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Application of a Portable FTIR for Measuring On-road Emissions

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ABSTRACT

The objective of this work was the development of an on-road in-vehicle emissions measurement technique utilizing a relatively new, commercial, portable Fourier Transform Infra-Red (FTIR) Spectrometer capable of identifying and measuring (at approximately 3 second intervals) up to 51 different compounds. The FTIR was installed in a medium class EURO1 spark ignition passenger vehicle in order to measure on-road emissions. The vehicle was also instrumented to allow the logging of engine speed, road speed, global position, throttle position, air-fuel ratio, air flow and fuel flow in addition to engine, exhaust and catalyst temperatures. This instrumentation allowed the calculation of mass-based emissions from the volume-based concentrations measured by the FTIR. To validate the FTIR data, the instrument was used to measure emissions from an engine subjected to a real-world drive cycle using an AC dynamometer. Standard analyzers were operated simultaneously for comparison with the FTIR and the standard analyzer results showed that most pollutants (NO_x, CO_2, CO) were within ~10% of a standard analyzer during steady state conditions and within 20% during transients. The exception to this was total HC which was generally 50% or less than actual total HC, but this was due to the limited number of hydrocarbons measured by the FTIR. In addition to the regulated emissions, five toxic hydrocarbon species were analyzed and found to be sensitive to cold starts in varying proportions. Finally, FTIR data was compared to results from a commercially available on-road measurement system (Horiba OBS-1000), and there was good agreement.

INTRODUCTION

In Europe there is a requirement for all cities to monitor and model their urban air quality. If European air quality targets are not met then action must be taken and in virtually every case of non-compliance, traffic-related pollution is responsible, especially in urban or industrialized areas [1-4]. To model urban air pollution, the mass emissions of road transport have to be modeled together with their dispersion. Traffic movement and emissions needs to be modeled on a second-by-second basis for incorporation in an air dispersion model that calculates the amount of pollutants present based on actual meteorological factors. To provide the dispersion model with emission data, the traffic model needs accurate information on the emissions of cars under different driving conditions. Normally this data is derived from legislated test cycle emissions data by applying various correction factors for speed. To improve the accuracy of these air pollution models, it is preferable to measure on-road vehicle emissions instead of deriving them from the legislated drive cycle data which may not be representative of real traffic conditions. Car manufacturers are continuously improving the emissions of their vehicles, especially with the latest EURO4 legislation in Europe. On-road testing is not part of the legislative process and therefore a vehicle is only subjected to the mild ECE15 drive cycle in Europe, and the slightly more aggressive FTP75 in the USA. It is not a legal requirement for the vehicle to maintain clean exhaust emissions outside the operating conditions needed to negotiate these standard drive cycles. Therefore a vehicle driven in real-world conditions where situations might require hard acceleration might not meet the legislated standards. Real-world on-road testing helps to ascertain this possibility.

It is widely accepted that legislated drive cycles such as the FTP75 and ECE15 underestimate emissions from cars under real-world conditions [5-9]. This is especially true for CO and HC but less so for NO_x [10,11]. Vogel et al. [10] found that CO emission factors were increased by a factor of two in real life. De Vlieger's [11] results

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(*) E. T. S. de Ingenieros Industriales, Universidad de Castilla-La Mancha, Spain were more extreme having determined CO to be four times, and HC+NO_x to be twice, the legislated levels for a EURO1 vehicle in real-world driving. Real-world emissions depend on many factors such as driving behavior, traffic conditions, weather and ambient temperature conditions, vehicle model, fuel used, traffic conditions and network geometry [6]. Hence it is unrealistic to predict atmospheric pollution from emission factors obtained from the standardized legislated drive cycles. Correction factors may be applied for various parameters but in the end it is much better to measure actual real-world emissions in real traffic flow conditions Also, if a city is to reduce emissions from traffic in order to control the air quality, it needs to know how emissions will be reduced as a result of traffic management measures. In-vehicle emissions measurement in real traffic conditions allows the impact of different traffic management measures on emissions to be directly determined.

The techniques developed in this study aim to address the shortcomings of rolling road dynamometer testing as conducted by most laboratories and emissions legislation bodies. The main limitations imposed by the use of a rolling road dynamometer are the limited acceleration rates possible (due to tire slippage) and the limited air flow rate around the car. In addition to the advantage of measuring exhaust emissions under real-world driving conditions, the technique also potentially permits the partial speciation of the emitted hydrocarbons so that toxic hydrocarbons such as benzene and 1,3-butadiene can be determined. The ability to measure individual HC components allows the calculation of the ozone forming potential (OFP) of the vehicle's emissions as well as indicating if any of the individual hydrocarbons are above any allowable health and safety limits.

PREVIOUS DESIGNS

The following is a literature review of the systems that have been proposed and used in the past for measuring real-world emissions.

REMOTE SENSING

Remote sensing was once considered by the EPA as the solution to the transport pollution problem. The plan was to install remote sensors across the US highways together with number plate recognition cameras and then issue fines to the polluting vehicles based on the amount of pollutants being produced. This was all too ambitious since this technique simply provides a 'snapshot' of the emissions of the vehicle in question as it passes through the remote sensor. This is obviously not an indication of the average level of emissions being produced by the vehicle and therefore it would be unfair to issue any fine based on this one 'snapshot' of emissions. The driver of an offending vehicle could simply let off the throttle as they passed through the sensor in order to avoid detection.

For determining emissions factors from road traffic in a Switzerland tunnel, Staehelin et al. [12] measured NO_x, CO and THC's at 5-minute intervals at the tunnel entrance and exit simultaneously. They also measured semi-volatile hydrocarbons using a GC-type Airmotec HC 1010 at 15-minute intervals. Air flow rate through the tunnel was measured with a Flowsic 400. Tracer SF_6 gas was injected at the tunnel entrance and then used to evaluate tunnel ventilation as well as the level of turbulent mixing at the tunnel exit using six sampling points on the periphery. Vehicle speed was also monitored in addition to the license plates. This tunnel study was one week long and provided information on tunnel ventilation as well as the necessary emissions factors to be used in air pollution prediction models.

In another 20-day remote sensing experiment, Vogel et al. [10] carried out a study on a stretch of German motorway to determine real-life emissions and compare those to data calculated from pollution models. VOC (Volatile Organic Compound) measurements were done by GC-MS at 55-minute intervals while NO, NO_x, CO and O_3 were averaged over 10 minutes. These measurements were done at various positions perpendicular to the highway (25m, 50m, 75m, 100m, 150m and 400m) and at various heights above the ground. It was found that pollution models correlated well (within error bars) with real-world measurements once the real traffic data (as opposed to modeled traffic data) was input into the models. The exception to this was CO where a discrepancy factor of two was found between real-world and predicted values.

ON-BOARD MEASUREMENTS

For large vans or buses, conventional engine test bed emission analyzers can be used with battery power packs to supply the power. However, such systems are difficult to fit into passenger car vehicles and more compact systems are required. Single component gas analysis systems are one approach. Sutela et al. [13] developed a fast response CO_2 sensor based on a miniaturized NDIR detector with a 5.6ms time constant. The problem with this sensor was the need for recalibration after ten minutes of operation due to the lack of a chopper wheel (continuous light beam experiences drift). Another proposed use for the CO_2 sensor was the determination of the air-fuel ratio when used together with a HEGO (Heated Exhaust Gas Oxygen) sensor. The HEGO determines the rich-lean bias and the CO_2 sensor determines the magnitude of the air-fuel ratio. This setup would provide a faster response time than the more commonly used UEGO (Universal Exhaust Gas Oxygen) sensor (5ms versus 30-100ms). Sutela et al. [14] later used this CO_2 sensor to make EGR (Exhaust Gas Recirculation) measurements during rapid transients. They observed EGR valve leakage at low loads and determined that intake and exhaust CO_2 readings must be made simultaneously to obtain accurate EGR information.

Hands et al. later modified this CO_2 [15] sensor to make a fast response (7ms response time) CO sensor. Under rich cold-start conditions the CO sensor allows a faster estimate of stoichiometry than the UEGO sensor. It can also be used to monitor air-fuel ratio on the rich side. Using this CO sensor, differences in cylinder to cylinder air-fuel ratios were also identified. However these ultra-fast response instruments are not required for real-world measurement, where a 1-second response would be adequate.

De Vlieger [11] developed an on-board system that was used in a Belgium investigation of 6 cars, 3 road types and 3 driving behaviors. The system consisted of NDIR for CO and CO_2, FID for THC's, and CLD for NO_x. These techniques are the measuring methods approved for legislation. Fuel consumption was accurately (1% within 0.5-60L/hr) measured. Exhaust flow rate was measured using the fuel consumption and calculated lambda value. Emission factor errors were within 10% for emissions compared to stationary equipment on a chassis dynamometer.

Honda and Nicolet also developed a system [16] that they used for measuring on-road emissions from a ZLEV (Zero Level Emissions Vehicle) car, which produces 1/10th the emissions levels of a ULEV (Ultra Low Emissions Vehicle) car. The system consists of two Nicolet FTIR detectors placed on the back seat of the car. One was used to sample intake air and the other sampled exhaust gases. It was shown in field tests [17] that the car was producing exhaust gases that were cleaner than the ambient intake air for some pollutants. The FTIR in this case was limited to measuring the gases of interest which were NMHC (Non-Methane HydroCarbons), NO_x and CO. Another challenge was the development of techniques that allow a 0.1ppm limit of detection (LOD). Multi-tube Nafion dryers were used to remove the water from the exhaust since it was decided that spectral corrections for the water cross-interference necessitated a tedious calibration procedure and the accuracy would suffer if water was allowed to stay in the analysis. A cell with a 10m path length was chosen to attain the 0.1ppm LOD. Spectral resolution was $0.5cm^{-1}$ and CO_2 cross interference was avoided by careful selection of analytical regions. The Mercury Cadmium Telluride (MCT) detector was cooled with liquid nitrogen for faster response. Cell pressure was kept constant at 700mmHg. It was found that the calculation of exhaust mass flow rate from the engine speed and fuel injection data was adequately accurate for the work [17]. Laboratory calibration was done in the ranges 0-2ppm Carbon, 0-20ppm CO and 0-2ppm NO. Excellent correlation was found between the FTIR-measured and actual propane, CO and NO. On the rolling road dynamometer, there was excellent agreement for CO and NO but not for NMHC since FID measures real THC's. The project probably has little practical applicability outside Honda's ZLEV since the measuring range is designed for a car producing ultra-low emissions.

Weaver et al. [18] developed the RAVEM (Ride-Along Vehicle Emission Measurement) system in order to accurately and repeatability measure NO_x, CO_2 and PM (Particulate Matter) on the road. The system is very much like the CVS (Constant Volume Sampling) system employed on rolling road dynamometers but it only samples a small fixed fraction of the total exhaust. To achieve proportionality, a stepper motor controls the throttle of the dilution air inlet based on pressure feedback signal from the exhaust probe thus making volume flow rate linearly proportional to the exhaust pipe flow rate. This is called isokinetic sampling and avoids the need for expensive equipment that measures the exhaust mass low rate. A FID was not used to measure THC's since that would have required heated sample lines. Therefore the system is limited to measuring CO and CO_2 by NDIR and NO_x by heated CLD. PM was gravimetrically measured on pre-weighed 37mm Teflon-coated borosilicate glass fiber filter papers. This system was tested on a refuse truck and found to correlate well with a rolling road dynamometer for CO_2, NO_x and PM. However this equipment will not fit in a passenger car.

