

PRACTICAL METHODOLOGY FOR CALCULATION OF SPECIFIC GASEOUS EMISSIONS

Maris Gailis^{1,2}, Ilmars Dukulis¹, Vilnis Pirs¹, Gints Birziētis¹

¹Latvia University of Life Sciences and Technologies, Latvia; ²Riga Technical University, Latvia
maris.gailis@rtu.lv, ilmars.dukulis@llu.lv, vilnis.pirs@llu.lv, gints.birziētis@llu.lv

Abstract. Different methods and tools are used to measure concentrations of various gaseous components in engine exhaust gas stream. The concentration usually is measured in parts per million or percent by volume. To compare results between different engines, automobiles or fuels, normalized parameters are more useful. Specific emissions are the pollutant mass flow per distance travelled or unit of power, such as $\text{g}\cdot\text{km}^{-1}$ and $\text{g}\cdot\text{kWh}^{-1}$. There is a lack of description of practically applicable methodology for calculation of specific emissions, particularly, if the FTIR analyser is used. The methodology, presented in this paper, requires measurement of ambient air pressure and humidity, fuel mass flow, engine power or driving speed and concentration of wet or dry exhaust gas components. The methodology includes calculation of absolute air humidity, exhaust gas mass flow and specific emissions.

Keywords: internal combustion engine, exhaust gas analysis, specific emissions.

Introduction

Gaseous emissions from internal combustion engines are an important source of air pollution and greenhouse effect gases. Emission levels are important engine operating parameters.

Exhaust gas analysis can be performed for legislative or research purposes. Legislative measurements are performed for type approval of new engines and motor vehicles and periodical inspection of used motor vehicles. In the European Union (EU), current legislation and its amendments require certain specific amount of carbon monoxide (CO), nitrogen oxides (NO_x), unburned hydrocarbons (THC), non-methane hydrocarbons (NMHC), mass (PM) and number (P) of particles [1]. Carbon dioxide (CO_2) is recognized as an important contributor to climate changes that creates the greenhouse effect [2]. Specific emissions of CO_2 by motor vehicles are legislatively limited in the EU [3]. Methodology for exhaust gas analysis for type approval purposes requires specific equipment for each pollutant species - non-dispersive infra-red analyser (NDIR) for CO and CO_2 , flame ionisation analyser (FID) for HC and chemi-luminescent (CLA) or non-dispersive ultra-violet resonance absorption (NDUVR) for NO_x . Gravimetric analyser is required for PM. Exhaust gas analysis is not performed in direct gas stream but using the constant volume sampling (CVS) system with sample dilution [4]. Calculation method to obtain specific emissions that is included in the type approval methodology is suitable for the CVS system and is somehow impractical for research purposes. Additionally, to standardise type-approval testing in laboratory conditions, car manufacturers in the EU are now required to conduct real driving emission (RDE) testing, using a portable gas analyser (PEMS). Procedure of calculation of specific emissions, included in the respective EU regulation, is simplified and requires additional measurement of the engine inlet air flow or exhaust gas flow [1].

Different methods and tools are used to measure concentrations of various gaseous components in engine exhaust gas stream. Types of gas analysers, recommended by the motor vehicle type approval legislation, have limited capabilities. For instance, the FID analyser cannot distinguish between different species of hydrocarbons and has lower sensitivity to oxygenated components [5]. For research purposes, it might be useful to measure the amount of specific pollutants, such as aldehydes or ammonia. Near simultaneous recognition of various species in a gas sample, if their molecules have dipole moments, can be performed by the Fourier Transfer Infrared Analyser (FTIR) [6]. Results, obtained using the FTIR, are not directly comparable with the results gained by other methods [7].

