Review

Fourier Transform Infrared (FTIR) Spectroscopy for Measurements of Vehicle Exhaust Emissions: A Review

Barouch Giechaskiel * and Michaël Clairotte

European Commission—Joint Research Centre (JRC), 21027 Ispra, Italy; michael.clairotte@ec.europa.eu

* Correspondence: barouch.giechaskiel@ec.europa.eu; Tel.: +39-0332-785-312

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Featured Application: The review showed that sampling with FTIR from the tailpipe of vehicles for the determination of various gaseous pollutants is a possible alternative to currently regulated techniques.

Abstract: Pollution from vehicles is a serious concern for the environment and human health. Vehicle emission regulations worldwide have limits for pollutants such as hydrocarbons, CO, and NO_x. The measurements are typically conducted at engine dynamometers (heavy-duty engines) sampling from the tailpipe or at chassis dynamometers (light-duty vehicles) sampling from the dilution tunnel. The latest regulations focused on the actual emissions of the vehicles on the road. Greenhouse gases (GHG) (such as CO_2, CH_4, N_2O), and NH_3 have also been the subject of some regulations. One instrument that can measure many gaseous compounds simultaneously is the Fourier transform infrared (FTIR) spectrometer. In this review the studies that assessed FTIRs since the 1980s are summarized. Studies with calibration gases or vehicle exhaust gas in comparison with well-established techniques were included. The main conclusion is that FTIRs, even when used at the tailpipe and not at the dilution tunnel, provide comparable results with other well-established techniques for CO_2, CO, NO_x, while for hydrocarbons, higher deviations were noticed. The introduction of FTIRs in the regulation needs a careful description of the technical requirements, especially interference tests. Although the limited results of prototype portable FTIRs for on-road measurement are promising, their performance at the wide range of environmental conditions (temperature, pressure, vibrations) needs further studies.

Keywords: FTIR; NDIR; NDUV; CLA; NH_3; formaldehyde; acetaldehyde; PEMS

1. Introduction

Vehicle emissions are regulated since the 1970s [1]. The measurements are conducted on chassis dynamometers (light-duty vehicles) or in engine test cells (heavy-duty engines). The instruments described in the regulations are sampling from the full dilution tunnel, where the whole exhaust gas is diluted, or directly from the tailpipe (undiluted exhaust). The control of the regulated pollutants (e.g., CO, NO_x) with advanced aftertreatment devices [2] has led in some cases to increased emission of non-regulated pollutants (e.g., N_2O, NH_3). The measurement techniques for regulated pollutants are well-defined in the regulation (e.g., non-dispersive infrared (NDIR) for CO and CO_2). For non-regulated pollutants, only recently, a Global Technical Regulation for light-duty vehicles (GTR 15) prescribes possible measurement techniques. One method that can measure many compounds is FTIR (Fourier transform infrared) spectroscopy (= study of the interaction between light with matter) [3]. Many compounds absorb infrared energy at an intrinsic wave number (or wavelength) proportionally to their concentration. In an FTIR spectrometer, some of the infrared (IR) radiation is absorbed by the sample, and some of it is passed through (transmitted). The resulting molecular absorption and transmission response can be used to identify the components of the sample and their concentration. FTIR, compared to other IR techniques, can measure many components in real-time due to the use of an interferometer.
that allows the collection of a broad range of wavelengths. By contrast, NDIR analyzers measure one compound due to the use of an optical filter that allows the selection of a narrow wavelength area, specific to the compound of interest.

FTIR is used in geology, chemistry, materials, medicine, and biology research fields on solid, liquid, and gaseous samples [4]. FTIR has been used in a wide range of air pollution-related studies in both ambient air and environmental chambers [5,6]. Already in the late 1970s, an FTIR system was installed in a van for air pollution measurements for the Environmental Protection Agency (EPA) of the United States of America (USA) [7,8]. FTIR has also been applied for aerosol analysis [9,10], for example, to assess the hygroscopicity of ambient particles [11] or analyze surface functional groups of particles [12]. Another application was the measurement of stack emissions from various processes, such as incinerators [13]. Other researchers have used open path FTIR to record CO, CO₂, and N₂O [14] or NH₃ [15] emissions from high traffic roadside sites or even emissions in aircraft exhaust [16]. Extractive in cell FTIR has been used in many applications, e.g., trains [17]. Extractive measurement with an activated charcoal tube was used to measure volatile organic compounds (VOC) of a heavy-duty engine [18]. Applications in atmospheric and environmental studies were reviewed elsewhere [19,20].

The application of FTIR spectroscopy to vehicles’ exhaust analysis began in the early 1980s [21–23]. It received a lot of attention for the study of alternative fuels due to its ability to discriminate oxidized species in tailpipe gases [24–27]. Other studies focused on TWC (three-way catalysts) [28–30] and low ambient temperatures [27,29]. Later FTIR was used to measure emissions from NOₓ reduction systems [31] due to its ability to simultaneously measure separately the oxides of nitrogen [27,32,33].

However, the technique did not spread out in the industry due to several practical problems, such as complexity of calibration (due to cross sensitivity of, e.g., CO₂ and H₂O), slow response, and poor concentration accuracy when compared to the regulated analytical techniques [31,34]. The evolution of computers and algorithms made it possible to have an instrument that can measure and analyze the data in real time. Since then, and especially in the last decade, the use of FTIR spectrometers has widespread.

It has been used for the measurement of gas concentrations for various studies, e.g., soot oxidation [35], or SCR (selective catalytic reduction for NOₓ) [36,37] and catalyst evaluation [38–40] with synthetic gases. It has also been used in engine test beds to assess ethanol [41,42], biodiesel [43] such as Jatropha [44], dimethyl ether (DME) [45], or hydro-treated vegetable oil (HVO) [46], homogeneous charge compression ignition (HCCI) engines [47], gasoline compression ignition engine [48], post injection effect on emissions [49], NH₃ sensors [50], or even modeling of emissions [51]. FTIR instruments have also been used on chassis dynamometers: Small gasoline engines [52] or even diesel trucks [53,54]. For example, for exhaust gas recirculation (EGR) [55], alternative fuels [56,57], reactive nitrogen compounds [58,59], impact of low temperature on non-regulated pollutants [60], and retrofit evaluation [61,62] of diesel vehicles. Similarly, chassis dynamometer studies with gasoline vehicles [63] focused on unregulated emissions [64–68], NH₃ [69–73], effect of exhaust gas reforming on emissions [74], low temperature [60,75,76], alternative fuels [65,77], and hybrids [78–80]. Motorcycles’ non-regulated pollutants emissions have also been assessed with FTIR [81–85].

The on-road application started in 2000 [86]. Since then other researchers measured emissions on the road [87–89], greenhouse gases (GHG) [90], nitrogen species [91], cold start emissions [92–96] of gasoline vehicles and the impact of ambient temperature [97]. A few also studied compressed natural gas (CNG) [98], diesel fueled vehicles [99–101] and their non-regulated pollutants [102].

Currently in the European Union (EU), FTIR is allowed for tailpipe (undiluted) NH₃ measurements for heavy duty engines (Commission Regulation (EU) 582/2011). The same applies globally with UNECE (United Nations Economic Commission for Europe) Regulation 49. It is also prescribed in the UNECE light-duty vehicles GTR 15 (Global Technical Regulation) for ethanol, formaldehyde, acetaldehyde and N₂O from the dilution
tunnel. The future Euro 7 regulation on light-duty and heavy-duty vehicles moves in a direction that these pollutants should be tested on the road [103]. Thus, using the FTIR for simultaneous analysis of various pollutants sampling from the tailpipe (undiluted exhaust) is an attractive option [104,105] that needs to be assessed.

The reviews on the topic are limited and 20 years old [31]. Furthermore, assessing FTIRs for regulatory purposes has not been discussed before. The objective of this paper is to review studies that have evaluated FTIR systems for automotive exhaust gas applications. Special emphasis is given to portable applications and low emission levels to assess the suitability for future regulations.

2. Materials and Methods

2.1. Regulatory Background

In the legislation of the EU, light-duty vehicles include passenger cars and light commercial vehicles, while heavy-duty vehicles include trucks and buses.

Originally emission regulations for light-duty vehicles were introduced in the 1970s with Directive 70/220/EEC (only CO and HC) [1,106]. In the years after, other pollutants were added, and various reductions of the emission limits were applied. In 2007 regulation 715/2007 defined Euro 5 and Euro 6 standards. The pollutants currently regulated are CO, HC (for positive ignition (PI) engines only), NOx, HC + NOx (only for compression ignition (CI) engines), particulate matter (PM), and particle number (PN) (only for CI and PI direct injection engines). CO2 has limits only as fleet-average. The measurements were conducted mostly from bags that collect a sample from a dilution tunnel with constant volume sampling (CVS), where the whole exhaust gas was diluted.

In 2017, with Euro 6d-temp, additional on-road testing was added to the laboratory type approval and in-service conformity testing. Limits were defined only for PN and NOx, while CO and CO2 had to be measured. The limits were the laboratory type approval limits taking into account the additional measurement uncertainty of the on-board portable emissions measurement systems (PEMS) with temporary conformity factors [107,108]. Since 2020, with Euro 6d the revised conformity factors were applicable. Regulation (EU) 2018/858 introduced a new EU type-approval framework (from September 2020), with an effective market surveillance system to control the conformity of vehicles already in circulation (new In-Service Conformity process from September 2019).

Heavy-duty standards were originally introduced with Directive 88/77/EEC (applicable from 1992). Current Euro VI emission standards were introduced by Regulation 595/2009 followed by a number of amendments that specified technical details. Limits are applicable for CO, non-methane hydrocarbons (NMHC), CH4 (for gas engines) NOx, PM, PN, and NH3. The measurements can be conducted from bags, directly from the full dilution tunnel, from a proportional partial flow system (PDFS), or directly from the tailpipe. Euro VI regulation introduced in-use testing with field measurement using PEMS. Conformity factors are applicable that take into account the additional measurement uncertainty of the PEMS.

At a global level, GTR 15 (global technical regulation) for light-duty vehicles includes additional pollutants (only methodology, not limits), and the EU is highly likely to adopt most of them in future regulations. None of these pollutants, however, are prescribed as candidates for on-board testing. Table 1 summarizes the pollutants, their principle of measurement and their inclusion or not in the current EU regulations. Some of them were recently introduced in other countries (e.g., N2O in China 6, aldehydes in Brazil, Korea, USA) [109].