Kihara et al. [19] developed an on-board system that measures and logs NO_x, fuel consumption and various other engine and vehicle parameters. Of note were the fast response ZrO_2 sensors used to measure NO_x (0-1000ppm) and air-fuel ratio (1-10λ). Fuel consumption was calculated from the inlet air mass flow meter and the inlet air conditions as well as the ZrO_2 lambda sensor. The other sensors were conventional pressure transducers and thermocouples. This set-up was installed on the passenger seat of a diesel vehicle and was monitored for over a year. NO_x emission patterns were found to correlate negatively with fuel economy. Seasonal influences on NO_x emissions were noted, with NO_x increasing during the lower humidity winter months. Compared to the standard CVS-bag method, the on-board system was found to be within 4% for NO_x mass emission and 3% for fuel consumption. This same NO_x sensor was used in the Horiba OBS-1000 system.

Gautam et al. [20] developed an OREMS (On-Road Emissions Measurement System) for use in heavy-duty diesel vehicles. They dubbed their system the MEMS (Mobile Emissions Measurement System) and it was capable of measuring NO_x and CO_2 over 30-second windows. This is too slow a response for resolving specific traffic movement influences on emissions. They sacrificed some CO and HC accuracy in order to maintain acceptable simplicity and size for the system. This decision was influenced by the fact that modern diesel engines produce very low CO emissions and any sample cell would have to be considerably long to provide the required CO resolution. Torque was calculated from engine speed and fuel quantity injected. The torque and engine speed were directly obtained from the engine ECU in the MEMS application. Exhaust flow rate was measured with a multi-port pitot tube sensor. The pressure difference across the device was measured by pressure transducers. Thermocouples were also placed to measure exhaust temperature. CO_2 was measured using an NDIR detector. A FID was deemed too dangerous to install on-board due to the He/H_2 bottle it requires. NO_x was measured with a zirconium oxide (ZrO_2) sensor and also verified with an electrochemical cell. Prior to drying the sample with a thermoelectric chiller, the sample gas was passed over a NO_x converter. This was done since a large portion of the diesel NO_x emissions is NO_2 and the sensor only measures NO. A GPS system was used to record vehicle speed and verify it against the ECU output. Based on standard FTP tests, the MEMS was found to be within 5% of laboratory measurements when measuring brake-specific emissions.

Vojtisek-Lom et al. [21] developed a portable on-board system to be utilized in heavy duty vehicles. They used NDIR for CO and CO_2, electrochemical cells for NO_x and O_2 and laser scattering detectors for PM. HC's were not considered since it was believed that only a fraction of the exhaust HC's reach the sample cell in gaseous form. Exhaust flow was calculated from engine operating data. Power consumption of the system was up to 15 Amperes and a backup battery capable of 1-minute power provision was also installed for cold starts. The sample line was 6m long, 6mm in diameter and unheated to avoid complexity and cost. Repeatability of the on-board system was found to be less than the bench equipment but fair correlation was established between on-board and bench measured NO_x and CO_2. Contrary to expectations, there were no problems with the response time of the electrochemical cells. PM measured on-board was validated against TEOM (Tapered Element Oscillating Mass) and gravimetric methods and the results were less than acceptable. More validation was recommended for the PM measurements. This system has been improved with HC analysis using NDIR [22].

PREVIEW (Portable Real-Time Emissions Vehicle Integrated Engineering Workstation) is an on-board emissions measuring system developed in-house by Ford and used by Nam et al. to calibrate an emissions model that provided output for use in a microscopic traffic model [23]. PREVIEW uses an NDIR for HC, CO and CO_2, and a UV (UltraViolet) analyzer for NO. Wet sample gas is used, therefore necessitating heated cells, sample lines and a separate power supply. Engine and vehicle data were obtained directly from the PCM (Powertrain Control Module). The detection limits were 38ppm for CO, 10ppm for HC (as propane), 10ppm for NO and 200ppm for CO_2, which means it would not be suitable for measuring low load conditions on a low emissions modern vehicle. The whole system weighed ~70kg and could be fitted on the back seat or in the trunk of a vehicle. Correlation with standard equipment on a dynamometer, using a 1997 sport utility vehicle driven over a US06 drive cycle, was very good.

Sensors Inc.'s previous experience helping Ford develop the PREVIEW system allowed it to develop the SEMTECH [24]. The SEMTECH-G (gasoline) and SEMTECH-D (diesel) were used by the EPA to generate data for facilitating the development and validation of a new generation of mobile emissions model called MOVES. The 36kg SEMTECH-D uses a heated sampling system where the lines, filter and pump are kept at 195°C to avoid HC condensation. NDIR is used for CO and CO_2, while a NDUV (Non Dispersive Ultraviolet) is used for NO and NO_2. Engine and vehicle data is obtained from the vehicle data port directly and a GPS is used to track position and speed. The 20kg SEMTECH-G is similar to the diesel model but it uses NDIR for THC measurements, with the heated FID being optional. The reasoning behind this is that gasoline produces a lot of hexane which has strong infra-red absorbing properties and does not condense at ambient temperatures, A heated sampling system is not used in order to reduce power consumption. NDUV is used to only measure NO since NO_2 is negligible in gasoline vehicles. Engine and vehicle data is obtained using the OBDII connector and a GPS is also used. Both systems are said to have a detection limit and uncertainty of 50ppm [24]. Correlation with rolling road dynamometer CVS is excellent.

Hawirko et al. developed an on-board emissions measurement system using a Vetronix PXA-1100 5-gas analyzer with a built-in sample handling system, a wide-band lambda sensor, a hot-wire Siemens mass air flow meter, and temperature probes for coolant, ambient and inlet temperatures [25], All parameters were logged on a laptop computer at an average of 1.5Hz along with engine and road speed. The analyzer used NDIR for HC, CO and CO_2, and electro-chemical cells for NO_x and O_2. The system was later used to investigate the relationship between ambient temperature and emissions [26]. In this later study, 2- and 3-factor emission models were developed and compared to other one-factor emission models currently in use.

North et al. have developed an on-board emissions system called VPEMS (Vehicle Performance and Emissions Monitoring System) [27]. This uses a Nafion impregnated tube to dry the exhaust sample before introducing it into a commercially available 5-gas analyzer. This analyzer uses NDIR for CO, CO_2 and HC, and electro-chemical cells for O_2 and NO_x. Engine and vehicle performance data is obtained from the CAN bus. On post-2001 European market cars this is possible via the standardized OBDII link, but on older cars it can be much harder. This data was then used to convert the concentration data from the analyzer into mass-based emissions. A GPS was incorporated and all sampling was done at about 1Hz. The VPEMS was referenced against a rolling road dynamometer CVS measure, and compensation factors were derived for all pollutants. Compared to bag results, the VPEMS aggregate mass emissions were off by 11% for CO, 8% for CO_2 and 17% for NO_x for the standard European drive cycle.

APPARATUS DESIGN

DESIGN REQUIREMENTS

For an on-board system to be successful, it must have the following properties:

- Low energy consumption, which limits the power supply options
- Robustness for vibration, which limits analyzer principle
- Fast response needed for modal analysis
- Wet measurement (hot sample gas) must be used otherwise condensable hydrocarbons would be lost. Condensation and removal of water could slow the response time and consume energy.

The US EPA also have their own set of guidelines outlined in US EPA Title 40 CFR part 1065 subpart J regarding on-road measurements. Subpart J is specific to field testing of vehicle emissions. It specifies requirements for the various analyzers and equipment needed to calculate brake-specific emissions from engines while they remain installed in vehicles.

EXHAUST FLOW MEASUREMENT

One of the more critical measurements to be made for the conversion of volumetric emissions measurements into mass is the exhaust mass flow rate. It is not much use measuring the emissions from a car only on a volumetric basis. To make any meaningful comparison between different cars of different weights and engine sizes, the emissions on a mass basis must be calculated. Emission Index (EI) is often used (g emission/ kg of fuel) which can be calculated from the volumetric measurements and the air-fuel mass ratio (computed by carbon balance from the exhaust gas analysis or measured directly) [6]. The equation used is:

$$EI = K * C * (1+ A/F) * 1000 \text{ g/kg fuel}$$

- K is the ratio of molecular weight of the component to the molecular weight of the whole sample gas. The molecular weight of the sample gas is close to that of air and does not vary more than 1% for H/C ratios of about 2 (i.e. gasoline), irrespective of the air-fuel ratio. For this reason, K is a constant and is 0.554 for THC (methane equivalent), 0.968 for CO, 1.590 for NO_x (taken as NO_2) and 1.521 for CO_2.
- C is concentration of the component. If this is measured in ppm or % then the equation has to be multiplied by 10^{-6} or 10^{-2} respectively
- A/F is the air fuel ratio on a mass basis determined by wet based carbon balance or measured using lambda sensor

Another unit used in legislation is (g emission/km). The g/km and EI units are related by the fuel consumption of the car and this was directly measured in the present work.

SOURCE OF POWER

The power needed for the on-board measuring system is around 1200 Watts and this would necessitate drawing up to 100 A at 12V from the car's electrical system. That would have required an upgraded alternator and increased the load on the engine, therefore affecting the emissions characteristics. Another possibility was to use a small dedicated generator but that option is only possible in large heavy duty vehicles. The only feasible option was to use two battery packs providing a total of 24V which is then converted to 240V AC via an on-board DC-AC converter. The two batteries used weighed a total of 90kg and were installed where the front passenger seat would normally be. They provided approximately 2-3 hours of operation before needing recharging.

SAMPLE CONDITIONING

In order to measure wet concentration, the raw undiluted sample gas extracted from the exhaust system had to be maintained at about 190°C otherwise some pollutants would drop out due to condensation. Furthermore, the extracted exhaust sample must be hot filtered so that the sample cell remains free of particulates which would contaminate it and shorten its lifetime. A sample handling unit was acquired to perform these functions. The sample handling unit uses a pump to continuously extract sample from the vehicle's exhaust system at a constant flow rate (~2L/min) via a heated line. This is then filtered using a 2 µm filter and introduced via another heated line into the sample cell of the FTIR. Both heated lines were controlled to 190°C by the sample handling unit. The sample handling unit consumes the most power since it performs heating and pumping functions. It was installed in the boot of the car along with the FTIR. The gas sample was taken downstream of the catalyst and the heated sample line was passed through a small hole in the car's floorpan. There was no possibility of dilution of the sample by pressure pulsations from the tailpipe.

MEASURING POLLUTANTS USING FTIR

The Temet Gasmet Fourier Transform InfraRed (FTIR) Spectrometer was used to measure on-road, real-world emissions from the vehicle. The model used, the CR-series is normally used for making ambient air measurements. This is capable of measuring concentrations as low as 0.5-3 ppm, depending on the application. The FTIR manual claims that accuracy is 2% of the measurement range and precision is 0.01% of the measurement range. Diatomic molecules such as N_2, O_2, H_2 and Cl_2 do not absorb infrared radiation and therefore cannot be measured using the FTIR. The same applies for noble gases such as He, Ne, Ar and Kr. H_2S absorbs very little radiation and is therefore not detectable at levels less than 200ppm.

