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Review of progress in solvent-extraction techniques for the determination of polyaromatic hydrocarbons as airborne pollutants

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ABSTRACT

In this review, we concentrate on sample-pretreatment options with the main emphasis on all aspects of solvent extraction prior to GC-based analysis of airborne polyaromatic hydrocarbons (PAHs). To this end, we review developments in these applications covering many different approaches that have commonly been used or introduced recently.

Generally, sample pretreatment comprises

(1) solvent extraction of PAHs from filters and sorbents;
(2) extract concentration;
(3) some form of liquid, or solid, chromatography clean-up;
(4) eluent concentration; and
(5) injection into a GC for analysis.

Recent developments in these areas include: cold-fiber solid-phase microextraction of PAH extracts; the “Quick, Easy, Cheap, Effective, Rugged, and Safe” (QuEChERS) extraction technique; and, using vehicle-engine air-intake filters to collect airborne particulate matter. We also discuss some aspects of “green chromatography”, used in recent years to reduce solvent usage.

Contents

Abbreviations: ACN, Acetonitrile; aiu, Arbitrary intensity unit; ASE, Accelerated solvent extraction; BaP, Benzo[a]pyrene; BaPeq, Benzo[a]pyrene equivalent; BSTFA, Bis(trimethylsilyl)trifluoroacetamide; BTV, Breakthrough volume; CF-SPME, Cold fiber solid-phase microextraction; DCM, Dichloromethane; DDT, Dichlorodiphenyltrichloroethane; H_{act}, Arrhenius activation enthalpy for PAH desorption of a sorbent into gas-phase; DSWE, Dynamic subcritical water extraction; EC, European Commission; ECD, Electron-capture detector (for a GC); FID, Flame-ionization detector (for a GC); GC, Gas chromatograph(y); GFF, Glass-fiber filter; HAP, Hazardous air pollutant; HPLC, High-performance liquid chromatography; HRMS, High-resolution mass spectrometry; HS, Headspace; HVAS, High-volume air sampler; IARC, International Agency for Research on Cancer; IS, Internal standard; LOD, Limit of detection; LOQ, Limit of quantitation; MAE, Microwave-assisted extraction; MEF, Mutagenic equivalency factor; MDL, Method detection limit, MS, Mass spectromet(er or ry); MW, Molecular weight; NIST, National Institute of Standards and Technology; PAH, Polyaromatic hydrocarbon; PFE, Pressurized fluid extraction; PM, (airborne) Particulate matter; POP, Persistent organic pollutant; ppm, parts-per-million; PUF, Polyurethane foam; QFF, Quartz-fiber filter; QuEChERS, Quick, easy, cheap, effective, rugged, and safe; SC-CO_2, Supercritical CO_2; SFE, Supercritical fluid extraction; SPE, Solid-phase extraction; SPME, Solid-phase microextraction; SRM, Standard reference material; TEF, Toxic equivalency factor; TPM, Total particulate matter; UV(F), Ultra-violet (fluorescence); XAD-n, a type of sorbent (n = 1, 2, . . . n).

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1. Introduction

Polyaromatic hydrocarbons (PAHs) are ubiquitous byproducts of incomplete combustion or pyrolysis of carbonaceous and organic matter (e.g., tobacco, coal, charcoal, diesel, gas, and wood) [1]. PAHs are hydrocarbons with two or more fused aromatic rings and there are several hundred of these compounds.

Zhang and Tao [2] reviewed the 2004 PAH emissions inventory both globally and by country, as Gg.y^{-1} of benzo[a]pyrene (BaP) equivalent (BaPeq) (together with the major sources): Global 8.5 (biofuel 57%), China 2.81 (biofuel 56%), India 1.56 (biofuel 91%) and the USA 0.20 (waste incineration 24%). The 1999–2004 levels of atmospheric PAHs in several Asian countries have also been reviewed; in China, cooking is the major source of PAHs in indoor air [3].

PAH emissions in Europe over the past 300 years have been reconstructed by analyzing snow and ice samples collected in the high Alpine regions; from ~1700–1900, PAH emissions were low but increased dramatically after ~1900 to peak during the 1940s. They decreased considerably until ~1970s and have only moderately increased until the early 2000s [4]. Similarly, Wang et al. [5] determined the historical trends (~1965–2005) of DDT, hexachlorocyclohexanes, and PAHs in an ice core from a Mount Everest glacier, central Himalayas, China and found good correlations with Indian economic and regulatory activities.

