following is an illustration of the MEXA-ONE and Ecophysics CLD64 distribution during Day 1 of background testing respectively.

Figure 13: Hour-by-Hour distribution of ambient NO_x concentrations via the MEXA-ONE instrument

Figure 14: Hour-by-Hour illustration of the mean ambient NO_x concentration via the MEXA-ONE instrument

As shown in Figure 14, the MEXA-ONE has a normal distribution and shows a mean of around 0.006 ppm as shown in Table 5. This data shows that the MEXA-ONE can handle such low concentrations and the readings are stable considering the nullification of the outlier points. Figure

13 also indicates that the distribution about the mean, not including the outliers, is within 0.01 ppm.

Figure 15: Hour-by-Hour distribution of ambient NO_x concentrations via the Ecophysics CLD64 instrument

Figure 16: Hour-by-Hour illustration of the mean ambient NO_x concentration via the Ecophysics CLD64 instrument

As shown in Figure 15, there is a non-normal distribution of the data. From the data, the detection limit of 0.002 ppm is being reached and thus adding to some outlier data. Comparing the MEXA-ONE and the Ecophysics CLD64, it can be hypothesized that the internal calculations of these instruments are different and thus can add to the non-uniform distribution. Another thing to note is the different DAQ systems used for the MEXA-ONE and the other analyzers. There can be some resolution issues in the MEXA-ONE DAQ system allowing for this non-normal binning of the data. This although, is outside of the scope of this study and so it was not investigated.

Figure 17: Continuous Measurement of Ambient THC Concentrations via MEXA-ONE

The THC and CH₄ ambient concentrations look stable, around 2.5 ppm, during Day 1 of background variability testing as shown in Figure 17. The MEXA-ONE had stable readings at these levels but the MKS MultiGas 2030HS had some signal noise and so not included in this summary. Although the concentrations are within the instrument range, the nature of the analyzer (IR) has some drawbacks thus indicating that such an analyzer is unadvised for CVS emissions testing for such species at these levels. The reason for taking THC measurements alongside NO_x measurements was due to the adverse effects HC plays during emissions testing. Understanding HC interference at these low levels helps with the reliability of the emission measurement results. This also gave a preview of what concentrations the dilution air filter would experience during operation and see which times of days the highest concentrations occurred.

3.5.1.1 Carbon Filtration Efficiency

The following table illustrates how effective the carbon filter is at removing NO_x and THC from background ambient air.

Table 6: Filtration efficiency of the Activated Carbon Filter with respect to NO_x and THC [2]

Test ID	H0003-001-330	H0003-001-332	H0003-001-334	H0003-001-336
MEXA-ONE THC	4.8%	3.6%	6.5%	5.5%
MEXA-ONE NO_x	40.9%	23.1%	51.5%	25.2%
Brandgaus 7705 NO_x	53.8%	-19.3%	21.2%	1.5%
Ecophysics CLD64 NO_x	22.0%	76.7%	45.8%	42.8%
Avg. Intake Temp [°C]	26	21	39	35
Avg. Intake Humidity [%]	75	84	26	36

A correlation study, using the correlation coefficient method, was performed on Table 6, and some insight can be understood of the effects temperature and humidity have on NO_x via several analyzer measurements. Table 7 is an illustration of such study.

Table 7: Correlation Coefficient of Intake Temperature and Intake Humidity on CLD Analyzers and Filtration Efficiency

	MEXA-ONE NO_x	Brandgaus 7705	Ecophysics CLD64	MEXA-ONE THC	Intake Temperature	Intake Humidity
MEXA-ONE NO_x		0.6939	-0.5238	0.7155	0.5502	-0.4505
Brandgaus 7705			-0.9235	0.3788	0.1858	-0.0531
Ecophysics CLD64				-0.4837	-0.3508	0.2394

The CLD analyzers should have the same positive correlation with each other but that is not the case. From the table we can conclude that the Brandgaus and Ecophysics have strong negative correlation when it comes to carbon filtration efficiency and how it affects them. The MEXA-ONE NO_x and MEXA-ONE THC have positive correlation. This is the most significant data set found during this study, but due to a limited sample pool, a clear conclusion is still undetermined. The filtration of the THC has a positive correlation with filtration of the NO_x for the MEXA-ONE instrument. Further investigation of such testing should be conducted to see a clear picture of the effects THC has on NO_x with respect to using a carbon filtration system. The results can only indicate that the carbon filter did remove NO_x and THC from the background ambient air, but no correlation is identified between intake temperature and humidity.

