Anal Bioanal Chem (2006) 386:859–881
DOI 10.1007/s00216-006-0771-0

REVIEW

Analysis of polycyclic aromatic hydrocarbons (PAHs) in environmental samples: a critical review of gas chromatographic (GC) methods

Dianne L. Poster · Michele M. Schantz · Lane C. Sander · Stephen A. Wise

Received: 18 May 2006 / Revised: 4 August 2006 / Accepted: 10 August 2006 / Published online: 21 September 2006

Abstract Polycyclic aromatic hydrocarbons (PAHs) are frequently measured in the atmosphere for air quality assessment, in biological tissues for health-effects monitoring, in sediments and mollusks for environmental monitoring, and in foodstuffs for safety reasons. In contemporary analysis of these complex matrices, gas chromatography (GC), rather than liquid chromatography (LC), is often the preferred approach for separation, identification, and quantification of PAHs, largely because GC generally affords greater selectivity, resolution, and sensitivity than LC. This article reviews modern-day GC and state-of-the-art GC techniques used for the determination of PAHs in environmental samples. Standard test methods are discussed. GC separations of PAHs on a variety of capillary columns are examined, and the properties and uses of selected mass spectrometric (MS) techniques are presented. PAH literature on GC with MS techniques, including chemical ionization, ion-trap MS, time-of-flight MS (TOF-MS), and isotope-ratio mass spectrometry (IRMS), is reviewed. Enhancements to GC, for example large-volume injection, thermal desorption, fast GC, and coupling of GC to LC, are also discussed with regard to the determination of PAHs in an effort to demonstrate the vigor and robustness GC continues to achieve in the analytical sciences.

Keywords Polycyclic aromatic hydrocarbons · Gas chromatography · Capillary columns · Mass spectrometry · Environmental samples

D. L. Poster (✉) · M. M. Schantz · L. C. Sander · S. A. Wise
Analytical Chemistry Division,
National Institute of Standards and Technology,
Gaithersburg, MD 20899-8392, USA
e-mail: poster@nist.gov

Introduction

When one thinks of the higher analogs of the simple, six-carbon benzene ring, familiar images of multiple-fused rings are often envisaged and the term "polycyclic aromatic hydrocarbons" (PAHs) comes to mind. PAHs, or polyarenes, constitute a large class of organic molecules that likely exhibits the most structural variety in nature relative to any other class of non-halogenated molecules in the eco- and biosphere. PAHs are ubiquitous environmental contaminants derived principally from combustion of fossil fuels in heat and power generation, refuse burning, coke ovens, and motor vehicle operation [1–3]. Although three PAHs—acenaphthene, acenaphthylene, and anthracene—are produced commercially in the United States in quantities greater than research level, commercial production is not regarded as a significant source of PAHs in the environment [4]. Open burning of biomass and fuel pools also emits PAHs, and PAH emissions have been noted in plumes from the combustion of polymers [5, 6]. Natural emission sources include forest fires, volcanoes, and hydrothermal processes [7–9]. Some PAHs are relatively potent carcinogens, and biological and mutagenic effects are well documented [10]. Given the right conditions, PAHs can persist in the environment and accumulate, for example in anaerobic sediments, to the extent that the potential for adverse health effects is high. As a result, characterization of PAHs in environmental compartments has been an important focus for decades. PAHs have been monitored in the marine environment since the 1960s and this continues today in local, regional, and national-scale programs [11, 12]. Major long-term monitoring programs, for example the Arctic Monitoring and Assessment Program (AMAP), the Baltic Marine Environment Protection Commission (Helsinki Commission), and the National

Status and Trends Program (US), focus on PAHs in marine biota and sediment as part of their strategies to assess marine environmental quality [12]. PAHs are also frequently measured in the atmosphere for air-quality assessment, in biological tissues for health-effects monitoring, and in foodstuffs for safety reasons.

Measurements of PAHs in environmental matrices tend to require difficult analytical chemistry procedures, largely because of the extreme complexity of environmental samples. This complexity is realized when one considers the general categories of phases into which environmental samples may be categorized; these include aqueous, air (gaseous or condensates/particulate matter), oil or organic liquids, solids or sludges, biological samples, and even multiphase samples. Multiphase samples may be a combination of these, and typically require some sort of phase separation, for example filtration, before the start of the analytical process. In addition, numerous structural isomers are often present in environmental samples, and in some matrices, for example fuel products or emissions, there may be heteroatoms (nitrogen, sulfur, oxygen) [13–16]. Hence, analytical methods must include processes for isolation of compounds that are part of complex phases, and separation and detection techniques for multi-component mixtures that consist of compounds with a wide range of polarities, volatilities, and molecular sizes and shapes. Chromatographic approaches offer avenues to address these elements and play a critical role in the determination of PAHs in environmental samples.

Chromatographic methods for PAH analyses in environmental media have been developed and evaluated extensively over the past few decades, as reviewed in the literature [11, 17–19]. Liquid and/or gas chromatography (LC and GC, respectively) are prominent techniques in US

Table 1 Selected US Environmental Protection Agency test methods for determination of PAHs[a] in environmental media

Method	Method focus	Document title	Ref.
TO-13A	Determination of PAHs in ambient air using GC/MS	Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air - Second Edition	[27]
525.2 Rev 2.0	Organic compounds by liquid–solid extraction and capillary column GC/MS[b]	Methods for the Determination of Organic Compounds in Drinking Water-Supplement III	[21]
550, 550.1	PAHs by liquid–liquid extraction and HPLC[b] with coupled UV[b] and FL[b] detection	Methods for the Determination of Organic Compounds in Drinking Water Supplement I	[20]
610	Methods for organic chemical analysis of municipal and industrial wastewater—Method 610, polynuclear aromatic hydrocarbons	Guidelines Establishing Test Procedures for the Analysis of Pollutants	[23]
625	Methods for organic chemical analysis of municipal and industrial wastewater—Method 625, base/neutrals and acids	Guidelines Establishing Test Procedures for the Analysis of Pollutants	[24]
1625	Methods for organic chemical analysis of municipal and industrial wastewater—Method 1625 Revision B, semivolatile organic compounds by isotope dilution GC/MS	Guidelines Establishing Test Procedures for the Analysis of Pollutants	[25]
8270C	Semivolatile organic compounds by GC/MS	Test Methods for Evaluating Solid Waste, Physical/Chemical Methods	[26]
8275A	Semivolatile organic compounds (PAHs and PCBs[b]) in soils/sludges and solid waste using thermal extraction–GC/MS	Test Methods for Evaluating Solid Waste, Physical/Chemical Methods	[26]
8100	Polynuclear aromatic hydrocarbons (GC)	Test Methods for Evaluating Solid Waste, Physical/Chemical Methods	[26]
8310	Polynuclear aromatic hydrocarbons (HPLC)	Test Methods for Evaluating Solid Waste, Physical/Chemical Methods	[26]
8410	GC/Fourier-transform infrared spectrometry for semivolatile organics: capillary column	Test Methods for Evaluating Solid Waste, Physical/Chemical Methods	[26]
Not specified	Methods for sampling and analyzing contaminants in fish and shellfish tissue	Guidance for assessing chemical contaminant data for use in fish advisories	[28]