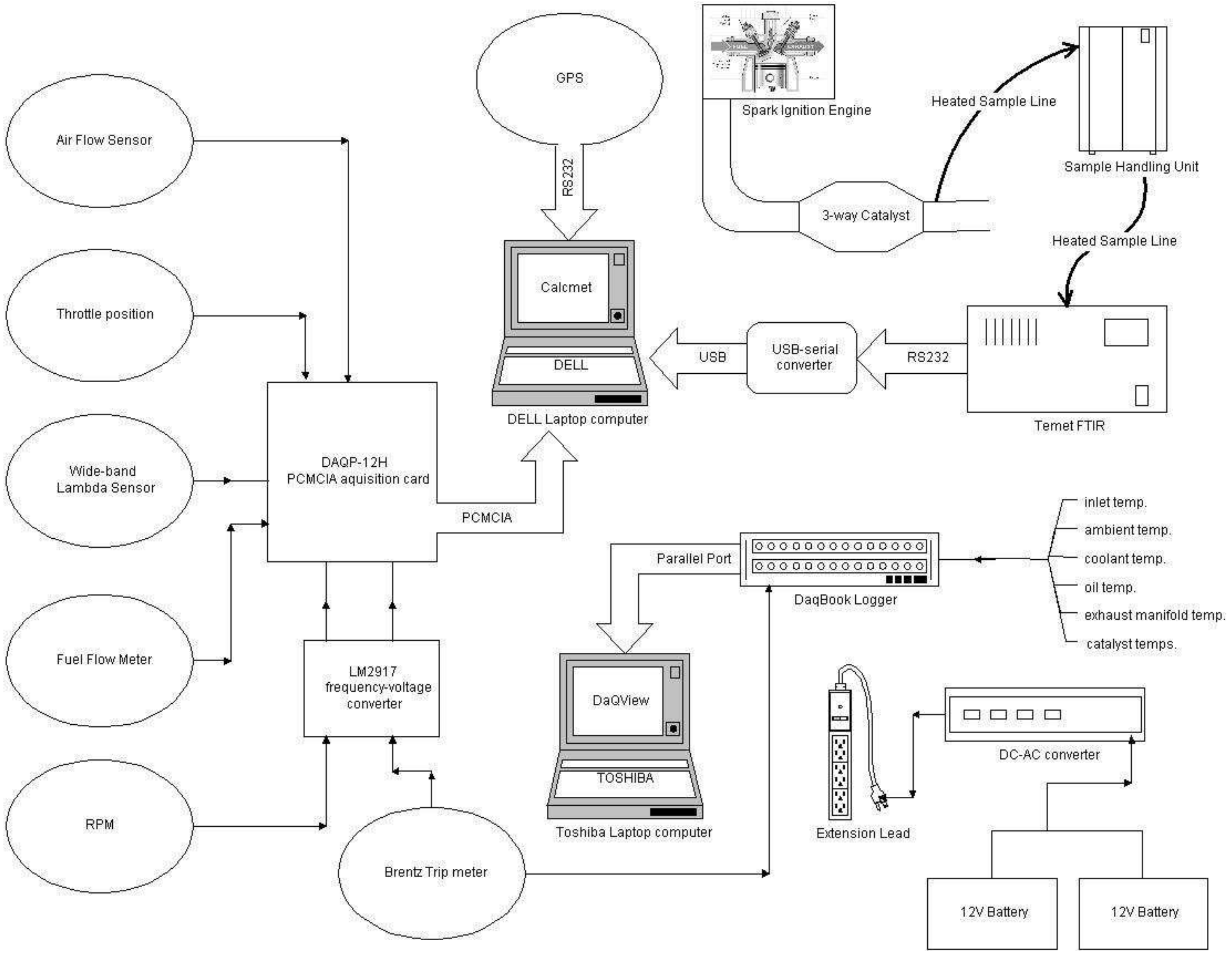

Figure 1: Block diagram of on-board system

An FTIR was chosen because of its ability to speciate hydrocarbons and NO_x. With lean-burn engines, the output of NO_2 increases relative to NO_x, and most of the current on-board systems cannot measure NO_2 and NO simultaneously. Another reason for the FTIR is the need to measure certain toxic hydrocarbons that are of interest to health-related studies.

The FTIR measuring principle is as follows: An infrared (IR) source produces a broad band IR radiation which is modulated by an interferometer. The interferometer performs an optical inverse Fourier transform. The modulated IR radiation passes through the sample cell, where sample gas absorbs certain wavelengths of the IR radiation. The detector detects the transmitted radiation and the signal is digitized. A computer then performs a mathematical Fourier transform on the digitized modulated signal and an absorbance spectrum is obtained. This spectrum is then compared to a background spectrum made initially before the measuring commenced. The Calcmet software then determines the concentrations of the components present based on absorption data from previous factory-performed gas calibrations. All the major species in the engine exhaust were included in the unique 51-species calibration performed by Temet for the particular instrument used in this work. A table of the measurement components and their ranges are included in the appendix. The Temet FTIR gives a warning if the calibrated compounds do not account for the observed infrared absorption in the spectra, indicating that a significant species was present that had not been calibrated for. This was not a significant problem in the present work.

Unlike traditional FTIR analyzers that use a Michelson interferometer, the GASMET uses a Carousel interferometer which is more rugged and stable [28] because its modulation is independent of any deformation or bending of the interferometer mount. The instrument is calibrated to measure up to 51 gas compounds simultaneously and has a response time of 2-10 seconds depending on the sample flow rate and number of compounds being analyzed. Furthermore, unlike traditional bench FTIR's, the GASMET has a low resolution of 8 cm^{-1}. This results in a better signal-to-noise ratio while providing enough resolution to distinguish most compounds using the Calcmet software.

The software uses a modified CLS (Classical Least Squares) algorithm for the multi-component analysis [29]. This algorithm is adequate provided that the number of data points in the spectral region used for the analysis is twice the number of analysis components. This means that for 50 components at 8 cm^{-1} wavenumber resolution, a minimum $800cm^{-1}$ of spectrum is required for the analysis. This condition is satisfied as the recorded spectrum in this instrument covers 900-$4250cm^{-1}$.

The detector is a liquid nitrogen cooled MCT (Mercury Cadmium Telluride) detector that scans 10 spectra per second. To enhance signal-to-noise ratio (SNR), several scans are co-added to produce a time–averaged spectrum. The SNR increases proportionally to the square root of the number of scans. Due to this averaging of spectra, the actual output interval is only 2-3 seconds. The multi-pass, gold-coated sample cell has a path length of 2m, a volume of 0.22 L and is maintained at ambient pressure and 190℃. The choice of path length and volume represents a compromise between a long path length for increased accuracy and a short path length for shorter response time. Whilst 2-3 seconds is not ideal for detailed modal emissions studies, it does provide adequate resolution for most applications. The response time will be improved in future with the shortening of the heated sample lines and the increase in the flow rate of the sample. New software will also be developed by the manufacturer in order to improve output time interval.

The Calcmet software has the additional capability of accepting analog inputs which can be logged together with the emissions spectra and analysis data. Some of these analog inputs were used to log road speed, fuel mass flow, air mass flow, throttle position, air-fuel ratio and engine speed. This then allowed the FTIR volumetric output to be converted to EI (g/kg) and g/km. The total hydrocarbons were not measured, but calculated by summing the 30 HC's identified in the analysis.

OTHER EQUIPMENT

Fuel flow

In addition to the FTIR and the sample handling unit, in the boot of the car is a fuel flow measuring device from Max Machinery Inc. This measures the fuel mass flow rate using a level controlled recirculation tank, transfer pump and a high-resolution flow meter. The pump maintains a constant pressure to the recirculation tank which feeds fuel to the engine. This recirculation tank collects return fuel from the engine and recirculates this fuel back to the engine instead of returning it to the fuel tank. This recirculation loop allows the use of a single meter to measure make-up fuel as it replaces the fuel consumed by the engine. Total fuel consumption was determined to better than 1% accuracy and the rate of fuel consumption was determined with a 1-second resolution. The device has an analog output which is logged on the same laptop computer used for the FTIR.

Temperatures

A DaqBook data acquisition unit was installed in the car in order to measure and log the output of the 27 K-type thermocouples attached to the various points along the exhaust and the vehicle. These outputs are recorded along with road speed on a separate laptop computer to the one being used for the FTIR. More details about the probe locations are reported by Andrews et al. [6].

Although the Temet FTIR instrument itself weighs only 21kg, the entire system as described in this paper weighs a total of ~180kg. The heaviest items are the batteries at 45kg each and the MAX fuel flow meter at 32kg. This weight is probably causing an increase in emissions as it is equivalent to carrying at least two passengers.

CALCULATIONS

Since the FTIR only measures gaseous emissions on a volumetric basis (concentration in ppm or %vol) some calculations must be performed to report the results in the requisite g/km unit. This is done by using the fuel flow rate and the air-fuel ratio. Using the equations described by Andrews et al. [6], the emission index (EI) can be calculated for each of the components under consideration. The unit of EI is (g pollutant/kg fuel). After the EI for each compound has been calculated, then the fuel flow rate is plugged into below equation giving the resulting g/s:

- Emission (g/s) = Emission EI (g/kg fuel) x Fuel flow rate (kg/hr) /3600

After calculating the emissions in g/s, the results were integrated using the trapezoidal method in order to obtain the total grams for the drive cycle. Finally, these results were divided by the drive cycle distance in order to obtain g/km for each pollutant. The instantaneous emissions could be displayed as g/kg or g/s.

VALIDATION DATA

Before any experimentation was conducted using the FTIR, a series of validation tests were performed in order to quantify the accuracy and precision of the FTIR measurements compared to the Horiba MEXA-7100D, which is an industry-standard analyzer that uses NDIR, FID and CLD for CO_2/CO, THC and NO_x respectively. Validation was done in three stages. First the FTIR was used to measure steady state emissions from a calibration bottle in addition to an operating engine. Then an AC dynamometer was used to test transient response, and finally for the third stage the FTIR was installed simultaneously in-vehicle with a Horiba OBS-1000 on-board sampling system. The OBS-1000 is a commercially available system specifically designed for installation in a vehicle [30]. The OBS uses hot NDIR capable of measuring CO and CO_2 under wet-based conditions (sample cell kept at 120°C) by correcting interference from co-existing gases with a specially developed algorithm. This system has been validated against CVS tests and found to be within 7% for fuel consumption, 5% for CO mass emission and 6% for CO_2 mass emission [30]. Exhaust flow is measured using a pitot tube attached to the tailpipe of the vehicle. THC's are also measured using the hot NDIR, but a correction factor of 1.66 is applied since NDIR uses the absorption intensity of infrared, which is not always proportional to the number of carbon atoms in hydrocarbons. NO_x and air-fuel ratio are measured using a heated ZrO_2 type sensor attached on the tailpipe. Velocity and position are obtained using a GPS.

STEADY STATE VALIDATION

Steady state validation involved measuring the concentrations of various calibration bottles with $CO/CH_4/NO/CO_2/N_2$ mixtures at exhaust concentration levels. Table 1 lists the results obtained from the FTIR alongside those from the MEXA-7100D and the actual certified values. The MEXA-7100D results are for an instrument calibrated on a different calibration bottle. The Temet FTIR calibration only involves zeroing the instrument using nitrogen gas. The species calibration was undertaken by Temet for 51 species and recalibration is not necessary unless any of the instrument's hardware is changed.

Table 1: Calibration bottle #1

	Certified values	*MEXA-7100D*	*Temet FTIR*
CO (ppm)	4900	4990	5324
CO_2 (%)	14.50	14.00	13.86
Methane (ppm)	1509	1594	1432
NO (ppm)	1451	1403	1456

Compared to the certified values, the FTIR is within 9% for CO, 6% for CO_2, 5% for methane and 0.5 % for NO. With the exception of methane, these results were deemed acceptable as they are close to the 2% of measuring range error claimed by the manufacturer. The measuring ranges are listed in the appendix. CO was within 3.3% of measuring range, CO_2 within 0.5%, methane 16% and NO 2.6%. One possible reason for the excessive methane deviation is that the measurement being made exceeded the maximum methane calibration (995ppm) of the instrument.

A different bottle containing only two species was also tested and the results shown in table 2 were also acceptable, with CO being off by 0.5% and CO_2 by 5.5%. In this case, CO was within 1% of measuring range and CO_2 within 2.1%.