The toxicity of PAHs is well known. Indeed, they are the key components of the 189 hazardous air pollutants (HAPs) in the U.S. Clean Air Act Amendments [6]. Their structure is complex enough to include not only compounds consisting of just carbon and hydrogen but also a wide range of nitro-(N-), oxy-(O-), and thio-(S-) related PAHs [7]. The nitro- and oxy- derivatives deserve special attention due their harmful health effects. It is suggested that these are potentially mutagenic and/or carcinogenic [8,9]. PAHs and their associated (more polar) heteroatom derivatives are present in not only ambient particles but also urban dust [10]. Furthermore, through long-range transport of polluted air masses, PAHs, particularly in the fine PM fraction, can be transported to receptor sites far from their original sources [11].

Based on laboratory tests on animals and human epidemiologic studies, a number of PAHs are known or suspected carcinogens and mutagens [12]. There is strong causal evidence (based on IARC criteria) that PAHs are lung cancer carcinogens and suspected carcinogens for bladder, laryngeal, and prostate cancers [13]. PAHs are shown to be male reproductive endocrine disruptors [14] and to induce lung cell tumorigenesis in mammals [15]. A number of PAHs have been assigned toxic equivalency factors (TEFs) for cancer [16] and mutagenic equivalency factors (MEFs) [17] relative to BaP to provide a more accurate risk assessment from environmental PAH exposure (e.g., for young children in New York City, NY, USA) [18]. The mutagenicity and the carcinogenicity of PAHs in rodents has been assessed [19]. Bostrom et al. [12] reviewed in detail the lifetime cancer risk for various PAHs; these were found to be in the range $23–430 \times 10^{-6}$ per ng.m^{-3} of BaP, thus showing wide epidemiological variability.

There have been a number of reviews in recent years concerning the sampling and the quantitation of PAHs in gaseous or particulate matter (PM) in both ambient air and from more potent sources (e.g., tobacco smoke). Davis et al. [20] reviewed many important issues involved in sampling PAHs in air [i.e., the choice of filters and sorbents [e.g., polyurethane foam (PUF), Tenax, and XAD-2], and active *versus* passive sampling]. These authors covered the period 1977–83 and described experimental artifacts, especially losses due to gaseous desorption of low-molecular-weight (MW) PAHs from PM and then prototype PAH-detection methods for near real-time spectroscopic analysis. Liu et al. [21] reviewed the developments of the analytical methods used to determine airborne PM PAHs (e.g., sampling and pretreatment methods) during 2000–05. Pandey et al. [1] extensively reviewed the techniques for the determination of PAHs in air with particular attention to collection methods, solvent-extraction efficiencies, limits of detection (LODs), and analytical reproducibility. Cecinato et al. [22] presented a short review of the sampling and analytical methods for assessing PAHs, phthalates, and psychotropic substances in the atmosphere; they summarized sample type, collection, extraction and recovery, clean-up and separation, and analytical instrumentation. Cullum et al. [23] provided an overview of high temperature (150–600°C) fluorescence and other *in situ* spectroscopic measurements of PAHs in flames and ambient air. Indeed, spectroscopic approaches for detection and quantitation of PAHs may be an important area for future research.

Over the past decades, analysts have introduced many options for post-sampling treatment prior to the analysis of airborne PAHs. Despite such developments, solvent-extraction techniques remain the most common option for PAHs in particle or gas phases.

In this article, we provide a review of the solvent-extraction techniques for the analysis of airborne PAHs. Our discussion mainly focuses on sampling and treatment of particulate PAHs, while focusing on the most important issues for the sampling of vapor-phase PAHs. This is because measurements of vapor-phase PAHs are not made commonly – unless the study targets certain industrial sources such as solvent factories [24]. In future work, we will turn our attention to other emerging pretreatment methods for PAH analysis (e.g., thermal desorption of PAHs off filters or sorbents and cryofocusing).

2. The collection of PAHs in air

The principal stages in the measurement of PAHs in ambient air generally consist of sampling, extraction, sample clean-up, and analysis. The sampling may be performed with a variety of samplers, both low- and high-volume sampling rates and even passive samplers. Sampling media include quartz-fiber [25], glass fiber [26], Teflon-coated glass fiber [27], and Teflon-membrane filters [28]. Quartz-fiber filters (QFFs) are commonly annealed at high temperatures for several hours to lower blank levels associated with the new filters. Materials used for sample handling, transport, and ambient sampling equipment must be free from organic substrates, although this is rarely a major problem. Because the PAHs are only extracted from the PM on a filter without the whole PM and filter material being digested, as is the case for inorganic analysis of elemental metals content, blank levels from extraction of unloaded filters are usually well below the LOD. It is worth pointing out the 3–5 ringed PAHs, which have relatively high vapor