[a] SAFETY PRECAUTIONS: Some PAH are highly carcinogenic and must be handled with extreme care. Before commencing any PAH analysis in a laboratory it is wise to discuss the facilities with the appropriate health authority. Publications such as Ref. [195] or their equivalent (several references are provided in ISO 13877:1998, see Table 2 for selected ISO methods, http://www.iso.org) should be studied before handling PAH

[b] GC/MS: gas chromatography / mass spectrometry; HPLC: high-performance liquid chromatography; UV: ultra violet detection; FL: fluorescence detection; PCBs: polychlorinated biphenyls

Environmental Protection Agency (EPA) PAH-related test methods, including (although not limited to): drinking water [20, 21]; municipal and industrial discharges [22–25]; soils, sludges, and solid waste [26]; ambient air [27]; and shellfish tissue [28] (Table 1). Many standard analytical methods approved by other US federal agencies, for example the National Institute for Occupational Safety and Health (NIOSH), and non-government organizations, for example the Association of Official Analytical Chemists (AOAC) and the American Public Health Association (APHA), make use of both LC and GC for the determination of PAHs. These methods have been compiled and reviewed by the US Agency for Toxic Substances and Disease Registry in a PAH toxicological profile [4]. Similarly, analytical methods for trace organic contaminants, including PAHs, used by laboratories associated with the National Status and Trends Program National Benthic Surveillance and Mussel-Watch Projects have LC and GC components, and these have been compiled by the National Ocean and Atmospheric Administration [29, 30]. Several international standard methods also stipulate use of LC and GC for determination of PAHs (Table 2), as well as European national-level reference methods for PAHs in air (France, Germany, and Italy [31]).

Each technique, LC or GC, offers unique information or has unique aspects. For example, the GC procedure in EPA Method 610 does not adequately resolve four of the sixteen PAHs targeted for measurement (Table 3)—anthracene and phenanthrene; chrysene and benz[*a*]anthracene; benzo[*b*] and benzo[*k*]fluoranthene; and dibenz[*a*,*h*]anthracene and indeno[1,2,3-*cd*]pyrene. If, however, the purpose of the analysis is not served by the determination of the sum of one of these unresolved pairs, the LC method in EPA Method 610, which resolves all 16 PAHs, can be used [23]. In contrast, EPA Method 625 [24] only provides gas chromatographic–mass spectrometric (GC/MS) conditions appropriate for qualitative and quantitative confirmation of results for the PAHs listed in Table 3, with many other compounds (base/neutrals and acids), in the extract produced by EPA Method 610.

The scope and application of EPA Method 610 applies to 16 PAHs, commonly referred to as the EPA 16 priority pollutants (Table 3). This list has evolved somewhat since the development of EPA Method 610, for example the list includes two additional analytes in EPA Method TO-13A for the analysis of air samples (Table 3). Moreover, the 16 PAHs listed for EPA Method 610 are often grouped with a wider range of semivolatile organic compounds or base/neutral extractable compounds in other environmental test methods (e.g. EPA Method 625 [24]), and are often the "common" range of analytes for national and international environmental/health studies. In a review on approaches to consider for the risk assessment of PAHs, the World Health Organization (WHO) lists 17 individual compounds over and above the 16 PAHs in EPA Method 610 [32] (Table 3), a total of 31 parent PAH plus two alkyl derivatives, and AMAP has an additional 23 groups of alkylated PAHs. (See a review of marine monitoring programs [12]). The WHO provides a summary of genotoxicity and carcinogenicity results for the 33 PAHs (reviewed in Ref. [32], Table 3). The International Agency for Research on Cancer (IARC) has identified a subset of these PAHs as probable (group 2A) or possible (group 2B) human carcinogens (Table 3) [33]. The Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR) lists up to 46 PAH compounds (or mixtures such as anthracene oil and different distillates) as Substances for Possible Concern (http://www.ospar.org).

The range of isomers to be examined or measured in any environmental survey will ultimately depend on its purpose (e.g. health-related, ecotoxicological, source inventory) [32], and often only specific PAHs are targeted, or PAHs are included as a class/group. For example, only four to six PAHs are typically used as markers of emissions or emission inventory compilations (Table 3). The persistent organic pollutant (POPs) protocol under the United Nations Economic Commission for Europe's Convention on Long Range Transboundary Air Pollution requires that emissions of only four PAH compounds have to be reported annually by European Union member states [31, 34]. For the assessment of human exposure to air pollutants in European cities, benzene was the only major aromatic compound measured in six cities, although in selected campaigns measurements were extended to include several PAHs, particulate matter, and heavy metals [35]. The European Union regulated pollutant list for the protection of human health includes only one PAH, benzo[*a*]pyrene (see Table 1 in Ref. [35] and a paper by Menichini et al. [36]). Similarly, the Great Lakes Binational Toxics Strategy [37] between Canada and the US lists only benzo[*a*]pyrene as the PAH under the category "Level 1 substance" [38] (a primary focus for the virtual elimination of the substance), although PAHs as a group, with selected specific PAHs (anthracene, benz[*a*]anthracene, benzo[*ghi*]perylene, perylene, and phenanthrene) are listed in the next category (Level 2 [39]). Level 2 compounds are those that have been identified by one or both countries as having the potential to cause a significant impact on the Great Lakes ecosystem.

