A review of techniques for the determination of polycyclic aromatic hydrocarbons in air

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We provide an extensive review of the common methodologies employed in the analysis of airborne polycyclic aromatic hydrocarbons (PAHs). The review focuses on gas-chromatography-based approaches, in the light of their universal application with excellent separation, resolution, and sensitivity.

We first describe collection methods for airborne PAHs in the gas and particle phases. We then evaluate the efficiency of extraction techniques employed for separating target PAHs from sampling media, using conventional solvent-based and emerging thermal-desorption approaches.

We also describe commonly employed analytical methods with respect to their applicability to PAHs in gas and particle phases, collected from diverse environmental settings. As an essential part of basic quality assurance, we examine each method with special emphasis on key parameters (e.g., limit of detection and reproducibility).

Finally, we address the likely directions of methodological developments, their limitations, and the future prospects for PAH analysis.

Keywords: Airborne polycyclic aromatic hydrocarbon; Analytical discrepancy; Analytical methodology; Extraction; Gas chromatography; Limit of detection (LOD); Polycyclic aromatic hydrocarbon (PAH); Reproducibility; Solvent-free; Thermal desorption

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of over 100 different chemicals that are known to be formed typically during incomplete combustion of organic matter at high temperatures [1]. Their major sources in the atmosphere include industrial processes, vehicle exhausts, waste incineration, and domestic heating emissions, while they can also be released naturally {e.g., forest fires [2]}. They are ubiquitous in the environment and contain two or more fused benzene rings in linear, angular or cluster arrangements. In addition to the frequency with which they occur in the environment, proof of their mutagenicity and carcinogenicity led to some of them being selected as priority pollutants (e.g., 16 PAHs) by the US Environmental Protection Agency (EPA) (Table 1). The World Health Organization (WHO) added 17 additional PAHs to make a total of 33 PAHs under its regulation [3]. (In Table 1, these 33 compounds are listed with their three-capital-letter acronyms). In Europe, ambient air legislation targets benzo[a]pyrene (with an annual target value of 1 ng/m^3) because this compound carries the highest toxic load (defined as concentration multiplied by toxicity) of any airborne PAH.

Because of their thermally stable structure, PAHs generally exhibit a high melting point, a high boiling point, and a low vapor pressure. In the atmosphere, they are distributed between gas and particle-bound phases [4–9]. This phase partitioning is largely regulated by changes in atmospheric conditions (e.g., temperature and relative humidity), and the physical properties of the PAHs themselves [10–13]. Consequently, lighter PAHs tend to be preferentially enriched in the gas phase, while the heavier ones show almost complete association with particles [14] – indeed, in Europe, air-quality legislation to limit PAH concentrations in air sets target values for only particulate-bound PAHs (benzo[a]pyrene in the PM_{10} particulate phase). For these reasons, it is a challenge to acquire an accurate profile of these

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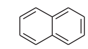
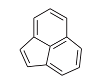
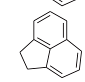
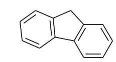
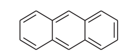
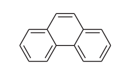
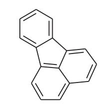
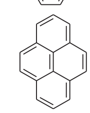
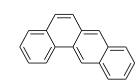
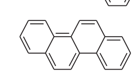
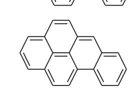
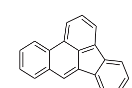
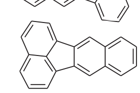
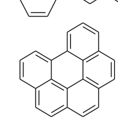
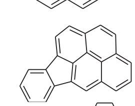
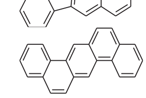
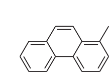
Table 1. Brief description of the 33 most common target polycyclic aromatic hydrocarbons (PAHs) (16 + 17 compounds)

Order	PAHs	Abbreviation	Chemical formula	CAS number	Number of fused benzene rings	Molar mass (g/mol)	Structure
[A] 16 priority PAHs designated by the US Environmental Protection Agency (EPA): most commonly referred in this review							
1	Naphthalene	NAP	$C_{10}H_8$	91-20-3	2	128	
2	Acenaphthylene	ACN	$C_{12}H_8$	208-96-8	3	152	
3	Acenaphthene	ACL	$C_{12}H_{10}$	83-32-9	3	154	
4	Fluorene	FLR	$C_{13}H_{10}$	86-73-7	3	166	
5	Anthracene	ANT	$C_{14}H_{10}$	120-12-7	3	178	
6	Phenanthrene	PHN	$C_{14}H_{10}$	85-01-8	3	178	
7	Fluoranthene	FLT	$C_{16}H_{10}$	206-44-0	4	202	
8	Pyrene	PYR	$C_{16}H_{10}$	129-00-0	4	202	
9	Benzo(a)anthracene	BAA	$C_{18}H_{12}$	56-55-3	4	228	
10	Chrysene	CHY	$C_{18}H_{12}$	218-01-9	4	228	
11	Benzo(a)pyrene	BAP	$C_{20}H_{12}$	50-32-8	5	252	
12	Benzo(b)fluoranthene	BBF	$C_{20}H_{12}$	205-99-2	5	252	
13	Benzo(k)fluoranthene	BKF	$C_{20}H_{12}$	207-08-9	5	252	
14	Benzo(ghi)perylene	BGP	$C_{22}H_{12}$	191-24-2	6	276	
15	Indeno[1,2,3-cd]pyrene	ICP	$C_{22}H_{12}$	193-39-5	6	276	
16	Dibenz(a,h)anthracene	DBA	$C_{22}H_{14}$	53-70-3	6	278	
[B] 17 PAHs based on their probable carcinogenic and mutagenic behavior by the World Health Organization (WHO)							
17	1-Methylphenanthrene	MPT	$C_{15}H_{12}$	832-69-9	3	192	
18	Benzo[a]fluorene	BAF	$C_{17}H_{12}$	238-84-6	4	216