Portable, on-board FTIR spectrometers: A universal tool for real-world monitoring of greenhouse gases, reactive nitrogen compounds, and other gaseous pollutants?

Michal Vojtíšek[1], Martin Pechout[2]

[1] Center for Sustainable Mobility, Czech Technical University in Prague, Czech Republic

[2] Department of Vehicles and Ground Transport, Czech University of Life Sciences, Prague, Czech Republic

Keywords: Greenhouse gases; reactive nitrogen compounds; real driving emissions; FTIR

Presenting author email: michal.vojtisek@fs.cvut.cz

Abstract

Exhaust emissions from internal combustion engines are one of the principal sources of greenhouse gas emissions, and one of the leading sources of air pollution in most metropolitan areas. Outdoor air pollution is associated premature death of about 0.1% population annually and associated economic damages on the order of 5% of the gross domestic product.

In addition to CO_2, the importance of methane (CH_4) and nitrous oxide (N_2O) is emerging as a result of the increased use of natural gas or biogas and of reduction catalysts. Of health relevant pollutants, most of the health effect is associated with particle bound semi-volatile organic compounds and with nitrogen monoxide (NO) and dioxide (NO_2), reported together as nitrogen oxides (NO_x). Ammonia (NH_3), owing to the potential to form secondary particles of ammonium nitrate, and potentially other reactive nitrogen compounds may be of interest. Of volatile organic gases, formaldehyde, acetaldehyde, and other fuel and technology dependent compounds may also be of a concern.

Fourier Transform Infra-Red (FTIR) analyzers have been increasingly used to analyze a wide range of compounds in exhaust gases, including all of the mentioned gases of interest, and have been recognized as a method for type-approval measurement of NH_3. Commercially available laboratory FTIR were shown to produce results comparable to laboratory analyzers for CO, CO_2, NO and NO_2, with the only potential downside being agreement with a flame ionization detector on total hydrocarbons.

Two pathways are suggested to exploit FTIR as a portable on-board instrument. In one, water is removed by cooling of the sample and/or selective membranes, after which greenhouse gases CO_2, CH_4, N_2O, and non-polar, non-water-soluble, highly volatile compounds such as NO and NO_2 can be readily quantified even at mediocre optical resolutions (units of cm^{-1}) and relatively short optical path lengths (on the order of 1 m), allowing small cells and detectors with thermoelectric cooling to be used.

For a more detailed and comprehensive analysis, water is kept in the sample, and the entire sampling train is heated to prevent condensation of water, ammonia, and less volatile compounds. Retaining the water allows for the detection of additional compounds such as ammonia, formaldehyde, or ethanol. Higher optical resolution ($0.5\ cm^{-1}$) is then typically required to resolve the compounds interfering with water and CO_2. Operating at a higher resolution, however, requires a faster detector and tighter tolerances in the optical path, and the increased noise needs to be balanced against the instrument response time. Another critical decision is the selection of the optical path length. Longer path lengths increase the instrument sensitivity, but also increase the occurrence of regions where analysis is prevented due to nearly complete attenuation by water, and typically require larger optical cell volumes, increasing the system response time. Optical path lengths of 2-10 meters have been used.

Several different FTIR systems used by the authors in moving vehicles as portable emissions monitoring systems will be discussed. Overall, FTIR technology may be useful for real-world emissions measurement of all gaseous pollutants of current interest with a single instrument.

1. Introduction

Internal combustion engines of various types and running on a variety of traditional and experimental fuels remain to be the principal source of motive power for the majority of automobiles and heavy on-road vehicles, as well as for the majority of most types of mobile machinery. The freedom of movement and the tremendous societal and economic benefits realized through mobility and work done by the machinery come at a major cost: Engines are one of the major sources of air pollution in urban areas, and one of the key sources of greenhouse gas emissions. Outdoor air pollution is listed within the top ten health hazards [1] and is associated with severe health and economic damages, including premature death of on the order of 0.1% of population annually (over half a million premature deaths per year in the EU [2], over an order of magnitude more compared to traffic accidents), and economic costs of approximately 5% of the Gross Domestic Product [3,4]. While engine exhaust emissions have improved considerably, and the number of premature deaths has a gradual downward trend, they remain one of the key problems. The persistence of the emissions problem is attributed not only to the high intensity of motor vehicle traffic and the close proximity of exhaust sources to the population, but also due to the discrepancy between type approval limit values and the actual emissions during everyday operation. The introduction and consequent gradual optimization of highly efficient exhaust aftertreatment has produced a situation where the distributions of emissions along a trip and among the vehicles are increasingly skewed, with large portion of fleet emissions attributed to a relatively small number of vehicles and large portion of trip emissions attributed to relatively short episodes of high emissions. Additionally, the quest to lower the emissions of the key pollutants that become subject of emissions limits (regulated pollutants) had an inadvertent side effects in the form of additional pollutants, which were, at the time, not of a grave concern. A meaningful characterization of the actual emissions from in-use vehicles requires, therefore, measurement under realistic conditions of a range of pollutants on a range of individual engines.

To assess the inherent characteristics of the design and systematic problems, portable, on-board monitoring instruments mounted on selected vehicles tested thoroughly under a variety of realistic conditions can be used during engine design and calibration, evaluation of drop-in fuels and aftermarket NO_x reductions, and independent verification of the in-use performance of vehicle or engine families [5]. To assess high emissions specific to individual vehicles, remote sensing approaches, offering high-volume testing at relatively low cost but at a limited range of operating conditions, can be used to identify individual vehicles with excess emissions due to tampering or malfunctions, and also to identify suspect engine design and calibration issues [6].

In this work, molecular spectroscopy in mid-infrared region, with the use of a Fourier Transform Infra-Red (FTIR) spectrometer, is suggested as a single universal tool for on-road assessment of all principal compounds that are known to be of interest at this time.