Based on Table 1, FTIR is permitted to be used for the measurement of NH3, N2O, C2H5OH, CH2O, and CH3CHO. However, with the current regulations, FTIR would have to be connected to the tailpipe for the measurement of NH3, but at the dilution tunnel for the rest of the pollutants. As FTIR can determine simultaneously many of the regulated pollutants (CO2, CO, NO, NO2, CH4), and has the capabilities to be used at the tailpipe (e.g., for NH3), it is an attractive candidate for on-road testing.
Table 1. Pollutants, principle of measurement, and the sampling option for light-duty (LD) vehicles and heavy-duty (HD) engines in the European Union (EU) regulation and the global technical regulation (GTR 15) for LD vehicles. PEMS (portable emissions measurement systems) refer to the EU regulation for both LD and HD vehicles. Measurements can be conducted directly from the dilution tunnel with constant volume sampling (CVS), the bags, the proportional partial flow dilution system (PFDS), or the tailpipe (TP), depending on the regulation.

| Compound | Measurement Principle | GTR15 (LD) | EU LD | EU HD | PEMS |
|----------|-----------------------|------------|-------|-------|------|
| PN       | VPR + PNC             | CVS        | CVS   | +PFDS | TP   |
| PM       | Gravimetric (filter)  | CVS        | CVS   | +PFDS | TP   |
| CO₂      | NDIR                 | bags       | bags   | +CVS, +TP | TP |
| CO       | NDIR                 | bags       | bags   | +CVS, +TP | TP |
| THC      | FID or HFID (for diesel) | bags     | bags   | +CVS, +TP | TP |
| CH₄      | NMC or GC combined with FID | bags   | bags   | +CVS, +TP | TP |
| NMHC     | Calculated (THC–CH₄)  | (bags)     | (bags) | calculated | TP |
| NOₓ      | CLA or NDUV           | bags       | bags   | +CVS, +TP | TP |
| NO       | CLA or NDUV (only bags) | CVS or bags | CVS or bags |    |
| NO₂      | NDUV, QCL (or CLA) or (NOₓbags–NOₓCVS) | CVS | CVS or bags |    |
| N₂O      | GC with ECD, QCL-IR, NDIR, FTIR¹ | CVS or bags |    |    |    |
| NH₃      | LDS or QCL or FTIR²  | TP         |        |        |      |
| C₂H₅OH   | Impinger + GC, FTIR, PAS, PTR-MS, dir. GC | CVS | CVS | CVS |    |
| CH₂O     | DNPH + HPLC, FTIR, PTR + MS | CVS | CVS | CVS |    |
| CH₂CHO   | DNPH + HPLC, FTIR, PTR + MS | CVS | CVS | CVS |    |

¹: interferences < 0.1 ppm; ²: with interference < 2 ppm at max CO₂ and H₂O; ³: only for heavy-duty vehicles; ⁴: LDS or FTIR for HD engines. C₂H₅OH = ethanol; CH₃CHO = acetaldehyde; CH₄ = methane; CLA = chemiluminescence analyzer; CO = carbon monoxide; CO₂ = carbon dioxide; DNPH = 2,4-Dinitrophenylhydrazine; ECD = electron-capture detection; FID = flame ionization detection; FTIR = Fourier transform infrared spectrometry; GC = gas chromatography; CH₂O = formaldehyde; HFID = heated flame ionization detection; HPLC = high-performance liquid chromatography; IR = infrared; LDS = laser diode spectrometer; N₂O = nitrous oxide; NDIR = non-dispersive infrared spectrometry; NDUV = non-dispersive ultra-violet spectrometry; NH₃ = ammonia; NMC = non-methane cutter; NMHC = non methane hydrocarbons; NO = nitrogen oxide; NO₂ = nitrogen dioxide; NOₓ = nitrogen oxides; PAS = photoacoustic spectrometry; PM = particulate matter; PN = particle number; PNC = particle number counter; PTR-MS = proton transfer reaction—mass spectrometry; QCL = quantum cascade laser; THC = total hydrocarbons; VPR = volatile particle remover.

2.2. FTIR Description

FTIR can be used to measure substances (solids, liquids, gases, powders, polymers, organics, etc.) that absorb in the mid-infrared (i.e., approximately 400–4000 cm⁻¹). As a basic principle of the interaction matter–radiation, absorption can occur at intrinsic energy levels, specific for each molecule. When mid-infrared radiations cross a molecule, some specific frequencies (or wavelengths) will be absorbed if they correspond to the transition of vibrational levels of the molecule. Consequently, FTIR can be used for qualitative and quantitative analysis. However, it cannot detect noble gases, such as helium (He) and argon (Ar), or diatomic gases, such as oxygen (O₂), nitrogen (N₂), and hydrogen (H₂), as their vibration does not create a dipole moment, thus do not have absorbance bands in the infrared region of the electromagnetic spectrum. Others molecules absorb very little radiation and are, therefore, not detectable at low concentrations (e.g., H₂S > 200 ppm [110]).

The heart of every FTIR instrument is an optical device called an interferometer (Figure 1) [3]. The oldest and most common type is the Michelson interferometer. The infrared source is usually a heated ceramic (at ca. 1200 °C). A collimating mirror collects light from the source and makes its rays parallel. A beamsplitter (in KBr) transmits approximately half of the light incident upon it and reflects the remaining half. A fraction of the light transmitted travels to a fixed mirror, while the other fraction travels to a moving mirror (see Figure 1). The lights are reflected by the two mirrors back to the beamsplitter, where they are recombined into a single light beam. This light beam interacts with the sample (exhaust gas) in a gas cell and finally strikes the detector. A multireflection cell is used to obtain a long optical path length with the minimum possible volume of the cell [111].
Figure 1. Principle of operation of FTIR (Fourier transform infrared) spectroscopy. IR = infrared.

Because the path that one beam travels is a fixed length and the other is constantly changing as its mirror moves, the signal which exits the interferometer is the result of these two beams “interfering” with each other. The resulting signal is called an interferogram (i.e., a plot of light intensity versus optical path difference). The interferograms measured are then Fourier transformed to yield a spectrum (i.e., a plot intensity versus frequency/wavenumber).

There is also a laser (not shown in the figure) whose light follows the infrared beam. This laser light is used to measure the optical path difference of the interferometer. The spectral resolution (in cm\(^{-1}\)) depends on the inverse of the optical path difference. This gives the wavelength accuracy (or Connes’ advantage) compared to dispersive instruments where the scale depends on the mechanical movement of diffraction gratings. Thus, the FTIR can give very accurate frequencies in the spectrum—this enables processing techniques such as spectral subtraction. It was shown that for automotive applications, a resolution of 0.5 cm\(^{-1}\) is the best compromise to obtain suitable fineness of the spectra (required to build robust calibration method) without compromising signal to noise ratio [8]. At lower resolutions (e.g., 1 cm\(^{-1}\)), water’s absorbance bands may create interference problems that affect the detection limits of many compounds [112]. The accuracy and detection limits of the individual compounds measured are dependent on the intensity of the respective absorbance bands and their interference, but also on the detector [113,114].

For most compounds, the detection limit is well below 1 ppm for 1 s resolution [55,115]. The resolution of 0.5 cm\(^{-1}\) is achievable only with a photonic detector (e.g., Mercury Cadmium Telluride—MCT) that needs to be cooled down with liquid N\(_2\). Peltier cooled MCT or heating detector (e.g., Deuterated TriGlycide Sulfate—DTG)) are less sensitive and reactive compared to photonic detectors. However, they might be more suitable for portable systems. Another advantage of the FTIR is the multiplex advantage (or Fellgett advantage) because all wavelengths are collected simultaneously and thus a spectrum can be obtained very quickly. In contrast, with “dispersive spectroscopy” a monochromatic light beam shines at a sample, the absorbed light is measured, and this is repeated for each different wavelength. The throughput advantage (or the Jacquinot advantage) arises because, unlike dispersive spectrometers, FTIR spectrometers have no slits, which attenuate the infrared light, resulting in a higher signal-to-noise ratio.

Other advantages of the FTIR systems are: measurement of many pollutants simultaneously, real-time operation, possibility to measure undiluted exhaust gas, the fast response time (at least as fast as the conventional analyzers) for transient engine operation, low minimum detection limits, large dynamic range for dilute and direct sampling, high accuracy with negligible cross-sensitivity [31]. On the other hand, the interference primarily from H\(_2\)O and CO\(_2\) can be high, and the signal-to-noise ratio can be affected by external vibra-
The selection of the absorption bands needs to be conducted between, e.g., H2O absorption regions for the analysis and interferences can be found in the literature [28, 47, 104, 118, 119]. Estimations of cross-sensitivities simulating exhaust gas gave an influence of <<1% for most absorption range, and between the CO absorption peaks. More detailed discussion on spectral regions for the analysis and interferences can be found in the literature [28, 47, 104, 118, 119]. CO2 measurement is relatively straightforward, but the selection of the bands needs to be conducted considering H2O interference, and between CO absorbance peaks.

CO requires the careful selection of infrared absorbance bands to stay within the desired absorbance range and in an area between H2O and potential N2O absorption region. NO and NO2 absorb only in regions with very high levels of water interference, as well as CO and CO2 interferences. Thus, for these compounds, the selection of the absorption bands needs to be conducted between, e.g., H2O absorption peaks, in the area between ca. 1850 and 1940 cm\(^{-1}\) for NO, and between 1570 and 1650 cm\(^{-1}\) for NO2. Figure 2b provides the example of NH3 calibration method, for which a rather straightforward selection of the absorption bands is possible within an area where no interference is expected (between 900 and 970 cm\(^{-1}\)). Figure 2c provides the example of the N2O, for which the absorption bands need to be selected in an area located outside the CO2 absorption range, and between the CO absorption peaks. More detailed discussion on spectral regions for the analysis and interferences can be found in the literature [28, 47, 104, 118, 119]. Estimations of cross-sensitivities simulating exhaust gas gave an influence of <<1% for most compounds (NO2, CO, NH3) [114], but >1% for acetaldehyde (CH3CHO), acetone (CH3COCH3), C6H6, and C7H8, because their absorption spectrums are not sharp and strong, and/or the region of possible quantification is small due to the co-existing components. The actual interference might be different if there are interfering compounds not included in the software, if some wavelengths are saturated due to high concentrations, and/or the resolution is not enough to resolve the species, e.g., water, NO, NO2, and NH3 [120].

![Figure 2a](image_url)  
Figure 2. Cont.
Figure 2. Example of absorbance versus wavenumbers: (a) for various species with concentrations of 398 ppm (CO), 97 ppm (NO), 136 ppm (NO\textsubscript{2}), 93 ppm (N\textsubscript{2}O), 93 ppm (NH\textsubscript{3}), 0.8% (CO\textsubscript{2}), 2.03% (H\textsubscript{2}O). For better visualization, the spectra of H\textsubscript{2}O and CO\textsubscript{2} were reduced by a factor of 10 and displayed in an inverted axis. For the same reason, NH\textsubscript{3} and HCN spectra were increased by a factor of 2 and 4, respectively; (b) NH\textsubscript{3}, area B of panel (a); (c) N\textsubscript{2}O, area C of panel (a).

Principally, transmission-FTIR spectroscopy follows the Lambert–Beer law. Consequently, for a given optical path length, a linear relationship between the compound concentration and the absorbance mediated by this compound can be assumed. However, the output voltage of the detector is not a linear function of the incident radiation power [121] and non-linearity can be seen for components such as CO\textsubscript{2}, H\textsubscript{2}O, CO, and NO\textsubscript{x} with a wide range of variations [8]. Thus, for some components, the calibration might not be a linear function, but quadratic, cubic, etc. Because the mirror travels only a finite distance, the interferogram is truncated, and the Fourier transform results in a spectrum with broader features and spurious oscillations at the wings of the features. An apodization function is applied to reduce the magnitude of these oscillations but further broadens the spectral features. This broadening causes the instrument to have a nonlinear response to
changes in absorption of the various gases being measured [122]. This can be modeled and corrected.

