Study of Measurement Systems for Determination of Polycyclic Aromatic Hydrocarbons in Vehicle Environmental Samples

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Polycyclic aromatic hydrocarbons (PAHs) are organic compounds with two or more aromatic rings. Their emission sources are anthropogenic, such as burning fossil fuels in vehicles. Due to their properties, these compounds are toxic in nature and have potential carcinogens, requiring attention to their detection in the environment. Several studies have already been conducted for construction-detection systems, nevertheless, the methods are expensive and complex. The objective of this work was to identify these measurement possibilities already used to propose a new, simpler, and cheaper system for determining PAHs. So, we carried out a literature review survey to build the necessary theoretical foundation for the proposed system development.
Keywords: Polycyclic Aromatic Hydrocarbons. Permanent Organic Pollutants. Measurement System. Vehicle Pollution.

Introduction

The exponential growth of the automotive industry in recent decades has increased concerns related to the impact of this large number of vehicles on urban air pollution. The emission of pollutants by vehicles is mainly caused by the burning of fossil fuels such as diesel or gasoline, and among the main pollutants emitted are polycyclic aromatic hydrocarbons (PAHs) [1]. These are organic compounds characterized by two or more condensed aromatics rings in their chain, and they come from the incomplete burning of organic matter [2]. Research studies indicate a strong correlation between the levels of PAH in the air and urban vehicle traffic [1,3,4] among these vehicles, those powered by diesel presented themselves as the source of PAHs [4].

As for the physicochemical nature of PAHs, they are chemically stable compounds, and many of them can be transported over long distances, being able to adhere to particulate material. In addition, when excited in the ultraviolet and visible spectrum, they present the phenomenon of fluorescence, which can be used for their detection [5]. Human exposure to these pollutants occurs through ingestion, inhalation, and through the skin, and during their metabolic process in the human and animal body, they interact with DNA, which could result in a tumor [6].

Due to their properties and interaction with the human body, they have been categorized by the US Environmental Protection Agency as priority pollutants and classified by the International Agency for Research on Cancer (IARC) as potentially carcinogenic compounds to humans and animals [2,6]. Because of the toxic nature of PAHs, several methods of detection of these compounds in samples have been studied over the years, however, the most commonly used methods apply expensive and time-consuming techniques, such as High-Performance Liquid Chromatography (HPLC), Gas Chromatography with Flame Ionizer Detector (GC - DIC) and fluorescence spectrophotometry [2].Therefore, this article aims to study the existing measurement systems and alternatives that could be used in an alternative simple, practical, and fast PAH detection system for vehicle samples.

Materials and Methods

A literature review survey was carried out in scientific databases such as Google Scholar,

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Science Direct, SciELO, and Research Gate, to select articles on the main polycyclic aromatic hydrocarbons, their characteristics, and their main physicochemical properties followed by a literature survey of methods for detection and identification of existing PAHs. And finally, at the beginning of the construction and characterization stage of the measurement system, we did a theoretical foundation for the construction of the proposed new measurement system.

Results and Discussion

Classification of PAHs

Growing emission of these toxic pollutants, the International Association for Research on Cancer (IARC) carried out experimental procedures and classified 19 main PAHs according to their carcinogenic potential, dividing them into groups (Table 1). Group 1 is a human carcinogen substance; group 2A: probably carcinogenic substance; group 2B: possibly carcinogenic substance; group 3: non-carcinogenic substance and group 4: probably non-carcinogenic [7].

PAHs in-Vehicle Samples

In 2020, in Brazil, it is estimated that there were approximately 107 million vehicles spread across the national territory according to the National Department of Transit (Departamento Nacional de Trânsito – DENATRAN) [8]. Additionally, according to the National Association of Vehicle Manufacturers (Associação Nacional dos Fabricantes de

Table 1. Classification of some PAHs according to the groups established by the IARC [2].

HPA	Classification
Anthracene	Group 3
Benzo [a] anthracene	Group 2B
Benzo [b] fluoranthene	Group 2B
Benzo [j] fluoranthene	Group 2B
Benzo [k] fluoranthene	Group 2B
Benzo [g, h, i] fluoranthene	Group 3
Benzo [c] fenanthrene	Group 2B
Benzo [a] pyrene	Group 1
Benzo [e] pyrene	Group 3
Chrysene	Group 2B
Coronene	Group 3
Dibenzo [a,c] anthracene	Group 3
Dibenzo [a,h] anthracene	Group 2
Dibenzo [a,j] anthracene	Group 3
Fluoranthene	Group 3
Fluorene	Group 3
Indeno [1,2,3-cd] pyrene	Group 2B
Naphthalene	Group 3
Pyrene	Group 3