4 Results and Discussion

The scope of this paper is to analyze and compare the performance of such state-of-the-art analyzers and their applicability for ULNO_x measurement while addressing the uncertainties of the technology and negative effects that can hinder their performance.

4.1 Analyzer Performance

4.1.1 Linearity

Linearity checks are performed during CVS system testing to check how the analyzers are performing at different steady state concentration levels and their respective accuracy. Such testing was conducted with the MKS MultiGas 2030HS, Ecophysics CLD64, and Brandgaus 7705 analyzers.

Table 8: Linearity check using a gas divider and a 19.5 ppm NO_x bottle with N₂ balance

Divider	Value NO_x (ppm)	MKS MultiGas 2030HS	Brandgaus 7705 NO_x 7705	Ecophysics CLD64
100	19.4	100.4%	100.2%	100.3%
90	17.5	102.0%	99.7%	100.0%
80	15.5	100.1%	99.2%	99.7%
70	13.6	99.0%	99.2%	99.5%
60	11.6	100.0%	98.6%	99.3%
50	9.7	101.6%	98.7%	98.9%
40	7.8	103.3%	98.3%	98.9%
30	5.8	101.1%	98.0%	98.2%
20	3.9	98.5%	96.7%	96.8%
10	1.9	101.8%	95.2%	95.5%
0	0.0	100.5%	100.1%	100.0%
10	1.9	86.8%	94.5%	94.2%
20	3.9	95.4%	97.2%	96.7%
30	5.8	102.6%	97.7%	97.9%
40	7.8	101.0%	97.6%	98.5%
50	9.7	99.0%	98.0%	98.8%
60	11.6	100.5%	97.5%	98.9%
70	13.6	100.0%	97.9%	99.1%
80	15.5	100.0%	97.8%	99.4%
90	17.5	100.3%	99.7%	99.8%
100	19.4	99.9%	100.3%	99.9%

Regardless of the specifications indicated for each analyzer, the accuracy falls below 99% of span at 60% of 19.5 ppm for Ecophysics CLD64, 70% for Brandgaus 7705, and 60% for MKS MultiGas 2030HS. As the concentration increases to above 10-12 ppm the analyzers perform well and are accurate at or above 18ppm. These results indicate several issues since Ecophysics claims measuring ranges of 0.5 to 100 ppm with limit of detection being 0.002 ppm. Brandgaus specifications show ranges of 1 to 500 ppm with span error noise of less than or equal to 0.25% of span. This data illustrates that the MKS MultiGas 2030HS, Brandgaus 7705, and Ecophysics CLD64 have trouble reading accurately during quasi steady state operation. One thing to note is that as stated in literature, there can be NO_x loss in the system due to chemisorption or condensation.

4.1.2 NO₂ Effects

Table 9: The effects of NO₂ on analyzers at 20.5 ppm with N₂ balance gas

Divider	Value NO₂ (ppm)	MKS MultiGas 2030HS	Brandgaus 7705	Ecophysics CLD64
100	20.5	92.3%	88.7%	88.8%
90	18.5	94.9%	91.1%	91.4%
80	16.4	96.6%	92.6%	93.2%
70	14.4	97.4%	94.1%	94.6%
60	12.3	98.7%	95.1%	95.8%
50	10.3	99.5%	96.0%	96.8%
40	8.2	99.8%	97.6%	97.5%
30	6.2	100.2%	98.5%	98.2%
20	4.1	100.3%	98.7%	98.7%
10	2.1	100.8%	99.3%	99.3%
0	0.0	100.5%	100.2%	100.0%
20	4.1	100.1%	98.4%	98.5%
40	8.2	99.6%	96.9%	97.3%
60	12.3	98.9%	95.4%	95.8%
80	16.4	98.5%	93.7%	94.5%
100	20.5	98.3%	94.1%	94.0%

From the table above the analyzer's accuracy decreases when an NO₂ gas bottle was used with a N₂ balance. The adverse effects of NO₂ on these analyzers can be seen on the accuracy as the concentration of NO₂ increases. The Brandgaus 7705 and Ecophysics CLD64 use converters that convert NO to NO₂ and in such a state the NO₂ gives off a photon after it leaves its excited state. These analyzers were not made to have such high concentrations of NO₂ without having NO present. This experiment was conducted to characterize the effects NO₂ had on these analyzers and the decrease in accuracy it had. This setup had the opposite affect from Table 8 and shows more accuracy at only N₂ being present. Another observation is that the NO₂ has negative effects on both the photomultiplier tube and solid-state photodiode technology.