Regardless of the gas analyser type, the concentration usually is measured in parts per million by volume (ppm) or percent by volume [8]. Volumetric composition of the exhaust gases does not provide information about the amount of pollutants [9]. To compare results between different engines, automobiles or fuels, normalized parameters are more useful. Specific emissions usually are the pollutant mass flow per distance travelled or unit of power. Practically applicable methodology for calculation of specific emissions typically is not included in major literature sources. Stone provides simplified approach for such calculation, but it is lacking correction factors for air properties and

requires exact information on fuel composition [9]. Researchers of the University of Pittsburgh developed exhaust gas mass emission analysis system using low-cost components [10]. Data of fuel and air flows are obtained using on-board diagnostics, which may increase uncertainty of the results. Italian researchers developed an advanced methodology for calculation of specific mass emissions [11-13]. The methodology includes measuring of the oxygen content in exhaust gases and relatively complicated calculation sequence. Stinvinder provides a fuel-based calculation method for exhaust gas mass emission calculation [14]. Application of the method in case of modern, oxygenated fuels requires corrections. Regulation No 49 of the Economic Commission for Europe of the United Nations (UN/ECE) contains a methodology for calculation of specific emissions, based on the exhaust gas volumetric composition, inlet air flow, exhaust gas flow or fuel mass flow. Practical application of this methodology is slightly problematic, as the structure of the regulation is complicated and contains a few numeric and typographic mistakes.

Therefore, the aim of this study is to develop the methodology for calculation specific emissions in mass units, such as $\text{g}\cdot\text{km}^{-1}$ and $\text{g}\cdot\text{kWh}^{-1}$, from emission measurements in relative units in parts per million by volume (ppm) or percent by volume.

Materials and methods

Humidity of ambient air is a necessary parameter for conversion of dry/wet emissions, normalizing of NO_x emissions and calculation of the exhaust gas mass flow. In case, when relative humidity of air is measured, absolute humidity can be calculated, using the methodology developed by NASA researchers [15]. Relative humidity of air is defined by the equation (1):

$$U = \frac{e_v}{e_s}, \quad (1)$$

where e_v – partial pressure of water vapor, Pa;
 e_s – partial pressure of water vapor at saturation, Pa;
 U – relative humidity of air [15].

Partial pressure of water vapor at saturation is given by the equation (2):

$$e_s = 10^{23.5518 - 2937.4/T} \cdot T^{-4.92830}, \quad (2)$$

where T – temperature of air, K [15].

Knowing the value of relative humidity and partial pressure of water vapor at saturation, partial pressure can be calculated (3).

$$e_v = U \cdot e_s, \quad (3)$$

Absolute humidity of air can be found by the equation (4):

$$H = \frac{e_v}{R_v \cdot T}, \quad (4)$$

where R_v – specific gas constant of water vapor, $461.5 \text{ J}\cdot(\text{kg}\cdot\text{K})^{-1}$;
 H – absolute air humidity, $\text{kg}\cdot\text{m}^{-3}$ [15].

Air density is calculated by the equation (5):

$$\rho_a = \frac{p}{R_a \cdot T}, \quad (5)$$

where R_a – specific gas constant of dry air, $287.058 \text{ J}\cdot(\text{kg}\cdot\text{K})^{-1}$;
 p – air pressure, Pa;
 ρ_a – air density, $\text{kg}\cdot\text{m}^{-3}$ [15].

Absolute gravimetric air humidity can be found by the equation (6):

$$H_a = \frac{H \cdot 1000}{\rho_g}, \quad (6)$$

where H_a – absolute air humidity, $\text{g} \cdot \text{kg}^{-1}$ [16].

Results of CO and CO₂ concentration sometimes are presented as dry emissions. Water vapor might be separated from the sample before the analysis by the NDIR analyzer. If the results are obtained using the FTIR analyzer, sometimes they are converted from wet to dry basis by the calculation routine of the analyzer.

Further calculation is based on the Regulation No 49 of UN/ECE [16]. Emissions on dry basis can be converted to emissions on wet basis by the equation (7):

$$c_w = k_w \cdot c_d, \quad (7)$$

where c_w – concentration in wet sample, ppm;
 c_d – concentration in dry sample, ppm;
 k_w – coefficient of dry/wet conversion [16].

Coefficient of dry/wet conversion can be calculated by the equation (8):

$$k_w = \left(\frac{1}{1 + \alpha \cdot 0.005 \cdot (c_{CO_2} + c_{CO})} - k_{w1} \right) \cdot 1.008, \quad (8)$$

where α – fuel molar (H/C) ratio, $\text{mol} \cdot \text{mol}^{-1}$;
 k_{w1} – coefficient for air humidity [16].

