



Ammonia emissions from a light-duty vehicle



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ABSTRACT

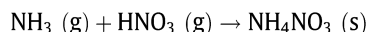
Ammonia (NH₃) is an air pollutant whose emission is partly caused by human activities. The objective of this study was to verify, in a vehicle with spark-ignition engine (Otto cycle), the values of ammonia emissions using the fuels gasohol 22 (gasoline plus 22% anhydrous ethanol), hydrous ethanol fuel (HEF) and compressed natural gas (CNG) with and without the presence of catalytic element (catalyst). The vehicle was tested on a chassis dynamometer following the method prescribed by the USEPA for measuring exhaust emissions and using the urban (FTP-75) driving cycle and highway cycle for measuring autonomy and the congestion (NYCC) and aggressive (US-06) driving cycles, which were also adopted by the US Environmental Protection Agency (USEPA). In addition to the methods of exhaust gas analysis prescribed in the standards, FTIR (Fourier transform infrared) spectroscopy was used for the measurement of NH₃.

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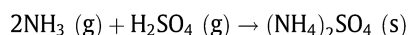
1. Introduction

Ammonia is a chemical compound composed of one nitrogen atom (N) and three hydrogen atoms (H). These atoms are distributed in a tetrahedral molecular geometry, and the chemical formula of the compound is NH₃ (NIST, 2011). After N₂ and N₂O, NH₃ is the most abundant nitrogen compound in the atmosphere (Seinfeld and Pandis, 2006).

The atmospheric concentration of NH₃ is highly variable, depending on the proximity to the emission source. The typical continental concentration is from 0.1 to 10 ppb (Seinfeld and Pandis, 2006). The ammonium ion (NH₄⁺) is an important component of continental tropospheric aerosol. Additionally, the reaction of NH₃ with nitric acid in the gaseous state generates ammonium nitrate, the main route for the formation of particulate nitrate, according to the following equation:



The reaction of ammonia with sulfuric acid in the gas phase also produces particulate matter:



Reactive nitrogen compounds are important inducers of air pollution by particles and may even be dominant in some regions. The high reactivity makes these compounds participate in reactions, some of which lead to particle formation. For example, particles made up of ammonium nitrate constitute approximately 65% of all particulate matter (total suspended particulates) in Southern California, USA (Malm et al., 2014). Schiferl et al. (2014) estimate that about 40–60% of sur-

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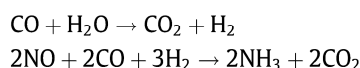
face inorganic PM 2.5 in California during the summer are attributable to anthropogenic sources of ammonia. Hasheminassab et al. (2014) affirmed that at eight distinct sampling locations in the state of California, including the Great Los Angeles area, secondary aerosols, including ammonium nitrate and sulfate, comprised the largest fraction of ambient PM 2.5, accounting for 26–63% of total, on an annual average basis.

Changes in the natural nitrogen cycle can significantly influence the air pollution in many ways. Studies have shown a positive correlation between the air pollution caused by fine particulate matter and cardiovascular and respiratory diseases, asthma, and a general increase in mortality (Pope et al., 2002).

Ammonium salt particles are capable of being respired and reach the alveoli, causing a number of respiratory disorders, such as asthma and bronchitis. This particulate form of ammonia is found in urban areas where gaseous ammonia reacts chemically with other compounds, leading to the formation of “smog”.

2. Ammonia emissions from vehicles

Although the use of three-way catalysts has led to a considerable reduction in emissions, the activity of these components has been identified as being responsible for the higher ammonia emissions by vehicles (Gandhi and Shelef, 1991). The formation of ammonia is attributed to nitric oxide reacting with the hydrogen gas produced by the reaction of CO with water (Livingston et al., 2009):



Durbin et al. (2002), Heeb et al. (2006), and Huai et al. (2003) reported an association between air/fuel ratio and ammonia emission. A low air/fuel ratio represents combustion of a rich mixture, which generally also leads to a higher CO emission. As vehicles generally tend to enrich the mixture during accelerations, a correlation between accelerations, CO emission and ammonia emission is expected.