Table 10: 20.5 ppm NO₂ bottle with 19.5 ppm NO_x bottle as balance and the effects on performance

Divider	Value NO	Value NO₂	Total NO_x	MKS MultiGas 2030HS	Brandgaus 7705	Ecophysics CLD64
0	19.5	0.0	19.5	100.6%	101.7%	101.9%
10	17.6	2.1	19.6	102.0%	101.1%	101.2%
20	15.6	4.1	19.7	100.3%	99.9%	100.5%
30	13.7	6.2	19.8	101.7%	99.5%	99.8%
40	11.7	8.2	19.9	101.1%	99.3%	99.1%
50	9.8	10.3	20.0	100.6%	97.9%	98.3%
60	7.8	12.3	20.1	101.1%	97.1%	97.6%
70	5.9	14.4	20.2	101.1%	96.7%	96.8%
80	3.9	16.4	20.3	100.3%	95.4%	96.1%
90	2.0	18.5	20.4	100.9%	94.8%	95.4%
100	0.0	20.5	20.5	100.5%	94.3%	94.6%
50	9.8	10.3	20.0	102.6%	98.5%	99.3%
0	19.5	0.0	19.5	100.7%	101.1%	102.1%
20	15.6	4.1	19.7	100.9%	99.7%	100.2%
40	11.7	8.2	19.9	100.8%	98.6%	99.0%
60	7.8	12.3	20.1	101.6%	97.4%	97.7%
80	3.9	16.4	20.3	101.7%	95.9%	96.2%
100	0.0	20.5	20.5	101.5%	95.9%	94.9%

Table 10 shows the effects NO₂ and NO_x ratios has on the performance of these analyzers. As shown, the concentration of total NO_x never went below 19 ppm but the constituent or ratio of NO₂ to NO did not change. This shows the susceptibility of these analyzers to different ratios of NO to NO₂. The Brandgaus 7705 and Ecophysics CLD64 are more accurate at 60% NO_x and 40% NO₂ and as NO₂ increase, their accuracy decreases. As shown in Table 10, error percentages of 5% are reached when there is only NO₂ present in the flue gas. Understanding that such conditions will rarely occur in a diesel system out emissions standpoint, it is good to note for future reference.

4.2 Analyzer Drift

Details outlined in 40 CFR 1065.550 allow a 4% gaseous analyzer equipment drift. This requires that for a NO_x limit of 0.2 (g/bhp-hr) the allowable analyzer drift is 0.008 (g/bhp-hr) and for a 0.02 (g/bhp-hr) NO_x limit the allowable drift is 0.0008 (g/bhp-hr). The concern for ULNO_x

measurement is whether laboratory grade gaseous analyzers can accurately detect such low levels [32].

Figure 18: Drift check after FTP test cycles with 20.4 ppm NO_x bottle, Day 1

Figure 19: Drift Check after FTP (3, 4, and 5) and RMC (1 and 2) test cycles with a 19.5 ppm NO_x bottle, Day 2

Figure 20: Drift check after FTP test cycles using 19.5 ppm NO_x bottle, Day 3

As the results indicate, Ecophysics CLD64 passed all drift checks during the FTP and RMC testing. Day 2, all analyzers passed the drift checks. Day 1 the Brandgaus 7705 failed during the second FTP and the MKS MultiGas 2030HS failed during the third FTP. Day 3 only the MKS MultiGas 2030HS failed during the second FTP. The following table shows the correlation coefficients between each analyzer and the test cycles.