Table 2: Calibration bottle #2

	Nominal values	*MEXA-7100D*	*Temet FTIR*
CO (%)	1.50	1.50	1.51
CO_2 (%)	10.0	10.1	9.46

Another steady state test condition was an actual sample of exhaust gas obtained by running an engine at a steady state load of 8 kW and 2500rpm on an engine dynamometer. Figure 2 shows good agreement for CO_2 except that the FTIR readings are more noisy. The MEXA results were corrected to wet because the MEXA removes water before introducing the sample to the NDIR analyzer while the FTIR samples wet exhaust. The FTIR reading is oscillating around the 13.2% mark while the MEXA is steady at 12.8%. All sampling was done immediately downstream of the catalyst.

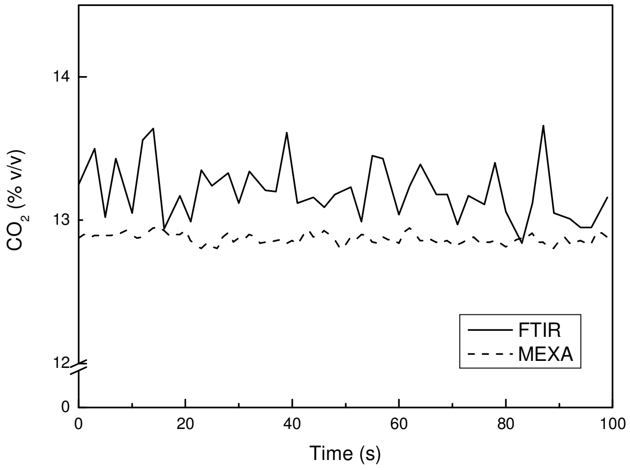

Figure 2: Steady state CO_2 comparison

Figure 3 shows CO measured by the FTIR following the MEXA well but missing the peaks that the MEXA detects. Just like CO_2, the MEXA CO results are corrected to wet for the sake of comparison with the FTIR.

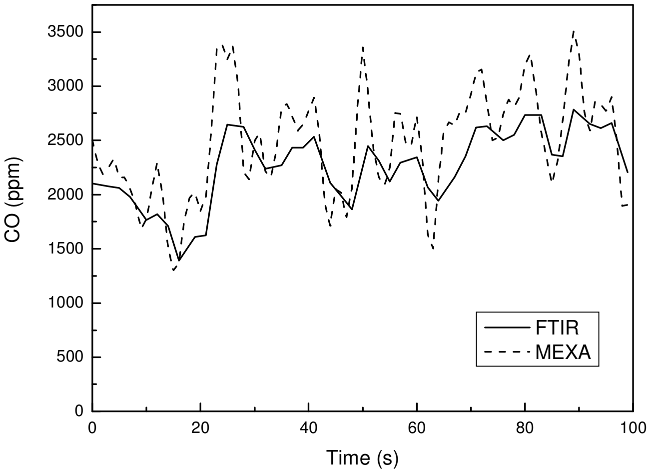

Figure 3: Steady state CO comparison

Figure 4 shows that the NO_x measured by the FTIR is higher than that measured by the MEXA. It can also be seen that the FTIR has a slower response time and cannot detect the fast changes in NO_x.

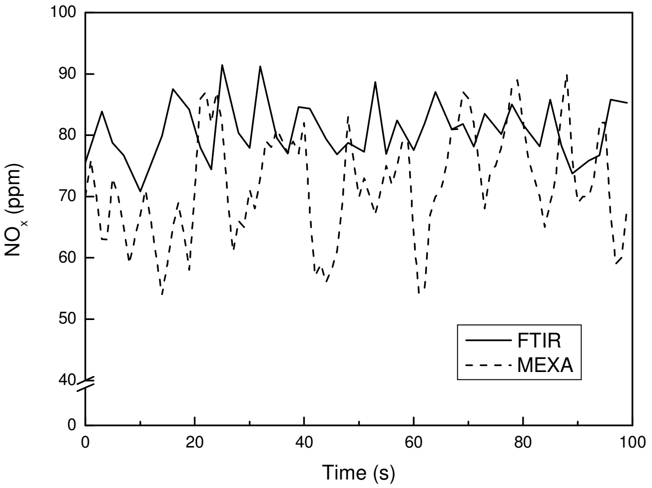

Figure 4: Steady state NO_x comparison

As expected, Figure 5 shows that the FTIR measured THC does not agree with the MEXA measurements. This is because the MEXA is a true total hydrocarbon analyzer and counts the number of carbon atoms using the FID technique, while the FTIR simply sums all the hydrocarbons it has identified in its analysis. This FTIR is calibrated for only 30 hydrocarbons, whereas there are typically ~160 present in exhaust gas [31]. It appears that a correction factor of approximately three needs to be applied to the FTIR readings if they are to agree with MEXA's total HC measurements. However, this factor may vary with the level and characteristics of the THC's and therefore no correction was applied to any data reported in the present work. The key advantage of the FTIR is to determine individual toxic HC's online, as will be demonstrated later.

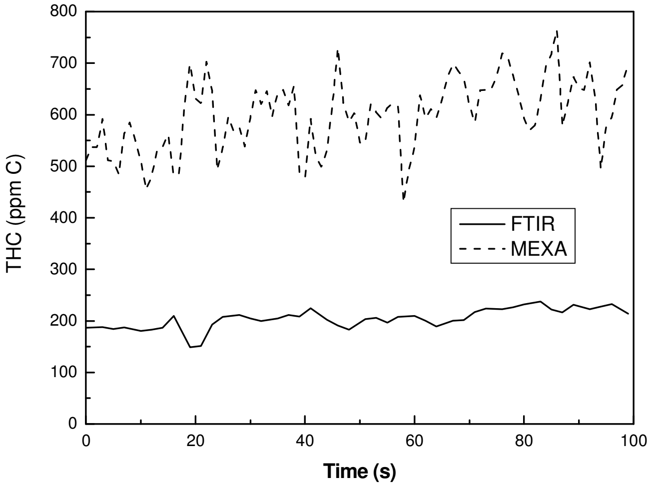

Figure 5: Steady state THC comparison

Table 3 summarizes the results from the steady state engine experiments and calculates the resulting error. The results reported in this table are the average readings taken over the 100 second sampling time. The error is substantial for the THC but the other components are well within the accepted limits of 20%. Possible causes of the discrepancy are the slow response time of the FTIR in addition to potential interference from other co-existing components including water. Error in the factory gas calibrations of the instrument is possible but unlikely.

Table 3: Steady state engine MEXA vs FTIR

	MEXA-7100D	*Temet FTIR*	*% Error*
CO (ppm)	2568	2260	-12
CO_2 (%v/v)	12.8	13.2	+3
THC (ppm)	599	205	-66
NO_x (ppm)	72	81	+13

TRANSIENT VALIDATION

Transient validation measurements were made in order to investigate whether the FTIR maintains its accuracy during real-world testing. To do this, the instrument was installed on a test-bed engine which is attached to an AC dynamometer. This computer controlled engine dynamometer uses an AC motor to load and power the engine so as to simulate real-world drive cycles. A real-world drive cycle was chosen which included hard accelerations in addition to normal everyday driving. Along with road speed, Figure 6 plots engine speed, torque and throttle position versus time for three different runs using the AC dynamometer. This is to show that the repeatability of the dynamometer is excellent. The three lines in Figure 6 overlap most of the time, and that is why only one solid is visible. Consequently, this means that emissions data can be compared from different experiments as long as the initial engine conditions are the same.

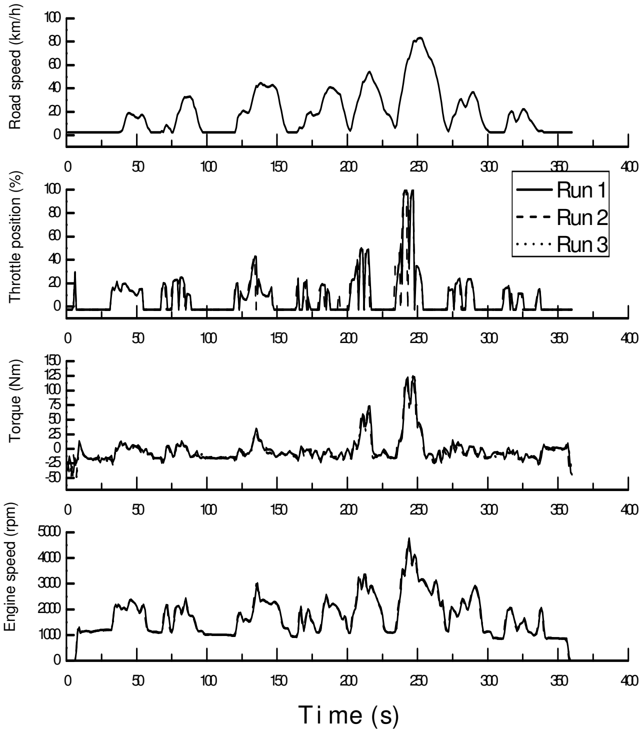

Figure 6: AC dyno repeatability

Figure 7 shows the CO_2 concentration from the FTIR and the MEXA overlaid. It appears reasonable to conclude that the FTIR follows the MEXA trend well but tends to slightly underestimate. The dry CO_2 readings from the MEXA were corrected to wet assuming a 12% water concentration in the exhaust, which is reasonable for stoichiometric operation [32]. It must be noted that this stage of the validation was done upstream of the catalyst in order to subject the FTIR to the worst possible conditions that can be experienced on the road.

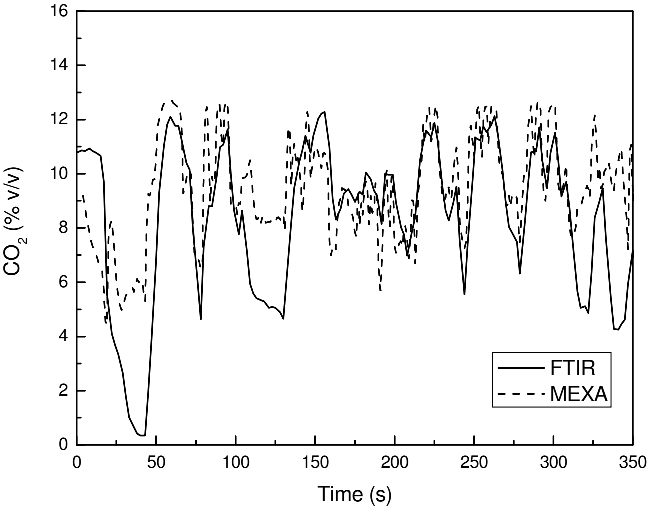

Figure 7: FTIR vs. MEXA for CO_2

Figure 8 shows the CO results from the FTIR are close to the MEXA. Figures 7 and 8 show that the FTIR has a slightly lower response than the MEXA-7100D, both readings having been corrected for the sample dead time due to the sample line length (as these were different for the two instruments). There are transients which are measured by the MEXA but not by the FTIR. To study these in detail, Figure 9 enlarges a 20-second section of Figures 7, 8, 10 and 11 in order to show the differences in response time for the MEXA and the FTIR. It can be seen from Figure 9 that the MEXA will respond in as little as 1 second whereas the FTIR needs at least 2 seconds and usually up to 4 seconds in order to measure a sudden change in emissions. This causes the FTIR to miss transients that last for less than 2 seconds. Also noticeable is the longer time required by the FTIR to recover from measuring a peak. This causes the total emissions to be slightly higher than they would be when the integral is calculated.