One of the factors identified as influencing the emissions of ammonia is the sulfur content in fuel. Mejia-Centeno et al. (2007) reported that the removal of sulfur from gasoline increases the formation of NH₃ and decrease the formation of N₂O. A similar assertion can also be found in Durbin et al. (2004). Since NH₃ is primarily formed over the catalyst, these results suggest that sulfur could inhibit NH₃ formation on the catalyst by poisoning reaction sites for NH₃ formation (Gandhi and Shelef, 1991). Durbin et al. (2004) showed for tests on two vehicles that NH₃ emissions increased as the sulfur content in the fuel was decreased over the FTP and US06 cycles.

Recently, studies on ammonia emissions by vehicles have emerged in Brazil. Daemme et al. (2013) found a substantial increase in the ammonia emissions measured when testing a gasoline-fueled motorcycle with a 300 cm³ engine. The emission before the catalyst was 0.732 mg km⁻¹, and after the catalyst was added, it was 87.441 mg km⁻¹. In the same test, the vehicle was equipped with an additional type of catalyst used in SCR (selective catalyst reduction) systems for NO_x reduction in diesel-powered vehicles. After this second catalyst was added, the emission of ammonia was reduced to 48.996 mg km⁻¹, indicating a possible additional use for this type of technology.

Daemme et al. (2014) performed a study to find a correlation between the sulfur content of fuels and the emission of ammonia. Although they observed a tendency of an increase in the ammonia emission when the sulfur content was reduced (in tests on motorcycles and one automobile), they indicated the need for further research due to the small number of vehicles tested.

Although several papers have been published about the measurement of NH₃ emissions from vehicles, there is a gap with respect to the Brazilian reality. Brazil is a pioneer country in the use of ethanol produced from sugar cane as an automotive fuel. Since the 1970s, anhydrous ethanol has been added to gasoline. As a result, it was possible to completely eliminate the use of tetraethyl lead as an antiknock agent, an action that has undeniable environmental and health benefits. Since the 1980s, the country has developed a large fleet of cars that run on ethanol. In 2003, flexible fuel engine technology, capable of operating with any proportion of gasoline and ethanol mixture, was introduced. In practice, when the ethanol price presents an economic advantage for the user, flexible vehicles run almost only with hydrated ethanol. In 2012, the fleet of the country was a little more than 27 million cars, and approximately 40% of the Otto-cycle vehicle fleet consisted of gasohol-22 (a mixture containing 78% gasoline and 22% anhydrous ethanol) powered vehicles, 3% hydrated ethanol powered vehicles and 57% flexible fuel vehicles (FFV) (MMA, 2013). There were also approximately 1.7 million vehicles adapted to run on CNG (IBP, 2014). These figures show the importance of this study, which aimed to increase the knowledge of how some specific variables found in the Brazilian automobile fleet can affect NH₃ emissions.

The objective of this study was to verify, in a vehicle with a spark-ignition engine (Otto cycle), the values of ammonia emissions using the fuels gasohol 22, hydrous ethanol fuel (EHC) and compressed natural gas (CNG), with and without the presence of the catalytic component (catalyst). In addition, we attempted to verify the existence of a relationship between the emission of ammonia and driving the vehicle (driving cycle), as well as the existence of a relationship between two sulfur contents in gasohol 22 and the emission of ammonia in the sample tested.

3. Materials and methods

3.1. Characteristics of the vehicle tested

The vehicle tested was a tetra-fuel spark ignition vehicle with a four-cylinder engine, a displacement volume of 1.4 L, year 2011, with 120,000 km, designed to run on plain gasoline, plain ethanol, any mixture of gasoline and ethanol, and CNG. The vehicle is certified to meet emission limits imposed for light duty vehicles by phase 5 of Brazilian legislation. This phase is equivalent to US Tier II for 50,000 miles, bin 6 for CO (3.4 g km^{-1}) and NMHC (0.075 g km^{-1}) and bin 8 for NO_x (0.20 g km^{-1}).

