

## **focal point**

# Spectroscopy Applied to On-Road Mobile Source Emissions

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## INTRODUCTION

Not to be confused with emission spectroscopy, the detection of mobile source emissions by means of a remote sensing device (RSD) is almost entirely an application of absorption spectroscopy. In this article we discuss the application to measurement of individual vehicle emissions remotely as the vehicle drives by in its normal driving mode. Most studies and commercial implementation have involved automobiles and light duty trucks.<sup>1-8\*</sup> However, the same technology has been applied to heavy duty trucks<sup>9</sup>, locomotives<sup>10</sup>, snowmobiles<sup>11</sup> and airplanes in taxi and takeoff modes<sup>12</sup>. The challenge in all these applications is to make precisely collocated absorption measurements at 100 Hz in both the UV and IR regions of the spectrum with low noise. The ability to measure 1/1000 absorbance units is necessary. The only compensating advantage is that an individual vehicle measurement cycle is over in one second or less, such that slow instrument drift becomes unimportant. The results are all measured as a ratio to the measured emission of CO<sub>2</sub> and calibrated by means of a certified cylinder with known ratios. Using these ratios, the end result for each vehicle can be expressed as mass emissions per kg or per L of fuel as well as the emissions % which would be measured were the vehicle equipped with a tailpipe probe and emissions measurement system (corrected for any excess air which might be in the exhaust manifold).

Some of the RSD systems and applications have been the subject of a prior review,<sup>3</sup> however at least one formula presented in that review turns out to be in error and there have been several new breakthroughs in instrumentation capability. An RSD instrument is shown in Fig. 1A schematically, and Figs. 1B-1F in typical in-use setups measuring light duty vehicles (LDV), heavy duty trucks, locomotives, snowmobiles, and airplanes respectively. The IR/UV light source and speed bar source (LDV and snowmobiles) are on one side of the road while the detector, computer, video camera, speed bar detectors (LDV and snowmobiles), and calibration gases are on the other.

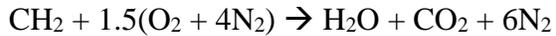
## COMBUSTION CHEMISTRY

The simplest approximation which illustrates the principle assumes an empirical formula for all hydrocarbon fuels by mole as CH<sub>2</sub>. This turns out to be a very useful approximation because it is close to correct for average gasoline and diesel fuels. Even

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\* Many of the referenced reports are available at <http://feat.biochem.du.edu> either as a report or as a link.

for fuels in which the mole ratio is very different, such as CH<sub>4</sub>, the majority of the mass remains the carbon. Using this approximation and the further approximation that air can be regarded as O<sub>2</sub> + 4N<sub>2</sub>, a simplified balanced equation for stoichiometric combustion can be written as:



Equation (1) provides the air/fuel ratio by mass (A/F)

$$A/F = C_2 * (m_{\text{O}_2} + C_3 * m_{\text{N}_2}) / C_1 * m_{\text{CH}_2} \quad (1)$$

where  $C_2$  is the reaction coefficient of air,  $m_{\text{O}_2}$  is the molar mass of O<sub>2</sub>,  $C_3$  is the reaction coefficient of N<sub>2</sub>,  $m_{\text{N}_2}$  is the molar mass of N<sub>2</sub>,  $C_1$  is the reaction coefficient for the fuel, and  $m_{\text{CH}_2}$  is the molar mass of the fuel. Using the simplified stoichiometric combustion equation above and equation (1) the A/F is 15.4. Further, the %CO<sub>2</sub> in the exhaust, corrected for water vapor (most exhaust gas analyzers remove the water vapor before analysis) is 1/7 x 100% or 14.3%. The CO/CO<sub>2</sub> ratio in the exhaust is 0 when combustion operates at stoichiometry.

If we now consider a situation in which there is 50% less air (or more fuel), the combustion will be in a fuel rich condition and to a first approximation can be written as:

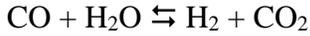


Using equation (1), the A/F ratio by mass is 10.3. The %CO corrected for water vapor is 20% and the CO/CO<sub>2</sub> ratio is infinite.

From the above simplified derivation it is apparent that a device which can measure the CO/CO<sub>2</sub> ratio from a passing vehicle can determine the engine's air/fuel ratio as long as the vehicle is operating in a fuel rich mode. Also, determination of the %CO and %CO<sub>2</sub> which would be observed if a tailpipe probe were inserted into the vehicle's exhaust and the result corrected for the presence of water vapor is possible. If the vehicle is running fuel lean then there is excess oxygen in the exhaust which can not be distinguished by means of remote sensing from the large amount of oxygen already present in the atmosphere. In this case (true for all compression ignition, diesel vehicles) the calculations above yield the % pollutant and A/F which would be measured were the probe readings not only corrected for water vapor but also for any excess air present.

In our observations of over 20,000,000 vehicle emissions we have never observed the extreme A/F ratio in which the exhaust contains only CO and no CO<sub>2</sub>. We have observed a CO/CO<sub>2</sub> ratio of 5.6 (once) and routinely observe a half dozen vehicles out of each 25,000 (about a week of on-road measurements) with CO/CO<sub>2</sub> ratios above 2.0. These extremely high emitters should be contrasted to typical measured mean ratios of 0.017 or median, 0.009.

