FINAL REPORT

Marine Engine Testing and Emissions Laboratory (METEL)

Led by Maine Maritime Academy

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Continuous Emission Monitoring System Project

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Abstract

Marine vessels contribute a significant portion of total pollutant gas and particulate matter emissions near ports and waterways across the United States. As such, current MARPOL, US Federal, and California Air Resources Board emissions regulations dictate engine exhaust emission limits on CO, NOx, Total Hydrocarbons (THC), and Particulate Matter (PM). The Marine Engine Testing and Emissions Laboratory (METEL) at Maine Maritime Academy (MMA) was created to assist and address the emission reduction needs of the marine industry due to regulatory requirements. This report outlines the development of a Continuous Emissions Monitoring System (CEMS) to quantify all gas and particulate emission from laboratory testing and on board vessel testing at sea. A Fourier Transform Infrared (FTIR) spectrometer was selected to measure gaseous emissions while a Scanning Electrical Mobility Spectrometer (SEMS) was employed to measure exhaust particulate matter emissions. This report outlines the instrumentation and testing procedures developed to create the continuous emissions monitoring system at the Marine Engine Testing and Emissions Laboratory at Maine Maritime Academy. Outstanding issues and suggested improvements are also outlined to aid the development of future CEMS.

1. Introduction

Marine vessels contribute a significant portion of total pollutant gas and particulate matter emissions near ports and waterways across the United States. As such, current MARPOL, US Federal, and California Air Resources Board emissions regulations dictate engine exhaust emission limits on CO, NOx, Total Hydrocarbons (THC), and Particulate Matter (PM) with SOx controlled via fuel sulfur content limits. These regulations also dictate a tiered schedule of increasingly stringent emissions limits be met for new engine families and new build vessels by date of construction. The Marine Engine Testing and Emissions Laboratory (METEL) at Maine Maritime Academy (MMA) was created to assist and address the emission reduction needs of the marine industry due to regulatory requirements. Several emissions reduction projects were undertaken at METEL including the development of a Continuous Emissions Monitoring System (CEMS) to quantify all gas and particulate emission improvements from laboratory testing and on board vessel testing at sea. The unique requirement of continuous emissions monitoring in a harsh marine environment requires rugged equipment on board a vessel capable of withstanding shock, vibration, and corrosion. For convenience, a simple calibration procedure is required with calibration stability over time.

Traditionally, gaseous emissions are measured with "five gas analyzers" capable of measuring carbon monoxide (CO), total unburned hydrocarbons (THC), carbon dioxide (CO_2), unreacted oxygen (O_2), and oxides of nitrogen (NO_x). These instruments consist of a suite of separate nondispersive infrared (NDIR) and chemical sensors to measure each gas and conform to test methods outlined in the code of federal regulations 40 CFR Part 1065 for engine testing. However, these five gas instruments are limited to the five gases they were designed to measure and require frequent recalibration. Instead, the CEMS system developed at METEL leverages Fourier Transform Infrared (FTIR) spectroscopy as a gas emissions monitoring device. FTIR has the potential to simultaneously quantify all currently regulated emissions and more than 100 of the 189 Hazardous Air Pollutants listed in the Clean Air Act Amendments of 1990 [1] and maintain calibration integrity. As such, the versatility of FTIR spectroscopy as a single source gas emissions measurement system was evaluated as an alternative to meet marine emissions regulations.

Engine exhaust particulate matter is measured with a variety of methods. The CEMS developed by METEL necessitates a continuous measurement device. Thus a continuous Scanning Electrical

Mobility Spectrometer (SEMS) was employed as a mature technology to measure exhaust particulate matter (soot) including particle size distribution, total number concentration, and total mass.

This report outlines the instrumentation, sampling, and supporting equipment and testing procedures developed to create the continuous emissions monitoring system at Maine Maritime Academy's Marine Engine Testing and Emissions Laboratory. Outstanding issues and suggested improvements are also outlined to aid the development of future CEMS.