2. Pollutants of interest

Realistic combustion processes yield, in addition to carbon dioxide (CO_2) and water, carbon monoxide (CO), various volatile organic compounds (VOC, also termed HC – hydrocarbons), particulate matter and nitrogen oxides (NO_x). While particulate matter, originating from incomplete combustion of fuel and engine lubricating oil and from uncombustible portion of fuel and oil and engine wear particles, has been viewed as the most critical health-relevant pollutant, its discussion is not within the scope of this work.

Nitric oxide (NO) is formed at high temperatures during the main phase of the combustion from atmospheric nitrogen and oxygen, and form nitric oxide (NO), a process known as Zeldovich mechanism [7,8]. Subsequent oxidation of NO in the atmosphere yields primarily nitrogen dioxide (NO_2), a brownish irritant gas. NO_2 in outdoor air has been associated with mortality and hospital admissions for a range of respiratory and cardiovascular endpoints [8-11]. Other oxides of nitrogen – N_2O_2, N_2O_3, N_2O_4, N_2O_5 – are generated in small concentrations, are unstable and short-lived in the atmosphere. The oxides of nitrogen are summarily referred to as NO_x, although there is no precise definition. Often, NO_x is evaluated as the sum of NO and NO_2. Technically, the sum of NO_x also includes nitrous oxide (N_2O), which is, however, not hazardous to human health, but is a potent greenhouse gas with global warming potential approximately 265 times higher relative to CO_2 [12]. NO_x lead to the formation of nitrous acid (HNO_2) [13,14], nitric acid (HNO_3), and a variety of salts such as ammonium nitrate, present in the atmosphere as particulate matter [15]. Photodissociation of NO_2 under the presence of sunlight produces NO and atomic oxygen, which reacts with molecular oxygen to form ozone [16], a highly reactive compound generally harmful to human health, organisms and plants. NO_x and ground-level (tropospheric) ozone are, together with particulate matter, the principal part of urban air pollution.

CO and VOC are principally a product of incomplete oxidation of fuel and to a lesser extent engine lubricating oil.

On spark ignition engines, CO and VOC, principally a product of incomplete oxidation of fuel and to a lesser extent engine lubricating oil, and NO_x have been successfully abated by the combination of three-way catalysts (TWC) [17] and by maintaining stoichiometric air-fuel ratio through closed-loop control of the quantity of fuel injected [18]. This technology has been remarkably efficient. On some vehicles tested at the turn of the millennium, the concentrations of CO and NO in the exhaust gases were lower than in the surrounding air [19], and even larger automobiles were capable of reaching the total sum of organic compounds and NO_x of less than 10 mg/km [20]. California type approval

documentation of a Honda car shows the total emissions of organic compounds and NOx during the type-approval test (FTP) of approximately 14 mg/km [21].

Larger stationary spark ignition engines fueled by natural gas achieve relatively low engine-out NO_x by operating at a very lean mixture. Such operation is, however, close to the lean limit of the engine, and often results in substantial emissions of methane.

On diesel engines, where three-way catalyst cannot be used due to excess air, some level of reduction of NO_x emissions has been achieved through reducing peak combustion temperatures via delaying injection timing, exhaust gas recirculation (EGR), and later by advanced combustion strategies such as low temperature combustion (LTC) and partially premixed charge compression ignition combustion [22,23]. Both EGR and advanced combustion concepts are, however, effectively limited to lower engine loads. More recently, various catalytic devices have been explored, of which LNT and SCR have shown relatively high potential [24] and are currently used in production vehicles. LNT (for overview, see [25]) operates alternately in a long (on the order of minute or minutes) "lean" accumulation mode, during which NO_x are stored (i.e., as barium nitrate) in the catalyst, and in a short (on the order of seconds) "rich" regeneration mode, during which the engine operates with excess fuel, NO_x are released, and reduced in a manner similar to a three-way catalyst.

SCR (reviewed in [26]) use a reducing agent, aqueous solution of urea, which is injected upstream of the SCR, is mixed with the exhaust, and thermally decomposes into NH_3, which is used to reduce NO_x; NH_3 is also stored in the SCR. Recently, solid ammonia storage has been demonstrated as an alternative to urea [27]. Except for very low exhaust temperatures associated with cold start and extended low-load operation, SCR catalysts achieve efficiencies over 90%. U.S. federal (EPA) 2010 NO_x limit for heavy vehicle engines of 0.2 g/bhp-h (0.27 g/kWh) and the Euro VI limit of 0.46 g/kWh represent over an order of magnitude reduction over early limits. SCR allows California trucks made after 2010 – and quite possibly also European heavy vehicles – are likely to produce lower NO_x emissions per km per vehicle than most Euro 5 diesel cars, with a further decrease in NO_x limit by additional 90 %, to 0.02 g/bhp-h, proposed [28], and found to be technically feasible by a California Air Resources Board assessment [29].

The most efficient catalytic devices – TWC and SCR rely on precise control of the air-fuel ratio for TWC, and of the dosing of the reducing agent for SCR. Excess air in TWC and insufficient amount of reducing agent in SCR reduce NO_x conversion efficiency, while excess fuel in TWC [30,31] and excess reducing agent in SCR results in the emissions of ammonia (NH_3), an important emerging pollutant. Large portion of NH_3 in urban air in the U.S. and China originate from motor vehicles [32]. NH_3 is a precursor of secondary inorganic aerosol, namely ammonium nitrate and sulfate [33,34] which are the most abundant atmospheric secondary inorganic aerosols in many regions [35,36].

Another emerging pollutant is NO_2, which is intentionally produced in diesel oxidation catalysts, as it aids passive regeneration of diesel particle filters and increases the speed of NO_x conversion in SCR. As a result, NO_2 from new engines accounts for tens of percent of NO_X [37,38]. When high NO_2 is not mitigated by the high efficiency of SCR, such as on many diesel cars operated in the EU, more NO_x is emitted as NO_2 instead of NO, and the concentrations of NO_2 on streets tend to increase.

The list, of course, does not end here. Decomposition of water-urea solution, the most popular SCR reducing agent (also known as Diesel Exhaust Fluid or AdBlue), into ammonia yields isocyanic acid (HCNO) as an intermediate product [39-41], and various nitrogen compounds have been found in diesel exhaust, including 3-nitro-benz[a]benzanthrone, one of the most mutagenic compounds known to date [42].