FTIR requires no daily calibration per se. This is possible because the daily background/zero scan is compared point per point to the measurement spectrum and compensates for any instrument drift in the final absorbance spectrum. Since the same number of molecules always absorb the same fraction of incident energy (independent of the total amount of energy), the calibration factor remains the same for a given compound and wavenumber and as a result there is no span drift or calibration drift [115]. However, since background and measurement spectrums are acquired successively, the FTIR needs to be very stable, in terms of infrared source, detectors, but also in terms of composition of the gas included in the instrument. Such stability is insured by keeping the instrument always on (heated), and by purging the optical system with dry gaseous N₂.

The sampling lines and the sampling cell for exhaust gas application need to be heated above 100 °C (usually 191 °C) to avoid water condensation, which would lead to an underestimation of the hygroscopic compounds (e.g., NH₃). In addition, the sampling line located upstream is usually equipped with a heated filter that prevents the deposition of particles on the mirrors’ surface of the multipath gas cell, and thus, the modification of the optical path length.

2.3. Processing of the Interferogram

The interferogram produced by the interferometer is converted mathematically (Fourier transform) into an intensity versus wavenumber plot known as a single-beam spectrum (Figure 3). The single-beam spectrum of the gas exhaust sample is ratioed (logarithmically) against the single-beam background spectrum (produced by passing nitrogen gas through the cell) to produce the absorbance spectrum [123]. Other processing of raw data (apodization) may be used to smoothen discontinuities at the beginning and end of the spectra, reduce, or eliminate noise [3,124].

Then, to utilize the complete information of the complex spectra and to handle the large data set, multivariate analysis is often used (i.e., data analytical methods that deal with more than one variable at a time). Some combinations of variables (wavenumbers) of a given data set are highly correlated with each other. Principal component analysis (PCA) is one such widely used dimensionality reduction technique to extract the informative region of the spectra for every individual species. Unlike classification or clustering, regression is used in the quantification of particular dependent variables (expected pollutants). Some of the commonly used multivariate regression methods are classical least squares (CLS), multiple linear regression (MLR), principal component regression (PCR), partial least squares (PLS) [125]. Such calibration methods can be appropriate when the gas composition of the mixture to be analyzed (here, the exhaust gas) is not known. In that case, the compound of interest can be added to the mixture (matrix) at different concentration levels (spiking) in order to build a suitable multivariate regression model. This model might, however, highly depends on the complexity and composition of the gas mixture (matrix) used to build it.

Another approach is to compare the spectra of the compound of interest to the foreseen interfering compounds (e.g., water or CO₂) in order to: (i) identify the wavelength region
where not too many interferences are expected, and (ii) identify the other wavelength regions where interferences are expected. The first region is then used to build the regression model, sometime in a straightforward way (see Figure 2b), or less straightforward way (see Figure 2c). The second set of wavelength regions will be used to foresee the possible interference brought by the compound of interest when building a regression model for other compounds. For illustration, Figure 2c shows how the N$_2$O model is built in a wavelength area where the possible interference of CO absorption was identified. In this case, the region used to build the regression model was selected to avoid the interference of CO$_2$ and H$_2$O (see Figure 2a). Typically, specific wavelengths where no other species absorb are used to predict the volume concentration of the compound, assuming a linear or quadratic relationship between concentration and absorption [28,47,118]. For each compound, standard gas cylinders of several concentration levels are used to calibrate the model. Such an approach has the advantage of being more robust and less dependent on the composition of the mixture. However, this approach requires to be exhaustive in consideration of the expected interferences, thus having a library including the pure spectra of all the compounds expected to be found in vehicle exhaust.

Once the regression model is built, analysis of the spectral residual is also a crucial step in order to identify potential interfering compounds in the models created. It is important to highlight that the reference spectra must be recorded at the same conditions, meaning the same instrument (same optical system, including optical path), and same temperature and pressure as used for the exhaust measurements [126,127]. The processing of the data is not standardized, but FTIR data can be re-processed differently with a different method to reveal the concentration data of other components. It is important to mention that FTIR is a non-destructive measurement technique. Thus, it could be possible to direct the analyzed gaseous sample toward another measuring instrument for complementary analysis. It should be, however, recalled that the sampling gas is heated (e.g., 191 °C) and filtered.

3. Results

The following sections summarize the results of the studies that assessed FTIRs against calibration gases or reference instruments. The sections present shortly the principle of operation of the reference instruments (details can be found elsewhere, e.g., [128–130]) and any advantages and disadvantages over FTIR. Then the results of the studies that have assessed FTIRs are summarized. The details of the studies can be found in Appendix A. Each table gives first the results with calibration gases. Then, the comparison of the FTIR and reference analyzers is divided into cases that both instruments were at the same location (dilution tunnel or tailpipe), or different (FTIR at tailpipe, reference at dilution tunnel). In the last case, the differences can be affected significantly by the uncertainty of the exhaust flow determination.

To put the assessed values into perspective, Table 2 presents Euro 6/VI limits for light-duty vehicles and heavy-duty engines, an approximation of the mass emissions of 1 ppm concentration of various pollutants. Exhaust flows of 2 kg/km and 10 kg/kWh were assumed as the highest values for large engine displacement light-duty vehicles and heavy-duty engines [103]. The density ratios u of the relevant regulations were used.

| Pollutant | CO [mg/km] | NO$_x$ [mg/km] | HC [mg/km] | NH$_3$ [mg/km] | N$_2$O [mg/km] |
|-----------|------------|----------------|------------|----------------|----------------|
| Euro 6 limits (min of LD) | 500 | 60 | 100 | - | - |
| 1 ppm uncertainty (LD) | 1.9 | 3.2 | 1.0 | 1.2 | 3.0 |
| Euro VI limits (min of HD) | 4000 | 460 | 660 | 10 ppm | - |
| 1 ppm uncertainty (HD) | 9.7 | 15.9 | 4.8 | 5.9 | 15.2 |
3.1. Carbon Monoxide (CO) and Carbon Dioxide (CO₂)

CO and CO₂ are typically measured with NDIR (Non-Dispersive Infrared) absorption type detectors. NDIR is one of the IR methods, which is not spectroscopic analysis but uses non-dispersive infrared light. In NDIR, the region of wavelengths used for analyzing the target component is selected by using an optical filter (multilayer interference filter) or a gas filter (a cell enclosing interfering gases). Other gases that show absorption in the same wavelength region will contribute to the measurement result of the target component. For example, when analyzing CO in the engine exhaust gas, CO₂ and H₂O also included in engine exhaust gas are likely to interfere with the measured CO concentration [131]. The CO NDIR analyzer may require a sample conditioning column containing CaSO₄, or indicating silica gel to remove water vapor, and containing ascarite to remove carbon dioxide from the CO analysis stream (USA EPA Title 40, Chapter I, Subchapter C, Part 86, Subpart B, §86.111-94). Many analyzers use coolers. The regulation requires interference checks of the CO analyzer with CO₂ and H₂O at concentrations expected during the tests. The CO response has to be within 2% or ±50 ppm (whichever is larger). For analyzers measuring from the dilution tunnel, the allowed interference is between −1 ppm to 3 ppm. Regarding CO₂ measurements of diluted exhaust, the regulation requires that the CO₂ concentration in the dilute exhaust sample bag is <3% for gasoline and diesel engines, <2.2% for LPG engines, and <1.5% for natural gas and biomethane engines. When the concentration of water is <3% H₂O the error is <1% [132].

For tailpipe sampling, in order to minimize the interference for non-diluted exhaust, additional detectors sensitive only to the interfering component can be added [133], or the H₂O can be removed (e.g., by a cooler) [134]. Errors after corrections with additional H₂O detector, the main interfering component in the exhaust gas, are <2% for H₂O concentration up to 12% [135]. Removal of the water needs a dry-to-wet correction, which has a low error, as long as no condensation takes place at the sampling lines, e.g., at cold start. In such cases errors of up to 10% have been reported during the cold start period [135].

Table A1 summarizes the studies assessing FTIR CO₂ readings with calibration cylinders or NDIR analyzers. Table A2 summarizes for CO. Regarding CO₂, in most cases, the differences were within ±5% (slope 0.95–1.05), with only a few exceptions that the differences were around 10%. There were no particular differences between gasoline or diesel vehicles. The correlation coefficient was high (>0.95). The only exception (R² = 0.70, FTIR at tailpipe vs. dilution tunnel) was when a calculated from the intake air exhaust flow was used instead of measured with exhaust flow meter. Higher differences (∼21%) were reported when the response of the FTIR was slow [34].

Regarding CO, the mean differences were within ±5% of the reference analyzers, but the scatter was very high in some cases, exceeding 50%. The slopes were within 0.8 and 1.2 with no indications of higher slopes when the FTIR connected at the tailpipe was compared to the dilution tunnel or bags. The worse performance of the FTIR CO compared to the CO₂ might have to do with the higher interference of water and CO₂, and the higher concentration range of CO compared to the CO₂.

3.2. Nitrogen Monoxide (NO) and Nitrogen Dioxide (NO₂)

NO and NOₓ (sum of NO and NO₂) are typically measured with chemiluminescence analyzers (CLA) developed in early 1970s [120]. NO reacts with O₃ and the excited NO₂ molecules spontaneously return to normal state emitting light (chemiluminescence) [136]. The sensitivity for NO is influenced by the existence of CO₂ or H₂O in the sample gas, because the excited NO₂ can react with CO₂ and H₂O (quenching effect) [128]. The effect is <1%, in particular for systems with H₂O sensors that can compensate for H₂O concentrations up to 14% [137]. The light can also be filtered before being measured by the photomultiplier to minimize interference [130].

The CLA can be used to measure NOₓ. In this case, a carbon or active metal-based furnace converts NO₂ into NO (NOₓ converter) [120,136]. Regulations require a conversion efficiency of >95%. However, NH₃ can also be converted to NO in the converter. The
conversion efficiency depends on the converter material, the temperature and the concentrations of NO and NH$_3$. With a 5:1 ratio of NH$_3$ to NO, an error of 30% was estimated for NO$_x$ [120]. Nevertheless, laboratory CLA today has a cross-sensitivity of <1 ppm for 1000 ppm NH$_3$. NH$_3$ could also cause a loss of conversion efficiency of the NO$_x$ converter over time. On the other hand, NO$_x$ can be converted to N$_2$ or NH$_4$NO$_3$ (ammonium nitrate), resulting in a lower concentration [120]. Ammonium nitrate formation is very rapid even at room temperature if NH$_3$ and HNO$_3$ are present. HNO$_3$, in turn, is readily formed when NO$_2$ dissolves in liquid water. Ammonia scrubbers can be used to avoid this problem with CLA [138]. The disadvantages over FTIR are the extra expenses required for an ozonizer, NO$_2$ to NO converter with converter efficiencies >95% (which need to be checked every month according to EU Regulation), possible NO$_2$ losses in the chiller, influence due to quenching from water and CO$_2$ [136,139]. FTIR was also found to provide accurate measurements of NO$_x$ in the presence of NH$_3$ [120].

Table A3 summarizes the studies that the FTIR NO$_x$ reading was compared to calibration cylinders or CLA. The comparisons with calibration gases were within ±5%, while with reference CLA within ±10%, with a few exceptions. For example, a study had 30% difference due to different exhaust flows used for the FTIR and the PEMS [110]. Higher differences were reported when the response of the FTIR was slow [34]. Comparison of tailpipe FTIR with dilution tunnel bags were also within ±10%, with only a few exceptions. In some cases, the laboratory analyzers were suspected [98].