2. Instrumentation

2.1 FTIR

A MKS 2030 Fourier Transform Infrared (FTIR) spectrometer was chosen to measure gaseous engine exhaust emissions. The instrument operates by measuring the infrared light absorption of species passing through the device with a Michelsen interferometer. An FTIR has the capability to measure any gaseous species with a unique identifying infrared absorption spectrum after calibration. The MKS 2030 FTIR is equipped with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector permitting a maximum scan rate of 5Hz for resolving engine transients. Instrument sensitivity is between 10 and 100 ppb depending on species. Calibration stability is maintained, negating the need for frequent recalibrations. Background subtraction of a clean infrared baseline spectrum is required every 24 hours however, for species calibrations to remain valid. Background subtraction requires purging the instrument with air or nitrogen free of moisture and VOCs for 5 minutes before a user initiates an automated background subtraction. Upon arrival at METEL, the MKS 2030 FTIR was marinerized in a customized watertight and shock mounted Pelican rackmount case equipped with ball bearing drawer slides for ease of instrument maintenance. Figure 1 shows the finalized installation of the FTIR.

Figure 1: Marinerized MKS 2030 Fourier Transform Infrared Spectrometer (FTIR).

2.2 FTIR Sampling System

A portion of the FTIR exhaust gas sampling system is shown in Figure 2. The sampling system consists of an exhaust probe, heated sampling lines, heated sampling pump, heated filter, and a three way heated solenoid valve. The exhaust probe consists of a 10-inch long, 3/8-inch stainless steel tube sealed at one end with a multitude of 1/8-inch sampling holes drilled down the length of the probe. The probe protrudes into the engine exhaust stack with sampling holes facing the flow to ensure a homogenous mixture of exhaust gas is sampled across the diameter of the exhaust stack. To prevent condensation of sampled exhaust gas, all components of the sampling system are heated to 191°C in conformance with CFR 40 Part 1065 "Engine Testing Procedures". A 60 SLPM heated dual head diaphragm pump provides exhaust gas sample flow through the system. A heated filter housing, located upstream of the sample pump and FTIR, filters the exhaust gas sample of particulate matter that would foul the optics in the FTIR gas cell. Filters are replaced daily to ensure optimal sampling performance. Heated sample lines connect the pump and filter to the engine exhaust and FTIR. Lastly, a three way heated solenoid valve directs either exhaust sample flow or purge air flow into the FTIR gas cell. The provision for purge air free of moisture and VOCs is required when conducting a daily background subtraction.

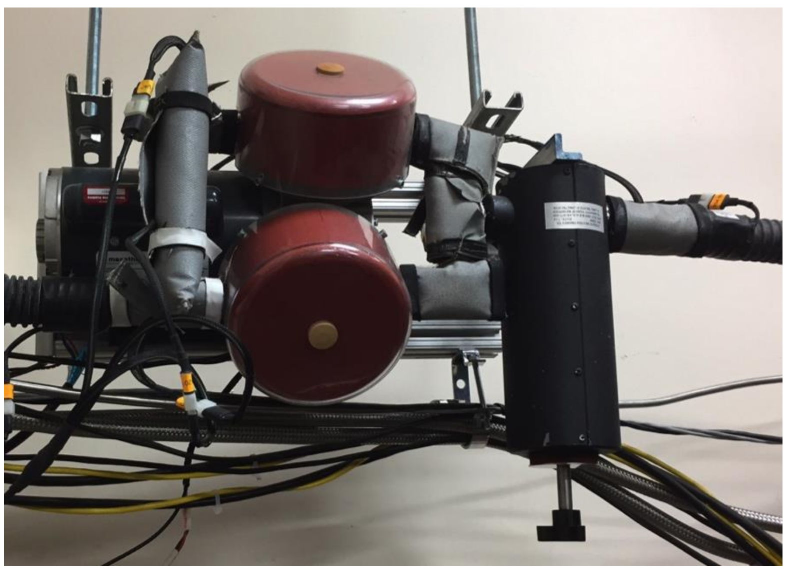

Figure 2: Primary components of FTIR gas sampling system including heated gas sampling pump, heated sampling lines, and heated filter.