At the National Institute of Standards and Technology (NIST), EPA Method 610 PAHs (sixteen, Table 1) plus many other PAHs (Table 4) are measured in environmental reference materials [40], and coupled LC and GC methods have been long standing parts of the analytical methods (Fig. 1) [18, 41–45]. The use of multiple methods of analysis provides examination of a wider range of analytes

Table 2 Standard methods for the determination of PAHs[a] in environmental media

Method	Title	General Approach	Number PAHs
ISO[b] 11338-1:2003	Stationary source emissions—Determination of gas and particle-phase PAHs—Part 1: sampling	Various isokinetic approaches for sampling flue gas PAH emissions (stack/waste) including (A) dilution method, (B) heated filter/condenser/adsorber method, and (C) cooled probe/adsorber method	Not listed
ISO 11338-2:2003[c]	Stationary source emissions—Determination of gas and particle-phase PAHs—Part 2: sample preparation, clean-up, and determination	Particulate phase is collected on a filter and gas phase is trapped on an adsorbent (e.g. XAD-2[d], PUF[d] or other of comparable efficiency). Filter(s) and adsorbent extracted with organic solvent (e.g. Soxhlet, PFE[d], or other validated method). Analysis by HPLC–UV[d] or GC/MS[d]. The concentration of each PAH is calculated from the mass of PAH (particle and gas phase) determined during analysis and the volume of flue gas sampled corrected to appropriate reference conditions	HPLC: 16 GC/MS: 22
ISO 12884: 2000(E)	Ambient air—Determination of total (gas and particle-phase) PAHs—Collection on sorbent-backed filters with gas chromatographic–mass spectrometric analyses	Air sample collected using appropriate sampler equipped with a fine-particle filter followed by a vapor trap containing PUF or XAD-2. The particle filter and adsorbent cartridge are extracted together in a Soxhlet extractor and analyzed by GC/MS. The results represent the combined gas and particulate PAH in air	22
ISO 16362: 2005	Ambient air—Determination of particle-PAHs by HPLC	Specifies sampling and analysis procedures for quantitative determination of low volatility (particle-bound) PAHs in ambient air. For sampling, a low-volume or a medium/high-volume sampling device may be used. Particulate matter is collected on a filter. Different solvent extraction methods are listed. Analysis with HPLC–FL[d] or HPLC–DAD[d] is possible. Combination of both detector types is also possible. Total suspended particulate matter is sampled. For PAHs with boiling points above 430 °C (vapor pressure less than 10^{-9} kPa at 25 °C, e.g. chrysene, benz[*a*]anthracene) can be collected efficiently on the filter at low ambient temperatures (e.g. below 10 °C). In contrast, at higher temperatures (above 30 °C, see also ISO 12884), PAHs having boiling points above 475 °C (vapor pressure less than 10^{-10} kPa at 25 °C) are determined quantitatively	Various
ISO 7981-1:2005	Water quality—Determination of PAH—Part 1: Determination of six PAH by high-performance thin-layer chromatography with fluorescence detection after liquid–liquid extraction	Screening and quantitative methods for PAHs in drinking water.[e] The whole test sample is analyzed (aqueous and particle-bound PAHs). PAHs extracted by liquid–liquid extraction and separated by HPTLC[d] on appropriate stationary phases and detected either visually or by in situ fluorescence measurement at constant or differing wavelength combinations	6
ISO 7981-2:2005	Water quality—Determination of six PAH by HPLC–FL after liquid–liquid extraction	Method for the determination of selected PAH in drinking, mineral, and table waters and ground and surface waters in mass concentrations above 0.005 μg L^{-1}.[f] The whole test sample is analyzed (aqueous and particle-bound PAHs). PAH are extracted by liquid–liquid extraction and separated by HPLC on suitable stationary phases under isocratic conditions, identified and quantified by means of fluorescence detection at a constant combination of excitation and emission wavelengths	6
ISO 17993: 2002	Water quality—Determination of 15 PAH in water by HPLC–FL after liquid–liquid extraction	Separate guides for sampling (ISO 5667-2, ISO 5667-3). Method for drinking and ground water in mass concentrations greater than 0.005 μg L^{-1} (for each compound) and surface waters in mass concentrations above 0.01 μg L^{-1}[g]	15

Table 2 (continued)

Method	Title	General Approach	Number PAHs
ISO 18287: 2006	Soil quality—Determination of PAH—GC method with MS detection	Separate guides are available for sampling (ISO 10381-1, ISO 10381-8). Solvent extraction by shaking thoroughly on a shaking machine using a one or two-step approach. Analysis by capillary GC/MS	16
ISO 13877: 1998	Soil quality—Determination of PAH—Method using HPLC	Separate guide for sampling (ISO 10381-5). Soil is extracted with acetone without drying (method A) or extracted with toluene after drying (method B). Analysis of the extract is by HPLC–UV or with fluorimetric detection with variable excitation and emission wavelengths[h]	16
ASTM[i] D 6209-98 (2004)	Standard Test Method for Determination of Gaseous and Particulate PAHs in Ambient Air (Collection on Sorbent-Backed Filters with GC/MS Analysis)	Air sample is collected using high-volume air samplers equipped with a fine particulate filter followed by a vapor trap containing PUF or resin XAD-2. Filter and adsorbent cartridge are extracted in a Soxhlet apparatus and analyzed by GC/MS	22 listed as common air analytes
ASTM D 5412-93 (2005)	Standard Test Method for Quantification of Complex PAH Mixtures or Petroleum Oils in Water	Method for quantifying or characterizing total PAHs by fluorescence spectroscopy in waterborne samples. The characterization step is to find an appropriate calibration standard with similar emission and synchronous fluorescence spectra. The method is applicable to PAHs resulting from petroleum oils, fuel oils, creosotes, or industrial organic mixtures	PAH mixtures
ASTM E2143-01	Standard Practice for Using Field-Portable Fiber Optics Synchronous Fluorescence Spectrometer for Quantification of Field Samples for Aromatic and Polycyclic Aromatic Hydrocarbons	Rapid method for screening of environmental samples (soils and water) by remote sensing with optical fibers. Useful for difficult-to-reach areas or potentially dangerous materials or situations	Not specified

[a] SAFETY PRECAUTIONS: Some PAH are highly carcinogenic and must be handled with extreme care. Before commencing any PAH analysis in a laboratory, it is wise to discuss the facilities with the appropriate health authority. Publications, for example Ref. [195], or their equivalent (several references are provided in ISO 13877:1998(e)[b]) should be studied before handling PAH

[b] All ISO methods are provided by the International Organization for Standardization (http://www.iso.org)

[c] Methods are in ISO 11338-2 and are intended to be combined with one of the sampling methods described in ISO 11338 to complete the whole measurement procedure for determination of PAHs in stationary source emissions

[d] XAD-2: styrene–divinylbenzene polymer resin; PUF: polyurethane foam; HPLC–UV: high performance liquid chromatography with ultra violet detection; FL: fluorescence detection; DAD: diode-array detection; HPTLC high-performance thin-layer chromatography

[e] Method may, with modification, be applicable to analysis of ground waters and moderately polluted surface waters

[f] Method may, with modification, be applicable to analysis of moderately polluted waste waters

[g] Method may, with modification, be applicable to the analysis of waste water, and possibly for additional PAH, if the method is validated for each case