The comparisons of FTIR and CLA for NO$_2$ did not always give acceptable differences, with differences exceeding 10% in particular at different sampling locations [140]. One explanation might be due to the fact that NO$_2$ is not directly measured but calculated from the difference between NO$_x$ and NO. Wrong CLA NO$_2$ measurements can also originate from different time delays in the analyzer for NO and NO$_x$ [141], and as mentioned before, converter-related side reactions. Partly lower NO$_2$ concentrations peaks due to reaction of NO$_2$ with soot contamination have also been reported [141]. Finally, despite the advantages of FTIR spectroscopy, the fundamental interference of NO$_2$ measurement by water vapor remains. It should be added that NO$_2$ (and NH$_3$) are considered “sticky” substances and the sampling setup is very important. NO$_2$ can be underestimated if it adsorbs on surfaces in the sampling system, dissolves in the condensed water [142], or forms a salt in the presence of NH$_3$ and remains in the sampling filter. Chiller penetration is defined in the USA regulation for analyzers that do not use NO$_2$ to NO converter upstream of the chiller. Heated CLA systems are used when high NO$_2$ concentrations are expected in order to avoid the loss of water-soluble NO$_2$ inside the dehumidifier. The dry-to-wet correction introduces an uncertainty, which is significant during cold start [135]. Lower NO$_2$ concentrations peaks over test cycle as reaction of NO$_2$ with soot contamination have been reported [141].

All reference instruments presented in the table applied the CLA principle. Only in one case the reference instrument was a PEMS applying the NDUV principle [102]. The NDUV measurement method is based on the absorption of ultraviolet (UV) radiation from a broadband UV source to quantify the amount of NO$_x$ in a given sample [139,143]. The NO and NO$_2$ signal occurs during the very large water wavelength in addition to other smaller contributing signals such as sulfur compounds [144]. For this reason, the sample is typically dried. The portable FTIR and the NDUV analyzer agreed well (slope 1.03, $R^2$ 0.97) [102]. This was expected as NDUV and CLA usually agree. For example, a study found the two principles within 5% for 20–130 ppm concentrations [145].

### 3.3. Nitrous Oxide (N$_2$O)

Nitrous oxide (N$_2$O) can be measured using FTIR, NDIR, QCL-IR, and GC with ECD. One study [102] compared two FTIRs measuring the tailpipe exhaust of diesel vehicle and found a slope of 0.96 ($R^2$ = 0.95) for concentrations up to 60 ppm. Another study compared the FTIR reading from bags with exhaust gas injected with N$_2$O and found differences
within 3% of the expected values [146], indicating no particular interference from H\textsubscript{2}O or other exhaust gas components.

3.4. Ammonia (NH\textsubscript{3})

Ammonia can be measured using FTIR, QCL or LDS from the tailpipe. A Quantum Cascade Laser (QCL) element emits an intermittent mid-infrared laser beam in a sample cell at a very specific wave number by applying a pulsed current [128,147,148]. During a pulse, the element temperature varies, and, consequently, the actual wave number continuously shifts within a narrow range. Compounds that absorb energy in this oscillation range will decrease the light intensity and will be detected at the relevant wave numbers.

The measurement principle of a Laser Diode Spectrometer (LDS) is based on single line molecular absorption spectroscopy [149]. A diode laser is used for emitting a near-infrared (compared to QCL mid-infrared) light beam through the sample gas, and the light is detected by a receiver. The laser diode output is tuned for a gas-specific absorption line. Cross-sensitivities of the method is insignificant as, spectrally, the laser light is much narrower than the gas absorption line.

Table A4 summarizes the studies that FTIR was assessed in measuring NH\textsubscript{3}. The calibration gases readings were within 5% of the specified values. In general, the agreement between FTIRs was good. Steady-state engine tests with NH\textsubscript{3} dosing showed the importance of the FTIR response time and the sampling line conditioning. The differences in dynamic response indicated buffering of NH\textsubscript{3} (known to “stick” on walls) within the sampling line before breakthrough to the analyzer cell [150].

The comparison of FTIRs with QCLs was also good on average. In one case, examining real-time graphs, higher and sharper peaks were obtained with the QCL due to the 10-Hz frequency [151]. Comparison of an FTIR with chemical ionization mass spectrometry (CI-MS) gave good agreement [152], and comparisons with an in-situ (cross-duct, without sampling line) LDS was also in good agreement [149].

There were only a few studies comparing tailpipe with dilution tunnel [152,153]. However, as pointed out by these studies, severe losses of ammonia can occur in the dilution tunnel resulting in lower emissions.

The sampling location and the sampling conditions are very important for NH\textsubscript{3} measurements. As it was mentioned in the NO\textsubscript{x} section, the formation of ammonium nitrate is also possible in the presence of HNO\textsubscript{3}. Low sample line temperature can result in condensation inside the heated line, which can lead to loss of NH\textsubscript{3}. On the other hand, upstream of the SCR in the presence of HNCO and H\textsubscript{2}O, a high sample line temperature can produce NH\textsubscript{3} [150]. For such cases, a temperature of 113 °C was recommended. Downstream of the SCR, no such phenomena were observed.

3.5. Hydrocarbons (HCs) and Methane (CH\textsubscript{4})

Total hydrocarbons (THC) and methane (CH\textsubscript{4}) are typically measured with Flame Ionization Detection (FID). In FID, the sample gas is introduced into a hydrogen flame, where some of the HCs in the sample gas are ionized [154,155]. Due to the ions, an electric current is generated at the applied electric potential, is nearly proportional to the amount of carbon atoms. For this reason, the HCs concentration is called “THC” and the unit is “ppmC”. A heated FID should be used in applications such as diesel exhaust that contains significant quantities of high boiling point HCs to avoid condensation and loss of heavier HCs [128]. The FID detector temperature should be set to 113 °C for alcohol-fueled vehicles (instead of 190 °C, which is used for diesel-fueled vehicles) (USA EPA Title 40, Chapter I, Subchapter C, Part 86, Subpart B, §86.111–94). This is based on the higher water vapor of methanol and the fact that methanol can undergo decomposition reactions if the oven is too hot [156].

The FID sensitivity for each HC is represented by a “response factor” that indicates the relative sensitivity compared to propane as the calibration gas. Generally, the FID has
lower sensitivity to oxygenated HC components such as alcohols, aldehydes [157–160] and no sensitivity to formaldehyde. For regulatory purposes, FIDs are calibrated to have a response factor of 1 for propane. Toluene and propylene have to be within 0.9 and 1.1. The FID has negligible interference from inorganic components such as CO, CO₂, H₂O, and NO, except for O₂ in the sample gas. The O₂ concentration in the sample can affect not only FID sensitivity for HCs but also the zero point. Some THC analyzers have a compensation function for O₂ interference using an additional O₂ analyzer. The regulation allows a maximum of 1.5% oxygen interference.

For measuring CH₄ in the engine exhaust gas with the FID analyzer, sample conditioning parts, i.e., Gas Chromatography (GC) or Non-Methane Cutter (NMC), are placed before the detector to extract or separate CH₄ from the other HC components. The GC-FID-based CH₄ analyzer is only suitable for batch measurement rather than continuous measurements. A Non-Methane Cutter (NMC) is a catalyst that selectively oxidizes HCs and only minimally CH₄. The regulation requires the determination of the methane conversion efficiency, which ideally should be 0%, and the ethane conversion as an approximation of the conversion efficiency of the non-methane hydrocarbons, which should be >98%. If the CH₄ response is <1.05, it may be omitted from the calculations of the emissions.

Non-Methane Hydrocarbons (NMHCs) are calculated as the difference of THC and CH₄. (details in regulation, it is not a simple subtraction as conversion efficiencies need to be considered). In EU for high ethanol content fuels a different density is used to calculate THCs and NMHCs (0.934 g/L E85 vs. 0.646 g/L E10). In USA, non-methane organic gases (NMOG) include NMHCs, alcohols and carbonyls. Therefore, to measure NMOG (gasoline with ethanol > 25%), one must separately measure the principle alcohols, aldehydes, and ketones, subtract their inaccurate contribution to the FID signal, and add in their correct concentrations. Ethanol is traditionally measured by impinger collection and GC. Alternatively, the ethanol levels in diluted emissions sampled into Tedlar bags can be read directly via a photoacoustic non-dispersive infrared method [161], thus avoiding the need for off-line impinge analysis. Aldehyde measurement is via DNPH cartridge collection and off-line high-pressure liquid chromatography. Thus, ethanol and acetaldehyde are measured via batch methods, thus precluding time-resolved NMOG data.

FTIR spectroscopy provides an attractive alternative because all of the species contributing to NMOG are infrared active. For FTIR, in general, the analysis of infrared spectra works best for components with strong and sharp absorbance bands [113]. It is progressively more difficult for FTIR to speciate hydrocarbons as the number of carbons increases for two reasons [162]: (i) the individual molecular rotation-vibration lines coalesce into broader bandshapes. (ii) they progressively overlap with each other.

Table A5 summarizes the comparisons of FTIR with FID systems for THC. There is a high scatter of the results. The differences are typically within 15%, but underestimation by a factor of 2 has also been reported [110,163]. Another study found FTIR measuring 34% higher than the FID from the dilution tunnel [164]. The explanation was the reduced sensitivity of FID to methanol and formaldehyde. It should be emphasized that this is a comparison of two technics, which are both estimating THC. None of them are specifically quantifying every single HC. FID is non-specific, and FTIR is non-exhaustive.

Table A6 summarizes the FTIR studies with CH₄. The differences were around 5% when measuring calibration gases and 10% compared to FIDs with NMC when measuring CH₄ from the tailpipe. The difference to other methods (GS) was within 5%. A few older studies found higher differences (up to 18%) at levels of <10 ppm CH₄. To put results into perspective of those older studies, when the FTIR was used at the tailpipe and then to measure the CH₄ from the bags, the differences remained the same (slope 0.88 and R² 0.96) [165], indicating uncertainties with the FTIR. Similarly, a study that measured CH₄ from cylinders found a 3.5 ppm offset due to interference from other gases [166]. The same study found more than double emissions compared to chemical ionization mass spectrometry (CI-MS).
Table A7 summarizes the FTIR studies with NMHC. The differences were around 5%, with some cases having >30% differences. For these cases, an uncertainty analysis revealed that the most likely reason for the differences was the reference method. The reference method uncertainty was around 80–100 ppm (almost 50–100%), while for FTIR was around 25 ppm (10–15%) [162]. Another study, even assuming ethane and ethylene to have an error of 10% and the other components to have an error of 50%, found that the FTIR had a lower absolute error than FID for NMHC [167].

A promising proposal to measure real-time NMHC and NMOG with FTIR is to use a group of HCs, as a surrogate to NHMC and then combined it with ethanol, acetaldehyde and formaldehyde to calculate NMOG [162]. That study also showed that typically the top five organic compounds account for about 60% of the HC emissions with CH₄ the most abundant, and the top 10 compounds account for 80% for fuels ranging from gasoline to 85% ethanol/gasoline blends. The same study concluded that FTIR can measure NMHC and NMOG within 5% to the regulatory method [162].