Correcting the above arithmetic for actual fuel C/H ratio and actual air O<sub>2</sub>/N<sub>2</sub> ratio makes only small differences but has been done by Johannes Brettschneider.<sup>13</sup> He included potential oxygen content in the fuel and included the fact that there is another reaction which occurs in exhaust, namely the water gas shift reaction. This reaction is an equilibrium:



Under typical combustion conditions, the equilibrium constant is reactant favored at 0.286 (1/3.5). Even so, this equilibrium is the reason why automobiles are a major source of the significant traces of hydrogen found everywhere in the earth's atmosphere.<sup>14</sup> The full Brettschneider equation rewritten in terms of potentially measurable exhaust ratios by RSD where CO/CO<sub>2</sub>, HC/CO<sub>2</sub>, and NO/CO<sub>2</sub> are Q, Q', Q'' respectively follows.

$$A/F = \{1+Q/2+O_2/CO_2+Q''+(1+Q)[(x/4)(3.5/(3.5+Q))-y/2]\}/\{(1+x/4-y/2)(1+Q+6Q')\}$$

The fuel is now CH<sub>x</sub>O<sub>y</sub> and Q, Q' and Q'' are the measured pollutant ratios. The factor of 6 which multiplies Q' is necessary because the filter-based IR HC measurement calibrated with propane only determines about half the HC mass (see later discussion). Since we do not measure O<sub>2</sub>/CO<sub>2</sub>, RSD can only provide A/F for vehicles running rich or stoichiometric

The inclusion of the hydrogen water gas shift reaction with an equilibrium constant of 3.5 = [CO]\*[H<sub>2</sub>O]/[H<sub>2</sub>]\*[CO<sub>2</sub>] in the equations derived in our 1996 review<sup>3</sup> significantly changes the air to fuel ratio result (for vehicles running rich only). The 1996 paper gave the result as

$$A/F = 4.93(3+2Q)/(1+Q+3Q')$$

The correct result including the water gas shift reaction is:

$$A/F = 4.93(10.5+9Q+Q^2)/[(3.5+Q)(1+Q+6Q')]$$

In 1989 when on-road remote sensing devices were first introduced, emission results in gm/kg of fuel or as ratios to CO<sub>2</sub> were not in common use. As a result, we caused our instrument output to report the % which would have been measured by a suitably corrected tailpipe probe. This provided a set of units familiar to laypersons and auto mechanics alike because, at that time, the annual emission test emission standards were expressed in units of percent (and ppm) in the exhaust. This may have been a mistake. RSD reports the percentage of four species. Only three ratios are measured and therefore one of the species percentages must be meaningless. The % CO<sub>2</sub> is derived from the other three and has no meaning except as a denominator. Occasionally, inexperienced RSD users have reported excellent agreement with these CO<sub>2</sub> data.

We now recommend to all users of RSD data to immediately ratio the reported pollutant readings to the reported CO<sub>2</sub>; this procedure resurrects the actually measured parameters.

The results for CH<sub>2</sub> fuel used in the combustion equation are fully derived on our website.<sup>1</sup> From these ratios the emissions in gm/kg of fuel can be calculated as given below.

gram pollutant/kg of fuel consumed:

$$\begin{aligned} \text{CO} &= 2007*Q/(1+Q+6Q') \\ \text{HC} &= 6307*Q'/(1+Q+6Q') \\ \text{NO} &= 2150*Q''/(1+Q+6Q') \end{aligned}$$

To get a feel for the size of the terms in these equations, the average Q, Q' and Q'' in Denver are 0.02, 0.001 and 0.002 for CO, HC and NO respectively.<sup>15</sup> In Denver, as well as all cities we measure, the medians are less than half the means because the means are dominated by a few high emitters.<sup>15-18</sup>

## SPECTROSCOPY TO MEASURE POLLUTANTS

Current commercial RSD units use the spectral features for CO and CO<sub>2</sub> at their well known fundamental absorptions in the IR region at 2150 and 2350 cm<sup>-1</sup> respectively. Laboratory calibration is achieved with known path lengths of the pure gases, usually diluted in nitrogen. Exhaust hydrocarbon measurement is more complicated, and is necessarily approximate by any technique.

The Federal emission standards for motor vehicles are in the interesting mixed metric units of gm/mile obtained by means of a very tightly specified dynamometer test, the Federal Test Procedure (FTP). One suspects that the mixed units are the result of chemists unwilling to provide gas measurements in units other than grams and engineers unwilling to supply dynamometers calibrated in units other than miles. The hydrocarbon results are determined using a flame ionization detector (FID). The FID is very sensitive to benzene, a rather unreactive compound for photochemical ozone formation, but a known carcinogen. By contrast, the FID does not respond to formaldehyde which is both carcinogenic and, by the Carter reactivity scale, about ten times more reactive than benzene towards ozone formation.<sup>19</sup>

Gasoline vehicle exhaust actually contains a variable mix of several hundred oxygenated and non-oxygenated hydrocarbons and there is no perfect metric for its measurement. Commercial RSD units use NDIR equipped with a band pass interference filter corresponding to the C-H stretching region around 2970 cm<sup>-1</sup>. This wavelength channel is, in turn, calibrated with known amounts of propane. Singer et al<sup>20</sup> have extensively reviewed the differences between FID and NDIR and suggest that multiplication by a factor between 2.0 and 2.3, depending on the fuel, be applied to the NDIR reading in order to obtain a result closer to the FID reported fuel mass. We have routinely used the factor of two since all HC results are necessarily approximate. This factor of two appears in the denominator of several above equations as 6Q'. The factor of six arises from the carbon atoms per molecule of propane (three) multiplied by the Singer et al. FID/NDIR

factor (two). We also report all our HC measurements as propane equivalents since it is the gas used for calibration.