Table 11: Correlation Coefficient between MKS MultiGas 2030HS, Brandgaus 7705, and Ecophysics CLD64 with drift

Day 1	MKS MultiGas 2030HS	Brandgaus 7705	Ecophysics CLD64
MKS MultiGas 2030HS		0.198001	0.469481
Brandgaus 7705			0.95842
Ecophysics CLD64			
Day 2	MKS MultiGas 2030HS	Brandgaus 7705	Ecophysics CLD64
MKS MultiGas 2030HS		0.585518	0.021581
Brandgaus 7705			0.773329
Ecophysics CLD64			
Day 3	MKS MultiGas 2030HS	Brandgaus 7705	Ecophysics CLD64
MKS MultiGas 2030HS		0.76177	0.630292
Brandgaus 7705			0.003359
Ecophysics CLD64			

The reason for such a comparison is to check whether these analyzers experienced the same drift effects during testing. As the table shows, there is no significant correlation between test cycles. The drift percentages are not indicative of major outside forces affecting the analyzers, e.g. large leak in the system while testing, water condensation, or even large changes in ambient concentrations. The data shows that no such correlation exists for this sample. One thing to note is that 4% of such span bottles equates to around 0.8 ppm drift which is well within the analyzer's specifications. Ecophysics CLD64 for Day 2 and Day 3 shows drifts less than 2%, being 0.4 ppm. Brandgaus 7705 did not consistently perform as well as the Ecophysics in Day 2 and Day 3 and the MKS MultiGas 2030HS had trouble maintaining a stable reading, which contradicts the 'no drift effects' the technology claims.

Figure 21: Integration of NO_x over the test cycle including RMC's (7 and 8) and FTP's (1 thru 6 and 9 thru 12)

During the transient testing portion of this study several FTP's and RMC's were performed. The data before the RMC's looks to be sporadic and shows no congruency with the MEXA-ONE. After the RMC's were conducted the data seems to align well, in terms of the analyzers showing the same behavior and being more aligned with each other than before. The tests prior to the RMC's show greater deviations from test to test and are well above ULNO_x concentrations. There are several indications that proper conditioning of these cycles is necessary to begin at the same point or to produce results that coincide with each other. Understanding that RMC's are higher temperature cycles with more steady state operation than FTP's, this can be indicative of the need to regenerate the system or purge the system in such a way that any unwanted constituents are blown out or burned. Another caveat is that the MKS MultiGas 2030HS, Brandgaus 7705, and Ecophysics CLD64 share the same heated manifold feeding these analyzers with the same flue gas constituents. The MEXA-ONE on the other hand, is drawn in a different direction as shown in Figure 10. This can have effects such as the MEXA-ONE reading concentrations much different than the MKS MultiGas 2030HS, Ecophysics CLD64 and Brandgaus 7705. The last observation

is that with each test conducted, the first six cycles, the Brandgaus 7705 read higher than the Ecophysics CLD64 and the Ecophysics CLD64 read higher than the MEXA-ONE excluding the MKS MultiGas 2030HS. After the RMC cycles were conducted the MEXA-ONE always read higher.

5 Conclusion

The improvements introduced in this study were made in order to decrease uncertainty and error for the CVS system. Some improvements such as the carbon filtration system and the heated tunnel introduction showed promise in that there was calculable proof that the improvements had positive effects on the system. Other improvements such as proportional bagging, not included in this paper, showed no improvements, rather contradicted findings in literature. Ambient concentrations can vary and be unpredictable and so the implementation of the carbon filter was used to try to mitigate these variations and smooth NO_x and THC concentrations to reduce spikes or high concentrations in the ambient environment. Tunnel heating also enabled the mitigation of water condensation inside the tunnel where the gas species mix prior to sampling by the analyzers. The SF_6 injection and propane check conducted to the CVS system verified that the system was leak proof.

Details outlined in 40 CFR 1065.550 allow a 4% gaseous analyzer equipment drift. This requires that for a NO_x limit of 0.2 (g/bhp-hr) the allowable analyzer drift is 0.008 (g/bhp-hr) and for a 0.02 (g/bhp-hr) NO_x limit the allowable drift is 0.0008 (g/bhp-hr). The concern for ULNO_x measurement is whether laboratory grade gaseous analyzers can accurately detect such low levels.