[h] Acenaphthylene cannot be measured using fluorimetric detection

[i] ASTM International, http://www.astm.org

than can be determined by a single method and also provides confirmation of measurements made by other methods [44]. For example, at low concentrations anthracene and perylene are best measured by use of LC coupled with fluorescence detection (LC–FL) because of their selective and sensitive fluorescence-detection characteristics [41]. This approach is also well suited for the determination of benzo[*a*]pyrene [46], often the only target analyte in environmental surveys (see discussion above). In contrast, GC/MS provides more accurate results than LC–FL for the determination of benzo[*ghi*]perylene because of its inherently low fluorescence sensitivity [41]. LC is also a useful fractionation technique for isolation of PAHs for subsequent analysis by other chromatographic and spectroscopic techniques, either in discrete fractions based on the number of aromatic rings or as a total PAH fraction [18, 47, 48]. LC–FL determinations of PAHs in LC fractions based on the number of aromatic rings and in a total PAH fraction were both part of the analytical scheme for value assignment of PAH concentrations in SRM 1941b Organics in Marine Sediment (Fig. 1 [45]). This fractionation approach is particularly suitable for high-molecular-mass PAHs (>300 amu) which are typically present at low concentrations in environmental samples and have many isomers [49, 50].

Table 3 Selected PAHs reported for environmental and health-effects studies

WHO EHC[a]	GENO[a,b]	CARC[a,b]	US EPA[c]	U.S. ATSDR[d]	IARC[e]	Borneff[f]	UNECE POPs[f]	ISO 17993[g]
Acenaphthene	(?)	(?)	X	X				X
Acenaphthylene	(?)	no data	X	X				
Anthanthrene	(+)	+						
Anthracene	−	−	X	X				X
Benz[*a*]anthracene	+	+	X	X	X (2A)			X
Benzo[*b*]fluoranthene	+	+	X	X	X (2B)	X	X	X
Benzo[*j*]fluoranthene	+	+		X	X (2B)			
Benzo[*ghi*]fluoranthene	(+)	(−)						X
Benzo[*k*]fluoranthene	+	+	X	X	X (2B)	X	X	X
Benzo[*a*]fluorene	(?)	(?)						
Benzo[*b*]fluorene	(?)	(?)						
Benzo[*ghi*]perylene	+	−	X	X		X		
Benzo[*c*]phenanthrene	(+)	+						
Benzo[*a*]pyrene	+	+	X	X	X (2A)	X	X	X
Benzo[*e*]pyrene	+	?	X*	X				
Chrysene	+	+	X	X				X
Coronene	(+)	(?)	X*					
Cyclopenta[*cd*]pyrene	+	+						
Dibenz[*a*,*h*]anthracene	+	+	X	X	X (2A)			X
Dibenzo[*a*,*e*]pyrene	+	+			X (2B)			
Dibenzo[*a*,*h*]pyrene	(+)	+			X (2B)			
Dibenzo[*a*,*i*]pyrene	+	+			X (2B)			
Dibenzo[*a*,*l*]pyrene	(+)	+			X (2B)			
Fluoranthene	+	(+)	X	X		X		X
Fluorene	−	−	X	X				X
Indeno[1,2,3-*cd*]pyrene	+	+	X	X		X	X	X
5-Methylchrysene	+	+						
1-Methylphenanthrene	+	(−)						
Naphthalene	−	(?)	X					X
Perylene	+	(−)						
Phenanthrene	(?)	(?)	X	X				X
Pyrene	(?)	(?)	X	X				X
Triphenylene	+	(−)						

[a] Reviewed in World Health Organization (WHO) Environmental Health Criteria Monograph on PAHs [32]
[b] GENO=genotoxicity; CARC=carcinogenicity; +, positive; −, negative; ?, questionable; parentheses, result derived from small database [32]
[c] US Environmental Protection Agency (EPA) Method 610 PAHs [23]; PAHs noted with asterisk (*) included in Method TO-13A for PAHs in air [27] (see Table 1 for methods)
[d] US Agency for Toxic Substances and Disease Registry (ATSDR) Toxicological Profile for PAHs [4]
[e] International Agency for Research on Cancer (IARC) identified as probable (2A) or possible (2B) human carcinogens (subset from review by Siemiatycki et al. [33])
[f] From Ref. [34]
[g] International Organization for Standardization (http://www.iso.org) Method 17993:2002 Water quality – Determination of 15 PAH in water by HPLC–FL after liquid-liquid extraction (see Table 2)

Obviously, the use of multiple methods of analysis, for example those shown in Fig. 1, for the determination of PAHs in environmental samples is often not possible for many laboratories, because the approach is not only costly and intense in terms of effort, but samples may be limited or even rare (e.g. an air particulate sample from the Arctic or a shipboard water sample from one cruise). A single method is therefore usually selected on the basis of the matrix (e.g. simple or complex), the target analytes (e.g. individual isomers or mixture), and sensitivity requirements (e.g. screening or quantification needs, expected concentration range). In contemporary analyses of environmental samples for the determination of PAHs, following carefully tailored matrix extraction and clean-up approaches (see examples in references on compilations of analytical methods [4, 29, 30], Tables 1 and 2, and Fig. 1), capillary GC, rather than LC, is usually the preferred analytical technique, for reasons discussed below. Incidentally, the term "capillary" typically refers to columns with inner diameters ranging from 0.18 mm to 0.32 mm whereas microbore inner diameters range from 0.05 mm to 0.10 mm and megabore inner diameters range from 0.45 mm to

Table 4 Number of PAHs[a] recently measured in selected environmental Standard Reference Materials (SRMs)

	Air particulate matter	House dust	Marine sediment	Marine sediment	Mussel tissue	Mussel tissue	Coal tar	Diesel particulate matter	Diesel particulate matter
SRM Number:	1649a	2585	1941b	1944	1974b	2977	1597a	1650b	2975
PAHs	30	29	30	29	29	25	43	32	25
Molecular mass 300 and 302 PAHs[b]	20	20	20	20			18	15	1
Methylnaphthalenes		2	4	2	4	2	3	2	
Methylphenanthrenes	5	5	7[c]	18[c]	6[c]	5	11[c]	13	14
Methylfluoranthenes		3	4	4			1	3	4
Methylpyrenes		3	3	3			3	3	2
Methylchrysenes		5					1	4	
Methylbenz[*a*] anthracenes		4						6	
Nitro-PAHs[c]	16							22	20
Sulfur-PAHs							10		
Total Compounds	71	71	68	76	39	32	80	100	66

[a] Some in combination
[b] Review on environmental SRMs by Wise et al. [40] in this issue
[c] Includes 2-methylanthracene