The federal standards for oxides of nitrogen in exhaust are written in gm/mi and whether the measured gas is NO or NO<sub>2</sub>, all NO<sub>x</sub> are given the mass as if they were NO<sub>2</sub>. It is important to bear this factor in mind if comparing RSD measurements (mostly measured as NO and reported, as above, as mass of NO) to computer models which routinely treat all NO<sub>x</sub> as having the mass of NO<sub>2</sub>.

## INSTRUMENTATION

**Infrared Channel.** Historically, the first attempt to monitor on-road emissions was not a success, probably largely because the IR system made use of an internally generated reference beam.<sup>21</sup> The precise absorption readings needed, coupled with the fact that the passing vehicle disturbs a layer of air near the road surface causing a “shimmering” effect lead to its lack of success.

Our first instrument<sup>2</sup> used LN<sub>2</sub> cooled InSb detectors with cold filters at the CO<sub>2</sub> and CO wavelengths and used a spinning gas cell (CO/N<sub>2</sub> versus N<sub>2</sub>) filter (gas filter correlation spectroscopy) to provide the across-road reference optical beam to which the other intensities are ratioed. This instrument was very successful, although criticized for being unable to monitor HC emissions. A beam splitter and third InSb detector with an HC filter removed that criticism. However, we considered that an instrument designed for routine roadside operation should be able to do without a source of liquid nitrogen. With this in mind we designed a system, FEAT 3000, using four thermo-electrically cooled PbSe detectors (Cal Sensors) with cooled filters. The acronym arises from the name Fuel Efficiency Automobile Test recognizing that high CO emissions, if properly repaired, lead to significant gas mileage improvements.

The IR source in both cases was the SiC 110V igniter used in many gas clothes driers (GE #WE4X444). This device is an amazing item. It operates at about 1700K with an emissivity close to a black body. It uses 110V at 300W with less than 7 ppm intensity ripple at 120 Hz and costs less than \$10 to replace. In our systems, several have operated continuously 24/7 for more than a year! The light from the igniter is collimated and passes across a single lane of traffic into the detector where it is refocused by a 50mm diameter f/6 mirror onto a twelve-sided spinning mirror (Lincoln Laser, 12,000 rpm). The IR beam is thus swept sequentially across four collimating mirrors each one of which focuses upon a separate detector (HC, CO, Reference, and CO<sub>2</sub>). The Reference wavelength, 3.9 microns (2600 cm<sup>-1</sup>), is chosen as a wavelength in the same general range as the pollutants but where no pollutants should absorb.<sup>7</sup>

The system has been tested on vehicles driving at speeds between 2 and 152 mph. Figure 2 shows a typical voltage trace (half second) from a low emitting vehicle driving at about 20 mph. Notice that significant absorption by the exhaust CO<sub>2</sub> only occurs during the first

hundred milliseconds. This result is typical for vehicles with small engines driving at moderate speeds.

Figure 3 shows the voltages from Fig. 2 converted, by means of laboratory and field gas calibrations, into estimated gas optical depths versus time. This intermediate result is then further analyzed as in Fig. 4 which shows a correlation graph between the measured CO<sub>2</sub> and the measured CO. The slope is essentially zero (also for HC from this vehicle) and thus this vehicle is given a Q and Q' reading (with a calculated standard error) of essentially zero, as expected for a typical low emitting vehicle. The analysis occupies about 0.3 seconds of computer time so the system is ready for the next vehicle as long as the inter-vehicle gap is longer than 0.8 seconds. A gap only this short is rare, and is certainly dangerous in view of the human 0.3 second reaction time and the following vehicle's significant braking distance. Notice that the graphs show a large intercept on the CO<sub>2</sub> axis which is caused by the fact that ambient CO<sub>2</sub> has a very significant absorption over the 24 ft optical path. The relatively constant optical depth of the ambient CO<sub>2</sub> significantly exceeds the optical depth added by the automobile exhaust.

Figure 5 shows the received voltages from a much higher emitter measured a few moments later at the same (Speer/I-25 in Denver) location. Figure 6 shows the derived correlation graph. In this case, the added CO and CO<sub>2</sub> are very well correlated and the ratio of 0.8 corresponds (when the also high emitting HC data are included) to a reading of 872 gm/kg or 7.6 %CO in the exhaust.

An artificial offset has been found in our HC measurements. This offset, restricted to the HC channel, has been reported earlier<sup>15-18</sup> but diagnosis has proved quite difficult. In the absence of a true diagnosis of the problem, we remove the offset with an adjustment of the data set. Calculation of the offset is accomplished by computing the mode and mean of the newest model year vehicles, and using the lowest of either of these values as the subtracted offset. Since we assume the cleanest vehicles to emit little hydrocarbons, such an approximation will only err slightly towards clean because the true offset will be a value somewhat less than the average of the cleanest model year.

In Denver 2003, the mode emissions for the three most recent model years 2001, 2002, and 2003 were all 20ppm. For the other Denver data sets, offsets were determined to be 70, 100, 5, 60, and -50 ppm for measurements conducted in 1996, 1997, 1999, 2000, and 2001, respectively.<sup>15</sup>

Recently, the IR detection of pollutants has evolved to the FEAT 4000 and now FEAT 5000 units.<sup>22,23</sup> This technology uses a single, peltier cooled PbSe detector and allows for the self calibration of the instrument in the field. The FEAT 3000 instrument described above is calibrated in the field at least twice in a typical day for varying ambient CO<sub>2</sub> concentrations. In principle, the voltages on the Reference and CO<sub>2</sub> detectors would allow the RSD to do a "self correcting" calibration. If the ambient CO<sub>2</sub> increases, the standing CO<sub>2</sub> detector voltage would be depressed while the Reference voltage would remain unchanged. For this to work there can be no effect on CO<sub>2</sub> and Reference voltages other than ambient concentrations. In practice, however, four independent detectors are very sensitive to instrument alignment and the ability to hold a constant

ratio for all factors except changing ambient concentrations is difficult. The newer FEAT models now being tested use a single detector and are equipped with a spinning wheel carrying five different NDIR band pass filters. This optical system should be immune from the alignment problem discussed above.