3.2. Test method

For the determination of emissions from exhaust gas, the vehicles were tested by the method described in the standard ABNT NBR 6601 (ABNT, 2012), which is similar to the procedure used by the US EPA (Code of Federal Regulation (CFR), 40 CFR part 86), through the use of the driving cycle FTP-75 - Federal Test Procedure.

This standard prescribes the method for the determination of total hydrocarbons (THC) and non-methane hydrocarbons (NMHC), carbon monoxide (CO), nitrogen oxides (NO_x), carbon dioxide (CO₂) and particulate matter emitted by the engine through the tailpipe of light duty vehicles under simulated conditions of normal use in medium urban transit. FTP-75 is a three-phase cycle that simulates driving under cold-start conditions (phase 1), hot stabilized conditions (phase 2) and hot start conditions (phase 3) over an urban route. A twin roll hydraulic dynamometer, model Clayton ECE-50, was used to simulate the inertia and the resistance power of each vehicle tested (Borsari and Assunção, 2012).

The highway driving cycle used in this study was described in the standard ABNT NBR 7024 (ABNT, 2010) and was developed by the US EPA to simulate a highway driving conditions. Combined with the FTP-75 cycle, this cycle is used to determine the fuel consumption of a vehicle. Two other cycles were also tested. The US-06 or SFTP (Supplemental Federal Test Cycle), which is used in the type approval process of new vehicles in US and simulates an aggressive driving condition with higher speed and accelerations, and the NYCC (New York City Cycle), which tries to duplicate the severe driving conditions usually found in urban congested traffic.

3.3. Fueling

For the gasohol and ethanol fuels, before pre-conditioning, the fuel tank was drained and refilled with the standard fuels required by the automotive emission control law. Between the gasohol and ethanol tests, the fuel tank was completely drained and filled with the test fuel. Then the vehicle was preconditioned by running the FTP driving cycle twice, followed by new drainage and refueling. This procedure is the same as that recommended by the manufacturer when performing the type-approval tests so that the learning process can be adjusted by the electronic control unit. For CNG, the vehicle was tested with commercial gas. The main features of the specifications for these fuels are in a supplemental section. The real sulfur content for the gasohol used was 17 ppm for gasohol 22 S50 and 300 ppm for gasohol 22 S400.

3.4. Sample collection and analysis

The exhaust gases were diluted with ambient air of the laboratory using a constant volume sampler (CVS) and were then collected in Tedlar bags. This is the routine procedure for the method described in ABNT standard NBR 6601 (ABNT, 2012), similar to the procedure used by the EPA (Code of Federal Regulation (CFR), 40 CFR part 86). Another probe was inserted, and a second set of sample bags was mounted (one for each of the three phases of the driving cycle) and the raw exhaust gas was sampled. Whereas the original setting was used for the routine analysis of regulated pollutants, the set of extra sample bags was used for the measurement of NH₃ by FTIR. NH₃ has a strong affinity for the metallic sample system interior (CARB, 2009). This can result in a significant loss of ammonia in the exhaust gas from the vehicle emission until injection, after being diluted with the ambient air, into the FTIR gas cell. Another characteristic of ammonia is the quick reaction with water and NO_x, which makes sampling loss a key feature in the measurement of the pollutant (Bielaczyc, 2012).

The regulated pollutants were measured by a Horiba analyzer bench series 200: total hydrocarbons (THC) by flame ionization detector (FID) and nitrogen oxides (NO_x) by chemiluminescence. The non-methane hydrocarbon (NMHC) concentration was obtained by subtracting the methane, measured by a gas chromatograph coupled with an FID, from the THC. Carbon dioxide (CO₂) was measured by a non-dispersive infrared (NDIR) detector and by FTIR to validate these measurements through the comparison of the results obtained by the two methods.