0.53 mm. The stationary phase is most often a uniform film affixed to the inner wall of the column (other configurations exist although the uniform thin film is the most widely used) [51], and lengths usually range from 15 m to 60 m for environmental applications. Several active test methods call for the use of packed columns, which are shorter (2 m to 5 m) and wider (1 mm to 5 mm) than capillary columns, and are filled with an inert granular support, each particle which is coated with the stationary phase [51]. For example, EPA Method 610 recommends a 1.8 m × 2 mm glass column packed with 3% OV-17 (50% phenyl methylsilicone; Table 1.9 in Ref. [52]) on Chromosorb W-AW-DCMS (100/120 mesh) or equivalent, although capillary columns can be used if the relative standard deviations of responses for replicate injections are demonstrated to be less than 6% and other quality-control requirements are met [23]. EPA Method 8100 describes the use of both packed and capillary columns for evaluation of solid

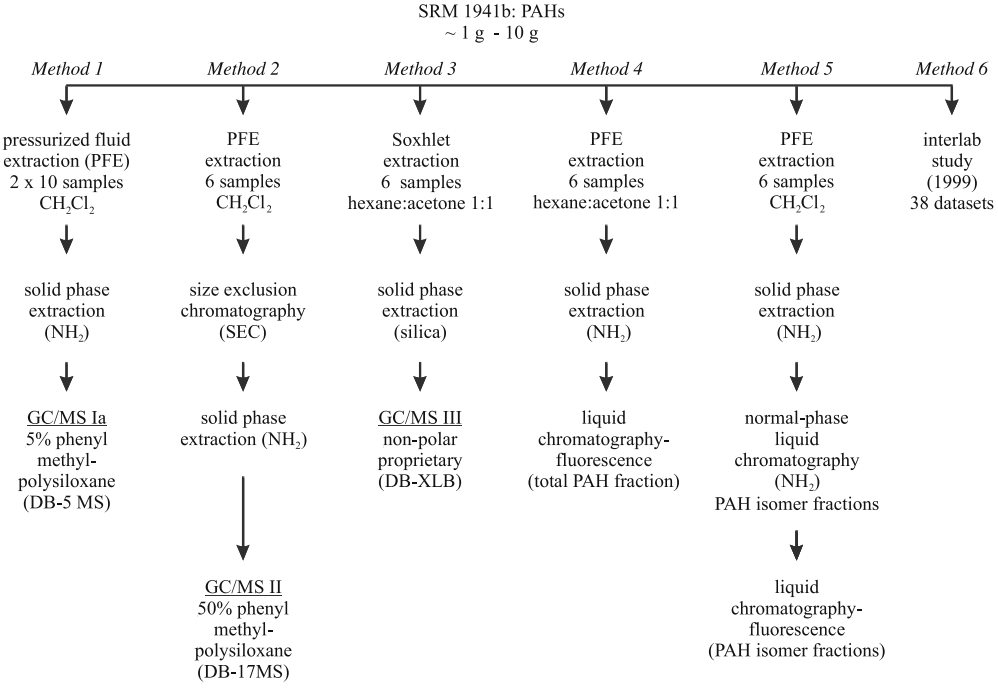

Fig. 1 Analytical scheme for the determination of PAHs in SRM 1941b Organics in Marine Sediment [45]