2.3 SEMS

A BMI 2100 Scanning Electrical Mobility Spectrometer (SEMS) was used to measure engine exhaust particulate mass, size distribution, and total number concentration in the particle size range of 5nm to 500nm. The instrument consists of a particle pre-impactor, particle charge neutralizer, differential mobility analyzer (DMA), and mixing condensation particle counter (MCPC). A pre-impactor was used to prevent particles larger than 500nm from entering the instrument and causing measurement errors. An x-ray particle charge neutralizer was adopted instead of a traditional radioactive neutralizer for ease of use and transport. The DMA separates charged aerosol particles in an electric field by aerodynamic mobility diameter due to size dependent changes in time of flight through the DMA. The DMA scans through the range of particle sizes from 5nm to 500nm, which are then counted by a MCPC. The MCPC operates by condensing n-butyl alcohol on the particles until they reach a large enough size to be detectable by laser light scattering on a detector. The MCPC differs from traditional CPCs through a redesigned condensation technique, resulting in dramatically improved response time. The MCPC was additionally modified by BMI to prevent flooding of the instrument due to tilting and rocking of the n-butyl alcohol reservoir while at sea. This modification is also often used for aerosol measurements by UAV. The combined SEMS instrument is a first-of-its-kind, capable of achieving particle size distribution scans at a significantly faster rate (approximately 5 seconds) in comparison to other particle mobility spectrometers currently on the market (approximately 30 seconds). Upon arrival at METEL, the BMI 2100 SEMS was marinerized in a customized watertight and shock mounted Pelican case. Figure 3 shows the finalized installation of the SEMS and supporting soot sampling equipment.

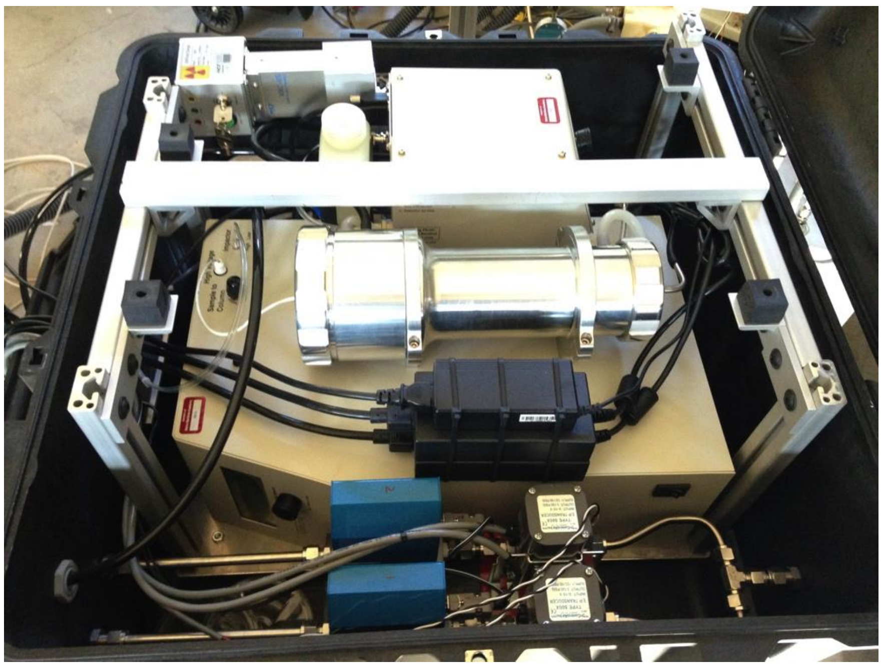

Figure 3: Marinerized BMI 2100 Scanning Electrical Mobility Spectrometer (SEMS) system and sampling equipment.

2.4 PM Sampling System

An illustration of the PM sampling system developed for the SEMS is shown in Figure 4. The sampling system consists of two calibrated flow orifices and two ejector pumps, providing a diluted sample to the SEMS with a dilution ratio of approximately 1000. Diesel engine exhaust PM sampling is historically complicated by the multiple phases inherent to the exhaust flow [2,3]. Improper sampling results in gaseous unburned volatile organic carbon (VOC) compounds condensing into liquid nanoparticles in the exhaust sample. An aerosol electrical mobility spectrometer erroneously reads the liquid VOC droplets as soot particles, resulted in corrupted soot measurements. Sampling at elevated temperature or diluted sampling avoids the issue of VOC condensation by maintaining VOC vapor pressures below saturation levels. Dilution tunnels often employ both sampling strategies, but suffer from particulate loss due to particle collisions with the dilution tunnel wall [2]. The problem is exacerbated by increased residence time in a dilution tunnel. To minimize the issue of particle losses and liquid VOC droplets, the dilution sampling system developed at METEL was built as small as possible. Soot aerosol laden exhaust is sampled through a calibrated flow orifice by an ejector pump and immediately diluted with air at 150°C from the ejector. Standard compressed air cleaned and filtered of moisture, oil, and particulate matter is used for dilution. A second calibrated flow orifice is placed in the exhaust of the first ejector and a second sample is similarly collected and diluted through a second ejector pump. The dual stage heated dilution sampling system dilutes the PM sample by a factor of 1000, which then travels back to the instrument for analysis. The compact design of the sampling system minimizes residence time and particle losses through the device. Particle losses through the diluted sample return piping to the SEMS were found to be negligible.

