Validation of Analytical Methodology for Determining Polycyclic Aromatic Hydrocarbons (PAHs) in Fine Particulate Matter Emitted by Diesel Engines

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Studies on determining toxic pollutants in particulate matter emitted by diesel engines are crucial for developing strategies to mitigate atmospheric pollution. However, the low levels of analytes and the complexity of the matrix pose significant challenges from an analytical chemistry perspective. This work aimed to evaluate the analytical parameters of a procedure for determining polycyclic aromatic hydrocarbons (PAHs) in delicate particulate matter emitted by diesel engines. The validation parameters indicated good linearity, with coefficients of determination (R^2) ranging from 0.9959 to 0.9995. The limits of detection and quantification were between 0.24 to 0.60 ng/mL and 0.78 to 2.0 ng/mL, respectively. Recoveries ranged from 66.1% to 121%, with relative standard deviations (RSD%) of less than 20%. Applying this method to determine PAHs in PM1.0 and PM2.5 samples revealed high levels of these compounds in S10 diesel samples.

Keywords: Atmospheric Pollution. Chromatography. Mass Spectrometry.

The growing concern about emissions of toxic compounds into the atmosphere, such as polycyclic aromatic hydrocarbons (PAHs), has generated renewed interest in researching more sustainable alternatives, such as biofuels. PAHs are products of incomplete combustion of organic matter, with fossil fuels being the primary sources of these emissions [1-3]. However, the low concentrations of these compounds in the samples (a few µg/g) combined with the high complexity of the particulate matter matrix present challenging conditions for most existing analytical methods [4].

Using gas chromatography coupled with mass spectrometry (GC-MS) offers a robust analytical approach for identifying and quantifying these compounds, allowing an assessment of the potential environmental impacts associated with using various fuels. Efficient sample preparation methods are often necessary to achieve adequate quantification limits for these determinations. This study aimed to evaluate the main analytical parameters for the validation stage of an analytical procedure for determining PAHs in particulate matter (PM) samples emitted by diesel engines.

Materials and Methods

We employed the analytical parameters reported by Santos and colleagues (2016) [4] and Paim and colleagues (2023) [3] to determine PAHs. The separation and identification of the compounds were performed using a gas chromatograph coupled with a mass spectrometer, model QP2010 SE (Shimadzu, Kyoto, Japan), equipped with a DB-5MS capillary column (30 m x 0.25 mm ID x 0.25 µm film thickness). Data acquisition was conducted in SIM (single ion monitoring) mode. To validate the method, the following analytical parameters were evaluated: selectivity, linear range and linearity, limit of detection (LD), limit of quantification (LQ), precision, and accuracy, using urban dust reference material (NIST Urban Dust 1649b).

Results and Discussion

Validation of the Analytical Method

Table 1. presents the analytical parameters evaluated in the method validation. The coefficients of determination (R^2) ranged from 0.9959 for acenaphthylene-d10 to 0.9995 for naphthalene, indicating excellent linearity.

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The detection and quantification limits ranged from 0.24 to 0.60 ng mL^{-1} and 0.78 to 2.0 ng mL^{-1}, respectively, demonstrating suitability for quantifying these compounds in the analyzed samples. The method's accuracy was assessed by analyzing urban dust's certified reference material (SRM) (Urban Dust 1649a, NIST). The recoveries obtained from the SRM analysis ranged from 66.1% for phenanthrene to 121% for naphthalene, with relative standard deviation (RSD%, n=3) values below 20%, within the recommended range for trace-level analysis [4,5].

After establishing the analytical parameters, the validated procedure was applied to determine PAHs in samples of $PM_{1.0}$ (aerodynamic diameter of up to 1.0 µm) and $PM_{2.5}$ (aerodynamic diameter of up to 2.5 µm) collected during studies with emissions from diesel engines mounted on a bench dynamometer, using different mixtures of biofuels with S10 diesel.

Figure 1 shows the chromatogram (GC-MS/SIM) obtained from the injection of an extract of a $PM_{2.5}$ sample from the combustion of S10 diesel.