The instruments used and their comparisons varied as the study progressed. The Brandgaus 7705 and Ecophysics CLD64 were analyzers added to this study in order to conduct an analysis of various ULNO_x instruments for automotive use. This study addressed linearity, drift, cycle-by-cycle performance, low concentration performance, and signal noise at various concentrations. This study concludes that the MEXA-ONE adhered to its specifications and had accurate performance in measuring ULNO_x background concentrations around 0.005 ppm and THC concentrations around 3 ppm. The Ecophysics CLD64 performed well in ULNO_x background concentration measuring and drift performance during the FTP and RMC cycles, the only analyzer to adhere to the 2% drift limit excluding the MEXA-ONE. No data was collected on the MEXA-ONE for drift due to DAQ system issues not addressed in time. The MKS MultiGas 2030HS is not suitable for ULNO_x measuring and should only be used as a supplemental analyzer for other constituents. The Brandgaus 7705 had subpar performance in NO_x background concentration measuring, drift, linearity, and cycle-by-cycle measurement. This analyzer had high signal noise at low concentrations (<0.02 ppm) as seen in ambient NO_x and so did the MKS MultiGas 2030HS. The MEXA-ONE and Ecophysics CLD64 had little noise in all comparisons since their detection

limits were (<1 ppm). All analyzers experienced adverse effects from NO_2 concentrations where NO was not present or in situations where the ratio of NO/NO_2 was close to 1.

The study also showed that NO_2 has negative effects on CLD analyzers regardless of photomultiplier tubes or solid-state photodiode detector technology. Given the specifications, Ecophysics CLD64 adhered to its specifications more so than the MKS MultiGas 2030HS and Brandgaus 7705. Further studies should also be conducted on the carbon filter to see how effective it is using known concentrations of NO_x and THC and calculate the residence time for such filtration. In addition, figuring out the saturation limit of such a filter.

To further address the ULNO_x measurement environment, the MEXA-ONE and Ecophysics CLD64 are suitable for steady state low NO_x concentrations but for transient operation such as engine testing, the MEXA-ONE is more suitable. Since the Brandgaus 7705 was made for CEMS applications in gas turbine environments, this instrument is not suited for ULNO_x automotive application. As stated before, the MKS MultiGas 2030HS should only be used as a supplemental analyzer for constituents such as SO_x and NH_3 . The greatest problem that should be addressed in future work is the effects a Nafion Dryer tube has on such analyzers and if the removal of water vapor caused desorption of NO_x species from the flue gas. This may shed light on the discrepancies seen in the consecutive FTP and RMC cycles.

6 Appendix

Table A 1: Comparison of different analyzers and their respective accumulated NO_x in grams for the entire cycle

TEST TYPE	MEAN x_dil_exh		Difference	Continuous Measurement - Accumulated Background NOx mass (g)						Bag Measurement - Accumulated Background NOx mass (g)			Bag Filling Method	Effect on (g/bhp-hr) due to Instruments			
	CVS	EFM			MEXA		BRAND GAUSS		ECOPHYSICS		BRAND GAUSS	ECOPHYSICS		FTIR	MEXA	BRAND GAUSS	ECOPHYSICS
FTP	0.9317	0.8174	12%	-0.0021	-0.0019	0.1060	0.0903	0.1051	0.0927	0.1259	0.1268	-0.6989	Constant	0.344 g/bhp-hr	0.87%	1.16%	
FTP	0.9317	0.8246	11%	0.0072	0.0063	0.1319	0.1168	0.1510	0.1342	0.1175	0.0725	-0.4597	Constant	0.366 g/bhp-hr	0.82%	1.09%	
FTP	0.9323	0.8255	11%	0.0092	0.0081	0.2124	0.1962	0.4370	0.4071	0.1363	0.0359	-0.5359	Proportional	0.442 g/bhp-hr	0.68%	1.13%	
FTP	0.9323	0.8245	12%	-0.0012	-0.0011	0.0962	0.0848	0.1553	0.1367	0.1558	0.0591	-0.5699	Proportional	0.302 g/bhp-hr	0.66%	1.32%	
FTP	0.9295	0.8329	10%	-0.0213	-0.0191	0.1457	0.1311	0.0207	0.0192	0.3632	0.2003	-0.4534	Proportional	0.348 g/bhp-hr	1.44%	0.29%	
FTP	0.9319	0.8404	10%	-0.0229	-0.0207	0.1548	0.1394	0.0705	0.0643	0.1813	0.0545	-0.4876	Proportional	0.426 g/bhp-hr	1.17%	0.47%	
RMC	0.8463	0.6951	18%	-0.0013	-0.0009	0.3133	0.2563	0.6353	0.5131	0.3698	0.1604	-0.7653	Proportional	0.244 g/bhp-hr	0.82%	1.64%	
RMC	0.8463	0.7004	17%	-0.0010	0.0007	0.2993	0.2471	0.4977	0.4084	0.3570	0.1455	-0.8161	Proportional	0.164 g/bhp-hr	1.22%	1.83%	
FTP	0.9318	0.8536	8%	0.0261	0.0240	0.2255	0.2064	0.0702	0.0640	0.2520	0.0248	-0.1656	Constant	0.26 g/bhp-hr	1.54%	0.38%	
FTP	0.9309	0.8656	7%	-0.0277	-0.0258	0.1936	0.1799	0.0481	0.0446	0.1667	0.0114	-0.3271	Constant	0.129 g/bhp-hr	3.88%	1.55%	
FTP	0.9310	0.8495	9%	-0.0060	-0.0055	0.1781	0.1625	0.1222	0.1118	0.1543	0.0243	-0.2341	Proportional	0.471 g/bhp-hr	1.06%	0.85%	
FTP	0.9316	0.8532	8%	0.0128	0.0118	0.1230	0.1126	0.1060	0.0979	0.0812	0.0152	-0.2649	Proportional	0.312 g/bhp-hr	0.96%	0.64%	