Veículos Automotores-ANFAVEA) [9], more than 2 million vehicles were produced in the country in 2019. All of these vehicles, before being launched on the market, undergo a rigorous process of analysis and inspection regarding their emissions to control and minimize their environmental impact. Although the vehicle emission control is targeted at regulated pollutants, the study, and control of non-regulated pollutant emissions, such as PAHs, is also relevant, due to their toxic and harmful nature to human beings. In a survey on air pollutants carried out in Portugal, the emissions of 16 HPAs classified by the United States Environment Protection Agency (USEPA) as priority pollutants were analyzed for 40 days in a row. This research concluded that in the urban area, the main source of PAHs was emissions from diesel-powered vehicles [4].

Other studies and surveys showed that in vehicular samples, it was mainly observed the presence of pyrene, naphthalene, phenanthrene, fluoranthene, and chrysene (Figure 1), with concentrations ranging from 1.133 to 5.801 mg km-1 [1,10].

<u>PAH Detection Methods</u>

Due to their carcinogenic potential, PAHs have long been the subject of study in the scientific community, not only regarding their properties but also regarding their detection methods. Table 2 shows the main detection methods for these compounds. All of them are well-founded methods, with proven accuracy and effectiveness. However, their complexity and cost limit the frequency of analyses. Fluorescence applied in the detection of PAHs The phenomenon of fluorescence is characterized by the emission of light by a substance when excited through energy absorption. Nowadays, the fluorescence detection methodology is widely used in the scientific community due to its high selectivity and low complexity [5]. Lakowicz (2006) describes fluorescence as follows: Fluorescence detection is highly sensitive, and there is no longer the need for the expense and difficulties of handling radioactive tracers for most biochemical measurements. There has been dramatic growth in the use of fluorescence for cellular and molecular imaging. Fluorescence imaging can reveal the localization and measurements of intracellular molecules, sometimes at the level of single-molecule detection. The PAHs have this property and as seen in Table 3, there are already studies on the wavelength needed to induce the fluorescence in each of these compounds and the wavelength emitted by them during this phenomenon [11].

Conclusion

In the present study, the main properties and emission sources of polycyclic aromatic hydrocarbons were addressed, their main detection techniques already used in the scientific community, and the theoretical foundation for the construction of an alternative measurement system was initiated. For the continuation of the research, it is necessary to acquire the materials to carry out experiments and demonstrate the technical feasibility of the proposed PAH measurement system. The acquisition process is already in progress, for further work on the study and development of this system.

Figure 1. Chemical structure of PAHs [2].

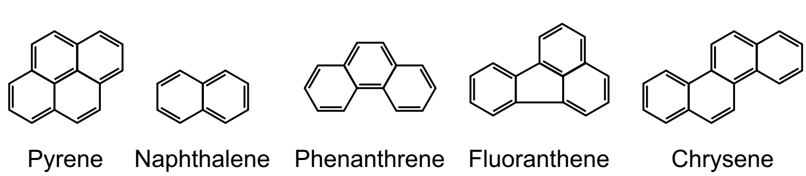

Table 2. PAH determinaton methods [2, 11-13].

Determination Method	Analysis Conditions	System Disadvantages
High Performance Liquid Chromatography (HPLC)	Most used technique for the analysis of PAHs and BaP in food	Equipment cost; complexity of the process by needing to separate the mix of PAHs.
Gas chromatography with flame ionizer detector (GC-DIC)	Allows the analysis of very complex mixtures of PAHs, widely used in oils and fats.	Equipment cost; complexity of the process by needing to separate the mix of PAHs.
Mass spectrometry	Highly sensitive and accurate analytical technique. For analysis, a preparation procedure is needed, which varies according to the sample.	In addition to the cost and complexity, as it is a highly sensitive technique, interference can significantly influence the result.
Fluorescence Spectroscopy	High sensitivity [...] without the need for any process to pre-concentrate numerous types of PAHs.	Equipment cost.
Gas chromatography with mass spectrometry (GC-MS)	Commonly used for qualitative and quantitative analysis of complex mixtures.	Equipment cost, sample preparation complexity, the analytes must be volatiles and thermally stable.

Table 3. Excitation and emission spectrum of some PAHs [11].

PAH	Excitation wavelength (energy absorption)	Maximum fluorescence emission wavelength
Pyrene	334nm	374nm
Benzo [a] pyrene	366nm	406nm
Phenanthrene	247nm	347nm
Chrysene	265nm	365nm
Benzo [a] anthracene	287nm	387nm
Dibenzo [a,h] anthracene	296nm	396nm
Benzo [k] fluoranthene	307nm	407nm
Anthracene	245nm	405nm

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