FTIR spectroscopy, in principle, can be used for the analysis of NH₃ in gas samples (Livingston, 2008). The equipment used was a Perkin Elmer FTIR Spectrum 100 equipped with a gas cell with a 10 m optical path and a resolution of 0.5 cm^{-1} . The concentration of NH₃ was determined by the relation between the absorbance and the concentration of a standard gas (Beer's Law) using a response curve obtained by dilution of the standard gas in nitrogen at various proportions using a gas divider. The resulting curve is shown in Fig. 1. The limitations of the equipment used in this study prevented the analysis to be performed by obtaining the emission values every second.

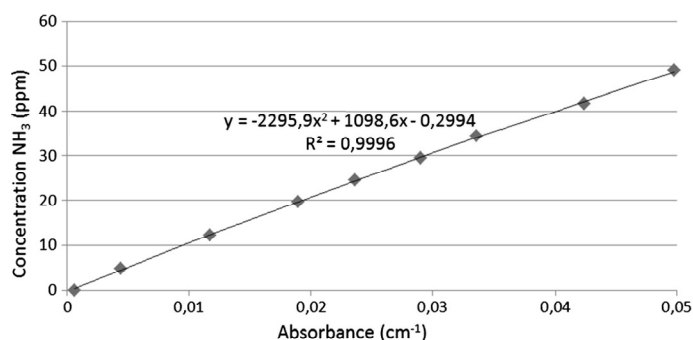


Fig. 1. FTIR calibration curve for NH₃.

A gas cylinder with a concentration of 48 ppm NH₃ was used, as certified by the manufacturer whose laboratory is accredited by the Brazilian Institute of Metrology and Industrial Quality (INMETRO) and traceable to the National Metrology Institute (NMI). The vehicle emission laboratory of CETESB is also accredited by INMETRO to perform emissions testing according to the ISO/IEC 17025 standard, which establishes the requirements for metrological competence in laboratory measurements. Although measurements of NH₃ are not within the scope of accreditation, the same requirements for quality and traceability were observed in these tests.

3.5. Test planning

Using the DOE (Design of Experiments) methodology, it was supposed that there were three factors that influence NH₃ emissions: the type of fuel, the presence of a catalyst and the sulfur content, with the latter only applied to gasohol fuel, given that the concentration of sulfur present in HEF and CNG fuel is non-existent or at least negligible. Fig. 2 shows the design of experiments.

In addition, the influence of different driving cycles on the ammonia emissions was verified. The tests were conducted using the US-06, NYCC and highway cycles, as described previously.

4. Results

4.1. Values of NH₃ emission by fuel type and driving cycle

The results of the NH₃ emissions obtained in the FTP-75 tests are shown in Table 1.

The graph of Fig. 3 shows the average values of the NH₃ emissions in the exhaust gas, measured before (pre) and after (post) the catalyst for each fuel.

The differences observed in the emission of ammonia in the tests performed with different fuels were not significant. One possible explanation is that although the composition of the three fuels used is diverse, the chemistry of ammonia formation is mainly associated with the availability of CO emissions, which did not appear to be very different between fuels. On the other hand, the fact that the ammonia emission was slightly higher in the tests using the CNG could be directly associated

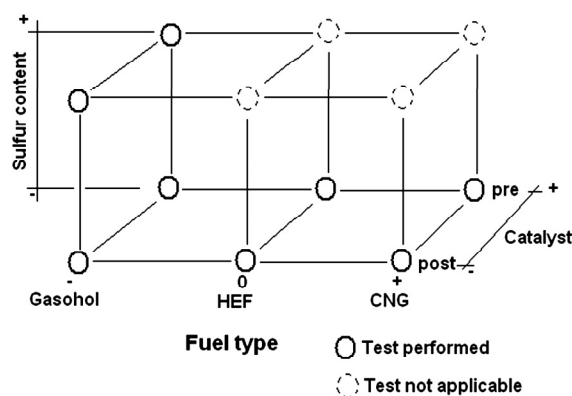


Fig. 2. DOE diagram.

Table 1NH₃ emissions - Results achieved for the FTP-75 tests. Emission is in mg km⁻¹.

