Polycyclic aromatic hydrocarbon emissions in diesel exhaust using gas chromatography–mass spectrometry with programmed temperature vaporization and large volume injection

Carolina Vieira de Souza, Sergio Machado Corrêa[*]

Rio de Janeiro State University, Faculty of Technology, 27537-000, Resende, RJ, Brazil

HIGHLIGHTS

- A GC–MS with PTV–LVI was optimized for the analysis of PAHs.
- Several injection parameters are presented that reduce the limit of quantification.
- Real samples from diesel with biodiesel were evaluated.
- Gas phase and stratified particulate matter were evaluated.
- PAHs were found in higher levels in the accumulation mode.

ARTICLE INFO

ABSTRACT

Diesel engines are significant sources of Polycyclic Aromatic Compounds (PAHs) in urban atmospheres. These compounds are widely known for their carcinogenic potential and mutagenic properties. In this study, a method was developed for the analysis of 16 priorities PAHs using gas chromatography–mass spectrometry (GC–MS) with programmable temperature vaporizer large volume injection (PTV–LVI), which allowed to be obtained detection limits below 2.0 ng mL^{-1}. This method was evaluated in samples from stratified particulate matter and gas phase from the emissions of diesel vehicle employing diesel commercial S10 (sulfur 10 mg L^{-1}) and B5 (biodiesel 5% v/v). A sampling system that does not employ exhaust products dilution was used to evaluate the PAHs gas-particle partition. Six PAHs were identified in extracts and gas-phase PAHs took percentage of 80% in the total PAHs emissions. The sampling system without dilution not caused a strong nucleation/condensation of the most volatile PAHs. PAHs size-particle distribution was found in higher levels in the accumulation mode.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are widely known for their carcinogenic potential and mutagenic properties (Finlayson-Pitts and Pitts, 2000; Guarieiro et al., 2014; Eiguren-Fernandez et al., 2004; Corrêa and Arbilla, 2006). Because of theses effects, the United States Environmental Protection Agency (U.S.EPA) listed 16 PAHs as priorities pollutants. Table 1 shows the number of aromatic rings and molecular mass of 16 priorities PAHs.

Diesel engines are significant sources of PAHs in urban atmospheres (Marr et al., 1999; Borrás et al., 2009; Finlayson-Pitts and Pitts, 2000; Guarieiro et al., 2014). PAHs emitted by diesel vehicles are originated from pyro-synthesis of aromatic compounds, un-burned fuel and lubricant oil (Borrás et al., 2009). Lower molecular weight PAHs in an unburned diesel fuel have shown to be the primary contributor to the exhaust emissions of a direct injection diesel engine (Marr et al., 1999), and high molecular weight such BBF and BAP are formed during the combustion processes (Turrio-Baldassarri et al., 2003). Although PAHs are toxic to humans, there is not any Brazilian law regarding PAHs emission for vehicles. PAHs may remain in the gas phase, absorbed and/or adsorbed at particles surfaces, or form new particles by nucleation (Secondary Organic Aerosol − SOA) (Burtscher, 2005). PAHs gas-particle partitioning depends on its sub-cooled liquid vapor pressure (Eiguren-Fernandez et al., 2004) and how samples are taken (location of sampling, temperature, dilution etc.) (Burtscher, 2005). According

* Corresponding author.
E-mail address: sergiomc@uerj.br (S.M. Corrêa).

Table 1
Number of aromatic rings and molecular mass of 16 priorities PAHs.

Compound	Number of rings	Molecular mass	Compound	Number of ring	Molecular mass
Naphthalene NAP	2	128	Benzo[a] anthracene BAA	4	228
Acenaphthylene ACY	2	152	Chrysene CRY	4	228
Acenaphthene ACE	2	154	Benzo[b] fluoranthene BBF	4	252
Fluorene FLU	2	166	Benzo[k] fluorantene BKF	4	252
phenanthrene PHE	3	178	Benzo[a]pyrene BAP	5	252
Anthracene ANT	3	178	Dibenzo[a,h] anthracene DBA	5	278
Fluoranthene FLT	3	202	Benzo[g,h,i] perylene BGP	5	276
Pyrene PYR	4	202	Indeno[1,2,3-cd] pyrene IND	5	276

to Burtscher (2005), the dilution system serves to (a) reduce the concentration in the raw exhaust to a concentration which can be handled by the measurement system, (b) reduce the temperature to an adequate value, usually close to ambient temperature, and (c) control the condensation and nucleation processes. Cooling the exhaust with no or moderate dilution will cause a strong nucleation/condensation. Most volatile material will then be found in the particle phase (Burtscher, 2005). Diesel particles are a complex mixture of elemental carbon (EC), a variety of hydrocarbons (HC), sulfur compounds and other species. Particles differ in size, composition, solubility and therefore also in their toxic properties (Burtscher, 2005).