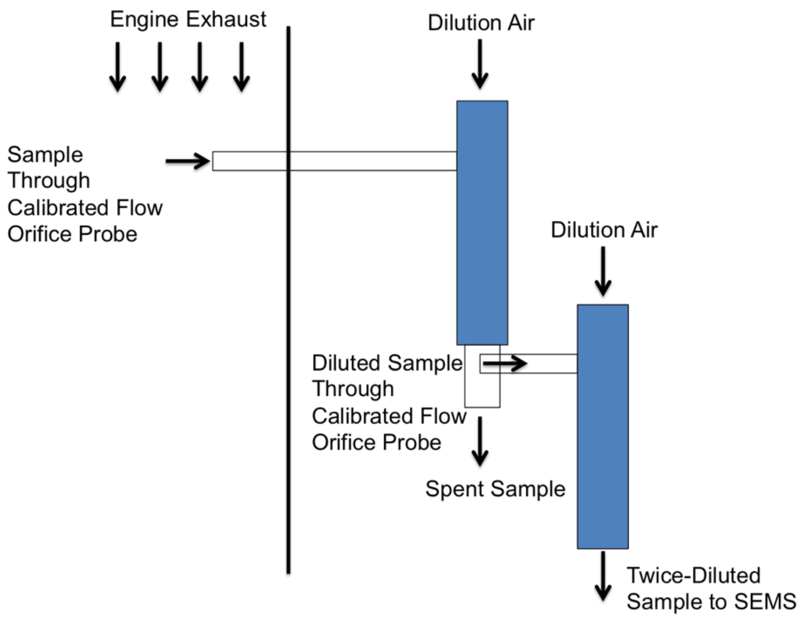

Figure 4: PM sampling system with dual stage heated dilution. The system consists of two calibrated flow orifices and two ejector pumps operated with clean filtered air at 150°C, serving to dilute the exhaust PM sample by a factor of 1000.

2.5 Control Instrumentation

The control box shown in Figure 5 houses all electronics for monitoring and control of all equipment and subsystems associated with the CEMS. The temperature of all heated sampling components are regulated with standalone PID controllers. PID controllers are monitored via MODBUS and a computer. The control box additionally includes relays for control of heated lines, valves, and pumps. A variety of analog inputs and outputs are also included for reading process variables and controlling sampling equipment. All connections to CEMS devices and sampling equipment are removable allowing for rapid disassembly and reassembly of the CEMS system.

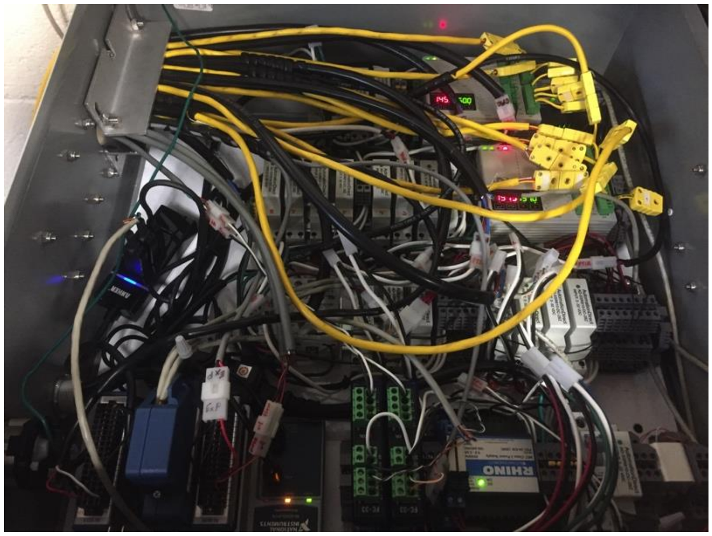

Figure 5: CEMS control system including relays, PID control, and digital and analog inputs and outputs.