Measurement of HC, with its broad spectrum across the band pass, allows for a linear relationship between concentration and absorbance. Carbon dioxide suffers from non-linearity because of its sharp and variable absorption lines across the  $130\text{ cm}^{-1}$  band pass at  $2350\text{ cm}^{-1}$ . One field calibration of HC/CO<sub>2</sub> compared to the HC linear calibration sets the other ratios and allows the instrument to correct for changes in ambient CO<sub>2</sub>, thus being “self calibrating”.<sup>22,23</sup>

In addition to self-calibration, the FEAT 5000 unit incorporates the ability to detect water droplets, often called “steam” plumes.<sup>22</sup> Liquid water absorbs in part of the HC band pass and on cold days when vehicles’ engines and exhaust systems are not warmed up, these steam plumes would be measured as high HC emitters. The FEAT 5000 renders the HC measurements invalid if both the HC and liquid water emissions are read as high and their ratio corresponds to that measured for liquid water.<sup>22</sup>

**Ultra Violet Channel.** After the HC channel was demonstrated, the criticism was that the instrument did not measure nitric oxide. We were beginning to realize at this stage that any instrument which could carry out 5,000-10,000 realistic emission tests in a single day of operation is bound to attract criticism. We surmised that, since the on-road system is so productive and could demonstrate the ineffectiveness of traditional emission testing such as the nearly half billion dollar pre year program in California,<sup>24</sup> several major private and public income sources were threatened. Nevertheless, we added the capability to monitor nitric oxide. The fundamental IR absorption band of NO ( $1800\text{ cm}^{-1}$ ) is buried amongst the strong lines of water vapor abundant in both the ambient air and the exhaust. As a result, we decided to monitor the strong electronic absorption at 227 nm in the UV (the 0,0 NO A ← X gamma band). The first attempt again involved gas filter correlation. This system<sup>25</sup> did measure NO, but aromatic hydrocarbons present in high emitting HC vehicles were a significant interference. The current version<sup>26</sup> uses a beam splitter that separates the coliner UV/IR beam and focuses the UV light onto the end of a quartz UV fiber bundle (Ceramoptec, East Longmeadow MA) optically coupled to a Czerny-Turner configured spectrometer with 0.3 nm resolution. The software requires the observed absorption band as a function of wavelength to correlate well with a standard spectrum of NO stored in the spectrometer’s memory. The observed NO as a function of time also must correlate well with the IR observed CO<sub>2</sub> or the NO reading is rendered invalid.

Since the introduction of NO measured by dispersive UV, the spectrometer has been adapted and its measurable range of wavelengths varied. The initial design used a 128-element photodiode array (Hamamatsu) and incorporated a spectral range of 16 nm from 218 nm - 234 nm. This system was adapted for use with two-stroke snowmobiles to measure toluene. Toluene absorbs at longer wavelengths than NO, peaking at 260 nm. Concurrent measurements were not possible, nor were they necessary, since no significant measurable quantities of NO exist in the fuel rich exhaust from two-stroke

engines. The grating was realigned in the spectrometer and a new standard spectrum recorded to compare in the software routines. The measurement of toluene was used to determine if certain types of two-stroke snowmobile engines released more HC than others as seen in an earlier study.<sup>27</sup> The previously measured difference in engines could have come from “steam” plumes but since the FEAT 5000 was still in development, toluene measurements were used. By measuring toluene near 260 nm where there are no water interferences, and plotting toluene versus HC, it was determined that indeed the differences could correctly be attributed to increased HC emissions.<sup>28</sup>

Current standards in the state of California limit combined NO<sub>x</sub> and non-methane emissions and particulate matter (PM) emissions. In 2007, new regulations will set a 10-fold reduction in both NO<sub>x</sub> and PM emissions from heavy duty diesel vehicles.<sup>29</sup> Continuously regenerating particle filters are the most effective current technology to remove PM but involve the production of primary NO<sub>2</sub>. Thus, a complimentary regulatory limit for vehicular NO<sub>2</sub> emissions is set to go into effect in 2007.<sup>30</sup> Therefore a need to measure primary NO<sub>2</sub> emissions separate from NO has become apparent. The NO<sub>2</sub> spectrum has the largest peak to valley absorbance differences between 425 nm and 450 nm. The upside to measuring NO<sub>2</sub> rather than NO is that the Xenon arc source has greater intensity at these wavelengths. The downside is that the absorbance cross section is much smaller. Like the adaptation for toluene, the spectrometer grating was shifted and aligned to 430 nm – 446 nm which does not allow for simultaneous NO and NO<sub>2</sub> and thus requires two RSD units to measure total NO<sub>x</sub>.<sup>31</sup>

At the same time that NO<sub>2</sub> is facing regulatory restrictions, other unregulated emissions are also under scrutiny. Ammonia and sulfur dioxide are two gases emitted from vehicles that are unregulated but form secondary aerosols that both limit visibility and are harmful to human health.<sup>32</sup> Ammonia is an unintended by-product of an over-reducing environment on the 3-way catalyst (now standard on all on-road spark ignition vehicles) which has been shown to be highly variable in its release.<sup>33,34</sup> Ammonia emissions from mobile sources are assumed to be dwarfed by agricultural emissions but in heavily urban environments, mobile sources could be the leading source. Sulfur dioxide, and to a lesser extent sulfur trioxide, is the natural oxidation combustion product of sulfur in the fuel.<sup>35</sup> Sulfur emissions should be directly calculable from the amount of sulfur in the fuel, but sulfur has been shown to be held on the catalyst and then mostly released during aggressive driving modes.<sup>36</sup> This affinity of sulfur for catalytic surfaces renders them less effective<sup>37</sup> and thus regulations are in effect to reduce sulfur levels in both gasoline and on-road and off-road diesel. To our knowledge there are no methods in place to determine if the fuel actually burned is this low sulfur fuel except for invasive methods based upon fuel sampling and later analysis.