In case, when fuel molar H/C and O/C ratio is not known, it can be assumed according to the values shown in Table 1 [16].

Table 1

Assumed H/C and O/C molar ratio

Fuel	H/C ratio	O/C ratio
Gasoline (E10)	1.930	0.093
Diesel (B7)	1.860	0.006
Ethanol-gasoline blend E85	2.740	0.385
Compressed natural gas (CNG)	4.000	0.000
Liquified petroleum gas (LPG)	2.525	0.000

Coefficient of air humidity can be found using the equation (9):

$$k_{w1} = \frac{1.608 \cdot H_a}{1000 + (1.608 \cdot H_a)}, \quad (9)$$

where H_a – absolute air humidity, $\text{g} \cdot \text{kg}^{-1}$ [16].

Concentration of NO_x on wet basis can be calculated using the equation (10):

$$c_{NO_x,w} = k_w \cdot k_{h,d} \cdot c_{NO_x,d}, \quad (10)$$

where $c_{NO_x,w}$ – NO_x concentration on wet basis, ppm;
 $c_{NO_x,d}$ – NO_x, concentration on dry basis, ppm;
 k_w – coefficient of dry/wet conversion;
 $k_{h,d}$ – humidity correction coefficient for NO_x [16].

Humidity correction coefficient for NO_x can be found by the equation (11):

$$k_{h,d} = \frac{15.698 \cdot H_a}{1000} + 0.832. \quad (11)$$

Flow of exhaust gas can be measured directly or calculated by the equation (12):

$$q_{mew} = q_{mf} \cdot \left(\frac{W_{BET}^2 \cdot 1.4}{(1.0828 \cdot W_{BET} + k_{fd} \cdot k_c) \cdot k_c} \cdot \left(1 + \frac{H_a}{1000} \right) + 1 \right), \quad (12)$$

where q_{mew} – exhaust gas flow, kg s^{-1} ;
 q_{mf} – fuel mass flow, kg s^{-1} ;
 W_{BET} – gravimetric part of carbon in fuel, %;
 k_{fd} – additional combustion volume of dry exhaust gas, $\text{m}^3 \cdot \text{kg}^{-1}$;
 k_c – specific factor of carbon [16].

Carbon content in fuel by mass can be found by the equation (13):

$$W_{BET} = \frac{M_C}{\alpha M_H + \varepsilon M_O + M_C} \cdot 100, \quad (13)$$

where M_C – atomic mass of carbon, u;
 M_H – atomic mass of hydrogen, u;
 M_O – atomic mass of oxygen, u;
 α – H/C molar ratio in the fuel;
 ε – O/C molar ratio in the fuel [16].

Additional combustion volume of dry exhaust gas can be calculated using the equation (14):

$$k_{fd} = -0.055594 \cdot W_{ALF} + 0.0080021 \cdot W_{DEL} + 0.0070046 \cdot W_{EPS}, \quad (14)$$

where W_{ALF} – hydrogen content in fuel by mass, %;
 W_{DEL} – nitrogen content in fuel by mass, %;
 W_{EPS} – oxygen content in fuel by mass, % [16].

W_{ALF} , W_{DEL} and W_{EPS} can be found in similar way as W_{BET} , by modifying equation (13).
 Specific factor of carbon can be calculated by the equation (15):

$$k_c = (c_{CO_2,d} - c_{CO_2,d,a}) \cdot 0.5441 + \frac{c_{CO,d}}{18522} + \frac{c_{HC,w}}{17355}, \quad (15)$$

where $c_{CO_2,d}$ – concentration of CO_2 on dry basis, %;
 $c_{CO_2,d,a}$ – concentration of CO_2 in the ambient air on dry basis, %;
 $c_{CO,d}$ – concentration of CO on dry basis, ppm;
 $c_{HC,w}$ – concentration of HC on wet basis, ppm [16].