2.6 Software

The FTIR came with control and data analysis software from MKS. However, control of sample equipment had to be developed at METEL. FTIR data collection and control of sampling equipment is illustrated in Figure 6, integrated into an engine monitoring program developed at METEL. The software allows for control of the FTIR gas sampling pump and three-way valve for sampling or purging. FTIR data acquisition can be started or stopped, and a background can be collected to maintain instrument calibration. All calibrated gases are user selectable for plotting.

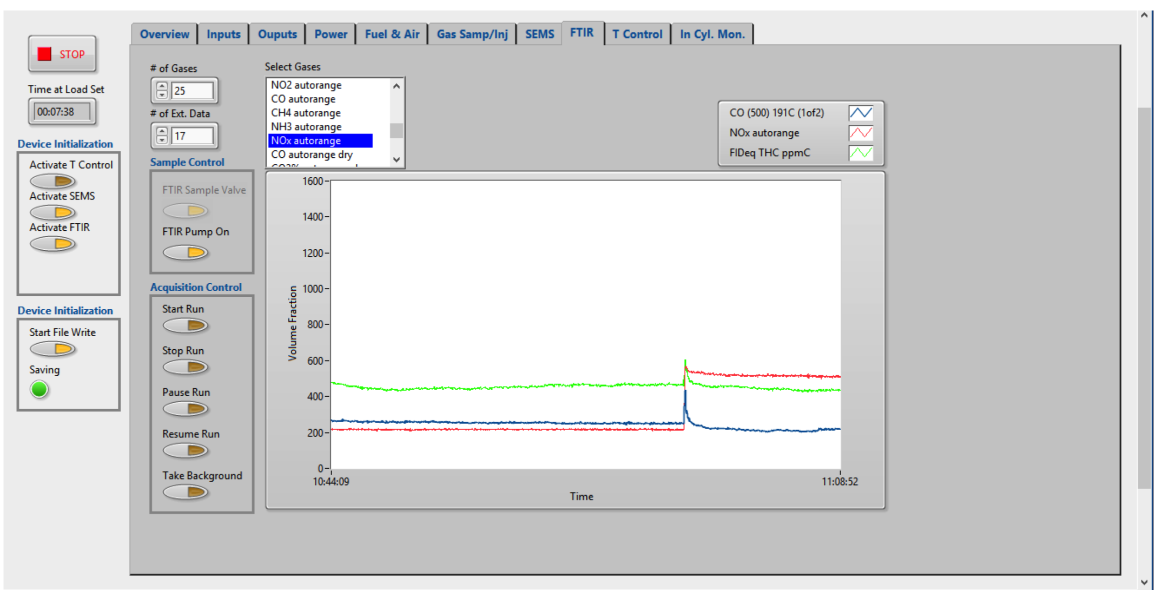

Figure 6: FTIR control tab integrated into engine monitoring software.

The SEMS came with control and data analysis software from BMI. However, the PM sampling system required extensive additional data collection and control. Figure 7 shows the SEMS control tab integrated into an engine monitoring program developed at METEL. The software controls the electro pneumatic transducers for sample dilution. Ejector sample pump flow rate, exhaust gas temperature, and pressure are measured to calculate sample dilution. Data from the SEMS is not currently integrated however, and must be post processed. BMI has plans to provide data integration in future firmware updates.