For the reasons above, another project has again adapted the RSD spectrometer. It was determined that both NH<sub>3</sub> and SO<sub>2</sub> could be measured simultaneously with NO emissions with one spectrometer. Sulfur dioxide is often measured from 280 nm – 320 nm but the absorbance cross sections are an order of magnitude smaller than those of the peaks near NO. The NO 0,0 gamma band at 227 nm is at the long wavelength end of the C ← X electronic bands of SO<sub>2</sub> with peaks from 200 nm – 230 nm while NH<sub>3</sub> has five

absorbance peaks between 200 nm – 220 nm from the A ← X transition. The current 128-element PDA was not large enough to measure this entire range and a 256-element PDA (Hamamatsu) was instead installed. The new PDA gave a spectral window from 200.8 nm to 235.6 nm. The next challenge came with detecting species at wavelengths shorter than 227 nm since the Xenon arc lamp inherently emits less light the deeper in the UV and the reflectivity of the mirrors also decreases. To compensate, beam splitters were optimized for shorter wavelengths and all of the reflective surfaces were coated with a special VUV-UV broadband coating (Acton Research Corp.) that increased the detected light intensity by almost 3 orders of magnitude at 215 nm.<sup>31</sup>

**Alternative Designs.** Most passenger vehicles have tailpipes that are located at the rear and under the vehicle. The majority of heavy duty trucks and all locomotives have elevated exhaust stacks. The FEAT instrument can measure these exhaust plumes but the optical beam must also be elevated. This elevated optical beam is currently (although inconveniently) achieved by means of two walk-up scaffolding systems. Figure 1c and 1d shows FEAT instruments on scaffolding at an interstate weigh station and a rail yard measuring passing trucks and locomotives. The plume from these vehicles is elevated above any obstacle to the light beam. For this reason an external optical trigger integrated with the software, rather than the blocked Reference signal, is used to initiate the measurement.

Small engine motorcycles pose a significant challenge because of their variable exhaust height and very small exhaust plumes. These two reasons made measurement of motorcycle emissions elusive with the standard FEAT arrangement of a single beam pass from the light source to the detector system on the other side of the roadway. To overcome this, a system capable of measuring absorptions at a variety of heights and plume sizes simultaneously was developed. The unit incorporates a FEAT 5000 detector in order to correct any artificially large hydrocarbon measurements which might arise from suspended water droplets in cold exhaust from these small engines. The motorcycle unit design consists of two posts on opposite sides of the test lane: one with three focusing mirrors and the other post with a 12 volt IR light source, two mirrors and the FEAT detector. The mirrors used have confocal distances of 2.25m. This width is wider than needed for motorcycles but the extra room allows 3 wheeled motor tricycles (common in Asia and South America) to pass through. The six passes of the IR beam between the mirror posts cover the range between 18 and 55 cm off of the ground.

## INSTRUMENT NOISE

Instrument noise can be measured in the laboratory using calibrated gas samples and provide excellent detection limits. Since we are often critical of measurements made in the laboratory and then applied to real world driving conditions, we employ a more realistic method to determine the inherent noise which the RSD contributes to on-road measurements. The method involves first calibrating an RSD unit then measuring a significant number of on-road vehicle emissions (preferably over 10,000). Since negative emissions can not truly exist, instrument noise is measured by graphing the logarithmic

slope of the negative portion of the emissions distribution functions. These emissions are binned and plots are constructed using the natural log of the frequency of occurrence versus the magnitude of the negative reading. Linear regressions give best fit lines whose slopes correspond to the inverse of the Laplace factor. See Fig. 7 for the determination of NH<sub>3</sub> noise. The Laplace factor describes the noise present in the measurements. This factor must be viewed in relation to the average measurement for the particular pollutant to obtain a description of noise. The Laplace factors from our most recent measuring campaign in Tulsa, OK in September 2005 were determined to be 17.1, 7.64, 0.57, 0.29 and 0.09 for CO, HC, NO, SO<sub>2</sub> and NH<sub>3</sub> respectively. These values indicate standard deviations of 24.2 g/kg (0.19%), 10.8 g/kg (254 ppm), 0.80 g/kg (59 ppm), 0.41 g/kg (17 ppm), and 0.12 g/kg (31 ppm) for individual measurements of CO, HC and NO, SO<sub>2</sub>, and NH<sub>3</sub> respectively. In terms of uncertainty in average values reported here, the numbers are reduced by a factor of the square root of the number of measurements. For example, with averages of 100 measurements, which is the low limit for number of measurements per a particular bin, the uncertainty reduces by a factor of 10. For fleet averages of 10,000 measurements, again a low number, the above uncertainties would reduce to 0.242 g/kg, 0.107 g/kg, 0.0080 g/kg 0.0041 g/kg and 0.0012 g/kg, respectively.