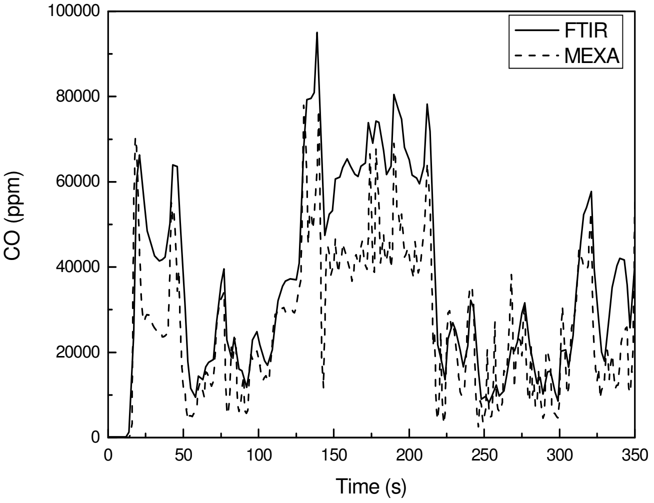

Figure 8: FTIR vs. MEXA for CO

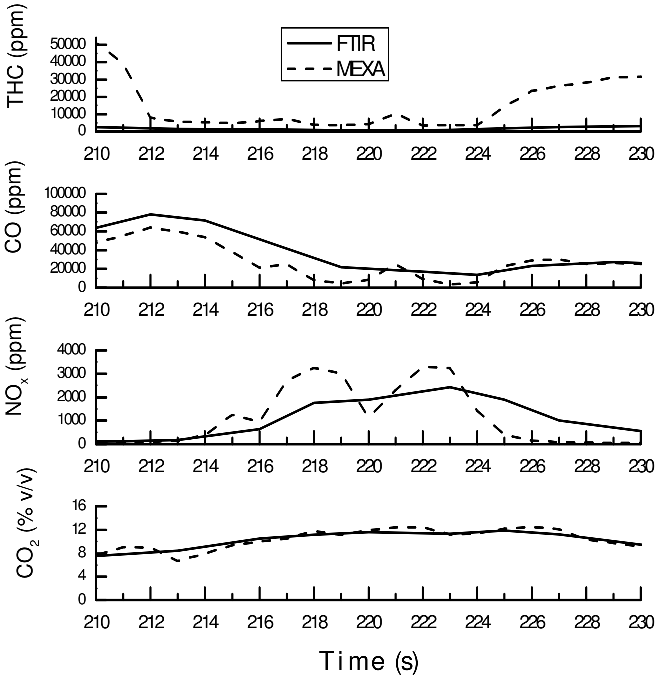

Figure 9: Detail of MEXA–FTIR response

Figures 10 and 11 plot NO_x and THC respectively. The MEXA-measured NO_x peaks are slightly higher than the FTIR readings, but this is probably a result of the FTIR's slower response time preventing it from measuring these momentary spikes in NO_x.

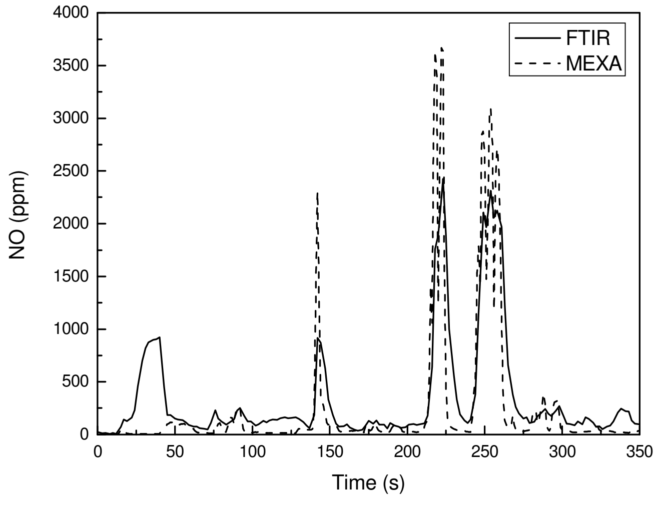

Figure 10: FTIR vs. MEXA for NO_x

THC measured by the MEXA counts every C atom in the sample, whereas the FTIR sums all of the hydrocarbons being analyzed to derive the THC (as methane equivalent). For this reason, the FTIR reading was expected to be a gross underestimation and Figure 11 confirms this. Had more HC components been analyzed for, then the FTIR reading might have been closer to the MEXA reading.

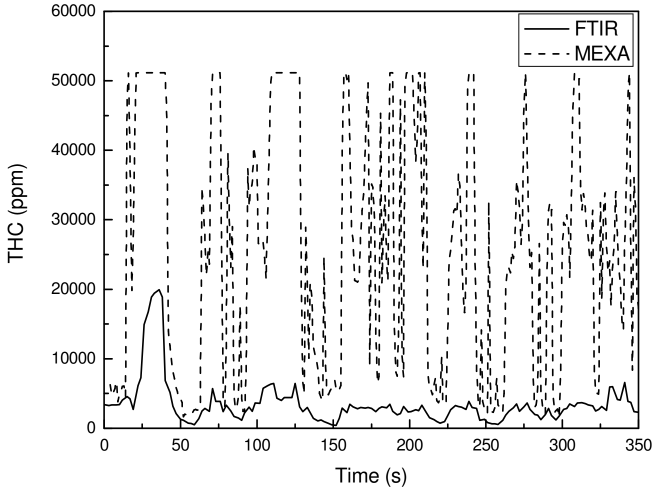

Figure 11: FTIR vs. MEXA for THC

The results from this transient validation were not as good as for steady state validation but they were still within acceptable limits (20%) apart from THC.

REPEATABILITY

To test the repeatability of the FTIR, two separate runs were made using the AC dynamometer (which had proven to be very repeatable). These two plots were overlaid for each of the four components measured. Figure 12 shows the CO_2 results and it can be seen that the repeatability is very good.

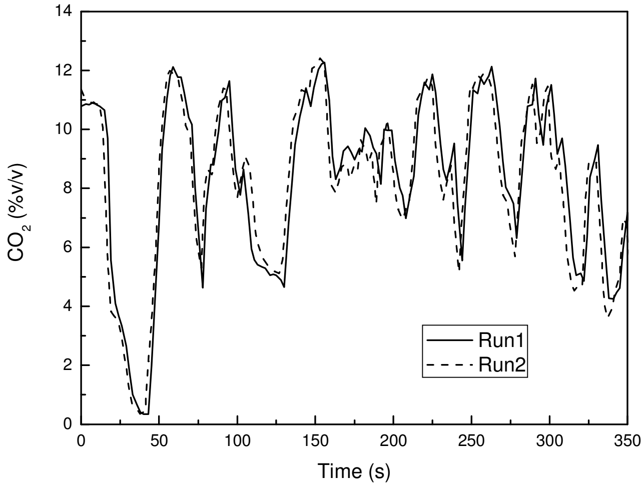

Figure 12: FTIR CO_2 repeatability

Figure 13 shows the CO repeatability. Again as with CO_2, the repeatability is very good. The same can be said for THC shown in Figure 14 and NO_x in Figure 15.

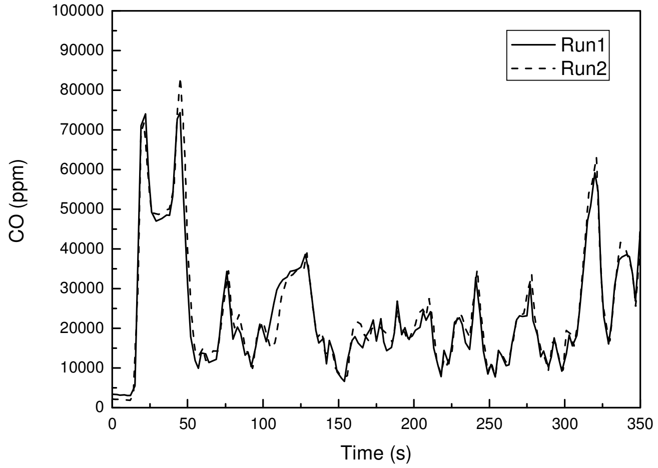

Figure 13: FTIR CO repeatability

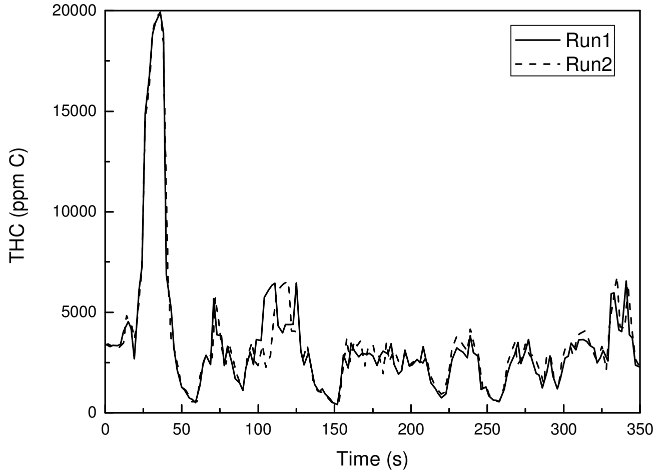

Figure 14: FTIR THC repeatability

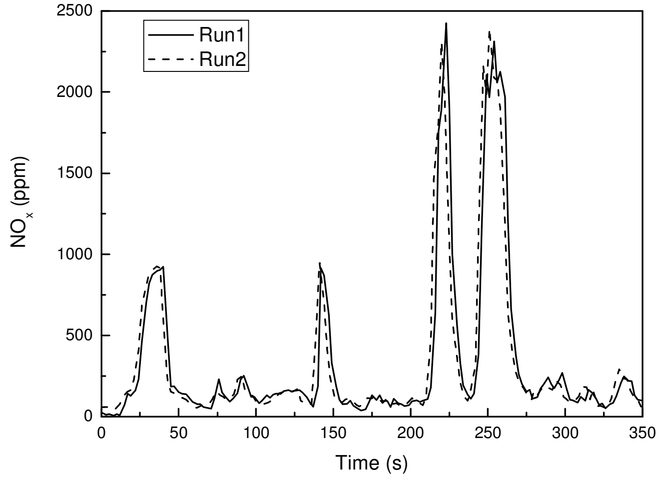

Figure 15: FTIR NO$_x$ repeatability

ADVANTAGES OF FTIR

One of the major factors why an FTIR analyzer was chosen for use in this system was its ability to differentiate between various hydrocarbon species in a gaseous mixture. The US EPA has identified 21 mobile source air toxics, including toluene, benzene, formaldehyde, 1,3-butadiene, acetaldehyde, and diesel particulate matter, all of which can cause cancer or other serious health problems [33]. Figure 16 plots the more important hydrocarbon species that are measured by the US EPA when assessing air quality. This is simply to demonstrate that the FTIR has the potential to be a very useful instrument in any work involving toxic emissions. The drive cycle used for these graphs was a cold start Leeds LU-UDTC [6], and it must be noted that the magnitude of the results should not be considered accurate because validation of the instrument's speciated hydrocarbon components has not been done yet. Future work will involve comparing the output of the FTIR to a standard GC-MS and a CI-MS (Chemical Ionization Mass Spectrometer).

All the hydrocarbons in Figure 16 show a dramatic drop after the first 200 seconds of the drive cycle. This is typical of a cold start. Formaldehyde seems to be less affected by the cold start than the others since it is dependent on oxygen availability, which is not present under the rich cold start conditions. After 200 seconds a combination of the catalyst lighting off and the ECU leaning the mixture to stoichiometric brings the emissions down to reasonable levels.