Only a few studies compared ethanol emissions from FTIR and other methods. In one study, the differences were <10% for emission levels ranging from 100–1000 mg/km [160]. Another study with three FTIRs found on average −7% (0% to −12%) compared to PTR-Qi-ToF-MS during the cold start phase (emissions 150 mg/km) [168].

Regarding methanol many studies in the 1990s gave good results: slopes 0.72–1.10 (FTIR vs. impinger + CS) [26,112,169–171]. One study compared alcohols and found an agreement of 22% (FTIR vs. impinger + CS) for emission levels up to 250 mg/km and fuels up to E100 [172].

3.6. Formaldehyde (CH₂O) and Acetaldehyde (CH₃CHO)

The accepted techniques for measuring formaldehyde and acetaldehyde are DNPH + HPLC, FTIR, and PTR + MS; all from the dilution tunnel. The most common and cheaper method is using HPLC (high-performance liquid chromatography) to separate and quantify the carbonyls after extraction of 2,4-DNPH (dinitrophenylhydrazine) cartridges [173,174], while PTR-MS (proton transfer reaction—mass spectrometry) [168] is the least common. The DNPH-HPLC method also has its uncertainties, as the quantification by HPLC is not always straightforward due to the chromatogram peak resolution. NO₂, NO, and CO can have an impact on the quantification of formaldehyde and acetaldehyde due to the consumption of the DNPH during sampling [175].

Table A8 summarizes the studies that assessed the FTIR measuring formaldehyde. Sampling from the dilution tunnel showed in general good agreement with the DNPH + HPLC methodology (slopes close to 1), with one exception where the FTIR was on average 20–25% higher. From the tailpipe, the differences were larger (±30%).

Table A9 summarizes the studies that assessed the FTIR measuring acetaldehyde. The scatter of the results is high. One study found more than double concentrations of acetaldehyde with the FTIR than with the DNPH + HPLC method. It seems that the reaction of acetaldehyde took place in the exhaust pipe [176]. Another study with a flexi-fuel vehicle found 30% higher concentrations with the FTIR (compared to DNPH-HPLC), but at the same study, the FTIR was 30% lower than the PTR-MS method [168]. The emission levels were around 0.4 mg/km. Other studies found differences within 10%. A study that checked the FTIR formaldehyde concentrations according to analyte spiking EPA method 301 on a coal-fired burner found differences on the order of 10% [177]. The same study found 5% differences for acetaldehyde.

3.7. Other Compounds

A few only studies assessed alkanes. For example, differences from propane (C₃H₈) gas cylinders were 3.3% at 3200 ppm [95], and 13% at 2 ppm or lower concentrations. One ppm interference from CO₂ and/or H₂O was found at 15 ppm levels [178]. Ethane was measured 5–10% lower [166].
Isocyanic acid (HCNO) was assessed in one study for SCR (selective catalytic reduction for NO\(_x\)) applications with a heavy-duty diesel engine, and all three FTIRs were within a few ppm for concentrations up to 15 ppm [150].

Aromatic hydrocarbons (benzene, toluene) from FTIR were compared to the analysis of bags after Tenax TA adsorption and GC-MS analysis. Benzene was from −6.5% to +1.5% from bags for various fuels (gasoline, ethanol, methanol) [179]. The emission levels were around 2.5 mg/km, and the peaks at the cold start were around 20–30 ppm. The same study found differences of −3.5% to 2.4% (spike 40–60 ppm, emissions 7.5 mg/km) for toluene.

A very good correlation has been found for propylene, ethylene, acetylene, and benzene [180]. Results from other gases such as ethane, ethyne, 1,3-butadiene [166], acetylene, propene [113,171,181,182] can be found in the literature.

4. Discussion

FTIR analysis is seeing increased use in engine exhaust measurements. Since the first prototype instruments in the 1980s, many laboratories use FTIRs as a standard technique for engine development (see introduction). This review summarized the differences between FTIR and other methods for various gaseous components of engine exhaust. The differences were in most cases at acceptable levels (5–10%), but in some cases and for some compounds, higher differences were noticed. The main question is whether FTIR can be used for on-road regulatory purposes. To answer this question, the following topics need some analysis:

- Can FTIR measure undiluted exhaust accurately enough?
- Can FTIR be used on-board?
- How the FTIR accuracy can be ensured for regulatory purposes?

4.1. Tailpipe Applications

Interestingly, GTR 15 allows the use of FTIR for ethanol, formaldehyde, acetaldehyde, and \(\text{N}_2\)\(_2\)O only from the dilution tunnel. This is because there is no exhaust gas measurement to determine the emissions from the tailpipe. Only \(\text{NH}_3\) has to be measured from the tailpipe. At the moment, there is a limit only for heavy-duty engines (in ppm) in the EU regulation (not in GTR). Such specifications would need two FTIRs for the measurement of non-regulated pollutants (e.g., one for \(\text{NH}_3\) at the tailpipe and one at the dilution tunnel for the other pollutants). Permitting measurement of all pollutants from the tailpipe would simplify the setup. Furthermore, FTIR could be used instead of other analyzers (NDIR for \(\text{CO}\) and \(\text{CO}_2\), CLD (for \(\text{NO}_x\)), and possibly for hydrocarbons (instead of FID). Indeed, the use of FTIR at the tailpipe is a commonly accepted technique for research and development (see “Introduction”).

Figure 4 gives an overview of the “Results” section summarizing the studies that FTIRs was compared with reference values: (i) calibration gases ("Cylinder"), (ii) reference instrument measuring in parallel with the FTIR at the dilution tunnel or at the tailpipe ("Parallel"), (iii) reference instrument at a different location (FTIR at the tailpipe versus reference at the dilution tunnel) (TP vs. CVS). Only cases where at least two studies were available were taken into account. It should be mentioned that the mean values of slopes or already averaged values do not give the complete scatter of the tests. Furthermore, a different number of tests in each case make any comparisons between different compounds doubtful. On the other hand, it has to be reminded that the results summarize 40 years of experience with a wide range of instruments manufacturers (and users).

The mean differences from the reference values were ±2.5% for \(\text{CO}_2\), \(\text{CO}\), \(\text{NO}_x\), and \(\text{NH}_3\), without any particular deviation when FTIR and reference instrument were at different locations. The variability (one standard deviation) of the means was 5% for \(\text{CO}_2\) and 10% for the other three gases. Again no particularly higher variability of the “TP vs. CVS” cases. For HCs (THC, NMHC) the mean differences were 5–30% and the variability 30%. Smaller mean differences and variability (10%) was calculated for \(\text{CH}_4\). The “TP vs. CVS” cases had similar means and variability. \(\text{CH}_2\text{O}\) had closer to \(\text{CH}_4\) behavior, while \(\text{CH}_3\text{CHO}\) was closer to \(\text{NH}_3\), but the number of tests was very limited to
draw any conclusions. The results are reasonable, considering that the uncertainty of the different equipment to which FTIR was compared was not the same. As it was discussed in the respective sections, the reference instruments for THCs, NMHCs, and carbonyls have higher uncertainty than those for, e.g., CO \(_2\) and CO. On the one hand, the THC measurement with FID is not specific, as different HCs can have different response factors in the flame; and on the other hand, THC estimate with the FTIR might be not exhaustive, as some HCs can be not quantified if they are not initially included in the calibration method. A proposal to bring closer the two methods was to use a group of HCs as a surrogate to NHMC and then combined it with ethanol, acetaldehyde, and formaldehyde to calculate NMOG [162]. Another way of research may be to apply chemometric tools, such as principal components regression (PCR) and partial least squares regression (PLSR), on the FTIR multivariate data to predict the THC estimated with FID. Either way, a higher uncertainty margin would be necessary when using FTIR to assess compliance to THCs standards.

The analysis was repeated considering only the studies of the last ten years (i.e., 2011 and afterwards), in order to see whether there were any trends of improvements (i.e., closer agreement with the references). For THCs, NMHC, CH\(_4\), and acetaldehyde there were no studies or only one study was available for each case, thus no conclusion could be drawn. For acetaldehyde, practically the same studies remained, thus there was no meaning for any comparison. For CO\(_2\), CO, NO\(_x\), and NH\(_3\), the mean differences and variabilities remained the same or slightly improved (in particular for CO), but without any statistically significant difference (only 2–6 studies available per case).

4.2. FTIR and Interferences

The higher differences for some components when measuring exhaust gas, compared to calibration gases, can be attributed to analytical and sampling interferences. Analytical interference (also called background or spectral interference) occurs when two or more compounds have overlapping absorbance bands in their infrared spectra. To minimize such interferences, appropriate resolution, selection of wave lengths, an appropriate library of expected components, and post-processing of the spectra are necessary [120].
Sampling system interferences are interferences that prohibit or prevent delivery of the target compounds to the FTIR gas cell (e.g., moisture condensation, reactive gases). Regulations, for example, require a heated sampling line (191 °C) when sampling undiluted exhaust in order to avoid the wall adsorption and/or dissolution of hydrophilic compounds (e.g., NH₃, NO₂, aldehydes, or ethanol) in condensed water. A study noticed the delay in oxygenated species reaching the tailpipe during cold start because of their condensation onto cold exhaust system surfaces and dissolution into condensed water [162]. FTIR systems might have differences in real-time operation. It was shown that an FTIR with a slower gas replacement rate and lower sampling frequency was not able to detect some of the rapid concentration fluctuations, e.g., for CO [183]. Another study noticed that during decelerations, the NH₃ concentration did not drop to near zero as it would be expected during fuel cut-offs (NH₃ formation is strongly inhibited by O₂) [184]. Partly the lower response time of the instrument could explain this. However, it was suggested that an important reason was the outgassing of NH₃ from metal surfaces, which act as temporary NH₃ storage reservoirs [184]. A dedicated study on NH₃ found that response attenuation rates were due to mixing and diffusion during transport as well as NH₃ wall storage. Mixing/diffusion effects caused attenuation with a mean time constant of around 1.6 s. Wall storage attenuation had a mean time constant of 72 s [185]. The stored NH₃ on the sampling lines was around 11 mg. It was concluded that, in practical terms, shorter lines at a higher temperature, with flow rates > 10 L/min proved the best for transient response testing [185].

4.3. On-Board Applications

In the previous paragraphs, it was shown that tailpipe application is possible, paying attention to analytical and sampling interferences. Are FTIRs robust enough for on-board applications? Portable systems were already available in the 1980s. However, portable does not necessarily mean suitable for on-board measurements. The main concerns are:

- Size, weight, power consumption.
- Effect of environmental conditions (temperature, altitude, vibrations).
- Safety (liquid N₂ for cooling, other gases on-board, e.g., N₂ for purging).

The importance of size, weight, and power consumption is different for light-duty and heavy-duty applications. The size and weight are very important for light-duty applications, especially for small city cars. Commercial portable FTIRs are split into units that can fit in the vehicle cabin and/or on the hook. The weight without accessories (e.g., pumps, batteries, and heated lines) is around 50 kg, but including accessories is around 100 kg, which is slightly heavier compared to commercial PEMS (portable emissions measurement systems). Even though in the 1980s the need for power generators of 10 kW was reported [186], today’s portable systems are <0.5 kW (after warming up in the laboratory). These values are still higher or comparable to PEMS based on other principles. An important point for energy consumption is the location of the sampling pump. If it is located upstream of the FTIR, it needs to be heated, thus the energy consumption will be higher compared to a downstream location. Furthermore, at the downstream location, the pressure can be lower than atmospheric pressure, which is an advantage for on-board measurement because it can be maintained and fixed easier. The liquid N₂ on-board is a concern. One solution is keeping the liquid N₂ in a sealed container, with only one small tube connected, venting the evaporating N₂ to the atmosphere or to the rest of the exhaust gases from the FTIR pump.