Test #	Fuel	Post catalyst	Pre catalyst
051-14	CNG	4.80	1.08
052-14	CNG	3.51	1.04
081-14	CNG	4.17	n.d.
053-14	HEF	4.98	1.63
054-14	HEF	1.98	0.80
089-14	HEF	4.45	n.d.
056-14	Gasohol A22 S400	3.92	1.15
057-14	Gasohol A22 S400	3.83	1.07
058-14	Gasohol A22 S50	2.73	n.d.
059-14	Gasohol A22 S50	3.32	n.d.
082-14	Gasohol A22 S50	3.74	n.d.

n.d. – not determined.

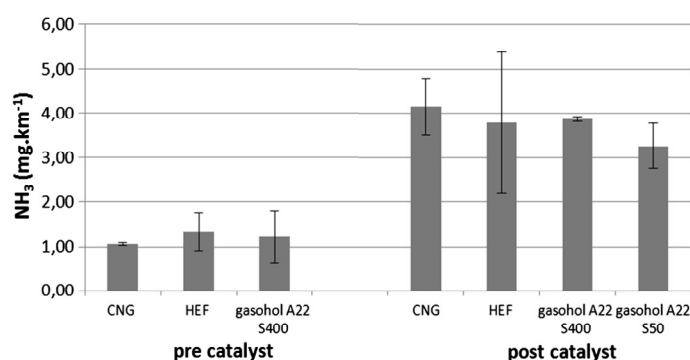


Fig. 3. Average values of ammonia emissions in mg/km considering the fuel variables and the presence of the catalyst. Vertical bars indicate the standard deviation ($\pm 1 s$).

with the fuel since the CNG combustion reaction is among the fuels used the one that produces the most water that will produce hydrogen through the water-gas shift reaction.

The averages and standard deviations in the test with gasohol fuel with two different sulfur contents were 3.88 ± 3.26 mg km⁻¹ and 3.26 ± 0.51 mg km⁻¹, respectively, for gasohol 22 S400 and gasohol 22 S50. These values were obtained only when the vehicle was tested in the FTP-75 cycle. Although the average value of the tests conducted with the higher sulfur content was higher than the average of the tests conducted with the lower sulfur content fuel, a comparison using *t*-student statistics showed no significant difference in the ammonia emissions when changing the gasohol sulfur content.

Further tests were performed with the measurement of the exhaust gas after the catalyst, using driving cycles other than the FTP-75. The results, expressed in mg km⁻¹ of NH₃, are shown in Table 2.

The graph of Fig. 4 shows the average values of NH₃ emissions present in the exhaust gas measured for different driving cycles for each fuel.

4.2. Relationship between NH₃ emissions and other pollutants

Although it is common to find data for vehicle emissions of regulated pollutants, for ammonia, as well as for other pollutants whose measurement is not mandatory, these data tend to be scarce. For this reason, it is important to establish relationships between the regulated pollutants and other compounds to estimate the latter from the available data of the first. One of the possible associations is the one that correlates the emission of CO with the emission of ammonia, which would make it theoretically possible to use that compound for a rough estimate of the NH₃ emissions.

The graph of Fig. 5 shows the dispersion of the obtained values for NH₃ and CO emissions.

The coefficient of determination of 0.30 observed in the tests conducted using the aggressive driving cycle (US-06) is greatly influenced by the high emissions of both ammonia and carbon monoxide.

Comparing the results of the NH₃ and NO_x emissions, a reasonable correlation is observed between the two compounds, as seen in the graph of Fig. 6. However, this correlation is greatly influenced by the results of four tests: those of the aggressive driving cycle (US-06) and with CNG and gasohol fuels. These tests showed the greatest emissions of both NO_x and NH₃. If these tests are not considered, the correlation between these compounds is negligible.

Table 2
NH₃ emissions - Results for other driving cycle tests. Emission is in mg km⁻¹.