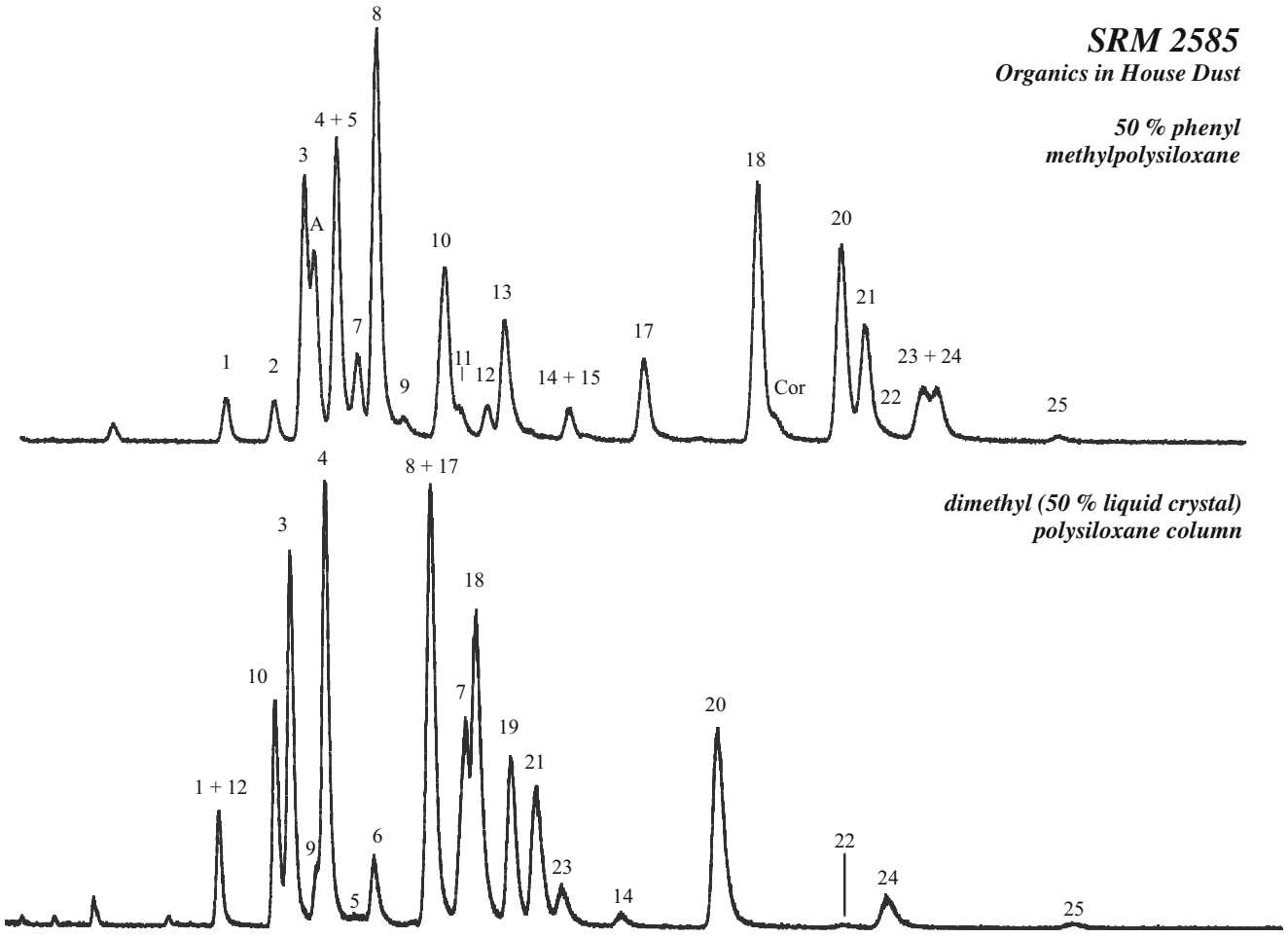

Fig. 2 Comparison of GC/MS single-ion chromatograms for PAHs of molecular mass 302 on two different GC stationary phases for SRM 2585 Organic Contaminants in House Dust. GC conditions for the 50% phenyl methylpolysiloxane column (DB-17MS, J&W Scientific, 60 m × 0.25 mm × 0.25 μm): 60 °C for 2 min, heat to 150 °C at 40° min^{-1}, hold for 3 min, heat to 300 °C at 2° min^{-1}, and hold for 120 min; on-column injection with a 5-m retention gap; carrier gas helium in the constant-pressure mode (33.4 psig). GC conditions for the dimethyl 50% liquid-crystalline polysiloxane column (LC-50, J&K Environmental, 15 m × 0.25 mm × 0.25 μm): 60 °C for 1 min, heat to 150 °C at 40° min^{-1}, hold for 2 min, heat to 270 °C at 1.5° min^{-1}, and a final hold for 220 min; on-column injection with a 5 m retention gap; carrier gas helium in the constant flow mode (1.8 mL min^{-1}). Peak identities are: #1 dibenzo[*b*,*e*]fluoranthene; #3 naphtho[1,2-*b*]fluoranthene; #4+5 naphtho[1,2-*k*]- and naphtho[2,3-*j*] fluoranthene; #7 naphtho[2,3-*b*]fluoranthene; #8 dibenzo[*b*,*k*]fluoranthene; #9 dibenzo[*a*,*k*]fluoranthene; #10 dibenzo[*j*,*l*]fluoranthene; #11 naphtho[1,2-*e*]pyrene; #12 dibenzo[*a*,*l*]pyrene; #14+15 naphtho[2,3-*k*] fluoranthene and naphtho[1,2-*a*]pyrene; #17 naphtho[2,3-*e*]pyrene; #18 dibenzo[*a*,*e*]pyrene; #20 naphtho[2,1-*a*]pyrene, #21 dibenzo[*e*,*l*] pyrene; #22 naphtho[2,3-*a*]pyrene; # 23 benzo[*b*]perylene; # 24 dibenzo[*a*,*i*]pyrene; # 25 dibenzo[*a*,*h*]pyrene (unknowns: #2, A, #6, #13, #19; Cor=coronene)

waste [26]. In contrast, only capillary columns are part of test methods for the determination of PAHs in ambient air (EPA Method TO-13A [27] and ASTM D 6209-98) and drinking water (EPA Method 525.2), and in environmental methods provided by the International Organization for Standardization (ISO) (Tables 1 and 2). Packed columns are rarely used in contemporary GC methods for PAHs. Even more than 20 years ago it was recognized that packed column GC would be rapidly replaced with "open tubular" (now denoted "capillary") columns [52], on which separations were noted as "vastly superior" (see Refs. in [51]). Nonetheless, ASTM International has active practice guides for both packed [53] and open-tubular capillary [54] columns.

The popularity of capillary GC for the determination of PAHs is based on a favorable combination of greater selectivity, resolution, and sensitivity compared to that achieved with LC [18, 19, 55]. In capillary GC of complex samples such as carbon black, coal tars, and shale oils it is not uncommon to resolve hundreds of components [17] whereas in LC a practical limit is a few dozen components, because of the limited peak capacity of LC columns. The easy use and compatibility of GC with mass spectrometers (GC/MS) are additional reasons for selection of GC in

preference to LC for the determination of PAHs in environmental samples [17]. Other advantages are that PAHs tend to have thermal properties amenable to GC, and MS techniques are fairly sensitive due to the projection of large molecular ion peaks or little fragmentation in common MS sources. The ongoing development of enhancements to GC for the determination of PAHs, for example large-volume injection, thermal desorption, and the coupling of GC to fast detectors, such as time-of-flight MS (TOF-MS), in which full range mass spectral acquisition rates on the order of hundreds of spectra per second enables a significant reduction in chromatographic analysis time, demonstrates the vigor and robustness of the technique. In addition, GC is usually the technique most often recommended in environmental test methods for the determination of PAHs (discussed above; Tables 1 and 2) and LC is typically more often used for clean-up or fractionation (as described previously) [29, 30] before GC analysis. Use of LC, as HPLC, is still stipulated in some test methods (Tables 1 and 2). For example, EPA Method 8310 makes use of HPLC for the determination of PAHs in ground water, soils, sludges, and non-water-miscible waste [26]. However, the decreasing popularity of LC for the determination of PAHs in environmental samples is reflected by actions such as the withdrawal of method ASTM D4657-92 (Standard Test Method for PAHs in Water, Table 1), which described HPLC methods for 16 PAHs in water and wastewater. The method was withdrawn in January 2005, due to lack of use and support to review and update the method.

As GC is so widely used for the determination of PAHs in environmental samples, this paper reviews contemporary state-of-the-art environmental PAH GC applications. An examination of modern GC separations of PAHs is followed by presentation on the properties and uses of selected mass spectrometric techniques. PAH literature on the use of GC with MS, including chemical ionization MS, ion trap MS, TOF-MS, and isotope-ratio MS (IRMS), is discussed. Enhancements to GC (large-volume injection, thermal desorption, fast GC and LC–GC) are reviewed. Purge-and-trap GC is not discussed, because this technique is not widely used for the determination of PAHs—it is more suited to the determination of volatile organic compounds (VOCs) [56, 57]. The determination of VOCs in ambient air is reviewed in this issue by Wang [58]. Relevant discussions pertinent to GC and PAHs, although beyond the scope of this review, are the use two-dimensional GC (GC×GC) and solid-phase micro-extraction (SPME), and the determination of PAH metabolites, nitro-PAHs, and polycyclic aromatic sulfur heterocycles (PASH). These topics are covered in this issue by Gorecki (GC×GC) [59], Ouyang and Pawliszyn (SPME) [60], Budzinski (PAH metabolites) [61], Zielinska (nitro-PAHs) [62], and Andersson et al. (PASH) [63].