Instantaneous molar mass of exhaust gas can be calculated by equation (15):

$$M_{e,i} = \frac{M_{CO_2}}{u_{gas,CO_2}}, \quad (15)$$

where M_{CO_2} – molar mass of CO_2 , $44.01 \text{ g} \cdot \text{mol}^{-1}$;
 u_{gas,CO_2} – molar mass ratio of exhaust gas and CO_2 [16].

Assumed molar mass ratios of exhaust gas and some of its components, $u_{gas,i}$, are shown in Table 2 [16].

Molar mass ratio for other components of exhaust gas, such as aldehydes or ammonia can be calculated, using the equation (16):

$$u_{gas,i} = \frac{M_{gas}}{M_{e,i}}, \quad (16)$$

where M_{gas} – molar mass of component, $\text{g} \cdot \text{mol}^{-1}$;
 $M_{e,i}$ – instantaneous molar mass of exhaust gas, $\text{g} \cdot \text{mol}^{-1}$ [16].

Mass flow of components of exhaust gas can be calculated by the equation (17):

$$q_{gas,i} = u_{gas,i} \cdot c_{gas,w} \cdot q_{mew} \cdot 10^{-3}, \quad (17)$$

where $q_{gas,i}$ – mass flow of component of exhaust gas, $g \cdot s^{-1}$;
 $c_{gas,w}$ – concentration of exhaust gas component on wet basis, ppm [16].

Table 2

Molar mass ratio of exhaust gas and its components

Fuel	Exhaust gas component					
	NO _x	CO	HC	CO ₂	O ₂	CH ₄
Gasoline (E10)	1.587	0.966	0.499	1.518	1.104	0.553
Diesel (B7)	1.586	0.966	0.482	1.517	1.103	0.553
Ethanol-gasoline blend E85	1.604	0.977	0.730	1.534	1.116	0.559
Compressed natural gas (CNG)	1.621	0.987	0.528	1.551	1.128	0.565
Liquified petroleum gas (LPG)	1.602	0.976	0.510	1.533	1.115	0.559
Propane	1.603	0.976	0.512	1.533	1.115	0.559
Butane	1.600	0.974	0.505	1.530	1.113	0.558

Power specific emissions of the components of exhaust gas can be calculated, using the equation (18):

$$m_{gas,i} = \frac{q_{gas,i} \cdot 3600}{P}, \quad (18)$$

where $m_{gas,i}$ – power specific emission, $g \cdot kWh^{-1}$;
 P – engine power, kW [16].

Distance specific emissions of the components of exhaust gas can be calculated, using the equation (19):

$$m_{gas,d} = \frac{q_{gas,i} \cdot 3600}{v}, \quad (19)$$

where $m_{gas,d}$ – distance specific emission, $g \cdot km^{-1}$;
 v – driving speed, $km \cdot h^{-1}$ [1].

In case of driving cycle, calculation of the specific emissions shall be divided in separate timing windows, based on the driving speed. For each timing window, data of the fuel flow, concentration of exhaust gas components and driving speed must be synchronised.

Results and discussion

Methodology that is presented in this paper is based on regulations and recommendations of the European Commission. It allows calculation of power or distance specific emissions, by using a relatively small number of experimentally obtained data:

- parameters of ambient air – pressure, temperature, humidity and concentration of CO₂;
- fuel type;
- fuel mass flow;
- engine power or driving speed;
- volumetric concentration of exhaust gas components on dry or wet basis.

Uncertainty of the results can be reduced, if the test fuel molar H/C and O/C ratio is known and the exhaust gas flow is directly measured. Regulation 49 of the ECE, which is the main source of the information for this methodology, contains 390 pages that makes it difficult to use. It contains typographic mistakes, such as mixed use of comma and point in decimal numbers throughout the text. Equation (15) in the regulation contains errors, 18.522 and 17.355 instead of 18522 and 17355:

$$k_c = (c_{CO_2,d} - c_{CO_2,d,a}) \cdot 0.5441 + \frac{c_{CO_2,d}}{18.522} + \frac{c_{HC,w}}{17.355}, \quad (20)$$

The authors also corrected values in Table 2 by multiplying them by 1000 and correcting equations (15-17).