Another useful application of the FTIR is the speciation of nitrogen-containing compounds such as NH_3, NO_2, NO and N_2O. This is shown in Figure 17. N_2O concentration peaks at around the 180s mark because catalyst temperature at that point is just under 300°C, which is a temperature conducive to N_2O production. NO and NO_2 have very similar trends but the NO_2 scale is approximately 2% of the NO scale. This is typical for spark ignition engines which do not produce as much NO_2 as diesel engines. The ammonia peaks seem to correspond to the NO_x peaks which correlate with high power situations. A rich excursion would normally result in some NH_3.

Even though the FTIR hydrocarbon measurements have not been validated against a GC-MS, preliminary comparisons made with previous literature are encouraging. Most of the species measured by the FTIR have also been detected by other researchers [34-36] in exhaust emissions using traditional bag sampling and GC or CI-MS. The major FTIR-measured species like benzene, alkyl-benzenes, methane, toluene and xylenes are in reasonable proportions to each other when compared to the literature data. The absolute quantities are not quoted since validation work on the FTIR has yet to be conducted.

OBS-1000 VS. FTIR

As a final validation, the FTIR was installed simultaneously with a commercially available on-board measuring system, the Horiba OBS-1000 [30]. Although data from various drive cycles was obtained, the only data reported in this paper will be from a cold start Leeds LU-UDTC. This drive cycle is an urban 1.5km loop described by Andrews et al. [6]. There are two right hand turns and four left hand turns in the cycle. There is also a 300-meter long steep downhill section followed immediately by a similar uphill section. This is where the highest engine loads are experienced. There are at least three first gear starts from a complete stop and sometimes more depending on the traffic conditions. Figure 18 shows the CO_2, CO, NO_x, THC and exhaust flow results from the OBS and FTIR plotted on the same graph. The CO_2 measured with the OBS is lower in places due to the exhaust sampling point at the tailpipe entraining ambient air so that dilution takes place. This mainly occurs at idle speeds when the air mass flow is measured too high by the OBS. There also appears to be some dilution of the CO_2 at idle. The THC, CO and NO_x measurements are very close between the OBS and FTIR and for this reason the two lines plotted in Figure 18 appear to be one solid line.

Figure 19 plots the cumulative mass emissions for the various gases measured by the FTIR and the OBS. There is very good agreement for CO and CO_2. Total THC measured by the FTIR was not expected to agree with the OBS, with the plot showing that the OBS measures higher than the FTIR by almost a factor of three. The large discrepancy in total NO_x is not due to any inaccuracies in the FTIR measurements, but rather the longer sampling interval of the FTIR (2-3s) compared to the 1 second interval of the OBS. The larger time interval of the FTIR means NO_x peaks are not as high as those detected by the OBS, and therefore when the instantaneous NO_x emissions are numerically integrated, some accuracy is lost. This time factor did not affect total CO and CO_2 as much as NO_x because the fluctuations in the instantaneous mass emissions for those gases were not as high as for NO_x. Once the FTIR software is modified to sample at shorter time intervals then the total NO_x will be closer to the value measured by the OBS.

In order to study the step throttle changes, Figure 20 zooms in on a 20-second section (210-230s) of the drive cycle. What is most noticeable is that the OBS detects the spikes in the sample whereas the FTIR tends to smooth out these spikes.

The main discrepancy between the OBS and the FTIR was the THC, as expected. This is because the FTIR simply sums all the hydrocarbons that it has identified in order to come up with a value for THC. The OBS on the other hand uses a NDIR cell to measure the infrared absorption of the THC. A correction factor of 1.66 is then applied in the OBS software in order to obtain true THC values. A similar correction factor is needed for the FTIR's THC readings, but one was not applied in the present work. Both THC's are based on a hot wet sample.

Comparison of exhaust flow measurements obtained from the OBS and the FTIR were made. The OBS uses a pitot tube at the tailpipe while the FTIR setup uses an air flow sensor and a wide-band lambda sensor to calculate the exhaust flow. Figure 18 shows the two exhaust flows plotted side by side. The trend is very similar but the only major discrepancy is that the OBS measured a higher exhaust flow rate at idle. Once again the reason for this is strong engine pulsations at idle. This does not affect the total emission results because of the low magnitude of emissions at idle and the low exhaust flow at idle. It was found that to reduce this erroneous exhaust flow reading, a small extension tube should be installed after the pitot tube. Adding a small 100mm extension to the tailpipe reduced exhaust flow rate at idle from ~430 L/min to ~280 L/min as measured by the OBS on the same vehicle used in this work, under similar ambient conditions. This was not discovered until after the present work had been completed.

Since the exhaust flows match up well, then it is expected that the total emissions will also agree. This is shown in Table 4 where the total emissions from the OBS and the FTIR are compared for this particular LU-UDTC drive cycle. Also listed in this table are the EURO1 (1992) emissions standards for passenger vehicles. Agreement is not too good because the EURO1 drive cycle allows a 40-second warm-up period before emissions are measured and also includes the EUDC (Extra Urban Drive Cycle). Emissions for this work were measured from the moment the engine started. Furthermore, the real-world drive cycle has more transients than the legislated test cycle. Another contributing factor is probably the well-aged catalyst being used in the current study, whereas the EURO1 data is for a fresh catalyst. The OBS is higher than the FTIR for CO_2 and NO_x. This could be due to the overestimation of the total exhaust flow at idle, so total idle emissions are overestimated. Also the difference in time responses will contribute to higher values for the OBS. The agreement on CO was very good. Both instruments clearly show that the real-world urban drive cycle had substantially higher CO, NO_x and THC emissions than the legislated drive cycle. These need to be taken into account in urban air quality modeling.

Table 4: Total emissions, FTIR vs. OBS

	OBS	*FTIR*	*EURO1 regulations*
CO_2 (g/km)	418	365	n/a
CO (g/km)	9.75	9.88	2.72
NO_x (g/km)	1.85	1.29	0.42*
THC (g/km)	1.08	0.40	0.55*

*EURO1 specifies a total NO_x+THC of 0.97g/km, but the EURO3 HC/NO_x ratio is listed for comparison

Table 5 lists the average EI results of the FTIR, OBS and bag sampling accumulated over a cold start LU-UDTC drive cycle. This bag sampling work was done by Andrews et al. [6] using the same vehicle driven over the same drive cycle. In these bag sampling tests, g/km were not reported since the fuel consumption measurement was not accurate enough to be used. There were some discrepancies in the speed-time profile since the traffic conditions during the FTIR/OBS testing were not as favourable as during the bag sampling. In addition, FTIR/OBS testing was done at 18℃ ambient temperature while the bag sampling data was only available for -2℃ and 32℃. The results shown in table 5 were corrected to 18℃ using graphs produced by Andrews et al. [6].

Table 5: EI for FTIR vs. OBS vs. Bag sample

g/kg fuel	*OBS*	*FTIR*	*Bag sampling*	*EURO1 regs.*
CO_2	4448	3889	2633	n/a
CO	104	105	83	34
NO_x	19.69	13.79	2.51	5.23*
THC	11.49	4.24	6.39	6.91*

*EURO1 specifies a total NO_x+THC of 12.14g/kg, but the EURO3 HC/NO_x ratio is listed for comparison

The on-board bag sampling system operates with water and higher boiling point hydrocarbons removed from the sample prior to the bag. This explains why the THC value of the bag sample is low. The bag sampling was not proportional and this will bias the sample towards low power conditions such as idle. Low power conditions produce less NO_x and therefore this explains the significantly lower NO_x collected in the bag. The same reasoning can be applied to CO_2. On the other hand, CO and THC are more complicated since the engine would be producing higher CO and THC at idle, but the catalyst might be less efficient at idle and low power conditions due to its lower temperatures compared to high loads. Overall, the results from comparing bag sampling to the OBS and FTIR appear reasonable, and reveal the deficiencies of the bag sampling technique.

CONCLUSION

A system was developed to measure on-road emissions (CO_2, CO, NO_x and 30 hydrocarbon species) in-vehicle using a portable FTIR. Validation work proved that the FTIR is robust enough to be used in the harsh in-vehicle conditions. Repeatability of the FTIR was proved to be good, while accuracy was acceptable when compared to the standard analyzers. When compared to a commercial on-board system (OBS-1000) the FTIR was very close for all emissions except for THC. The FTIR is a relatively compact instrument that is considered suitable for in-vehicle real-world emissions investigation, particularly when information on toxic hydrocarbon emissions is also required. The poor correlation between the FID and the FTIR must not be taken as poor THC performance from the FTIR. The FTIR was not intended to be a direct replacement for a FID, but rather it is an instrument that can speciate a large number of hydrocarbons. In future, the FTIR data can be further analyzed to obtain hydrocarbon speciation data for use in calculating ozone forming potentials.

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CONTACT

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ACRONYMS

LU-UDTC: Leeds Univ. Urban Drive Test Cycle
HPL: Hyde Park Loop
FTIR: Fourier Transform InfraRed
NDIR: Non-Dispersive InfraRed
ECE: Economic Commission for Europe
FTP: Federal Test Procedure
EI: Emission index
SI: Spark Ignition
FID: Flame Ionization Detection

CLD: ChemiLuminescence Detector
ADC: Analog Digital Converter
THC: Total HydroCarbons
AC: Alternating Current
LOD: Limit of Detection
ECU: Electronic Control Unit
OFP: Ozone Forming Potential
CVS: Constant Volume Sampling
NMHC: Non-Methane HydroCarbons
VOC: Volatile Organic Compound
EUDC: Extra Urban Drive Cycle
HEGO: Heated Exhaust Gas Oxygen [sensor]
UEGO: Universal Exhaust Gas Oxygen [sensor]
PM: Particulate Matter

APPENDIX

Table 6: FTIR measurement components and their ranges

Species	***Calibrated range***		***Species***	***Calibrated range***	
Water vapor	20	%	1,3-Butadiene	100	ppm
CO2	30.1	%	Benzene	500	ppm
CO	9960	ppm	Toluene	500	ppm
N2O	500	ppm	m-xylene	500	ppm
NO	2008	ppm	o-xylene	500	ppm
NO2	4885	ppm	p-xylene	500	ppm
SO2	1000	ppm	1,2,3-trimethylbenzene	500	ppm
COS	200	ppm	1,2,4-trimethylbenzene	500	ppm
NH3	503	ppm	1,3,5-trimethylbenzene	500	ppm
HCN	500	ppm	Ethylbenzene	*	ppm
HCl	489	ppm	Indene	*	ppm
HF	91	ppm	Methanol	500	ppm
Methane	995	ppm	Ethanol	500	ppm
Ethane C2H6	506	ppm	Propanol	500	ppm
Propane C3H8	500	ppm	Butanol	*	ppm
Butane C4H10	500	ppm	MTBE	500	ppm
Pentane C5H12	500	ppm	Dimethyl Ether	*	ppm
Iso-pentane C5H12	*	ppm	Formaldehyde	96	ppm
Hexane C6H14	500	ppm	Acetaldehyde	200	ppm
Heptane C7H16	500	ppm	Formic acid	500	ppm
Octane C8H18	*	ppm	Acetic acid	500	ppm
Iso-octane C8H18	500*	ppm	Acrolein	500	ppm
Cetane C16H34	*	ppm	Naphthalene	305	ppm
Acetylene C2H2	98.8	ppm	1-ethylnaphthalene	500	ppm
Ethylene C2H4	493	ppm	Sulfur hexafluoride	49.4	ppm
Propene C3H6	500	ppm			

*asterisks indicate the component was not uniquely calibrated for this particular instrument and therefore generic libraries were used in the software for any quantitative analysis of this component