Gas chromatography and PAHs

In 2002, *TrAC—Trends in Analytical Chemistry* released an issue devoted to GC which provides detailed reviews on the history, principles, and applications of GC [64]. Environmental analyses were reviewed by Santos and Galceran, and the use of GC for the determination of selected families of environmental contaminants is discussed, although this is somewhat limited with respect to PAHs [55]. Capillary GC is one of the most widely used and successful chromatographic techniques for the determination of the concentrations of PAHs in environmental matrices, owing mainly to its high resolving power. In the GC process the stationary phase is a thin immobilized film confined to a column that is continuously swept by a stream of mobile phase (carrier gas) [51]. A compound subjected to this process partitions between the stationary and mobile phases and separations occur on the basis of the fraction of time the compound spends in the stationary phase relative to its total transit time through the column. Component separation, i.e. resolution, is strongly related to the optimization of chromatographic conditions [18]. Berezkin and Viktorova have reviewed how important chromatographic conditions, for example column length and diameter, film thickness, stationary liquid phases, and separation temperature mode, have evolved over the period 1970–2000 [65]. The retention and separation of PAHs is affected by such conditions as solvent type and amount, solvent effects, injection conditions (speed, liner size, sample size, temperature), and temperature programming [66–70]. Capillary columns are often used in conjunction with a retention gap—a piece of empty (i.e. uncoated), deactivated, capillary glass tubing (approx. 0.25 mm × 5 m). The retention gap is used to remove non-volatile compounds, minimizing contamination of the column, and to reconcentrate analytes, thus improving peak shape [51]. Cold on-column injection is preferred for PAH analysis, because this improves the resolution of low-molecular-mass PAHs (i.e. early eluting compounds) and reduces discrimination of high-molecular-mass PAHs. Such biases are difficult to avoid when using splitless injection [11].

PAH separations by capillary GC

The most critical aspect of GC method development is selection of an appropriate stationary phase for a specific PAH separation problem [42–45]. Methyl and phenyl-substituted polysiloxanes are the most widely used capillary column stationary phases for separation of PAHs in environmental samples. Columns prepared with polysiloxane stationary phases give relatively low background from column bleed, even at high temperatures (>300 °C) and with nonselective detectors such as the flame ionization

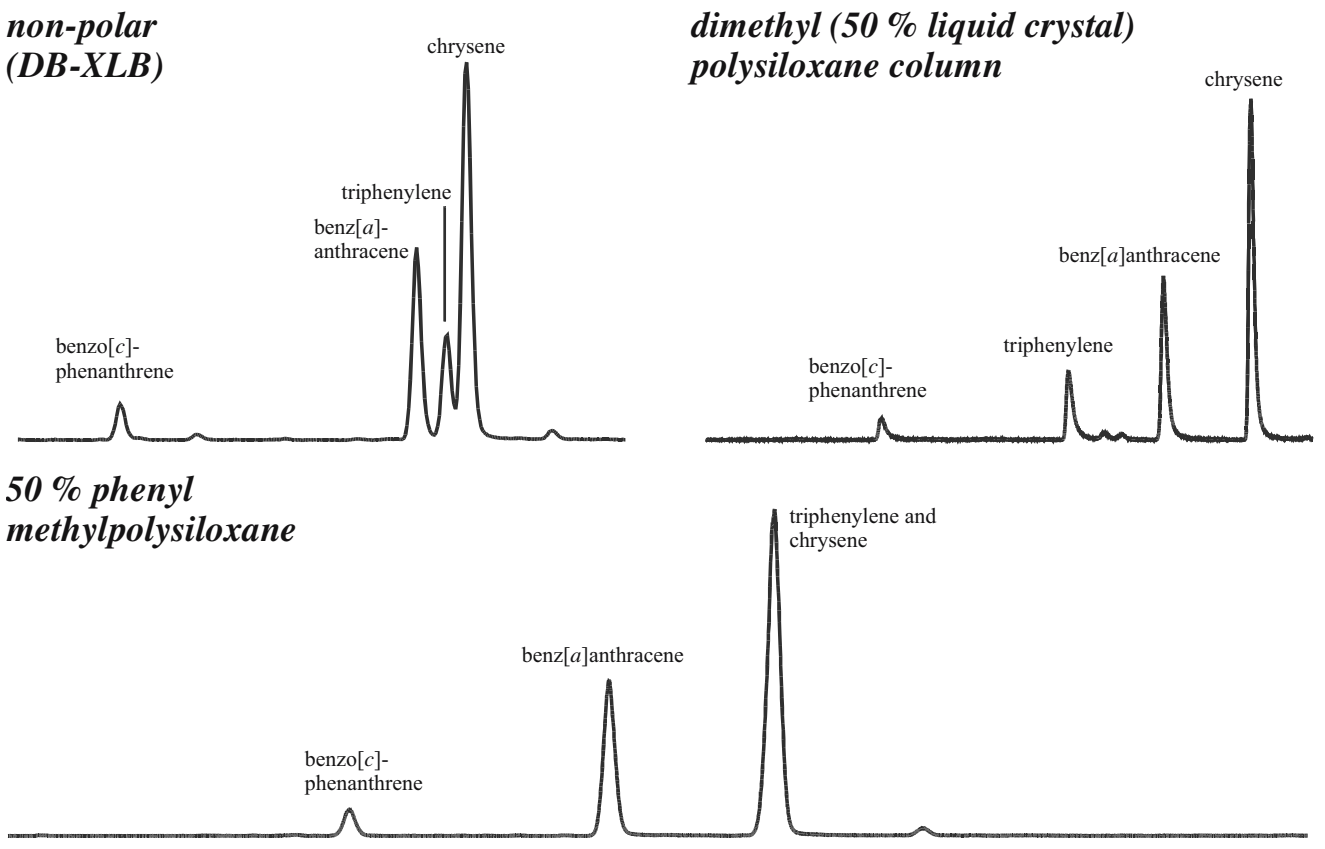

Fig. 3 Comparison of GC/MS single ion chromatograms for PAHs of molecular mass 228 on three different GC stationary phases for SRM 2585 Organic Contaminants in House Dust (representative GC conditions are given in Fig. 2)

detector (FID). Methylpolysiloxane phases containing 0%, 5%, 50%, and even 65% phenyl substitution are commercially available. Method TO-13A (Table 1) for GC/MS determination of PAHs in ambient air calls for use of a 5% phenyl methylpolysiloxane column (30 m × 0.32 mm i.d., 1.0 μm film thickness), although other columns may be used if specific criteria are met. This is the general recommendation in most standard test methods (Tables 1 and 2). Proprietary phases with unique selectivity for selected compounds are also available (DB-XLB). Columns containing liquid-crystalline stationary phases have shape selectivity aspects that are well suited to the separation of PAH isomers.