Test #	Cycle	Fuel	NH ₃
081-14	Highway	CNG	3.97
082-14	Highway	Gasohol A22 S50	1.90
083.1-14	NYCC	Gasohol A22 S50	10.44
083.2-14	NYCC	Gasohol A22 S50	8.58
084.1-14	NYCC	CNG	14.66
084.2-14	NYCC	CNG	19.93
091.1-14	NYCC	HEF	10.73
091.2-14	NYCC	HEF	12.20
087.1-14	US-06	Gasohol A22 S50	14.19
087.2-14	US-06	Gasohol A22 S50	17.44
088.1-14	US-06	CNG	22.99
088.2-14	US-06	CNG	26.82
092.1-14	US-06	HEF	5.78
092.2-14	US-06	HEF	5.15

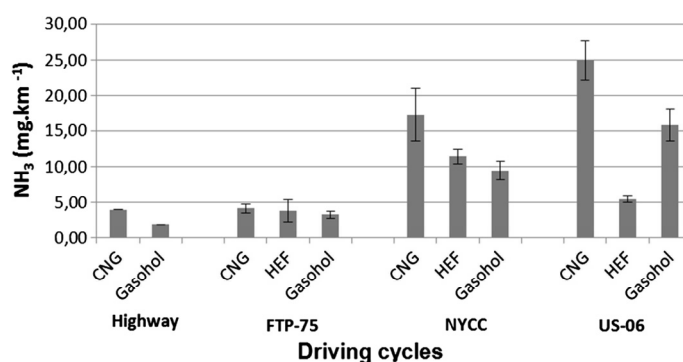


Fig. 4. Average values of ammonia emissions in mg km⁻¹ measured after the catalyst and considering the fuel and driving cycles. Vertical bars indicate the standard deviation (± 1 s).

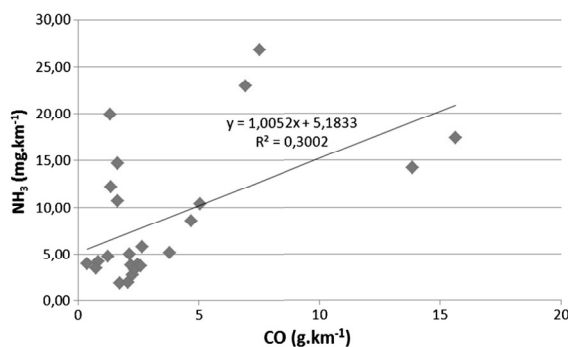


Fig. 5. Relationship between NH₃ and CO emissions.

During the tests, a momentary engine malfunction occurred with the vehicle, probably caused by fuel switching over very short time intervals. When the vehicle was first fueled with gasohol A22, the monitoring device of the engine operating conditions, known by the acronym OBD (“On Board Diagnosis”), showed a dysfunction indicated by lighting the indicator lamp MIL) on the dashboard. The indication was “ignition faults on cylinders 1 and 2” and the codes was P0301 and P0302. After the test, during the preconditioning of the vehicle the engine returned to its normal operation without any repair. It is possible that the transient failure has been caused by the frequent fuel changes and consequently a deficiency in adaptation. The vehicle was tested before it was returned to normal operation conditions. The emissions of regulated pollutants were severely increased, and there was an observed increase in NH₃ emission. The average emission of the vehicle under normal operating conditions was 3.88 mg km⁻¹, whereas the emissions detected in the unregulated vehicle was 18.56 mg km⁻¹, an increase of 378%.

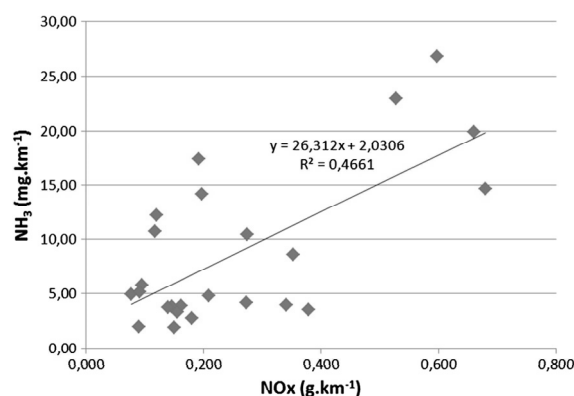


Fig. 6. Relationship between NH_3 and NO_x emissions.