The effect of the environmental conditions should be well characterized. FTIRs are sensitive to vibrations: the better the resolution is, the longer the displacement of the moving mirror in the interferometer, and the higher the effect of the vibrations on the optical system. Vibration tests in the late 1990s concluded that FTIRs were best isolated by simply placing them on the rear seat of the vehicle [86]. Today FTIR suppliers claim that their systems are vibrations robust. For example, wire rope isolators can be used [187]. Static single mirror solutions have also been presented [188]. Experiments with NOₓ
PEMS (based on CLA or NDUV) showed that sudden temperature changes resulted in zero drift [189]. FTIR results are also sensitive to temperature. The recent CEN standard on PEMS performance prescribes appropriate testing procedures to properly assess the influence of temperature, pressure, and vibrations [190]. Long-term stability and robustness due to vibrations, contamination of optics, etc., should also be assessed.

As with all portable systems, comparison with laboratory versions or other well-established techniques are necessary to increase their confidence in them. Sometimes portable systems might not have the appropriate spectral resolution, response time, or detection limits [104]. For example, in the past, drying of the sample has been used [86], slow response (30 s) [78], or the low optical resolution of 4 cm⁻¹ [110] might have negatively affected the accuracy of the results. It should also be emphasized that the studies in Appendix A were with prototype portable systems, thus further studies with commercial systems are needed.

4.4. Regulatory Requirements

It is clear that regulations cannot prescribe in detail all technical aspects of FTIRs. Some basic and important parameters can be described, but appropriate tests are necessary to confirm the instrument’s internal hardware and software performances. Table 3 summarizes the technical specifications for FTIRs for NH₃ measurements in the current regulations. Most of them are based on the experience of the users and the capabilities of the instruments. Nevertheless, some specifications could be further restricted or better be controlled for future low emissions vehicles. Such recommendations can be based on recent (2019–2020) standards and methodologies for FTIRs [191–194].

Table 3. Example of technical requirements for FTIR for NH₃ measurements in UNECE Reg. 49.

| Specification          | Requirement                                                      |
|------------------------|------------------------------------------------------------------|
| Sampling line          | Stainless steel or PTFE, as short as possible, heated at 190 °C (±10 °C) |
| Spectral resolution    | 0.5 cm⁻¹                                                          |
| Linearity              | offset ≤ 0.5% max, slope 0.99–1.01, SEE ≤ 1% max, R² ≥ 0.998       |
| Detection limit        | <2 ppm under all conditions of testing                           |
| Accuracy               | ±3% of the reading or ±2 ppm, whichever is larger                |
| Zero and span drift    | <2% of full scale                                                |
| Rise time              | ≤5 s                                                              |
| Response time          | ≤20 s                                                             |

PTFE = polytetrafluoroethylene; SEE = standard error of estimate.

For example, SAE J2992 [192] includes a few more requirements (e.g., repeatability and noise). The detection limit, typically determined with zero gas [191,192], could also be determined using interfering gases [193]. Similarly, in addition to the accuracy test, defined as the deviation of the analyzer reading from the reference value, an interference test could be added. SAE J2992 requires interference testing with a gas containing CO₂, CO, NOₓ, and N₂O (mix or separately). For most gases (e.g., NH₃, N₂O, etc.), the maximum total permitted interference is 1%. A spectral residual test is also recommended [191]. USA regulations require appropriate analytical procedures for the interpretation of infrared spectra [193,194].

In the EU RDE regulation, a maximum zero drift of 5 ppm and span drift of 2% is allowed for NOₓ. This is much stricter than the 2% of full scale currently prescribed for FTIR. Actually, the drift of FTIR should be negligible as it was discussed before, not only for NH₃, but for all compounds. Thus these drift requirements could be even stricter.

In USA EPA regulations, FTIR analyzer may be used to measure CH₄, C₂H₆, NMHC, and non-methane-non-ethane hydrocarbon (NMNEHC) for continuous sampling for natural gas engines (Title 40/I/U/1065/C/§1065.266). The FTIR analyzer must have combined interferences that are within ±2% (recommended ±1%) with CH₄, NMHC, or NMNEHC concentrations expected at the standard (Title 40/I/U/1065/D/§1065.366). Such uncertainties are at the same levels permitted for oxygen interference for FID analyzers.
Furthermore, for regulatory purposes, more quality checks should be included. SAE J2992 has a separate chapter of tests performed prior to and after an emissions cycle test (leak, zero, span, pre- and post-drift checks) [192]. As in CEN/TS 17337, adjustment factors for zero and span, or even zero and span drift could be allowed [191].

4.5. Measurement Uncertainty

One important aspect for future regulations is the uncertainty topic. At the moment, the uncertainty for PEMS analyzers is based on a simple (single point—worst case) model. Assuming a 2 ppm accuracy (including interferences), a 2.5 mg/km uncertainty is calculated for a 3 L engine for the analyzer [107] (see also Table 2). Combining the uncertainty of the exhaust flow, the distance, the trip dynamics, this value could be doubled. This value can be 5 times higher for heavy-duty engines. The values are half of the proposed future NH₃ limits [103]. This means that the accuracy requirement instead of “±3% of the reading or ±2 ppm, whichever is larger”, should change, for example, to “±2% of the reading for concentrations > 50 ppm, and ±1 ppm for lower concentrations”. This change would significantly reduce the uncertainty if mass limits are set (and not concentration in ppm). CEN/TS 17337, applicable to stationary sources emissions provides a detailed analysis [191]. A big step was the publication of CEN PEMS performance standard, where a second by second calculation is provided for the calculation of the final uncertainty [190]. Related to the uncertainty is also the traceability topic. The regulated gases have reached high levels of accuracy and traceability. However, this is not the case for non-regulated gases. For example, formaldehyde is tricky to calibrate because it tends to polymerize against the cylinder walls of the gas container. An old study found transfer efficiency of formaldehyde of 95.5% (±13.5%) for all vehicle types (gasoline, diesel, methanol) [24]. At the time of writing, the uncertainty of the formaldehyde calibration gas is much higher than the 2% uncertainty of the regulated gases. In another study, acetaldehyde standard (25 ppm in N₂) could not be used because an impurity was detected in the gas bottle [168].

5. Conclusions

This review summarized the studies that assessed FTIRs performance on the measurement of vehicle exhaust emissions. The mean differences compared to regulated or other methods were around ±2.5% for CO₂, CO, NOₓ, and NH₃ with a variability (one standard deviation) of 5% for CO₂ and 10% for CO, NOₓ, and NH₃. For CH₄, acetaldehyde, and formaldehyde, the mean differences were ±10% (variability 10–20%), but for total hydrocarbons, much higher differences were noticed. The differences were similar regardless of the sampling location of the FTIR (dilution tunnel or tailpipe). Assessment of prototype portable FTIRs on the road confirmed these findings also on-board, but for a narrow range of environmental and driving conditions. Based on these results, FTIRs may be an alternative for on-road testing. However, more studies with commercial portable systems are necessary to cover a wider range of environmental and driving conditions. The introduction of FTIRs in the regulation will require strict technical and performance requirements and procedures based on recently developed standards.

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The following tables summarize the studies that evaluated FTIRs comparing them with reference values. The following terminology applies:

- **Year**: Year of the study (published). The studies are given in chronological order; separately for laboratory and portable systems.
- **Instrument**: Manufacturer and model of the FTIR (as given in the study). In italics in case the FTIR was portable (and the letter “P” is added).
- **Difference**: Difference of FTIR from the reference value. If many points were available, the mean and the range (in brackets) is given.
- **Slope**: Linear regression analysis slope.
- **$R^2$**: Coefficient of determination of linear regression.
- **Range**: Concentration or emissions range (from plots or tables of the studies).
- **Points**: Number of points that the mean or the slope and $R^2$ were calculated.
- **Comment**: Particularities of the tests and additional information: CNG = compressed natural gas; D = diesel; E = ethanol; FFV = flex-fuel vehicle; G = gasoline; M = methanol; x = number of cars; y = years.
- **Ref**: Citation of study.

For each study, the following subdivisions were made whenever data were available:

- FTIR measuring cylinder (calibration gas).
- FTIR and reference, both sampling from the dilution tunnel.
- FTIR and reference, both sampling from the tailpipe.
- FTIR sampling from the tailpipe, reference from the dilution tunnel.
Table A1. Comparisons of FTIR with CO\textsubscript{2} analyzers (all NDIR).

| Year   | Instrument | Difference | Slope | \(R^2\) | Range   | Points | Comment          | Ref. |
|--------|------------|------------|-------|---------|---------|--------|------------------|------|
| 2010   | MKS MultiGas 2030 | −10.5%          |       |         | 12%     | 1      | mix with CO, NO, C\textsubscript{3}H\textsubscript{8} | [95] |
| 2010   | AVL Sesam | -           | 1.01  |         | 1–14%   | 10     |                  | [195]|
| 2019   | AVL Sesam | <1%         | -     | -       |         | 2      |                  | [196]|
| 2005   | P: Temet Gasmet CR2000 | −4.4%       |       |         | 14.5%   | 1      | mix with CO     | [110]|
| 2005   | P: Temet Gasmet CR2000 | −5.4%       |       |         | 10.0%   | 1      |                  | [110]|
| 2015   | P: Spectrum 2, PerkinElmer | 0.4% (−9%–4%) | 1.02  | 1.00   | 0–20%   | 17     |                  | [181]|
| 1990   | Nicolet Sesam | −0.6%       |       |         | 300–370 g/mi | means G, Dx2     | [165]|
| 1990   | Mattson Horiba | -           | 0.92  | 0.99   | 0.4–2.0% | 25     |                  | [112]|
| 1993   | Mattson REA | 13.7% (0.8%–22%) | 1.05  | 0.98  | 0.2–1%   | 380    | 2.5 y (G, CNG)   | [170]|
| 1993   | Nicolet REGA | 3.0% (−13%–18%) | 0.93  | 0.97  | 0.2–1%   | 268    | 2.5 y (G, CNG)   | [170]|
| 1994   | Nicolet REGA | −2.8% (−9%–7.5%) | 0.96  | 0.89  | 0.4–0.6% | 12     |                  | [146]|
| 1994   | Nicolet REGA 7000 | 2.1%       | -     | -       | 0.4%    | 1      | G, fuel M85      | [171]|
| 1990   | Nicolet Sesam | −1.3%       |       |         | 300–370 g/mi | means G, Dx2     | [165]|
| 2010   | AVL Sesam (MKS) | −5%         |       |         | 600–1200 g/kWh | 25     | G, fuels        | [123]|
| 2019   | AVL Sesam | ±2%         | -     | -       | 4–13%   | 9      |                  | [135]|
| 2005   | P: Temet Gasmet CR2000 | 3.1%       |       |         | 12.8%   | 1      |                  | [110]|
| 2005   | P: Temet Gasmet CR2000 \(^2\) | −12.6%     |       |         | 400 g/km | 1      |                  | [110]|
| 2006   | P: Temet Gasmet CR2000 | -           | 1.02  | 0.96  | 8–15%   | 12     |                  | [163]|
| 2020   | P: Bruker Matrix MGS \(^2\) | -           | 0.99  | 0.99  | <13%   | cycle D     | [102]|
| 1985   | Prototype | -           | 0.95  | 0.94   | 30–340 g/mi | 80     | G                | [164]|
| 1998   | VW Sesam | -           | 1.01  | 0.96   | 300–550 g/mi | 65     | Gx10            | [113]|
| 2013   | MEXA-6000FT | 10% (±1%)   |       | -       | 200 g/km | 6      | Gx2 (E0–10–20, M15–30) | [179]|
| 2017   | Gasmet CR2000 | ±4%        | 1.06  | 0.97  | 140–250 g/km | 20     | Dx2, Gx2, CNG | [197]|
| 2018   | AVL Sesam | -           | 1.01  | 0.90  | 200–440 g/km | 9      | D                | [198]|
| 2021   | AVL Sesam | 0.2% (±0.8%) | -     | -       | 140–650 g/km | 37     | G                | [199]|
| 2006   | P: Temet Gasmet CR2000 | −2.1% (−5%–1%) | -     | -       | 180–230 g/km | 11     | G                | [163]|
| 2018   | P: Nicolet Antaris IGS | 6.4% (−19%–61%) | 0.96  | 0.70  | 85–300 g/km | 18     | D, CNG         | [98]|