## VERIFICATION

Studies sponsored by the California Air Resources Board (CARB) and General Motors Research Laboratories have shown that the remote sensor is capable of CO measurements that are correct to within  $\pm 5\%$  for the values reported by an on-board gas analyzer, and within  $\pm 15\%$  for HC.<sup>38,39</sup>

It is difficult to imagine how absorption spectroscopy could fail to work correctly even when carried out at 100 Hz. However, it is always encouraging when one can compare the results from one instrument with a totally independent set of results. The USEPA has required a number of states to implement so called "Inspection and Maintenance" (I/M) programs and in several cases the required vehicle emission test is an EPA test called the IM240. This dynamometer-based test, often performed in a centralized testing lane, is intended to simulate on-road driving. We have shown that RSD correlates to lane IM240 by model year very well in 1999-2001 for HC and CO and NO in Chicago, Denver, and Phoenix. Fourteen of these correlations have been reported by Pokharel et al., all with  $R^2 > 0.96$ .<sup>40</sup>

Lane IM240 results have been criticized recently for unreliable results.<sup>41</sup> However, when one looks more carefully at the EPA laboratory IM240 results, measured twice on the same automobile, together with the concurrent FTP data, it is apparent that this variability is not caused by the test but by the fact that broken cars frequently have an intermittent malfunction (such as a loose connection) and this causes one test to be different from the next regardless if the test is RSD, IM240 or the legally "perfect" FTP.<sup>42</sup> Low emitting, well maintained, unbroken cars do not show significant variability regardless of test procedure, again vindicating the accuracy of the test and pinpointing the (broken) car as the source of the test to test variation.

## FURTHER APPLICATIONS

Current commercial applications include several “Clean screen” programs. The major ones are in Colorado and Missouri. In Colorado, vehicles identified twice by on-road sensing as low emitters are mailed a postcard when their registration renewal is required. The postcard allows them to pay, with the cost of their registration, the cost of their next scheduled emission test without having to take the test.<sup>43</sup>

Texas has undertaken what is called a “dirty screen” program.<sup>44</sup> Vehicles identified routinely entering the Dallas-Fort Worth area (now expanded to other areas) which are identified as on-road high emitters are notified that they must take the inspection and maintenance test required of all in-city cars. In actual fact, all regular commuters are required to pass the test, but this program is designed to enforce the requirement on those that are most relevant to poor air quality.

The City of Denver is home to a unique public/private program of voluntary motor vehicle emissions control.<sup>45,46</sup> Initiated in 1995, the world’s first SMART SIGN gives passing drivers their emission readings as they exit from I-25 southbound to Speer Blvd, southbound.<sup>†</sup> The 8 ft x 11 ft variable message sign illuminates one of three possibilities, GOOD, FAIR, or POOR, triggered by <1% CO in the exhaust, >1% <3.5% and >3.5%, respectively. GOOD readings, accompanied by a green smiley face on a cartoon car, account for about 93% of the measurements per day. FAIR readings get an “Ooh!” face and account for about 5% of the measurements. Of the CO emitted at this site, 40% comes from just 2% of the vehicles which receive a POOR reading and which get a frown in red. In view of the importance of ozone to Denver’s air quality and our air quality “close to violation” status, the Regional Air Quality Council asked the University of Denver to add gross HC emitters (more than 2500 ppm propane) to the POOR category. This change took place on July 1, 2003 and added about 20 vehicles per day to the 200 vehicles per day whose drivers receive POOR readings due to CO emissions of which many also are high HC emitters.

During the inaugural year of the SMART SIGN, independent surveys by Colorado State University<sup>46</sup> showed that it was responsible for removing as much as 700 tons of CO and HC from Denver’s air and gave 3,000,000 emission readings to 250,000 drivers in its first year of operation. The survey also showed that the benefits increase the longer the sign remains in operation. This was an interesting observation. It arises because drivers who routinely drive past the sign and obtain GOOD readings become convinced that the sign is correctly reporting the emission of their car. When their car develops an emissions failure and reads FAIR or POOR they are motivated to act upon the information immediately. For this reason, the longer the sign continues in routine operation, the more vehicles which drive by routinely suffer emissions failures, and the more repairs are initiated. By contrast, drivers whose (broken) vehicles initially receive POOR readings sometimes take action, but some become instantly convinced that the sign is not working

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<sup>†</sup> Readers can see the Smart Sign via live webcam at [www.sign.du.edu](http://www.sign.du.edu). If the image does not appear, accept “axis” software (about 25 kb) with a “yes”.

despite evidence to the contrary such as failing their next scheduled emission test.<sup>45</sup> The world's second SMART SIGN is currently operating in Gothenburg, Sweden.<sup>47</sup>

Motor vehicle inspection and maintenance I/M programs, for instance "Smog Check" in California are intended to reduce on-road emissions. I/M programs cost the affected citizens between \$25M/year (in Colorado) and as much as \$450M/year in California. Remote sensing would seem to be a perfect tool with which to evaluate the extent to which these programs actually reduce on-road emissions, were it not for the legal, political and financial implications of actually achieving an accurate evaluation. There are several techniques by means of which remote sensing can achieve this evaluation.<sup>48</sup> The most unequivocal method can only be applied when there is a step change in an affected area; for instance when a biennial I/M testing program is introduced in a new region. The on-road evaluation is then carried out at the end of the first year of application. Half of the evaluated vehicles have been subjected to the program and half have not, and the socioeconomics of the two halves is identical. In this application, as few as 25,000 readings, which can be obtained at only a little over \$1.00 each, can evaluate the program benefits to within about +/- 2%.<sup>49,50</sup> The introduction of the, then new, IM240 centralized emission testing I program in Denver in 1995 allowed for such an on-road evaluation of the emissions benefits. The study was able to compare on-road emissions from vehicles which had been through the new program and which had not. The results showed that the program benefits were significantly less than the computer models predicted, and that a significant fraction of failing vehicles (from an emissions point of view) were avoiding repair by registering outside the I/M district.<sup>49,50</sup>