The methodology was tested and validated using volumetric and mass specific exhaust gas data from another research [7]. Experimental validation was performed using different vehicles and fuels. Results of the validation will be included in the future publications.

Conclusions

1. Methodology for calculation of specific emissions, presented in this paper, requires measurement of ambient air pressure, temperature and humidity, fuel mass flow, engine power or driving speed and exhaust gas volumetric composition (at least CO₂, CO and HC).
2. Any component of exhaust gas measured by analyser in parts per million by volume (ppm) or percent by volume units can be calculated as specific mass in g km⁻¹ and g kWh⁻¹ units using the provided methodology.

References

- [1] Commission Regulation (EU) 2016/427. Official Journal of the European Union, vol. 82, no. 1, 2016, pp. 1-98.
- [2] Solomon S., Qin D., Manning M., Marquis M., Averyt K., Tignor M., Miller H. L., and Chen Z. Climate Change 2007 – The Physical Science Basis. New York: Cambridge University Press, 2007, 996 p.
- [3] Regulation (EC) No 443/2009 of the European Parliament and of the Council. Official Journal of the European Union, vol. 140, no. 1, 2009, pp. 1-15.
- [4] Regulation No 83 of the Economic Commission for Europe of the United Nations (UN/ECE). Official Journal of the European Union, vol. 375, no. 223, 2012, pp. 1-273.
- [5] Cheng W. K., Summers T., and Collings N. The fast-response flame ionization detector. Progress in Energy and Combustion Science, vol. 24, no. 2, 1998, pp. 89-124.
- [6] Wallner T., Frazee R. Study of Regulated and Non-Regulated Emissions from Combustion of Gasoline, Alcohol Fuels and their Blends in a DI-SI Engine. Proceedings of International Powertrains, Fuels & Lubricants Meeting, 2010, Rio de Janeiro, Brazil, 26 p.
- [7] Emissions Challenge SESAM-FTIR Emissions Data Summary. AVL, Graz, 2009, p. 30.
- [8] Heywood J. B. Internal Combustion Engine Fundamentals. New York: McGrawHill, 1988, 930 p.
- [9] Stone R. Introduction to Internal Combustion Engines. Third edition. New York: Palgrave Macmillian, 1999, 641 p.
- [10] Vojtisek-Lom M., Cobb, T. J. Jr. Vehicle mass emissions measurement using a portable 5-gas exhaust analyzer and engine computer data. Proceedings of Emission Inventory: Planning for the Future Conference Air & Waste Management Association, 1997, Pittsburgh, USA, pp. 656–669.
- [11] d'Ambrosio, S., Spessa, E., Vassallo, A. Methods for Specific Emission Evaluation in Spark Ignition Engines Based on Calculation Procedures of Air-Fuel Ratio: Development, Assessment, and Critical Comparison. Journal of Engineering for Gas Turbines and Power, vol. 127, no. 4, 2005, p. 14.
- [12] d'Ambrosio, S., Finesso, R., Spessa, E. A General Procedure to Calculate Air-Fuel Ratio, Mass Emissions and EGR Mass Fraction from Dyno Data in Diesel and SI Engines. The Proceedings of the International symposium on diagnostics and modeling of combustion in internal combustion engines, 2008, Tokyo, Japan, vol. 2008.7, pp. 613–623.
- [13] d'Ambrosio, S., Finesso, R., Spessa, E. Calculation of Mass Emissions, Oxygen Mass Fraction and Thermal Capacity of the Inducted Charge in SI and Diesel Engines from Exhaust and Intake Gas Analysis. Fuel, vol. 90, no. 1, 2011, pp. 152–166.
- [14] Stivender, D. L. Development of a Fuel-Based Mass Emission Measurement Procedure. SAE International Mid-Year Meeting, 1971, p. 19.
- [15] Parish O., Putnam T. Equations for the Determination of Humidity from Dewpoint and Psychrometric Data. Washington: NASA, 1977, 25 p.
- [16] Regulation No 49 of the Economic Commission for Europe of the United Nations. Official Journal of the European Union, vol. 171, no. 1, 2013, pp. 1-390.