Limitation of engine design by many manufacturers to the type approval procedures has resulted in marginal design, where catalysts on passenger cars are often properly sized only for low and intermediate loads, and infatuation by high horsepower rating on car engines has resulted in marginal practices to achieve high loads by, for example, disabling exhaust gas recirculation or fuel enrichment on gasoline engines (for examples, see [43-47]). Savings on sophisticated controls of air-fuel ratio or SCR reducing agent dosing have resulted in achieving low NO_x at the expense of considerable emissions of NH_3.

Furthermore, savings of fuel, reducing agent or motorist effort (to replenish diesel exhaust fluid on passenger cars) have motivated, over the last few decades, manufacturers, aftermarket sector, and motorists to modify or adjust their engines to achieve meager savings at the expense of several-fold or even order of magnitude increase of NO_x emissions. Examples of convictions include dual-mapping of engines in 90's on heavy-duty vehicles [48] and later on EU light-duty vehices (later commonly known as Dieselgate), manufacture of defeat devices (i.e. [49]), disabling of exhaust gas recirculation on cars, and SCR emulators for heavy trucks widely abundant on the internet.

Of all NO_x emissions from passenger cars in Europe, 56% were estimated to be excess emissions, which could be eliminated if the average on-road NO_x emissions were at the level of the respective diesel limit values [50]. These excess emissions represent about 15% of all NO_x emissions in Europe [50] and were associated with about 5000 premature deaths annually [51].

To minimize excess emissions associated with sub-optimal performance of engine and associated exhaust aftertreatment devices, at a minimum, the following compounds should be monitored throughout the operation of the vehicle fleet:

- a) Principal greenhouse gases CO_2 (all engines), CH_4 (gaseous fuel engines) and N_2O (lean-burn engine aftertreatment)
- b) Reactive nitrogen species, at the minimum, NO (primary engine-out pollutants from all engines), NO_2 (lean-burn engines with aftertreatment), NH_3 (all engines with NO_x aftertreatment)
- c) CO and fuel-specific VOC (formaldehyde, acetaldehyde)

3. Spectroscopic techniques

The absorption spectra of the principal compounds of interest in engine exhaust – water, greenhouse gases CO_2, CH_4, N_2O, health relevant pollutants CO, NO, NO_2, NH_3 – in the spectral range from approximately 4000-600 cm^{-1} (2.5 – 13.3 μm) are shown in Figure 1; omitted are various organic gases (alkanes, alkenes, aromatics, aldehydes, …), for which only general regions are shown. This range, useful for molecular spectroscopy measurements, is generally considered mid-infrared range, although some parts of it may be considered near (short wave) or far (long wave) infrared depending on varying classifications. Water is not considered a pollutant but absorbs in many spectral regions and its spectra overlaps with the spectra of many other measured compounds, creating an interference issue. Nitrogen, oxygen and inert gases absorb only minimally in this region.
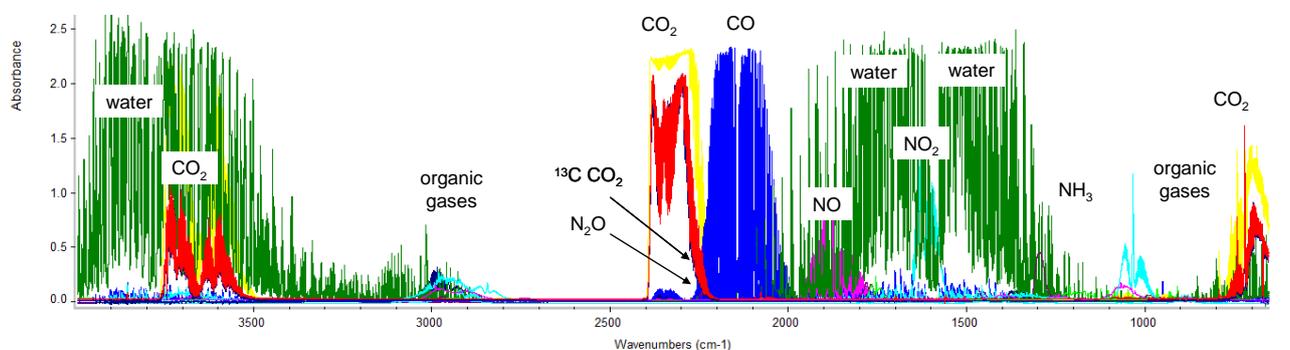

Figure 1: Mid infra-red spectra of principal compounds of interest in vehicular exhaust

Several spectroscopic techniques are available for quantitative analysis, mostly based on absorption spectroscopy and the Beer-Lambert law. When light of intensity I_o at specific wavelength is passed through a mixture measured gas and gases not absorbing at this wavelength, the resulting intensity I_r at this wavelength is a function of the absorption properties of this gas (dependent on temperature, pressure, wavelength, and other conditions), its molecular concentration, and the path length:

$$I_r = I_o \exp(-\varepsilon_\lambda LC) \qquad (1)$$

Where ε_λ is cross-absorption coefficient in m^{-1} at wavelength λ, L is path length in m, and C (dimensionless) is the concentration of the measured species. Absorbance A is defined as negative decadic logarithm of transmittance T, defined as the ratio I_r/I_o:

$$A = -\log T = -\log(I_r/I_o) = k\varepsilon_\lambda LC \qquad (= \varepsilon_\lambda LC) \qquad (2)$$

where constant k is given here only for formal reasons (conversion of logarithm base) and is typically reflected in the constant ε_λ. Typically, constant ε_λ is determined empirically for each given analyzer and summarily accounts for different additional factors. In reality, the absorption at any wavelength λ is the sum of absorptions of all compounds absorbing at that wavelength. Infrared spectroscopy is therefore prone to interference from other compounds, which need to be accounted for, regardless of whether the knowledge of their concentration is desired.