Smoking vehicles are an easily perceived motor vehicle emission problem. This human perception is achieved by observing the absorption or scattering of ambient light by the exhaust plume. Potentially, remote sensing could detect smoking vehicles day and night and without the need for a human presence and a sky for backlighting. In practice the first attempts involved observing the correlation between IR opacity at the Reference channel ( $2600\text{ cm}^{-1}$ ) and  $\text{CO}_2$  absorption. The signal/noise achieved was such that fleet average emissions of gasoline and diesel fueled vehicles could easily be distinguished and fleet average deterioration as a function of age addressed, but individual vehicle readings were rather imprecise.<sup>51</sup> The commercial RSD4000 and 5000 series units have developed a much improved measurement system for opacity in which the total optical depth (scattering plus absorption) at about 230 nm in the UV is correlated to the measured  $\text{CO}_2$ . This instrument shows a noise level for individual vehicle readings of as low as 500mg smoke/kg of fuel.<sup>52</sup> The commercial RSD instruments are better equipped than the above described FEAT instruments to measure opacity at this wavelength because of the different UV light sources chosen. The FEAT instrument uses the much brighter, but inherently greater flickering, Xe arc lamp source, whereas the commercial systems operate a more stable  $\text{D}_2$  lamp UV source.

#### ALTERNATIVE SYSTEMS FOR RSD

Detection of CO,  $\text{CO}_2$  and HC using dispersive spectroscopy equipped with an IR detector array was proposed<sup>53</sup> but apparently was never developed with success. CO and

CO<sub>2</sub> absorptions in the IR can be measured using laser based techniques. Tunable lasers in the fundamental region are available but are very expensive. Less expensively (although remaining three orders of magnitude more expensive than the drier igniter) one can obtain tunable lasers in the 1.2 micron region where one can also find very closely spaced overtone lines for both CO and CO<sub>2</sub>, allowing both gases to be determined with each scan of a single laser.<sup>54</sup> There are unfortunately no sharp IR lines which can be used as an adequate surrogate for HC. Methane and ethylene both have sharp lines but neither gas is at all well correlated to total exhaust HC (however measured). Nitric oxide and nitrous oxide have both been measured remotely from automobiles by tunable diode laser absorption spectroscopy.<sup>55-58</sup>

There have been commercial RSD units using other principles, for instance attempting to determine NO in the IR by means of measurement and subtraction of the very large water interference.<sup>59</sup> These systems are not currently commercially available to our knowledge.

## RESULTS

In the early 1990s, when we initiated this research, the distribution of on-road emissions was skewed and the mean was dominated by the ten percent of the fleet which caused half the emissions.<sup>3</sup> The introduction of newer and lower emitting vehicles has lowered the mean and caused the distribution to become even more skewed to the point that half the emissions now come from less than five percent of the fleet.<sup>12</sup> The impressive improvement in the on-road emissions of new vehicles was noted by Pokharel et al.<sup>60</sup> and expanded upon by Schwartz.<sup>61</sup> Figure 8 updates the results from Pokharel et al. and shows that the improved emissions from new vehicles continues through to the most recent data. The trend towards reduced CO emissions continues at over 10% per year. To the extent that on-road emissions remain a problem, then only a very small fraction of the fleet are the major contributors. On-road remote sensing techniques can identify them very efficiently. Ensuring that the identified vehicles are properly repaired is a sociopolitical problem beyond the scope of spectroscopy.

In view of the excellent correlation between RSD readings and IM240 it is apparent that both tests are measuring essentially the same parameter, namely the emissions of vehicles under at least somewhat realistic real driving conditions. The fact that 25,000 RSD readings can be well correlated against 750,000 IM240 readings and the RSD readings cost about one hundred fold less, implies that RSD can perform a very cost-effective emission inventory role. Singer and Harley,<sup>62</sup> Pokharel et al.,<sup>63</sup> have used RSD data in this way and compared the results to Federal computer models. The major difference is that RSD measures mass emissions per gallon or per kg of fuel and so fuel sales must be known. The computer model usually predicts emissions per vehicle mile. In the U.S.A. and most other countries it is easier to obtain estimates of fuel sales than estimates of vehicle miles (or km) traveled.

**Pattern failures.** Ross et al. analyzed RSD data showing that amongst fifteen year old cars the least expensive models were very significantly more likely to be gross emitters than the more expensive models.<sup>64</sup> This pattern was present to a greater or lesser extent

regardless of the manufacturer's country of origin. A typical result was 30% gross emitters in the cheaper models, 3% in the most expensive. They attributed this phenomenon to a manufacturer failure. Our attitude is that 30% gross emitters implies 70% not gross emitters and that the fault may lie with the individual owners and not the manufacturers. The truth probably lies in between, since the lower cost cars must be manufactured with minimum cost emission controls and the owners of these vehicles are statistically those least likely to engage in proper maintenance.

In 1991,<sup>65</sup> we were able to show that Hyundai manufactured vehicles from model years 1987-1989 had almost double the emissions of other manufacturers. We were later able to show that in 1990 and subsequent model years the Hyundai vehicles were statistically indistinguishable from other manufacturers. The United States Environmental Protection Agency assured us that this was the result of an action by their enforcement branch.