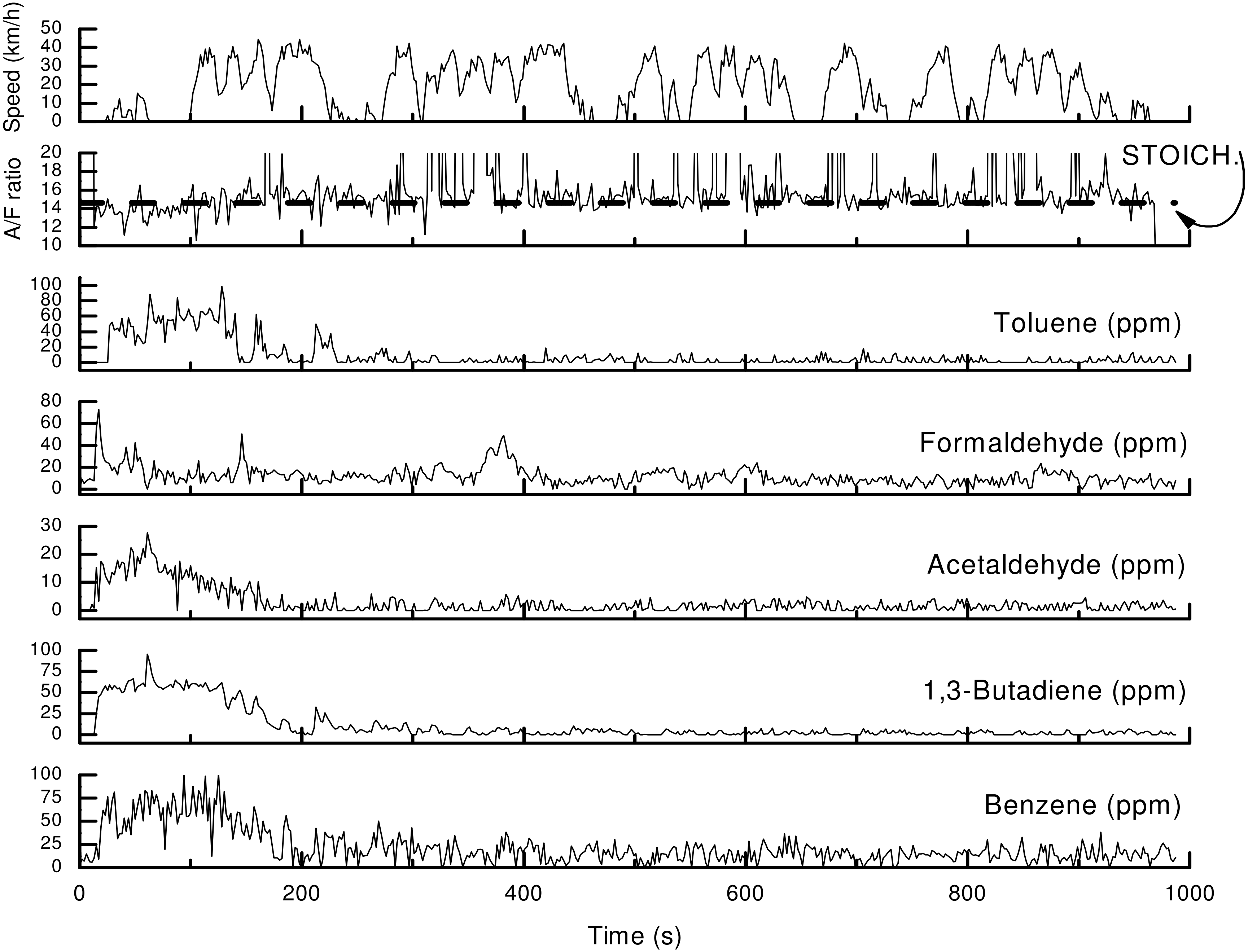

Figure 16: Speciated hydrocarbons from FTIR

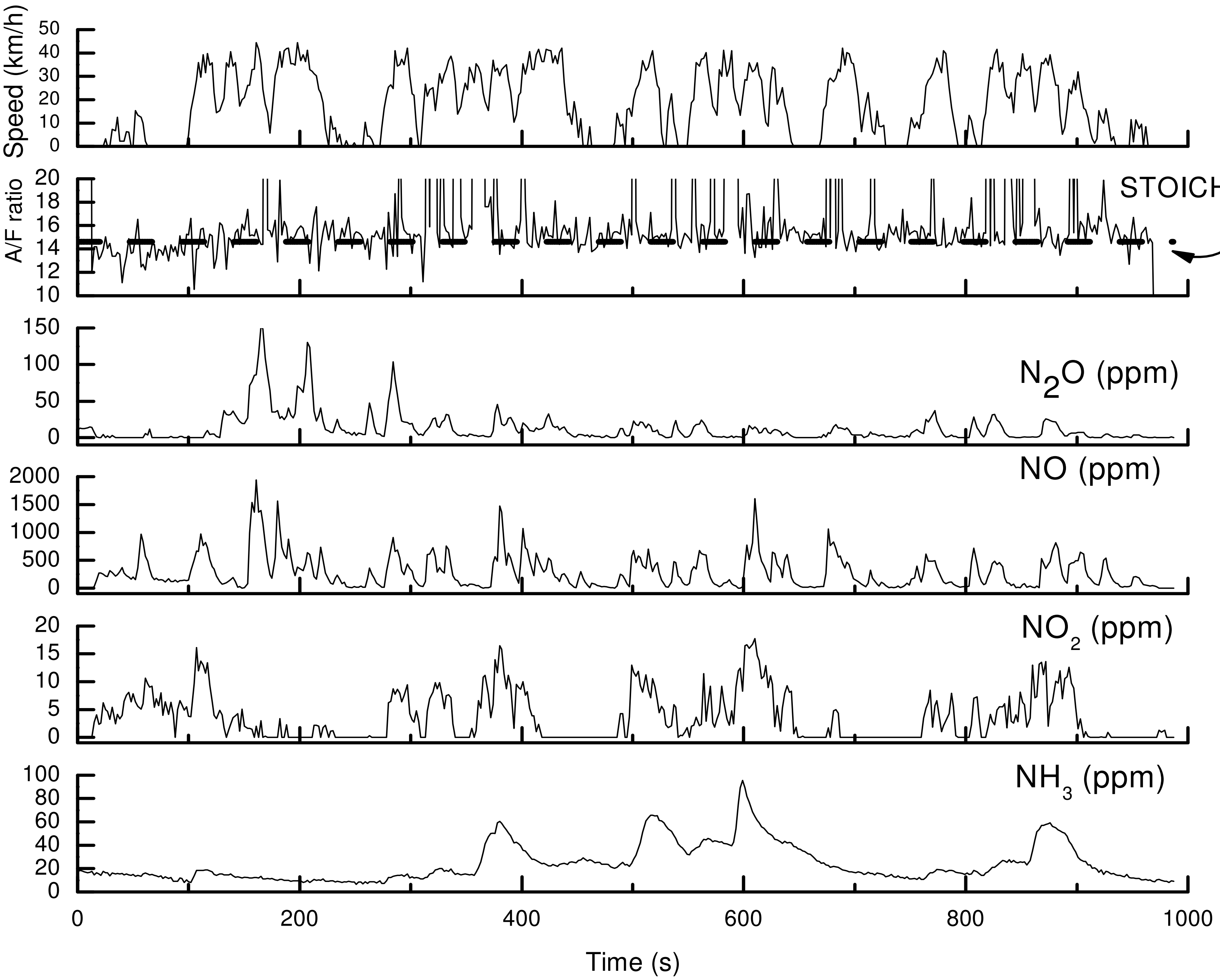

Figure 17: Speciated nitrogen-containing compounds from FTIR

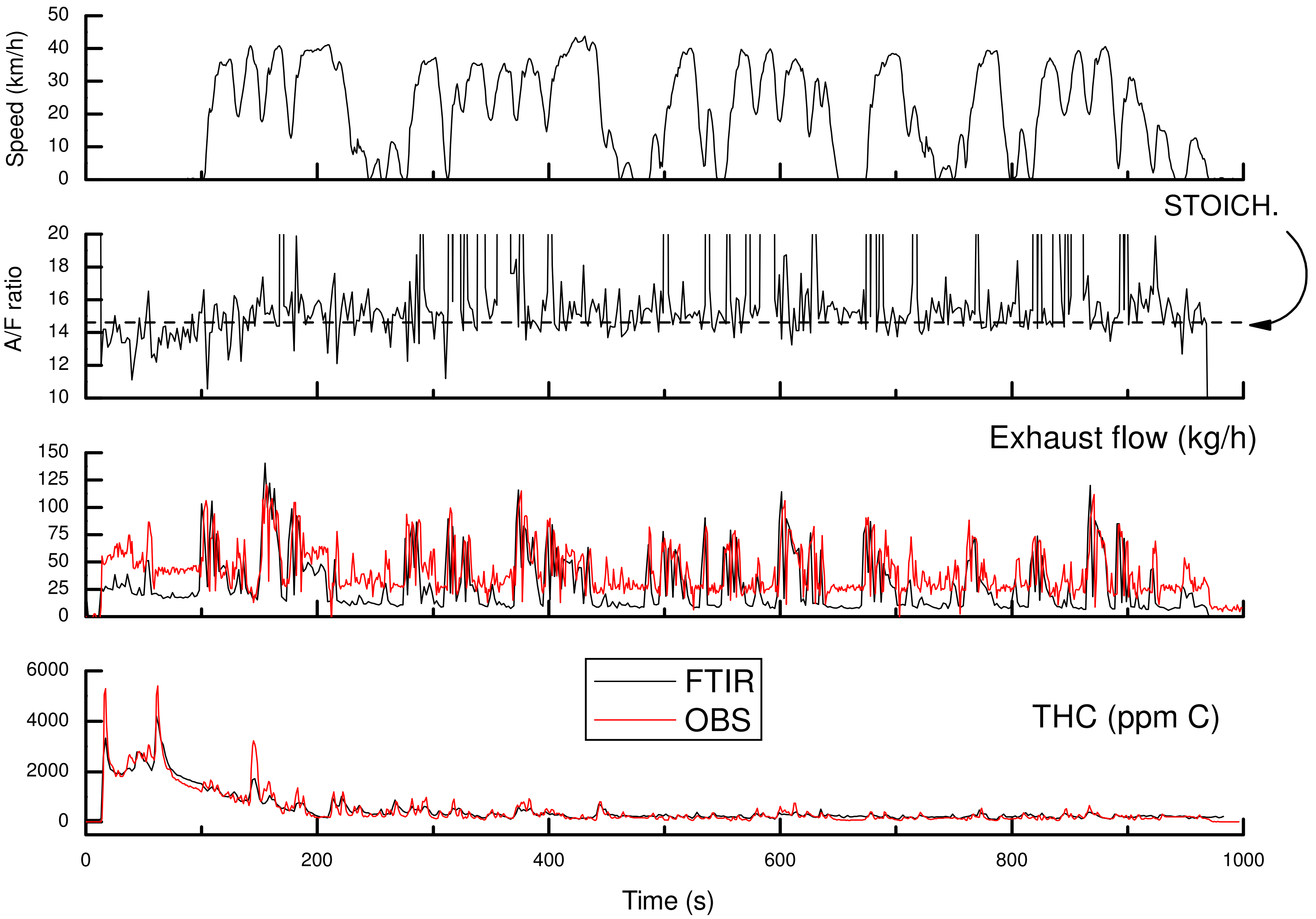

Figure 18a: FTIR vs. OBS comparison for exhaust flow and THC