The simplest technique, used in garage-grade analyzers (used for vehicle diagnostics and repair and for periodic technical inspections) and a variety of inexpensive sensors, is non-dispersive infra-red (NDIR) spectroscopy, where analysis is performed on a wavelength range pre-selected by the choice of source (LED diode), detector, or, most frequently, the source is a glowing element and the wavelength is selected by an optical filter. NDIR requires compensation for interfering gases (quantification at a different wavelength and subtraction), or most frequently, their removal. This is why NDIR is used for CO and CO_2, which have absorption bands generally free of interference, but not for many other gases. In industrial settings, NDIR is also used for NO with the removal of water by thermoelectric cooler. NH_3, and to some extent NO_2, are soluble in, and are removed with, water.

For NO_2, NH_3 and N_2O in vehicular exhaust, "broad band" NDIR cannot be used, due to strong interference of water (NO_2 and NH_3) and CO_2 and CO (N_2O). The analysis regions for these compounds are fairly narrow, with example

analysis regions shown in Figure 2. Further, water in the exhaust (typically up to 10% for diesel engines, up to 13% for gasoline engines, up to around 20% on engines running on methane; 4% is shown in Figure 2) leads to nearly complete absorbance (band saturation) at many wavelengths (absorbance 2.0 corresponds to 99% attenuation, 3.0 to 99.9% attenuation). Typically, high-resolution techniques, such as Fourier Transform Infra-Red (FTIR) spectroscopy, tunable diode laser absorption spectroscopy (TDLAS), or quantum cascade lasers (QCL) are needed, and have been successfully deployed. The example in Figure 2 are calibration spectra used with FTIR analyzer sampling undiluted engine exhaust, representing (except for water, deliberately shown at 4%, relatively low end of the range) values around the upper end of the desired quantification ranges (20 ppm N_2O, 100 ppm NH_3, 200 ppm NO_2, 3000 ppm NO). Often, interference cannot be avoided, and the absorption of the interfering compounds needs to be quantified separately at different wavelengths and subtracted. Fortunately, higher N_2O emissions are typically limited to diesel engines with NO_x aftertreatment (LNT, SCR), which exhibit, thanks to the oxidation catalyst, very low CO emissions, except for LNT regeneration.
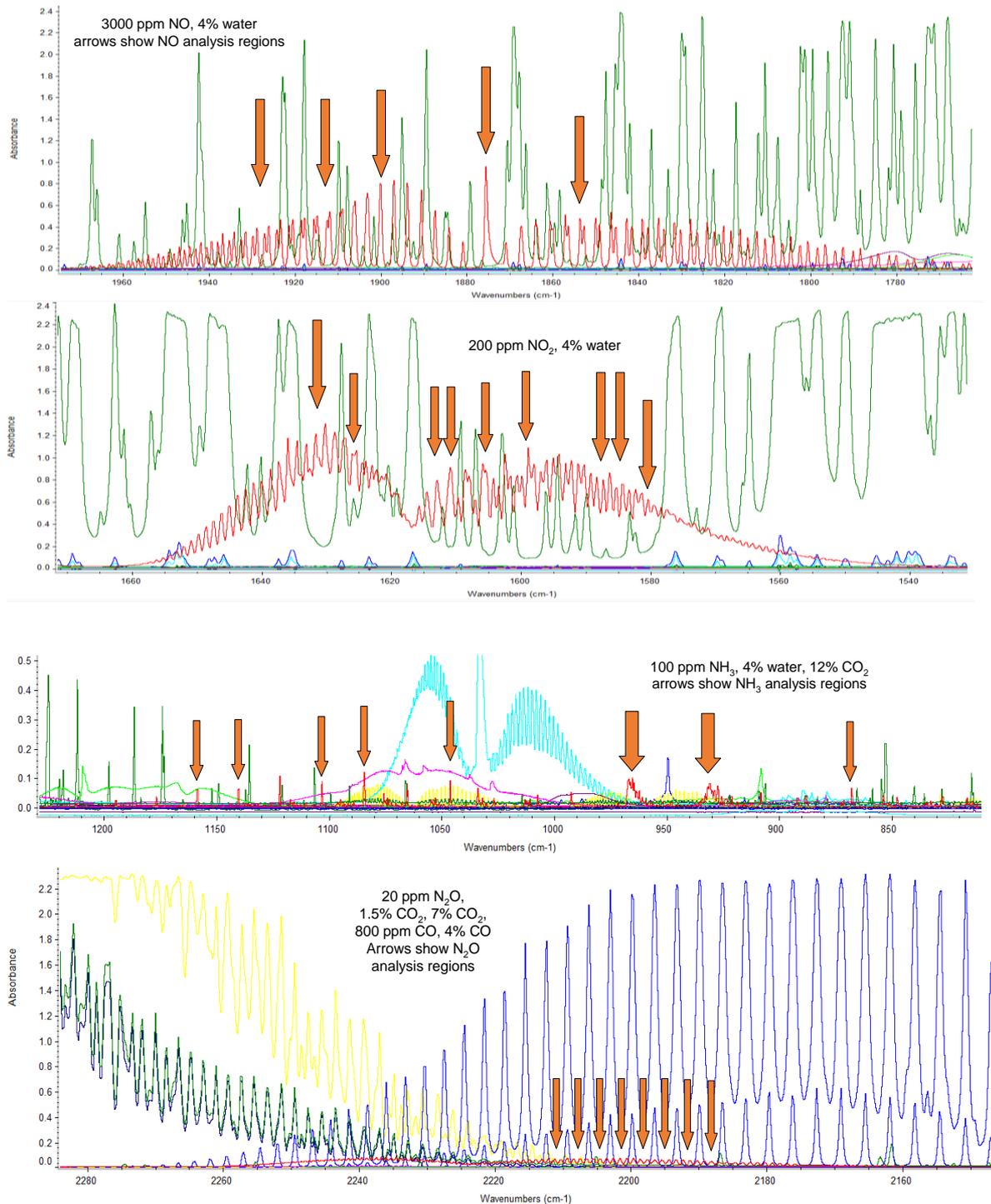

Figure 2: Possible analysis regions for (top to bottom): NO, NO₂, NH₃, N₂O

4. FTIR

In an FTIR analyzer, an infrared source producing a wide and continuous range wavelength light, such as a heated tungsten wire, is used. The beam is divided in a Michelson type interferometer by a beam splitter into two beams, one reflecting from a fixed mirror and the other reflecting from a mirror moving along the beam direction. The two beams are then joined, creating, for each difference between the optical path lengths, an interference pattern. The resulting beam is passed through a multi-pass sample cell filled with the analyzed exhaust, and the total intensity recorded, for each difference in optical path lengths, by a detector. The interferogram is transformed by a Fast Fourier Transform into a transmission spectra in the frequency domain. This approach leads to a higher signal to noise ratio than if the transmission at each wavelength was to be measured separately [52].

