STUDY OF MEASUREMENT SYSTEMS FOR THE DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN VEHICLE ENVIRONMENTAL SAMPLES

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Abstract: Polycyclic aromatic hydrocarbons (PAHs) are organic compounds that have two or more aromatic rings and their emission sources are mostly anthropogenic, such as burning fossil fuels in vehicles. Due to their properties, these compounds are toxic in nature and are considered to be potential carcinogens, requiring attention to their detection in the environment. Several studies have already been conducted for the construction of detection systems, however, the methods are very expensive and complex. In view of this scenario, the objective of this work was to identify these measurement possibilities already used so that a new, simpler and cheaper system for determining PAHs can be proposed. In order to do so, it was carried out a bibliographic survey in order to build the necessary theoretical foundation for the proposed system development.

Keywords: Polycyclic aromatic hydrocarbons; permanent organic pollutants; measurement system; vehicle pollution.

ESTUDO DE SISTEMAS DE MEDIDAS PARA A DETERMINAÇÃO DE HIDROCARBONETOS POLICÍCLICOS AROMÁTICOS EM AMOSTRAS AMBIENTAIS VEICULARES

Resumo: Os hidrocarbonetos policíclicos aromáticos (HPAs) são compostos orgânicos que possuem dois ou mais anéis aromáticos e suas fontes de emissão são principalmente antropogênicas, como a queima de combustíveis fósseis em veículos. Devido às suas propriedades, esses compostos são tóxicos por natureza e considerados potencialmente cancerígenos, exigindo atenção para sua detecção no meio ambiente. Vários estudos já foram realizados para a construção de sistemas de detecção, porém os métodos são muito caros e complexos. Diante desse cenário, o objetivo deste trabalho foi identificar essas possibilidades de mensuração já utilizadas para que um novo, mais simples e barato sistema de determinação de HPAs possa ser proposto. Para isso, foi conduzida uma pesquisa bibliográfica a fim de construir a fundamentação teórica necessária para o desenvolvimento do sistema proposto.

Palavras-chave: Hidrocarbonetos policíclicos aromáticos; poluentes orgânicos permanentes; sistema de medida; poluição veicular.

1. 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 there are polycyclic aromatic hydrocarbons (PAHs) [1]. These are organic compounds characterized by the presence of two or more condensed aromatics rings in its chain, and they come from the incomplete burning of organic matter [2]. Research studies indicate that there is a strong correlation between the levels of PAH in the air and urban vehicle traffic.[1,3,4] And among these vehicles, those powered by diesel presented themselves as the main source of PAHs [4].

As for the physicochemical nature of PAHs, they are chemically stable compounds and many of them have the ability to 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 can result in tumoration [6].

Due to their properties and the way they interact 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]. In view 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 the development of an alternative simple, practical and fast PAH detection system for vehicle samples.

2. METHODOLOGY

A bibliographic survey was carried out in scientific databases such as Google Scholar, 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, the necessary theoretical foundation for the construction of the proposed new measurement system was made.

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3. RESULTS AND DISCUSSION

Classification of PAHs

Taking into account the 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 being 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].

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

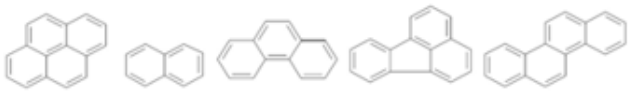
PAHs in vehicle samples

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 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 in order 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 were 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]

Figure 1. Chemical structure of PAHs Pyrene, Naphthalene, Phenanthrene, Fluoranthene and Chrysene.[2]



Pyrene Naphthalene Phenanthrene Fluoranthene Chrysene

PAH detection methods

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.

Table 2. PAH determination methods.[2,11,12,13]

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 the 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.

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].

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

4. 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 in order 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.

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