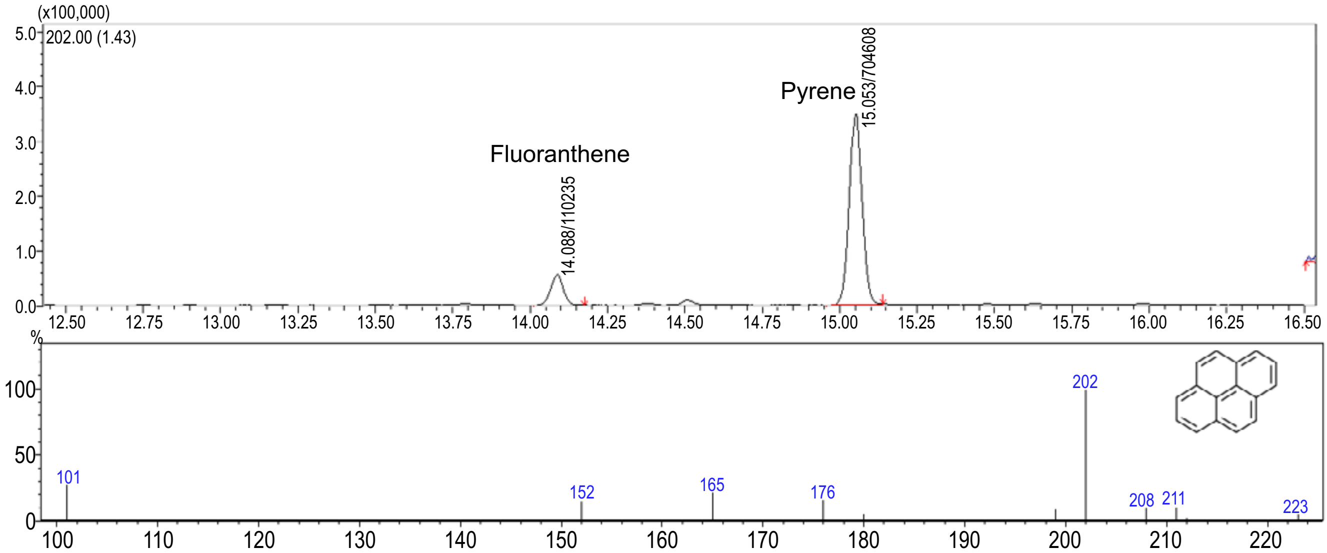
The concentrations of PAHs quantified in the samples were reported as the sum of low molecular weight PAHs (LMWPAH) and high molecular weight PAHs (HMWPAH). The final concentration was expressed as the mass of the analyte per mass of PM (µg g^{-1}). In general, the total concentrations of HMWPAH in the analyzed samples were higher than the concentrations of LMWPAH. This was expected, as HMWPAH are predominantly emitted by pyrogenic sources, which involve the combustion of organic matter.

Table 1. Analytical parameters of the method used in the analyses.

PAHs	Linear Range (ng mL^{-1})	R²	LD (ng mL^{-1})	LQ (ng mL^{-1})	Recovery (mean±RSD) SRM Nist 1649b
Naphthalene	0.78-40	0.9995	0.24	0.78	121±3
Acenaphthylene	1.18-400	0.9991	0.36	1.18	112±1
Acenaphthylene-d10*	0.5-400	0.9959	-	-	-
Acenaphthene	1.19-40	0.9991	0.36	1.19	86.1±7.2
Fluorene	2.00-60	0.9988	0.60	2.0	96.1±5.4
Phenanthrene	1.77-60	0.9988	0.53	1.77	66.1±10.9
Phenanthrene-d10*	0.5-400	0.9981	-	-	-
Anthracene	1.09-40	0.9990	0.33	1.09	99.7±12.4
Fluoranthene	1.09-40	0.9990	0.33	1.09	91.0±12.3
Pyrene	1.89-60	0.9986	0.57	1.89	91.4±11.7
Benzo[a]anthracene	1.24-40	0.9987	0.37	1.24	87.3±13.6
Chrysene	1.28-40	0.9986	0.38	1.28	99.6±6.4
Benzo[b]fluorene	1.32-40	0.9985	0.4	1.32	116.4±15
Benzo[a]pyrene	1.22-40	0.9988	0.37	1.22	80.7±13.6
Benzo[e]pyrene	1.22-40	0.9988	0.37	1.22	75.1±6.8
Perylene	1.30-40	0.9986	0.39	1.3	81.0±13.1
Indeno[1,2,3-*cd*]pyrene	0.82-40	0.9990	0.25	0.82	94.0 ± 14.9
Dibenzo[*a,h*]anthracene	1.14-40	0.9990	0.34	1.14	84.9±7.8
Benzo[*ghi*]perylene	1.43-40	0.9987	0.43	1.43	80.5±9.0
Coronene	1.07-400	0.9991	0.32	1.07	96.7±13.7

LD: limit of detection; LQ: limit of quantification; R²: coefficient of determination. *Internal standard.

Figure 1. GC-MS/SIM chromatogram obtained from the analysis of a PM2.5 sample from the combustion of S10 diesel.



The PAHs with high molar mass fluoranthene and pyrene (M+ m/z 202) were the compounds with the highest concentrations. The mass spectrum of pyrene obtained in SIM mode is also shown.

Despite all fuel mixtures undergoing combustion in the engine (dynamometer) under controlled conditions, higher concentrations of both LMWPAH and HMWPAH were observed in the $PM_{2.5}$ samples obtained from the combustion of pure S10 diesel and a mixture of S10 diesel with second-generation ethanol. In contrast, LMWPAH concentrations were lower than those observed for HMWPAH. Unlike HMWPAH, LMWPAH is characteristic of petrogenic sources, such as petroleum and by-products from fuel refining [1,2].

Conclusion

The results obtained from the validation of the analytical procedure were satisfactory, demonstrating good linearity, precision, accuracy, and low LD and LQ values. The analysis of PM2.5 and PM1.0 samples from the combustion of different diesel mixtures with biodiesel indicated that the highest concentrations of PAHs were observed in the S10 diesel sample, particularly PAHs with high molar mass. Conversely, the concentrations of these PAHs were reduced in mixtures of diesel with first-generation ethanol.

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