The use of FTIR for exhaust measurement has been reviewed in [53,54]. The use of FTIR in a moving vehicle has been, so far, limited due to technical challenges. Jeter [55] has used a pair of laboratory FTIR with a membrane sample dryer (a technique not compatible with NH_3 measurement) and a 10 m optical path length mounted in an instrumented vehicle to assess very low emission levels from a passenger car. A smaller but still relatively bulky and relatively slow (30 s time resolution) instrument with a 13 m optical path length was used by Reyes [56]. A portable, fast system has been used by Daham [57], however, the system worked at a relatively low (4 cm^{-1}) optical resolution, while a substantially higher resolution – at least 0.5 cm^{-1} – has been recommended, along with the tunable laser diode approach, for NH_3 measurement [30]. An on-board system built at the Technical University of Liberec using an industrial grade MIDAC FTIR analyzer with a custom optical cell, providing 6 m path length in a relatively low 0.2 liter volume, has been validated for NO and NH_3 measurement in the laboratory and for NO measurements on the road [58]. The limits of detection, calculated assuming 3 times the standard deviation of the background measured, for NH_3 and NO were 1 ppm. The system has been used on a range of vehicles from passenger cars [58] to locomotives [59] (shown in Fig. 3 on the left). A similar setup using faster (1 Hz) industrial FTIR (Nicolet Antaris IGS) with a 0.3 dm^3, 5 m path length cell, with about double the mass and double power consumption, but a faster time resolution of 1 Hz, has been prepared and validated at the Czech Technical University (shown in Figure 3 on the right) and recently used for evaluation of emissions of compressed natural gas vehicles [60] both on the road and in the laboratory, with laboratory measurements done in parallel using a full-flow dilution tunnel and standard instruments as a reference. A relatively compact setup using a Bruker Matrix FTIR system, with a series of modifications, has been developed and used at the Czech University of Life Sciences [61,62].

The path length and spectral and temporal resolutions are a careful compromise among contradicting goals. A longer path length and longer averaging time decrease the detection limit, but longer path length also increases the regions where the beam is excessively attenuated by carbon dioxide and water. Higher optical resolution increases noise but allows for discrimination of, for example, nitric oxide from order of magnitude higher concentrations of water vapor.

The TU Liberec, Czech Technical University and Czech University of Life Sciences systems used on the road, as well as the reference laboratory FTIR in [58] (MKS 2030), see [63,64] for additional description, used mercury cadmium telluride detectors cooled by liquid nitrogen, heated 5-6 m optical path length multipass cells, and run at the spectral resolution of 0.5 cm^{-1}. The reported sample train and optical cell temperatures ranged from 121 to 191 °C.
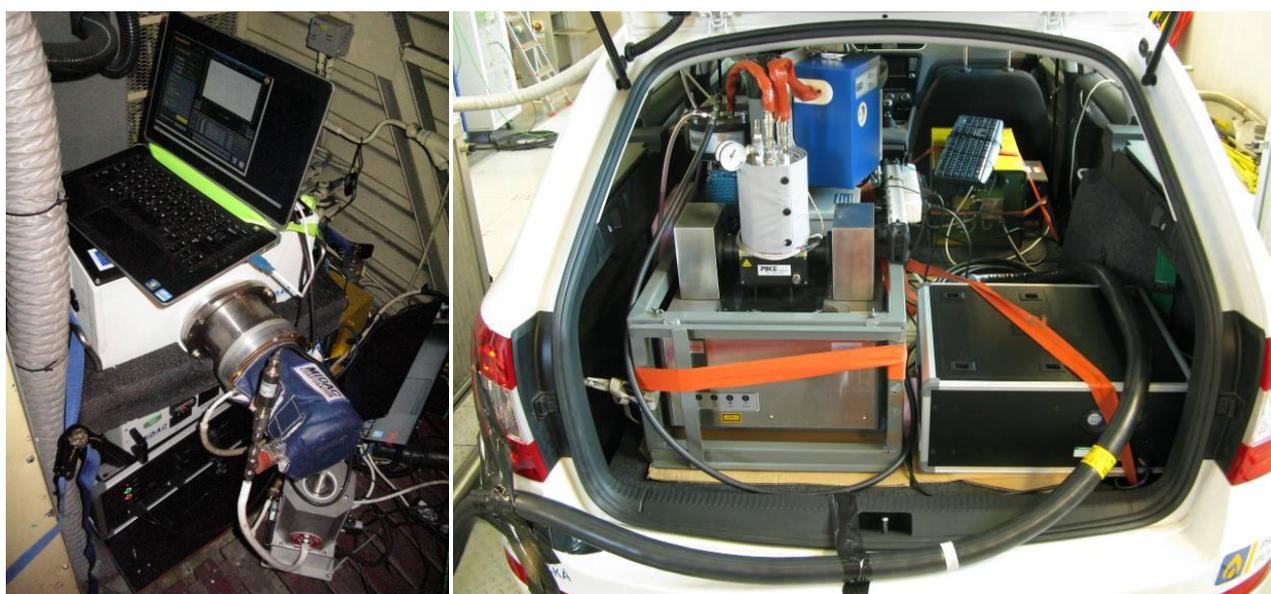

Figure 3: On-road FTIR setups: Left: MIDAC, TU Liberec, Czech Republic [58,59]; Right: Laboratory grade Nicolet Antaris, Czech Technical University [60]

There are two major caveats with FTIR. One is the possible distortion of the spectra due to contamination of the optics with semi-volatile organic species, excessive vibrations and jolts, fluctuations in various temperatures (instrument internals, optical cell, sample), and other reasons. The quality of the spectra can be checked by evaluating certain regions of the spectra and/or by comparing the concentrations of at least some gases for which reference measurement is available (CO_2 calculated from exhaust gas oxygen sensor, NO_x measured by a sensor in exhaust). This can be, with proper care, minimized, or at least such distortions could be detected.