Table A 2: The effects Tunnel Heating has on NO_x recovery in a CVS system and the error associated with it

Injected Bottle	Test ID	Tunnel	Tunnel Flow [scfm]	Injected Flow [scfm]	Injected Mass [g]	Recovered Mass [g]	Error [%]	Sample RH [%]	Sample Temperature [degC]	Dilution Air Temp [degC]
NOX [1504ppm]	H0003-001-446	Heated	396.4	2.514	0.086	0.081	6.0	20.0	38.9	23.6
			591.7	2.509	0.100	0.095	5.2	21.5	38.1	23.9
			886.4	2.504	0.074	0.070	5.4	22.8	36.8	24.0
			1186.8	2.496	0.058	0.055	5.5	24.2	35.5	23.9
NOX [1504ppm]	H0003-001-447	Heated	395.7	2.426	0.064	0.067	-4.9	22.4	35.8	23.4
			589.3	2.287	0.060	0.064	-6.5	21.4	36.6	23.5
			886.1	1.638	0.046	0.050	-9.5	22.3	36.0	23.5
			1185.9	0.873	0.020	0.022	-7.6	23.8	35.0	23.7
Propane [9885 ppm]	H0003-001-447	Heated	395.3	2.114	0.201	0.203	-0.7	18.5	38.9	24.6
			590.3	2.114	0.199	0.201	-1.2	18.9	38.6	24.9
			885.3	2.114	0.178	0.179	-0.7	19.8	37.5	24.9
			1186.9	2.115	0.173	0.174	-0.8	21.4	36.1	24.9
NOX [1504ppm]	H0003-001-444	Not Heated	396.6	0.846	0.037	0.033	10.2	37.5	27.8	26.2
			591.8	0.846	0.047	0.042	11.2	37.6	27.6	26.2
			886.9	0.846	0.063	0.055	12.5	38.0	27.1	26.0
			1187.9	0.846	0.060	0.052	13.3	38.5	26.9	26.0
			1492.8	0.846	0.074	0.064	13.6	38.9	26.7	25.9
			1798.0	0.846	0.170	0.147	13.7	39.3	26.4	25.7
NOX [1504ppm]	H0003-001-442	Not Heated	395.9	0.9	0.0	0.0	8.2	37.3	29.4	26.5
			788.1	0.9	0.1	0.1	9.5	37.7	29.1	26.6
			1187.8	0.9	0.0	0.0	10.2	38.2	28.7	26.6
			1492.7	0.9	0.1	0.1	10.4	38.3	28.4	26.7
			1798.0	0.9	0.1	0.1	10.3	38.5	28.3	26.7
Propane [9885 ppm]	H0003-001-445	Not Heated	395.8	0.846	0.063	0.063	-0.7	40.2	26.2	25.1
			590.6	0.846	0.056	0.056	-0.5	40.5	26.1	25.2
			886.9	0.846	0.095	0.096	-0.7	41.1	26.0	25.1
			1187.3	0.846	0.070	0.071	-1.0	41.8	25.9	25.2
			1490.7	0.846	0.038	0.039	-2.3	41.7	25.9	25.2
			1797.7	0.846	0.084	0.086	-2.7	41.9	25.7	25.1

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