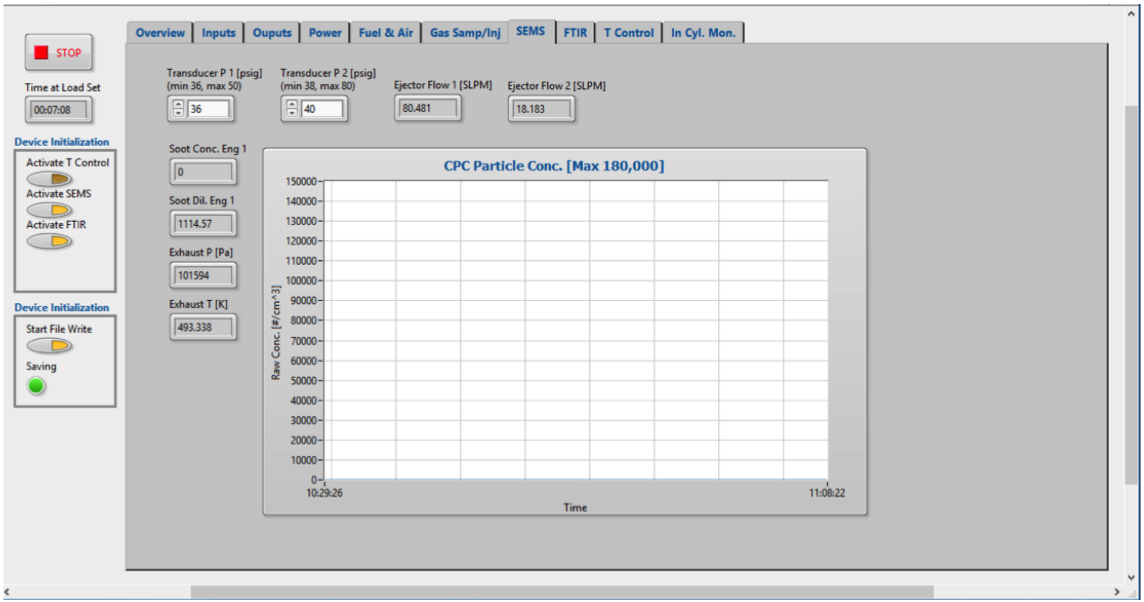

Figure 7: SEMS control tab integrated into engine monitoring software.

3. Measurement Procedures

Emissions measurements from testing were presented as energy weighted mass and number (g/kW-hr and #/kW-hr) and required conversion from the raw measurements provided by the emissions equipment. For gaseous emissions, volume fraction measurements were provided by the FTIR. All significant exhaust gas species were measured via FTIR except for nitrogen and oxygen, where intake air mass fractions of 0.767 and 0.233 were assumed, respectively. Assuming conservation of N_2 mass through the engine, the intake air mass fraction is corrected for the total exhaust flow rate according to Eq. 1.

$$Y_{N2,e} = Y_{N2,a} \frac{\dot{m}_a}{\dot{m}_a + \dot{m}_f} \tag{1}$$

Where $Y_{N2,e}$ is the mass fraction of N_2 in the exhaust, $Y_{N2,a}$ the mass fraction of N_2 in the intake air, $\dot{m}_a$ intake mass air flow, and $\dot{m}_f$ fuel mass flow. The mass flow of fuel was measured with Emerson coriolis meters integrated into the fuel supply and return lines. The mass flow of air was measured with a Sierra hot wire based flow meter. The measured emissions mole fractions are converted to mass fractions assuming O_2 balances the total exhaust mole fraction to 1. Lastly, energy weighted mass emissions of all exhaust gas species are calculated by multiplying the mass fraction of species *n* by the total exhaust mass flow rate and dividing by engine output power.

Particulate emissions for particle mass and number are measured as volume concentrations, and thus require a different procedure for calculating energy weighed number and mass emissions. Once all exhaust volume fractions are calculated, the exhaust density is estimated at standard temperature and pressure using Eq. 4.

$$\rho_e = \sum_n X_n \rho_n \tag{4}$$

Where ρ_n is a single exhaust species density at standard temperature and pressure. Next, the exhaust volume flow rate is calculated by dividing the exhaust mass flow rate by the exhaust density. Lastly, the soot particle number and mass concentrations are multiplied by the exhaust volume flow rate and divided by the engine output power to arrive at the energy weighted emissions of particulate matter.

4. Results/Improvements

The CEMS system was used to conduct a variety of fuel, fuel additive, and lubricating oil testing at METEL. Sample results of CEMS measurements can be found in the Diesel Glycerin Emulsion Fuel Final Report. The CEMS functioned as designed for laboratory and at sea testing. However, several design improvements were identified to facilitate using the CEMS system at sea over long periods of time.

4.1 Gaseous Measurements

The FTIR at METEL uses a MCT detector for maximum instrument response, which requires cooling with liquid nitrogen. Liquid nitrogen is inconvenient for long term testing on board vessels. It is suggested that an FTIR with a DTGS detector be used for continuous monitoring on board vessels with the advantage of reduced capital cost but at the expense of reducing instrument scan time from approximately 5 Hz to 0.125 Hz. Alternatively, a peltier cooled MCT detector may be able to be used.