The second and probably more serious caveat is that the measured absorption spectra is the sum of the absorptions of all absorbing compounds, and that the contributions of each compound are calculated from often overlapping individual absorption spectra obtained by deconvolution of the measured spectra. Therefore, detection limits, uncertainties, or even the capability to obtain a meaningful reading for a given compound, are specific to the composition of the mixture. For example, the detection limit achieved with a mixture of calibration gas with dry nitrogen is unlikely to be achieved in the presence of several orders of magnitude higher concentrations of CO_2 and water vapor. This is, however, a known issue, common to both on-road and laboratory measurement, and is dealt with, to various degree of success, by spectroscopy specialists. It should not, however, be underestimated. For example, in a study by Li et al. [65], multiple commercial FTIR instruments were reported to provide different results. On a positive note, if such problem is discovered and resolved, interpretation of the spectra can be done ex-post.

5. Conclusions

Several FTIR analyzers have been successfully used on a variety of moving vehicles, from cars to a diesel locomotive, suggesting infrared absorption spectra can be obtained on the road. Combined with the general use of FTIR in laboratory settings to measure a variety of regulated and unregulated compounds, it seems that FTIR analyzers can be, and have been, used to measure the three principal greenhouse gases CO_2, N_2O and CH_4, principal reactive nitrogen compounds NO, NO_2 and NH_3, and a variety of other gases such as CO and formaldehyde, making it a universal instrument for essentially all gaseous pollutants at least of current interest.

6. References

1. Health Effect Institute (2018): State of Global Air. https://www.stateofglobalair.org/sites/default/files/soga-2018-report.pdf
2. EEA (European Environment Agency): Air quality in Europe - 2020 report. EEA, Copenhagen, 2020.
3. Nam, K.-M., Selin N.E., Reilly J.M., Paltsev S. (2010). Measuring Loss in Human Welfare Caused by Air Pollution: A CGE Analysis for the European Region. Energy Policy 38(9): 5059-5071.
4. World Bank and Institute for Health Metrics and Evaluation. 2016. The Cost of Air Pollution: Strengthening the Economic Case for Action. Washington, DC: World Bank.
5. VOJTISEK-LOM, M.; COBB, J. T. (1997). Vehicle mass emissions measurement using a portable 5-gas exhaust analyzer and engine computer data. Proceedings: Emission Inventory, Planning for the Future, 1997.
6. BISHOP, G.A.; STARKEY, J.R.; IHLENFELDT, A.; WILLIAMS, W.J.; STEDMAN, D.H. (1989): IR long-path photometry: a remote sensing tool for automobile emissions. Analytical Chemistry, 61 (10), 671A–677A.
7. ZELDOVICH, Y. B. (1946): The Oxidation of Nitrogen in Combustion Explosions, Acta Physicochimica USSR, 21, 577–628.
8. LAVOIE G.A., HEYWOOD J.B. & KECK J.C. (1970): Experimental and Theoretical Study of Nitric Oxide Formation in Internal Combustion Engines, Combustion Science and Technology, 1:4, 313-326.
9. FAUSTINI, A., RAPP, R., FORASTIERE, F., 2014. Nitrogen dioxide and mortality: review and meta-analysis of long-term studies. Eur. Respir. J. 44, 744-753.
10. US EPA, 2015. Integrated Science Assessment for Oxides of Nitrogen - Health Criteria (Second External Review Draft), EPA/600/R-14/006. http://cfpub.epa.gov/ncea/isa/recordisplay.cfm?deid=288043 [Accessed February 2016]. United States Environmental Protection Agency, Washington DC.
11. BRAND, Christian. Beyond 'Dieselgate': Implications of unaccounted and future air pollutant emissions and energy use for cars in the United Kingdom. Energy Policy, 2016, 97: 1-12.
12. IPCC (Intergovernmental Panel for Climate Change) Fourth Assessment Report: Climate Change, 2007.
13. GUTZWILLER L., ARENS F., BALTENSPERGER, U., GÄGGELER H.W., AMMANN M. (2002): Significance of Semivolatile Diesel Exhaust Organics for Secondary HONO Formation. Environmental Science & Technology 2002 36 (4), 677-682.
14. KURTENBACH, R., et al. (2001). Investigations of emissions and heterogeneous formation of HONO in a road traffic tunnel. Atmospheric Environment, 35.20: 3385-3394.

15. HEEB, N.V., et al. (2011). Reactive nitrogen compounds (RNCs) in exhaust of advanced PM–NO x abatement technologies for future diesel applications. Atmospheric environment, 45.18: 3203-3209.

16. SEINFELD J.H., PANDIS S.N. (1998): Atmospheric chemistry and physics: from air pollution to climate change. John Wiley & Sons.

17. MOONEY, J. J.; THOMPSON, C. E.; DETTLING, J. C. (1977). Three-Way Conversion Catalysts Part of the New Emission Control System. SAE Transactions, 1553-1562.

18. FALK, C. D., & MOONEY, J. J. (1980). Three—Way Conversion Catalysts: Effect of Closed—Loop Feed—Back Control and Other Parameters on Catalyst Efficiency. SAE Transactions, 1822-1832.

19. JETTER, J., MAESHIRO, S., HATCHO, S., AND KLEBBA, R., "Development of an On-Board Analyzer for Use on Advanced Low Emission Vehicles," SAE Technical Paper 2000-01-1140, 2000, doi:10.4271/2000-01-1140.