Usually the toxicity of PAHs increases with its molecular mass. The high molecular masses PAHs are absorbed in particulate matter, so the toxicity of gas-phase PAHs is lower than that of particle-phase PAHs (He et al., 2010). A lot of researches have been reported on the particle-phase PAHs emissions of diesel engines or vehicles do not give much attention to gas-phase PAHs emissions (Borrás et al., 2009; Casal et al., 2014; Guarieiro et al., 2014; Marr et al., 1999). Homogeneous gas-phase reactions of volatile 2 and 3-rings and semi-volatile 4-ring PAHs are important secondary source of quinones (Wang et al., 2007; Eiguren-Fernandez et al., 2007) and Nitro-PAHs (Finlayson-Pitts and Pitts, 2000; Bamford and Baker, 2003). Quinones and nitro-PAHs are known to have toxic, carcinogenic, mutagenic and estrogenic properties, which are frequently more pronounced than those of their corresponding parent-PAHs (Bamford and Baker, 2003; Eiguren-Fernandez et al., 2007). Quinones (Eiguren-Fernandez et al., 2007) and nitro-PAHs (Bamford and Baker, 2003) can cause the overproduction of reactive oxygen species resulting in oxidative stress, which is a casual factor in the pathology of many diseases.

The PAHs concentration in the combustion products emitted by diesel vehicles depend on many factors, including the load applied to the engine during the test, the fuel characteristics, the use of emission-control systems, and the vehicle model and year (Abrantes et al., 2004; Guarieiro et al., 2014; Martins et al., 2012; Casal et al., 2014; He et al., 2010; Marr et al., 1999; Borrás et al., 2009). According He et al. (2010), high engine speed increase PAHs concentrations because the short time duration in cylinder at high speed resulting in incomplete combustion. The diesel fuel quality is constantly changed to improve the engine performance and reduce pollutants emission. Recently most Brazilian cities began to commercialize diesel fuel with lower sulfur (S10 – 10 mg L^{-1}). The sulfur in the fuel can work as a nucleation site and/or adsorption site PAHs (Burtscher, 2005). Since 2009, Brazilian

commercial diesel fuel has contained 5% v/v biodiesel (NEPC, 2009), and at the end of 2014, the biodiesel content was increased to 7%. Several studies showed a reduction in PAHs emissions by diesel engines with the addition of biodiesel up to 20% by volume (Tsai et al., 2010; He et al., 2010; Guarieiro et al., 2014; Martins et al., 2012; Corrêa and Arbilla, 2006). This reduction is explained by the absence of PAHs contents in biodiesel and the improved combustion rendered by oxygen content in biodiesel. It is important to understand how pollutant emissions like PAHs are influenced by fuel characteristics.

Due to low PAHs concentrations in the combustion products, analyzing PAHs in diesel emissions requires analytical methods to concentrate the sample and instruments with low detection limits. PAHs sampling in the gas phase is usually performed using polystyrene divinylbenzene resin (PS-DVB) cartridges in the form of Amberlite XAD-2 (Corrêa and Arbilla, 2006; Abrantes et al., 2004; He et al., 2010; Lim et al., 2005) or Amberlite XAD-16 (Tsai et al., 2010). Due to their hydrophobic characteristics, these resins may interact with the analytes, mostly through van der Waals interactions or through aromatic ring π−π interactions present in the resin structure. Sampling of PAHs associated with particulate matter is usually performed using fiberglass or Teflon (PTFE) filters with porosity between 0.45 μm and 1.0 μm (ARB, 2006; Corrêa and Arbilla, 2006; Abrantes et al., 2004; Tsai et al., 2010; He et al., 2010; Lim et al., 2005; Casal et al., 2014; Borrás et al., 2009).

PAHs extractions from the cartridge and filter samples are usually performed using Soxhlet extraction or ultrasonic baths with dichloromethane or acetonitrile (Corrêa and Arbilla, 2006; Yusa et al., 2006; Casal et al., 2014; Guarieiro et al., 2014; Martins et al., 2012; Abrantes et al., 2004).

The most-used instrumental methods in the analysis of PAHs are high-performance liquid chromatography with fluorescence detection (HPLC−FLU) and gas chromatography coupled with mass spectrometry (GC−MS) (Goméz-Ruiz et al., 2009; Crimmins and Baker, 2006; Yusa et al., 2006; Ramos et al., 2000; Pavón et al., 2008; Hoh and Mastovska, 2008; Tsai et al., 2010; ARB, 2006; Corrêa and Arbilla, 2006; Dobbins et al., 2006; Wilson and De Andrade, 1996; Abrantes et al., 2004). HPLC−FLU has greater sensitivity than GC−MS. However, GC−MS using single ion monitoring (SIM) provides structural information of compounds, thus reducing matrix effects (Casal et al., 2014). Some studies have used programmable temperature vaporizer large volume injection (PTV−LVI) associated with GC−MS for analyzing PAHs in environmental samples (Yusa et al., 2006; Gómez-Ruiz et al., 2009; Casal et al., 2014; ARB, 2006) to increase the analytical sensitivity and thus obtain lower detection limits. This technique allows injecting volume from 30 to 100 μL (Yusa et al., 2006). PTV−LVI has many experimental variables that need to be optimized before its use in analytical procedures.

The objective of this work is to propose a methodology to identify and quantify the 16 priority PAHs in stratified particulate matter and gas phase samples from diesel engine exhaust using GC−MS with programmable temperature vaporizer and large volume injection (PTV−LVI). After, this method was evaluated in samples from stratified particulate matter and gas phase from diesel vehicle exhaust used in Brazilian cities employing diesel commercial S10 (sulfur 10 mg L^{-1}) and B5 (biodiesel 5% v/v). A simple sampling system that does not employ exhaust products dilution was used to evaluate the PAHs gas-particle emission. There are no studies that used this sampling system to evaluate PAHs emissions.