The FTIR gas cell requires cleaning on the order of several days of continuous operation even with a heated sample filter installed in the sampling system. Installation of two filters in series may improve the cleaning frequency. Alternatively or in conjunction, the sampling system could be adjusted for shorter duration periodic sampling instead of continuous sampling. Periodic sampling was adopted in the lab during engine lubricating oil tests and was found to improve gas cell cleaning frequency in proportion to sampling duration and frequency. This strategy has the potential to improve cleaning frequency from days to week or months depending on sampling periodicity.

Lastly, the FTIR requires moisture and VOC free air or nitrogen for continuous purging of the instrument interior and periodic purging of the gas cell during background subtraction. Cylinders of zero air are required for purging, which is inconvenient for long term testing on board vessels. This gas requirement could be remedied with a small pressure swing absorption system, providing a continuous and unlimited supply of moisture and VOC free air.

4.2 PM Measurements

The first stage calibrated flow orifice of the soot sampling system was cleaned daily during testing to ensure the orifice never clogged with soot over time. During emission testing, some evidence suggests that the PM sampling orifice was automatically cleaned while sampling with an engine under moderate to high load. Additional studies should be conducted to further confirm this hypothesis.

Periodic cleaning of the ejector dilution system is required on the order of several months of use. The system could be improved by heating the sampling system to at least 400°C while sampling air. The elevated temperature would facilitate soot oxidation and clean the sampling system of soot contaminants. Additional studies would need to be conducted to determine the cleaning cycle duration and to source ejector pumps that could tolerate the elevated temperature of the cleaning cycle.

5. Conclusion

A standalone continuous emission monitoring system (CEMS) was built for use in laboratory and vessel testing of engine emissions. The CEMS consists of a Fourier Transform Infrared Spectrometer (FTIR) for measuring a variety of gaseous emissions including CO, total unburned hydrocarbons (THC), oxides of nitrogen (NOx), and a variety of hazardous air pollutants (HAPs). The CEMS is additionally equipped with a Scanning Electrical Mobility Spectrometer (SEMS) for measuring particulate matter (PM) size distribution, mass, and number concentration. Gaseous and particulate sampling systems were developed at METEL to facilitate accurate and repeatable emissions measurements. The CEMS system was used to conduct a variety of fuel, fuel additive, and lubricating oil testing at METEL. Sample results of CEMS measurements are found in the Diesel Glycerin Emulsion Fuel Final Report. The CEMS functioned as designed for laboratory and at sea testing. However, several design improvements were identified to facilitate using the CEMS system at sea over long periods of time:

1. The requirement of liquid nitrogen should be eliminated and a FTIR with a DTGS detector should be used in place of an MCT detector with the advantage of reduced capital cost but at the expense of reducing instrument response.
2. The FTIR requires gas cell cleaning every few days to maintain sensitivity. Additional filtering and periodic gas sampling as opposed to continuous sampling would improve cleaning frequency of the FTIR gas cell. Real improvements of cleaning frequency of weeks to months could be realized.
3. The FTIR requires moisture and VOC free air for instrument purging, requiring high purity gas cylinders on board. This gas requirement could be remedied with a small pressure swing absorption system, providing a continuous and unlimited supply of moisture and VOC free air.
4. The PM sampling probe was cleaned regularly to avoid clogging. Some evidence suggests that the PM sampling orifice was automatically cleaned while sampling with an engine under moderate to high load but additional studies should be conducted to further confirm this hypothesis.
5. Periodic cleaning of the PM ejector dilution system is required on the order of several months of use. The system could be improved with a heated oxidation based cleaning strategy.

References

[1] United States Environmental Protection Agency. (1992). *FTIR Technology Development.* Retrieved from http://www.epa.gov/ttn/emc/ftir/reports/entrop01.html

[2] Kittelson, D., Watts, W., & Johnson, J. (2002). *Diesel Aerosol Sampling Methodology - CRC E-43: Final Report*.

[3] Burtscher, H. (2005). Physical characterization of particulate emissions from diesel engines: A review. *Journal of Aerosol Science*, *36*(7), 896–932.