20. ANTHONY J.; KUBSH, J. (2007). The Potential for Achieving Low Hydrocarbon and NOx Exhaust Emissions from Large Light-Duty Gasoline Vehicles. SAE Technical Paper 2007-01-1261.

21. California Air Resources Board: Executive Order no. A-023-0683, 2018, https://www.arb.ca.gov/msprog/onroad/cert/pcldtmdv/2018/honda_pc_a0230683_1d5_s3-30.pdf

22. KIMURA, S., AOKI, O., KITAHARA, Y., AND AIYOSHIZAWA, E. (2001). Ultra-Clean Combustion Technology Combining a Low-Temperature and Premixed Combustion Concept for Meeting Future Emission Standards. SAE Technical Paper 2001-01-0200.

23. JACOBS, T.J.; ASSANIS, D.N. (2007). The attainment of premixed compression ignition low-temperature combustion in a compression ignition direct injection engine. Proceedings of the Combustion Institute, 31.2: 2913-2920.

24. JOHNSON, T.V. (2002). Diesel emission control: 2001 in Review. SAE Technical paper 2002-01-0285.

25. MRÁČEK D. (2016): Analysis and Modelling of Spatiotemporal Concentration Profiles in NOx Reduction Automotive Catalytic Converters. Ph.D. dissertation, VŠCHT Praha. https://repozitar.vscht.cz/theses/phd/fchi/2016/CHINZ4/14126

26. GUAN, Bin, et al. Review of state of the art technologies of selective catalytic reduction of NO x from diesel engine exhaust. Applied Thermal Engineering, 2014, 66.1: 395-414.

27. GIECHASKIEL, B., SUAREZ-BERTOA, R., LAHDE, T., CLAIROTTE, M., CARRIERO, M., BONNEL, P., & MAGGIORE, M. (2019). Emissions of a Euro 6b Diesel Passenger Car Retrofitted with a Solid Ammonia Reduction System. Atmosphere, 10(4), 180.

28. US EPA, NOx memorandum – NOx petition response. https://www.epa.gov/sites/production/files/2016-12/documents/nox-memorandum-nox-petition-response-2016-12-20.pdf

29. California Air Resources Board (2015): Draft Technology Assessment: Lower NOx Heavy Duty Diesel Engines. https://www.arb.ca.gov/msprog/tech/techreport/diesel_tech_report.pdf

30. SUAREZ-BERTOA, R., ZARDINI, A.A., ASTORGA, C. (2014). Ammonia exhaust emissions from spark ignition vehicles over the New European Driving Cycle. Atmos. Environ. 97. doi:10.1016/j.atmosenv.2014.07.050

31. HEEB N.V., et al. (2006): Three-way catalyst-induced formation of ammonia—velocity- and acceleration-dependent emission factors. Atmospheric Environment, 40, 31, 5986-5997, doi 10.1016/j.atmosenv.2005.12.035.

32. SUN, K., et al. (2017). Vehicle emissions as an important urban ammonia source in the United States and China. Environ. Sci. Technol, 51.4: 2472-2481.

33. FINLAYSON-PITTS, B. J., PITTS J.N. (1999). Chemistry of the Upper and Lower Atmosphere, Elsevier, New York.

34. BEHERA, S.N. AND SHARMA M. (2010). Investigating the potential role of ammonia in ion chemistry of fine particulate matter formation for an urban environment. Science of The Total Environment, 408(17), 3569-3575.

35. KIM, B.M., TEFFERA, S., ZELDIN, M.D. (2000). Characterization of PM25 and PM10 in the South Coast Air Basin of Southern California: Part 1—Spatial Variations. Journal of the Air & Waste Management Association, 50 (12), 2034-2044.

36. SILLANPÄÄ, M., ET AL. (2006). Chemical composition and mass closure of particulate matter at six urban sites in Europe. Atmospheric Environment, 40, Supplement 2 (0), 212-223.

37. CARSLAW, D.C., 2005. Evidence of an increasing NO2/NOX emissions ratio from road traffic emissions. Atmos. Environ. 39. doi:10.1016/j.atmosenv.2005.06.023

38. OLSEN, D.B., KOHLS, M., ARNEY, G., 2010. Impact of oxidation catalysts on exhaust NO2/NOx ratio from lean-burn natural gas engines. J. Air Waste Manag. Assoc. 60. doi:10.3155/1047-3289.60.7.867

39. GUTZWILLER L., ARENS F., BALTENSPERGER, U., GÄGGELER H.W., AMMANN M. (2002): Significance of Semivolatile Diesel Exhaust Organics for Secondary HONO Formation. Environmental Science & Technology 2002 36 (4), 677-682

40. BAIK, J.H., YIM, S.D., NAM, I.S. et al. Topics in Catalysis (2004) 30:37, doi: 10.1023/B:TOCA.0000029725.88068.97

41. KOEBEL M., ELSENER M., KLEEMANN M. (2000). Urea-SCR: a promising technique to reduce NOx emissions from automotive diesel engines. Catalysis Today, 59, 3-4, 2000, 335-345.

42. ENYA T., et al. (1997): 3-Nitrobenzanthrone, a Powerful Bacterial Mutagen and Suspected Human Carcinogen Found in Diesel Exhaust and Airborne Particulates. Environmental Science and Technology, 31, 2772-2776.

43. FRANCO, V., SÁNCHEZ, F.P., GERMAN, J., MOCK, P. (2014). Real-word exhaust emissions from modern diesel cars a meta-analysis of PEMS emissions data from EU (EURO 6) and US (TIER 2 BIN 5/ULEV II) diesel passenger cars. ICCT Int. Counc. Clean Transp.

44. LIGTERINK, N., KADIJK, G., MENSCH, P. VAN, HAUSBERGER, S., REXEIS, M. (2013). Investigations and real world emission performance of Euro 6 light-duty vehicles.