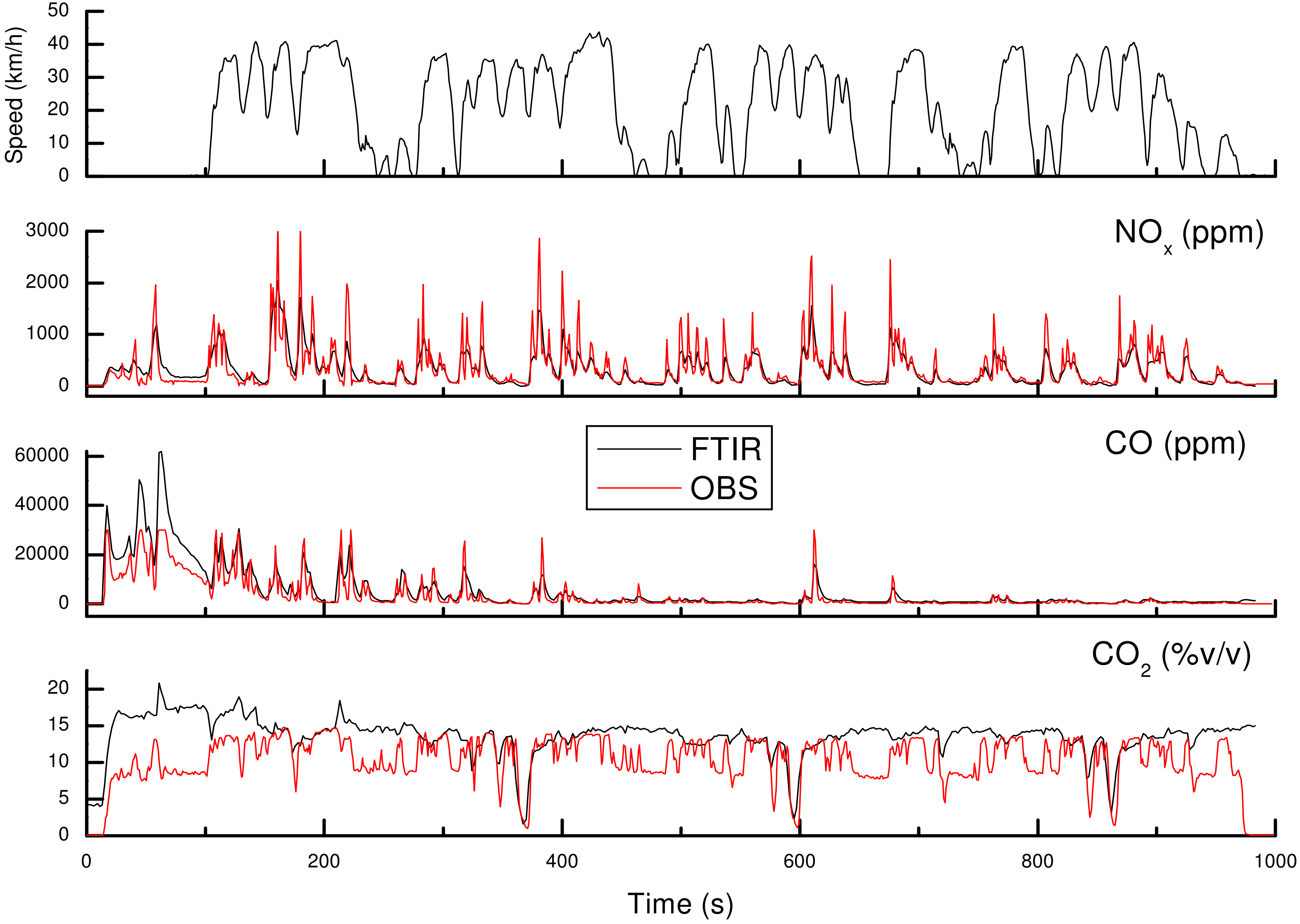

Figure 18b: FTIR vs. OBS comparison for NO$_x$, CO and CO$_2$

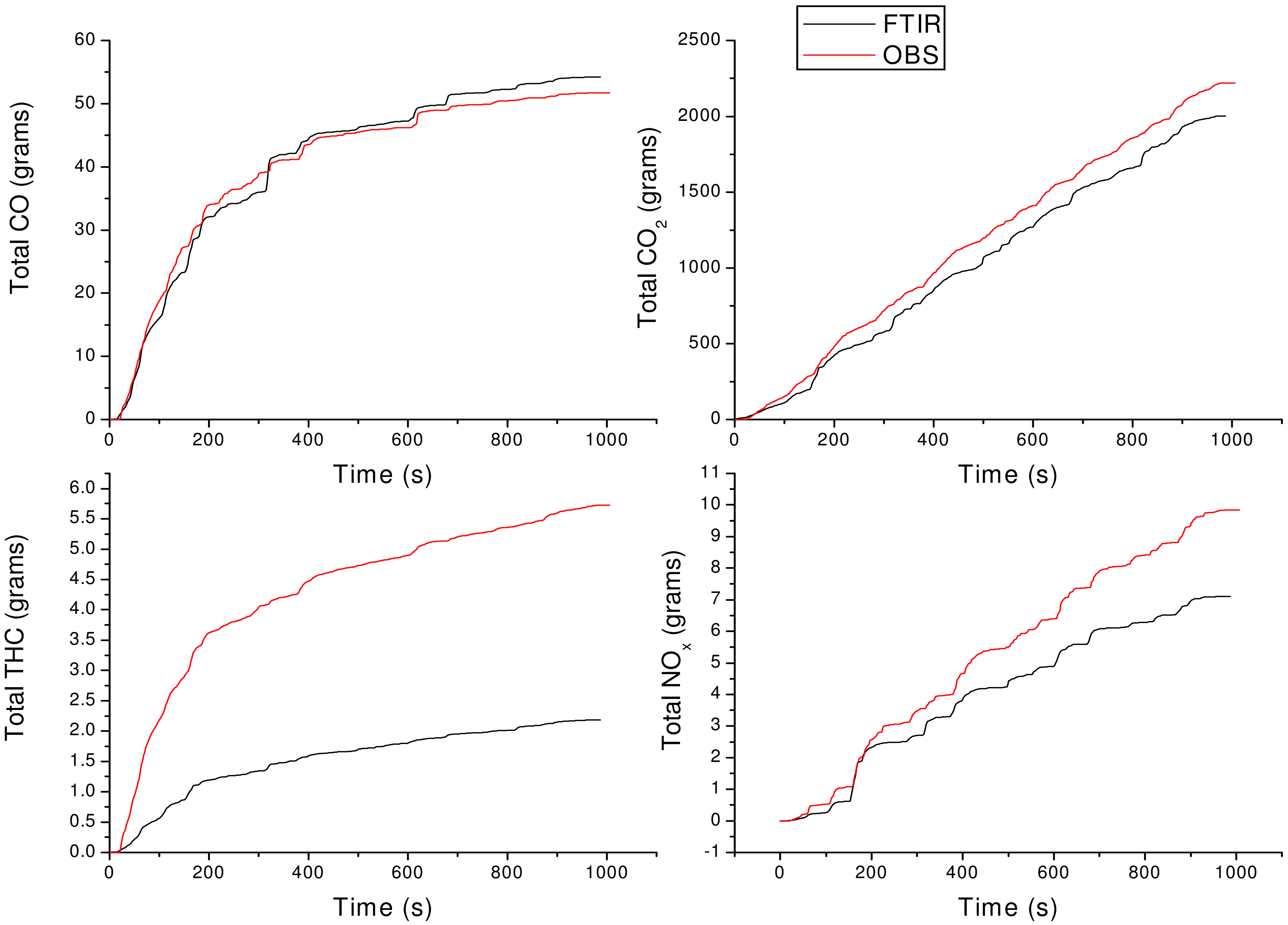

Figure 19: FTIR vs. OBS cumulative plots

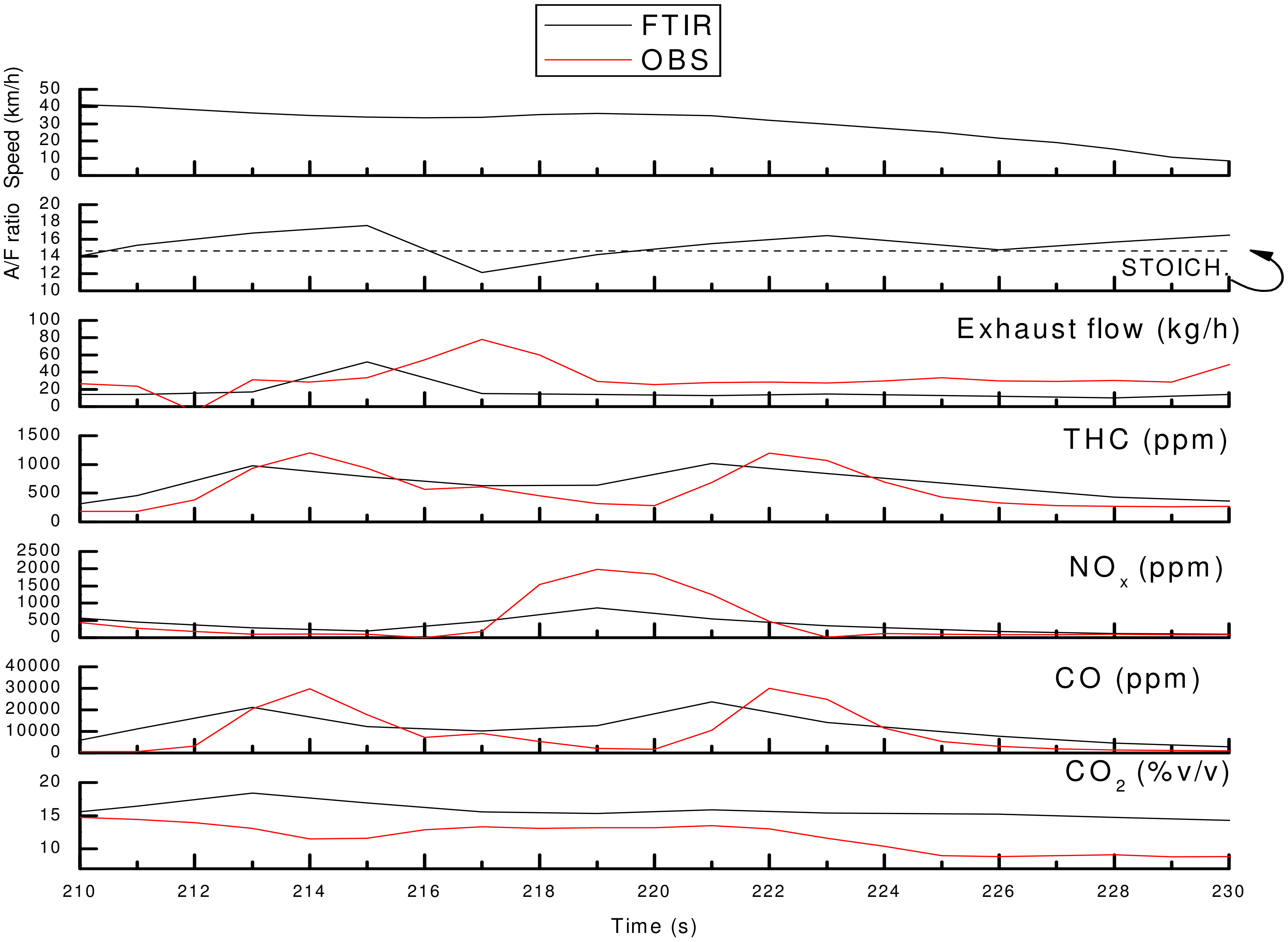

Figure 20: FTIR vs. OBS comparison for 20 second segment of drive cycle