In Melbourne, Australia, our measurements showed that the taxicab fleet which had recently been required to retrofit liquefied petroleum gas (LPG) fuel kits was actually higher emitting than on-road gasoline vehicles of the same model year.<sup>66</sup> We were not invited back. Several studies in Mexico City based upon on-road remote sensing and more recently on long-path spectroscopic correlation have shown that there has been significant reductions in the emissions of CO and HC but compared to the U.S.A. there remains room for further improvement.<sup>67</sup>

**Potential applications.** The success of the SMART SIGN in encouraging voluntary emission control suggests several possible similar applications. The simplest would be to include an RSD at the drive-through toll booths where significant numbers of drivers pass with automatic vehicle identification. These drivers now receive a monthly toll bill. Monthly emissions information with the monthly toll bill would, in most cases, serve to inform the driver that the vehicle remains well maintained and unbroken, however if a failure should occur, relatively immediate notification is provided. Another concept is self service I/M lanes to which the driver could report 24/7 at his/her convenience for a drive-by emission test.

More radical ideas include gates which only open to allow low emitting vehicles into certain locations such as "clean car only" lanes. After extensive snowmobile testing we proposed to the National Park Service that they should set up a year-round gate which allows no gross polluters in the park. This would level the playing field between summer and winter entrants and could also include screening for excessive noise. There have been unpublished pilot projects looking at nitric oxide and smoke emissions from trucks at border crossings. We have suggested that such a border crossing facility could ideally be combined with on road testing of adequate engine power and adequate brakes for the load. Further, RSD can certainly be used to evaluate compliance with emissions directives such as CARB's diesel NO<sub>2</sub> requirement and the rules requiring that on-road diesel fuel should not contain significant amounts of sulfur.

**Future challenges.** There is always room for improved signal/noise, particularly for species such as NO<sub>2</sub> and formaldehyde for which the emissions are normally very small.

Smoke readings might benefit from measurement at several wavelengths to provide some discrimination between “black” and “white” smoking vehicles.

Routine remote measurement of emissions from individual vehicles in a multi-lane environment has yet to be demonstrated. An unmanned, self-calibrating, multi-lane, array of remote sensors has been envisaged. For a FEAT 5000 unit to be unmanned during operation it must have measurements that are temperature and pressure independent. In an unmanned system, response to these variables will need to be eliminated or modeled and measured so that the instrument can automatically correct for them. For multi-lane, individual measurements the best approach we believe would be an array of overhead mounted systems looking at reflectors in the roadway. A rugged reflector in the roadway must be harder than concrete or road grit and must be expected to maintain reflectivity for long periods of time. A gold coated, back reflecting sapphire mirror has been embedded in a local roadway experimentally, but the gold to sapphire bond proved insufficient to hold the sapphire against the tire friction.

## CONCLUSION

There have been many advances in both the instrumentation and in the reduction of pollutants since the first reported attempt at remote sensing of on-road vehicle emissions in 1973. Remote sensing has been able to measure transportation using wheels, tracks, and wings. As these vehicles continue the trend in reduced emissions of regulated pollutants, remote sensing will continue to adapt to be able to measure new species of concern, in new locations, and with new instrumental arrangements. Remote sensing has provided real-world, in-use, and on-road measurements of millions of vehicles around the world. On a cost per vehicle basis, remote sensing remains the least expensive emission testing method available. Remote sensing can be used for regulatory, enforcement, and repair purposes or simply to inform the public and allow for voluntary action. However used, remote sensing has provided a wealth of data to on-road emissions and will continue to do so until all of the world's vehicles are zero-emitting or non-combusting.

## ACKNOWLEDGEMENTS

The authors acknowledge Environmental Systems Products, the Coordinating Research Council, the University of Denver, the City and County of Denver, and the National Science Foundation under grant ATM-0450466 for their financial support to make this project possible. Special thanks go to the late John R. Starkey, Arun Ramesesham, and Rachel Willson.

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## Figure Captions

Fig. 1 RSD systems illustrated. (A) A schematic diagram of a typical RSD system set-up across a single lane on-ramp to an expressway, (B) an actual on-road set-up in Los Angeles, (C) at a interstate weigh station measuring heavy duty trucks, (D) in a rail yard measuring locomotives, (E) in Yellowstone National Park measuring snowmobiles, (F) at Heathrow airport U.K. measuring airplanes.

Fig. 2 Fundamental measurements used to calculate emissions from IR absorbing species from a low emitting vehicle at Speer and I-25 in Denver, CO. The data are individual 10 ms voltages from each of the four detectors.

Fig. 3 Calculated % cm of each gas species from the original voltages from Fig. 2 plotted versus the time after the vehicle has passed the instrument.

Fig. 4 The calculated % cm of CO versus % cm of CO<sub>2</sub> from each 10 ms interval from Fig 3. This ratio is essentially zero and a low emitting vehicle and does not pass through the origin because of background CO<sub>2</sub>.

Fig. 5 Detector voltages versus sequential 10 ms intervals from a vehicle a few minutes after the low emitting vehicle from Figs. 2 - 4.

Fig. 6 The calculated % cm of CO versus % cm of CO<sub>2</sub> from each 10 ms interval from Fig 5. This ratio is 0.80 or 872 g CO/ kg fuel and a high emitting vehicle.

Fig. 7 Linear regression of natural logarithm of the occurrences versus binned negative NH<sub>3</sub> values for Laplace factor determination. From this plot, on-road noise for the NH<sub>3</sub> channel was determined to be 0.12 g/kg for individual measurements.

Fig. 8 Average model year CO emissions from twelve of the last 17 years in Denver, CO are plotted. Each calendar year includes average measurements from the five most recent vehicle model years. The 10% per annum trend in decreasing emissions shows that newer vehicles have become progressively lower emitting.