45. WEISS, M., et al. (2012). Will Euro 6 reduce the NOx emissions of new diesel cars? - Insights from on-road tests with Portable Emissions Measurement Systems (PEMS). Atmos. Environ. 62, 657–665. doi:10.1016/j.atmosenv.2012.08.056

46. YANG, L., FRANCO, V., MOCK, P., KOLKE, R., ZHANG, S., WU, Y., GERMAN, J. (2015). Experimental Assessment of NOx Emissions from 73 Euro 6 Diesel Passenger Cars. Environ. Sci. Technol. 49, 14409–14415. doi:10.1021/acs.est.5b04242

47. VOJTÍŠEK-LOM, M.; FENKL, M.; DUFEK, M.; MAREŠ, J. (2009). Off-cycle, real-world emissions of modern light-duty diesel vehicles. Society of Automotive Engineers Technical Paper 2009-24-0148.

48. United States Department of Justice (2015): Clean Air Act diesel engine cases. [WWW Document]. URL https://www.justice.gov/enrd/diesel-engines

49. US EPA (United States Environmental Protection Agency, 2019) : Performance Diesel Inc. Clean Air Act Settlement Sheet. Online at https://www.epa.gov/enforcement/performance-diesel-inc-clean-air-act-settlement-information-sheet. In reference to: United States of America v. Performance Diesel, Inc., Civil Action No. 4:19-cv-00075-DN, United States District Court for the District of Utah.

50. JONSON, J.E.; BORKEN-KLEEFELD, J.; SIMPSON, D.; NYÍRI, A.; POSCH, M.; HEYES, C. (2017): Impact of excess NOx emissions from diesel cars on air quality, public health and eutrophication in Europe. Environ. Res. Lett., 12, 094017, doi 10.1088/1748-9326/aa8850

51. CHOSSIÈRE, G. P., MALINA, R., ALLROGGEN, F., EASTHAM, S. D., SPETH, R. L., & BARRETT, S. R. (2018). Country-and manufacturer-level attribution of air quality impacts due to excess NOx emissions from diesel passenger vehicles in Europe. Atmospheric environment, 189, 89-97.

52. FELLGETT, P. B. (1949). "On the Ultimate Sensitivity and Practical Performance of Radiation Detectors". J. Opt. Soc. Am. 39 (11): 970–6. doi:10.1364/JOSA.39.000970

53. ADACHI, M. (2000). Emission measurement techniques for advanced powertrains. Meas. Sci. Technol. 11. doi:10.1088/0957-0233/11/10/201

54. REYES, F., et al. (2006). Technical Note: Analysis of non-regulated vehicular emissions by extractive FTIR spectrometry: tests on a hybrid car in Mexico City. Atmospheric Chemistry and Physics, 6.12: 5339-5346.

55. JETTER, J., MAESHIRO, S., HATCHO, S., AND KLEBBA, R. (2000). Development of an On-Board Analyzer for Use on Advanced Low Emission Vehicles. SAE Technical Paper 2000-01-1140, doi:10.4271/2000-01-1140.

56. REYES F., GRUTTER M., JAZCILEVICH A., GONZALEZ-OROPEZA R. (2006). Analysis of non-regulated vehicular emissions by extractive FTIR spectrometry: tests on a hybrid car in Mexico City. Atmospheric Chemistry and Physics Discussions, European Geosciences Union, 6 (4), pp.5773-5796.

57. DAHAM, B., ANDREWS, G., LI, H., BALLESTEROS, R., BELL M.C., TATE J., ROPKINS K. (2005). Application of a Portable FTIR for Measuring On-road Emissions. SAE Technical Paper 2005-01-0676, doi:10.4271/2005-01-0676.

58. SUAREZ-BERTOA, R., MENDOZA-VILLAFUERTE, P., RICCOBONO, F., VOJTISEK, M., PECHOUT, M., PERUJO, A., ASTORGA, C. (2017). On-road measurement of NH3 emissions from gasoline and diesel passenger cars during real world driving conditions, Atmospheric Environment, 166, 488-497.

59. VOJTISEK-LOM, M., JIRKŮ, J., PECHOUT, M. (2020). Real-World Exhaust Emissions of Diesel Locomotives and Motorized Railcars during Scheduled Passenger Train Runs on Czech Railroads. Atmosphere, 11.6: 582.

60. VOJTÍŠEK M., BERÁNEK V., KLÍR V., JINDRA P., PECHOUT M., VOŘÍŠEK T. (2018): On-road and laboratory emissions of NO, NO2, NH3, N2O and CH4 from late-model EU light utility vehicles: Comparison of diesel and CNG. Science of the Total Environment, 616-617, 774–784.

61. PECHOUT, M., KOTEK, M., JINDRA, P., MACOUN, D., HART, J., & VOJTISEK-LOM, M. (2019). Comparison of hydrogenated vegetable oil and biodiesel effects on combustion, unregulated and regulated gaseous pollutants and DPF regeneration procedure in a Euro6 car. Science of the Total Environment, 696, 133748.

62. SUAREZ-BERTOA, R., PECHOUT, M., VOJTÍŠEK, M., & ASTORGA, C. (2020). Regulated and non-regulated emissions from Euro 6 diesel, gasoline and CNG vehicles under real-world driving conditions. Atmosphere, 11(2), 204.

63. CLAIROTTE, M., et al. (2012). Online characterization of regulated and unregulated gaseous and particulate exhaust emissions from two-stroke mopeds: A chemometric approach. Anal. Chim. Acta 717:28–38. https://doi.org/10.1016/j.aca.2011.12.029.

64. SUAREZ-BERTOA, R., ZARDINI, A.A., KEUKEN, H., ASTORGA, C., 2015. Impact of ethanol containing gasoline blends on emissions froma flex-fuel vehicle tested over theWorldwide Harmonized Light duty Test Cycle (WLTC). Fuel 143:173–182. https://doi.org/10.1016/j.fuel.2014.10.076.

65. LI, N., ROBINSON, J., BARRETT, R.,WHEATLEY, A., 2016. Nitrogen Species Measurement Investigation Using Two Different Ftir. Iastem Int. Conf, pp. 24–29 (doi:IJASEAT-IRAJ-DOI-4984).