4.3. Comparison with other studies

Due to the limitations of the equipment used, the results obtained in this study should not be used as ammonia emission factors to quantify the total emission of the compound by a fleet of vehicles, for example. In addition, the results obtained refer only to the vehicle tested and cannot be extrapolated to other vehicles. Although the results obtained should be understood as explaining only the differences in ammonia emission due to the variables involved, it may be useful to compare them at least in a relative way with other studies in which measurements of vehicle ammonia emission were made.

Other studies indicated that the formation of ammonia is associated with the presence of the automotive catalyst. Penteado et al. (2012) measured ammonia emission on four motorcycles, finding much higher emissions in the measurements made after the catalyst. Daemme et al. (2013) also found a substantial increase in the emission of ammonia after the catalyst in a test on a gasoline motorcycle. Livingston et al. (2009) and Bielaczyc (2012) also suggest this phenomenon.

Livingston (2008) measure ammonia emissions on different dynamometer test cycles and expected to find higher ammonia emissions for the more aggressive driving cycles, since aggressive driving cycles have been associated with higher emissions of ammonia precursors (CO and NO_x). The results show higher ammonia emissions for the US06 cycle, consistent with previous studies (Durbin et al. (2002), Huai et al. (2003), and Heeb et al. (2008)). Those studies are consistent with the chemistry of ammonia formation; which requires rich air/fuel ratios to produce hydrogen gas via the water-gas shift reaction. Since vehicles must provide rich air/fuel mixtures during acceleration events, an association between acceleration, CO emissions and ammonia emissions was expected.

Huai et al. (2005) found average values of 6.6, 13.3 and 36.3 mg km^{-1} of ammonia emissions, though with high dispersion values, in a study running 8 gasoline vehicles using the FTP-75, NYCC and US-06. This study found, respectively, 3.7, 12.8 and 15.4 mg km^{-1} .

Several results found on studies that measured ammonia emissions in light duty vehicles are shown in Table 3.

5. Conclusions

The ammonia emission after adding the catalyst was consistently higher than the values measured upstream of the control device. The results confirm the claims in the literature that account for induction in the formation of this compound within the automotive catalyst. Ammonia emission downstream from the catalyst was three to four times higher than upstream from the catalyst in tests performed according to Brazilian Standard ABNT NBR 6601, i.e., using the FTP-75 driving cycle (ABNT, 2012).

Although there were differences between the average values, when comparing emissions obtained with different fuels, the statistical analysis showed that these differences were not significant at the 95% confidence level.

There was also no significant difference between the results of the tests with gasohol containing 50 ppm or 400 ppm sulfur, although some studies (Durbin et al., 2004; Mejia-Centeno et al., 2007; Daemme et al., 2014) have claimed that higher sulfur content generally leads to lower ammonia emissions. The sulfur present in the fuel has a deleterious effect on the catalyst, causing a loss of efficiency. This effect, however, is caused over the long-term, throughout its lifetime.

An increase in ammonia emissions was observed, regardless of the driving cycle used, when using CNG. Ammonia emission values with the congestion driving cycle (NYCC) were three to four times higher compared to the urban driving cycle according to the Brazilian Standard ABNT NBR 6601 (FTP-75). With the aggressive driving cycle (US-06), ammonia emissions were approximately 50–60% higher compared to the congestion cycle drive, for both CNG and gasohol. Under these conditions, dissonant behavior in ammonia emissions was detected when using EHC, resulting in lower ammonia emissions when tested with the NYCC cycle and slightly higher than values obtained with the FTP-75 cycle.

Table 3
Average emissions of NH₃ from light duty vehicles from several studies.