\(^1\) Portable (in italics), \(^2\) Comparison on the road with PEMS.
Table A2. Comparisons of FTIR with CO analyzers (all NDIR).

| Year     | Instrument          | Difference | Slope | $R^2$ | Range           | Points | Comment | Ref. |
|----------|---------------------|------------|-------|-------|-----------------|--------|---------|------|
| 2010     | MKS MultiGas 2030   | −0.8%      | -     | -     | 8%              | 1      |         | [95] |
| 2019     | AVL Sesam           | <1%        | -     | -     | 1000 ppm        | 4      |         | [196]|
| 2000     | P: Nicolet Protégé 460 | <0.5%    | -     | -     | 0–10 ppm        | 3      |         | [86] |
| 2000     | P: Nicolet          | -1.02      | 1.00  |      | 0–19 ppm        | 5–10   |         | [178]|
| 2000     | P: Nicolet          | −3.6%      | -     | -     | 19 ppm          | 2      | Mix (CO$_2$, H$_2$O) | [178]|
| 2005     | P: Temet Gasmet CR2000 | 8.7%     | -     | -     | 4900 ppm        | 1      |         | [110]|
| 2015     | P: Spectrum 2, PerkinElmer | −1.2% (−30%–15%) | 0.99  | 1.00 | 0–5000 ppm      | 15     |         | [181]|
| 1990     | Nicolet Sesam       | −4.2%      | -     | -     | 1–10 g/mi       | means | G, Dx2  | [165]|
| 1990     | Mattson Horiba      | -          | 0.80  | 0.87 | 0–2500 ppm      | 25     | G, fuels M85 | [112]|
| 1991     | Bio-Rad Digilab FTS-60 | -        | 0.82  | 0.96 | 0–400 ppm       | 20     | Many G, fuels | [169]|
| 1993     | Mattson REA         | 4% (−51%–68%) | 0.94 | 0.98 | 0–0.8%          | 390    | 2.5 y (G, CNG) | [170]|
| 1993     | Nicolet REGA        | 0% (−87%,109%) | 1.20 | 0.86 | 0–0.8%          | 268    | 2.5 y (G, CNG) | [170]|
| 1994     | Nicolet REGA        | −0.8% (−6%–7%) | 0.96 | 1.00 | 4–265 ppm       | 12     | G        | [146]|
| 1994     | Nicolet REGA 7000   | 0.4%       | -     | -     | 178 ppm         | 1      | G, fuel M85 | [171]|
| 2000     | P: Nicolet Protégé 460 | 3.5%     | -     | -     | 5–26 ppm        | 2      | G        | [86] |
| 1990     | Nicolet Sesam       | −4.2%      | -     | -     | 1–10 g/mi       | means | G, Dx2  | [165]|
| 2010     | AVL Sesam (MKS)     | −5%        | -     | 0.99 | 20–45 g/kWh     | 25     | G, fuels | [123]|
| 2010     | AVL Sesam           | −2.5% (0% ... 9%) | -     | -     | 5–170 g/kWh     | 6      | 6 snowmobiles | [195]|
| 2005     | P: Temet Gasmet CR2000 | −12%     | -     | -     | 2500 ppm        | 1      | engine   | [110]|
| 2005     | P: Temet Gasmet CR2000 2 | 1.3%     | -     | -     | 10 g/km         | 1      | G        | [110]|
| 2006     | P: Temet Gasmet CR2000 | -        | 0.87  | 0.99 | 0–6000 ppm      | cycle  | G        | [163]|
| 2020     | P: Bruker Matrix MG5 2 | -        | 1.00  | 0.98 | 0–2000 ppm      | cycle  | D        | [102]|
| 1985     | Prototype           | -          | 1.04  | 0.98 | 0–37 g/mi       | 80     | G        | [164]|
| 1998     | VW Sesam            | -          | 1.08  | 0.99 | 0–6 g/mi        | 65     | Gx10     | [113]|
| 2013     | MEXA-6000FT         | 5.8% (−4%–8%) | -     | -     | 0.27–0.37 g/km  | 6      | Gx2 (E0–10–20, M15–30) | [179]|
| 2017     | Gasmet CR2000       | 0.95       | 0.97  |      | 50–3000 mg/km   | 15     | Dx2, Gx2, CNG | [197]|
| 2006     | P: Temet Gasmet CR2000 | −1.5% (−11%,4%) | 0.95 | 0.98 | 0.5–1.1 g/km    | 11     | G        | [163]|
| 2007     | P: Nicolet          | 0.90       | 0.90  | 0.1–1.1 g/mi   | 15     | Gx4       | [92] |
| 2018     | P: Nicolet Antaris IGS | −4.7% (−75%–69%) | 1.01 | 0.92 | 10–400 mg/km    | 18     | D, CNG   | [98] |

1 P: portable (in italics). 2 Comparison on the road with PEMS.
### Table A3. Comparisons of FTIR with NO\textsubscript{x} analyzers (all CLD unless otherwise specified).

| Year | Instrument \(^1\) | Difference | Slope | \(R^2\) | Range | Points | Comment | Ref. |
|------|------------------|------------|-------|--------|-------|--------|---------|------|
| 2010 | MKS MultiGas 2030 | 3.5%       | -     | -      | 4000 ppm | 1 | FTIR measuring cylinder | [95] |
| 2010 | AVL Sesam        | -          | 1.00  | -      | 0–4000 ppm | 14 | | [195] |
| 2000 | P: Nicolet       | -0.95      | 1.00  | 0–3 ppm | 5–10 | | | [178] |
| 2000 | P: Nicolet       | -2.1% and 1.1% | - | - | 3 ppm | 2 | Mix (CO\textsubscript{2}, H\textsubscript{2}O) | [178] |
| 2000 | P: Nicolet Protégé 460 | ±10% | - | - | 1–10 ppm | 5 | | [86] |
| 2005 | P: Temet Gasmet CR2000 | 0.3% | - | - | 1451 ppm | 1 | | [110] |

Both FTIR and reference connected at the dilution tunnel

| Year | Instrument | Difference | Slope | \(R^2\) | Range | Points | Comment | Ref. |
|------|------------|------------|-------|--------|-------|--------|---------|------|
| 1990 | Nicolet Sesam | -5.2% | - | - | 0.5–1 g/mi | means | G, Dx2 | [165] |
| 1990 | Mattson Horiba | - | 0.95 | 0.94 | 0–50 ppm | 25 | G, fuels M85 | [112] |
| 1991 | Bio-Rad Digilab FTS-60 | - | 0.93 | 0.89 | 0–40 ppm | 20 | Many G, fuels | [169] |
| 1993 | Mattson REA | 4% (-40%...48%) | 1.04 | 0.78 | 0–100 ppm | 368 | 2.5 y (G, CNG) | [170] |
| 1993 | Nicolet REGA | 32% (-31%...86%) | 1.36 | 0.97 | 0–100 ppm | 217 | 2.5 y (G, CNG) | [170] |
| 1994 | Nicolet REGA | -6.6% (-11%,1%) | 0.96 | 1.00 | 4–14 ppm | 12 | G | [146] |
| 1994 | Nicolet REGA 7000 | 1.0% | - | - | 3 ppm | 1 | G, fuel M85 | [171] |
| 2015 | AVL Sesam | 1.3%...10.5% | - | - | 40–80 ppm | 2 | Dx2 | [140] |
| 2000 | P: Nicolet Protégé 460 | 0.5% | - | - | 0.5–3 ppm | 2 | G | [86] |

Both FTIR and reference connected at the tailpipe

| Year | Instrument | Difference | Slope | \(R^2\) | Range | Points | Comment | Ref. |
|------|------------|------------|-------|--------|-------|--------|---------|------|
| 1990 | Nicolet Sesam | 8.0% | - | - | 0.5–1 g/mi | means | G, Dx2 | [165] |
| 1996 | Nicolet REGA 7000 | -10% | - | - | 0–4000 ppm | cycle | G | [30] |
| 2010 | AVL Sesam (MK5) | 5% | - | 1.00 | 8–20 g/kWh | 25 | G, fuels | [123] |
| 2010 | Nicolet Magna 560 | 5.4% (3%,9%) | - | - | 20–100 ppm | 4 | CNG + NO\textsubscript{2} injection | [142] |
| 2016 | Not disclosed | <5% | - | - | 300–1000 ppm | steady | D | [200] |
| 2018 | AVL Sesam (MK5) | - | 1.03 | 1.00 | 0–600 ppm | 600 | various | [141] |
| 2018 | AVL Sesam | 4% (±9%) | - | - | 50–1200 mg/km | 22 | D | [61] |
| 2000 | P: Nicolet | ±5% | - | - | 0–70 ppm | cycle | G | [178] |
| 2005 | P: Temet Gasmet CR2000 | 13% | - | - | 70 ppm | 1 | engine | [110] |
| 2005 | P: Temet Gasmet CR2000 | -30% | - | - | 1.9 g/km | 1 | G | [110] |
| 2006 | P: Temet Gasmet CR2000 | - | 1.05 | 0.94 | 0–800 ppm | cycle | G | [163] |
| 2017 | P: MIDAC I-series | 1.09 | 0.99 | 0–400 ppm | cycle | D | [201] |
| 2020 | P: Bruker Matrix MG5 | - | 1.03 | 0.97 | 0–1000 ppm | cycle | D | [102] |

FTIR at the tailpipe and reference at the dilution tunnel

| Year | Instrument | Difference | Slope | \(R^2\) | Range | Points | Comment | Ref. |
|------|------------|------------|-------|--------|-------|--------|---------|------|
| 1985 | Prototype | - | 0.98 | 0.97 | 0–3.2 g/mi | 80 | G | [164] |
| 1998 | VW Sesam | - | 0.98 | 0.99 | 0–0.8 g/mi | 65 | Gx10 | [113] |
| 2013 | MEXA-6000FT | 7.1% (5%...10%) | - | - | 0.5 g/km | 6 | Gx2 (E0–10–20, M15–30) | [179] |
Table A3. Cont.