Study	Sample number	Measurement method	Analysis method	NH ₃ (mg km ⁻¹) ⁽³⁾
Fraser and Cass (1998)	Fleet	Tunnel	Colorimetric	61
Kean et al. (2000)	Fleet	Tunnel	Ion chromatography	49
Durbin et al. (2002)	39	Dynamometer (FTP-75 cycle)	FTIR	33.5
Karlsson (2004)	5	Dynamometer (NEDC)	Mass spectrometer	17.3
Huai et al. (2005)	n.d.	Modeling	Several	9.4 (SULEV) ⁽²⁾ 13.5 (ULEV) 21.7 (LEV)
Reyes et al. (2006)	1 (hybrid)	Dynamometer (2 cycles)	FTIR	1.5 (FTP-75) 9.2 (5)
Burgard et al. (2006)	Fleet	Traffic	Remote sensing	37 (1)
Kean et al. (2009)	Fleet	Tunnel	Ion chromatography	30 (4)
Livingston et al. (2009)	41	Dynamometer (several cycles)	FTIR	46
Bishop et al. (2010)	Fleet	Traffic	Remote sensing	37 (1)
Bielaczyc (2012)	3	Dynamometer (NEDC)	IR	16.9 (gasoline) 6.2 e 6.2 (gasoline, LPG) 3.7 e 1.6 (gasoline, GNV) 5.2 (gasohol) 3.7 (diesel)
Daemme et al. (2014)	3	Dynamometer (FTP-75 cycle)	FTIR	5.2 (gasohol) 3.7 (diesel)
This study	1	Dynamometer (several cycles)	FTIR	9.0 (gasohol, HEF, CNG)

(1) The original result of 0.49 g kg⁻¹ was transformed into g km⁻¹ assuming autonomy of 10 km L⁻¹ and a gasoline density of 0.75 kg L⁻¹.

(2) California State Control Legislation Designations - USA: SULEV – super ultra-low emission vehicles; ULEV – ultra-low emission vehicles; LEV – low emission vehicles.

(3) Unless indicated otherwise, the fuel is gasoline, or, in the case of traffic studies, undefined.

(4) The original result of 0.40 g.kg⁻¹ was transformed into g.km⁻¹ assuming autonomy of 10 km.L⁻¹ and a gasoline density of 0.75 kg.L⁻¹.

(5) Five specific cycles were used to simulate urban traffic in five regions of Mexico City.

Starting from the assumption of the formation of ammonia induced by the presence of the catalyst, we can conclude that, as a rule, it is likely that when using the congestion cycle, which reproduces sudden accelerations, and the aggressive cycle, which is characterized by sudden accelerations and extreme speeds, the conditions facilitate the formation of ammonia. These conditions include the presence of a higher concentration of ammonia precursor pollutants, together with the fact that the catalyst must stay at a higher temperature for a longer period compared to the FTP-75 cycle, which tends to optimize its operation.

It was also possible to determine, for all tests, the emissions of CO and NO_x, in addition to other regulated pollutants. Some conclusions and assumptions can be made based on the analyses conducted on these pollutants:

- A low correlation was observed between the emissions of NH₃ and CO, which is indicated as being a precursor of ammonia. However, the highest ammonia emissions were associated with high CO emissions, in tests performed with the aggressive driving cycle and with the test conducted with the unregulated vehicle, which had the highest CO emission. The use of CO as a predictor of ammonia emissions requires more testing on a representative sample of the fleet.
- There was not a strong correlation for the relationship between NH₃ and NO_x emissions. NO_x formation is due to the high temperature and pressure within the engine's combustion chambers, and its reduction is performed by the catalyst activity. The extreme conditions of the US-06 cycle, however, were of such magnitude that the emissions surpassed the performance capacity of the catalyst, even when operated under the optimized conditions, leading to increased ammonia emissions.

To achieve the objectives proposed in this study, the decision to perform the tests in a single vehicle was adequate. However, this decision restricted the ability to generalize the ammonia emission factors with respect to the entire vehicle fleet. It is recommended that additional tests are conducted, preferably in a sample that is representative of the current fleet.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.trd.2016.12.008>.

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