| Year | Instrument       | Difference      | Slope | $R^2$ | Range      | Points | Comment | Ref. |
|------|------------------|-----------------|-------|-------|------------|--------|---------|------|
| 2015 | AVL Sesam        | $-8.8\%...3.0\%$ | -     | -     | 190–310 ppm | 4      | D       | [140]|
| 2018 | AVL Sesam        | 11\% ($\pm 10\%$) | -     | -     | 50–1200 mg/km | 22     | D       | [61] |
| 2020 | AVL Sesam        | -               | 0.94  | 0.79  | 0–350 mg/km | 9      | D       | [198]|
| 2017 | Gasmet CR2000    | -               | 0.79  | 0.99  | 10–1200 mg/km | 12     | D, G, CNG | [197]|
| 2006 | P: Temet Gasmet CR2000 | 3.6\% ($2.7\%...4\%$) | -     | -     | 0.2–0.3 g/km | 11     | G       | [163]|
| 2007 | P: Nicolet       | -               | 1.02  | 0.96  | 5–40 mg/mi | 8      | Gx4     | [92]  |
| 2018 | P: Nicolet Antaris IGS | 32\% ($−22\%...117\%$) | 1.21  | 0.92  | 5–650 mg/km | 18     | D, CNG  | [98]  |

1 P: portable (in italics). 2 Comparison on the road with PEMS.

Table A4. Comparisons of FTIR with NH$_3$ analyzers (FTIR, QCL, LDS).

| Year | Instrument        | Difference | Slope | $R^2$ | Range      | Points | Comment | Ref. |
|------|-------------------|------------|-------|-------|------------|--------|---------|------|
| 2009 | AVL Sesam         | ± 5\%      | -     | -     | 20 ppm     | 1      | Daily checks | [202]|
| 2012 | AVL Sesam         | $−0.2\%$  | -     | -     | 100 ppm    | 1      | D       | [203]|
| 2016 | Horiba            | <2.5\%    | -     | -     | 100 ppm    | 1      | D engine NH$_3$ injection | [150]|
| 2016 | Not disclosed     | <5\%       | -     | -     | 0–350 ppm | 3      | D       | [200]|
| 2011 | Horiba            | <2.5\%    | -     | -     | 50 ppm     | 1      | D       | [150]|
| 2017 | P: MIDAC I-series | -          | 1.03  | 0.80  | 0–300 ppm  | cycle G | G       | [201]|
| 2020 | P: Bruker Matrix MG5 | -          | 0.82  | 0.96  | 0–100 ppm  | cycle D | D       | [102]|
| 2011 | Horiba            | 0–5\%     | -     | -     | 0–350 ppm | many D and NH$_3$ injection | [147]|
| 2015 | MKS 2030-HS       | $−6\%$    | 1.09  | 1.00  | 0–25 ppm   | 4      | D, G, FFV | [151]|
| 2020 | Not disclosed     | -          | 0.98  | 0.99  | 25–100 ppm | cycle D | D       | [204]|
| 2018 | Gasmet DX4000 2  | $−9\%$ ($−19\%...1\%$) | -     | -     | 0–25 ppm   | 5      | D       | [149]|
| 2004 | Nicolet Avatar 370 3 | -          | 1.01  | 0.99  | 25–100 ppm | cycle G | G       | [152]|

1 P: portable (in italics). 2 vs. LDS. 3 vs. CI-MS.
### Table A5. Comparisons of FTIR with THC analyzers (FID).

| Year | Instrument ¹ | Difference | Slope | \( R^2 \) | Range | Points | Comment | Ref. |
|------|--------------|------------|-------|-----------|-------|--------|---------|------|
| 1985 | Prototype    | -          | 1.34  | 0.97      | 0–3.7 g/mi | 80 | G | [164] |
| 1990 | Nicolet Sesam| 1.9% (−2%...1%) | - | - | 0.2–0.9 g/mi | means | G, Dx2 | [165] |
| 1990 | Mattson Horiba | - | 1.13 | 0.99 | 0–1200 ppm | 25 | G (fuels, M85) | [112] |
|      | Both FTIRs connected at the dilution tunnel | ¹ | \( P: \) portable (in italics). |
| 1990 | Nicolet Sesam | 17.6% (1%...38%) | - | - | 0.2–0.9 g/mi | means | G, Dx2 | [165] |
| 1996 | Nicolet REGA 7000 | −15% | - | - | <10,000 ppm | cycles | G | [30] |
| 2005 | \( P: \) Temet Gasmet CR2000 | −66%, −63% | - | - | 600 ppm | engine G, G | [110] |
| 2006 | \( P: \) Temet Gasmet CR2000 | −55% | 0.41 | 0.99 | 0–1600 ppm | cycle G | [163] |
| 1994 | Nicolet REGA 7000 | 1.8% (−4%...4%) | - | - | 50 ppm | 5 | CNG | [171] |
| 1998 | VW Sesam | 1.09 | 0.97 | <0.4 g/mi | 65 | Gx10 | [113] |
| 2000 | \( P: \) Nicolet | 5% | - | - | 550 mg/mi | 1 | G | [178] |
| 2006 | \( P: \) Temet Gasmet CR2000 | −55% (−5% cal.) | - | - | 160 mg/km | 10 | G | [163] |
| 2018 | \( P: \) Nicolet Antaris IGS | 46% (−63%...280%) | 0.63 | 0.69 | 0–300 mg/km | 16 | D, CNG | [98] |

¹ \( P: \) portable (in italics).
### Table A6. Comparisons of FTIR with CH\(_4\) analyzers (FID), unless specified otherwise.

| Year | Instrument \(^1\) | Difference | Slope | \(R^2\) | Range | Points | Comment | Ref. |
|------|------------------|------------|-------|--------|-------|--------|---------|------|
| 1992 | Nicolet REGA 7000 | 15%        | -     | -      | 15–17 ppm | 2     | Mix     | [166] |
| 2005 | *P: Temet Gasmet CR2000* | -5.1% | -     | -      | 1509 ppm | 1     |         | [110] |
| 2015 | *P: Spectrum 2, Perkin Elmer* | 1.0% (−2.4%...7.1%) | 1.02  | 1.00   | 0–50% | 17     |         | [181] |
| 1991 | Bio-Rad Digilab FTS-60 | -      | 0.89  | 0.96   | 0–10 ppm | 20    |         | [169] |
| 1994 | Nicolet REGA 7000 | -17.9%   | -     | -      | 3 ppm | 1      | G (M85) | [171] |
| 2016 | Thermo Fisher Antaris IGS | 2.4% (0.8%...4.2%) | - | - | 1500–3000 ppm | 12 | D-CNG | [167] |
| 1998 | VW Sesam | -      | 1.09  | 0.99   | 0–0.07 g/mi | 65 | Gx10 | [113] |
| 2020 | AVL Sesam | -      | 0.96  | 0.99   | 0–40 mg/km | 9 | D | [198] |
| 1994 | Nicolet REGA 7000 \(^2\) | 5%       | -     | -      | 43 ppm | 1 | CNG | [171] |
| 1994 | Sesam II \(^3\) | 5% (−29%...20%) | 1.11  | 0.99   | 40–250 ppm | 12 | G | [180] |
| 2017 | Gasmet CR2000 \(^2\) | -      | 0.97  | 0.95   | 3–105 mg/km | 17 | Dx2, Gx2, CNG | [197] |
| 2020 | *P: Bruker Matrix MG5* \(^3\) | -      | 1.07  | 0.93   | 0–6000 ppm cycle | | D | [102] |

\(^1\) P: portable (in italics). \(^2\) vs. GS. \(^3\) vs. FTIR.

### Table A7. Comparisons of FTIR with NMHC analyzers (FID).

| Year | Instrument \(^1\) | Difference | Slope | \(R^2\) | Range | Points | Comment | Ref. |
|------|------------------|------------|-------|--------|-------|--------|---------|------|
| 2000 | *P: Nicolet Protégé 460* | 0–9% | - | - | 1–10 ppm | 3 | | [86] |
| 1991 | Bio-Rad Digilab FTS-60 | - | 1.03 | 0.96 | 0–120 ppm | 20 | Many G, fuels | [169] |
| 2000 | *P: Nicolet Protégé 460* | −14%...−5% | - | - | 2 and 8 ppm | 2 | G | [86] |
| 2016 | Thermo Fisher Antaris IGS | 97% (31%...292%) | - | - | 50–350 ppm | 12 | D-CNG | [167] |
| 2007 | *P: Nicolet* | 9.5% (−32%...52%) | 1.04 | 0.99 | 3–51 mg/mi | 8 | Gx4 | [92] |
| 2017 | AVL Sesam | 5% | 0.95–1.05 | - | 0–2500 ppm many | G, FFV (E10, E50, E85) | [162] |

\(^1\) P: portable (in italics).
Table A8. Comparisons of FTIR with formaldehyde (CH\(_2\)O) methodology (DNPH + HPLC).

| Year  | Instrument ¹ | Difference | Slope | \(R^2\)  | Range Points | Comment |
|-------|--------------|------------|-------|---------|---------------|---------|
| 1986  | Prototype    | -          | 1.01  | 0.99    | 0.3–8.5 ppm  | 78      | G (methanol) [24] |
| 1990  | Mattson Horiba | -         | 1.03  | 0.99    | 0–80 ppm     | 25      | G, fuels M85 [112] |
| 1992  | Nicolet REGA 7000 | 17%      | 1.14  | 0.99    | 0–45 mg/mi   | 6       | G [166] |
| 1993  | Mattson REA   | 18% (−60%...98%) | 1.25  | 0.91    | 0–4 ppm      | 206     | 2.5 y (G, CNG) [170] |
| 1993  | Nicolet REGA  | 34% (−33%...96%) | 1.04  | 0.95    | 0–4 ppm      | 229     | 2.5 y (G, CNG) [170] |
| 1994  | Nicolet REGA 7000 | 0.9%     | -     | -       | 10 ppm       | 1       | G, fuel M85 [171] |
| 1994  | Sesam II     | −13% (−21%...−6%) | 0.88  | 0.88    | 2–16 ppm     | 6       | G [180] |

Table A9. Comparisons of FTIR with acetaldehyde (CH\(_3\)CHO) methodology (DNPH + HPLC).

| Year  | Instrument ¹ | Difference | Slope | \(R^2\)  | Range Points | Comment |
|-------|--------------|------------|-------|---------|---------------|---------|
| 2010  | Gasmet CR2000 | −20%, +5% | 2.45  | 0.79    | 0–2 ppm      | 27      | D [176] |
| 2013  | MEXA 6000 FT | 2.2% (−1%...5%) | -     | -       | 1–2 mg/km (<100 ppm) | 3 | Gx2 (E0–10–20, M15–30) [179] |
| 2016  | AVL Sesam    | −5%...27% | 1.32  | 0.98    | 0–20 mg/km   | 20      | D, Gx2, CNG [197] |
| 2017  | MKS, Sesam, MEXA | 8% (−4%...32%) | -     | 0.82-0.94 | 0–8 mg/km | 8 | FFV [168] |

¹ FTIR connected at the dilution tunnel or FTIR at the tailpipe and reference at the dilution tunnel
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