The shape selectivity of stationary phases used for gas chromatography of PAHs has been extensively studied [71, 72], and PAH separations using liquid-crystalline columns have been reviewed [18]. Liquid-crystalline columns have been part of the NIST analytical scheme for the determination of PAHs in environmental SRMs [73–75] including selected mussel tissue and marine sediment SRMs [44, 45]. Three important pairs of PAHs that typically coelute on traditional 5% phenyl methylpolysiloxane columns (chrysene and triphenylene; benzo[*b*]- and benzo[*j*]fluoranthene; and dibenz[*a*,*c*]- and dibenz[*a*,*h*]anthracene) are separated by liquid-crystalline columns [18, 76]. The greater selectivity of liquid-crystalline columns has also been used for the separation of methyl-substituted PAHs [18]. Liquid-crystalline columns have some limitations, including variations in selectivity, changes in the order of elution of PAHs among different columns, and a limited temperature range [72]. The relatively low temperature limit of early developed liquid-crystalline columns resulted in a limited mass range for the determination of PAHs. More recently, a liquid-crystalline column in the form of a 50% dimethyl 50% (mole fraction) liquid-crystalline polysiloxane phase has become commercially available and has a greater operating temperature range than previous smectic versions [77]. Even the higher-molecular-mass PAHs, for example dibenz[*a*,*c*]- and dibenz[*a*,*h*]anthracene, coronene, and the six-ring $C_{24}H_{14}$ PAHs (molecular mass 302) can be determined by use of this new liquid-crystalline phase [78]. Many higher-molecular-mass PAHs (molecular mass >300) give a positive mutagenic response when isolated from environmental and combustion-related samples [78], and several have been identified by IARC as possible human carcinogens (Table 3). It is, therefore, of great interest to develop analytical methods enabling accurate isolation, separation, and quantification of this group of PAHs. This novel liquid-crystalline column, which was recently used as part of the analytical scheme for the

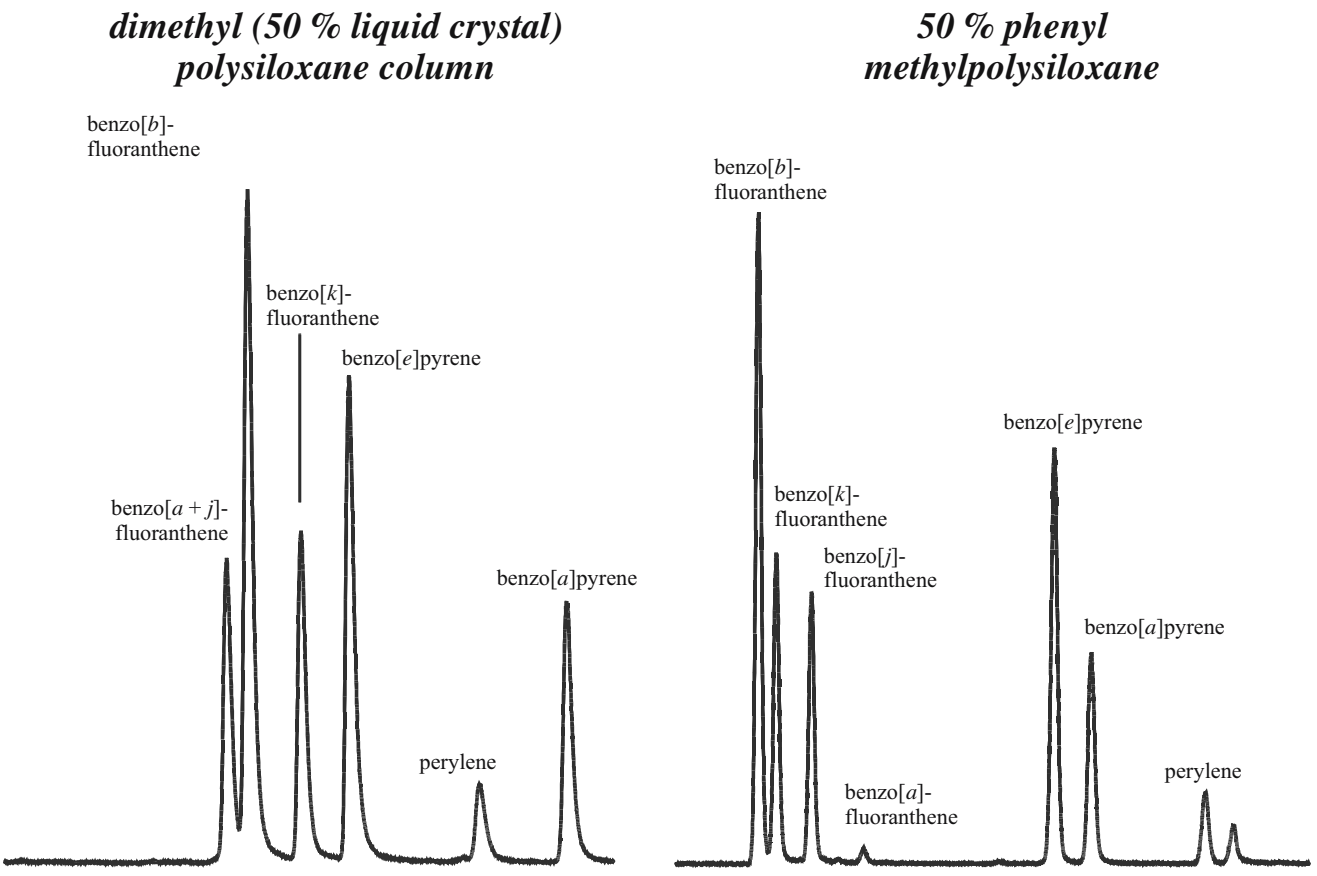

Fig. 4 Comparison of GC/MS single ion chromatograms for PAHs of molecular mass 252 on two different GC stationary phases for SRM 2585 Organic Contaminants in House Dust (representative GC conditions are given in Fig. 2)

determination of PAHs in a house dust SRM (SRM 2585 Organic Contaminants in House Dust) and a diesel particulate SRM (SRM 1650b Diesel Particulate Matter), has some advantages for separation of the $C_{24}H_{14}$ PAHs compared with use of a 50% phenyl methylpolysiloxane column (Fig. 2). For example, dibenzo[*e*,*l*]pyrene (#21) and naphtho[2,1-*a*]pyrene (#20) in a house dust sample are completely separated on the liquid-crystalline column, as are benzo[*b*]perylene (#23) and dibenzo[*a*,*i*]pyrene (#24). These compounds are poorly separated on the 50% phenyl methylpolysiloxane column (Fig. 2). It should be noted that long retention times are usually necessary to obtain the resolution needed for the accurate quantification of the higher-molecular-mass PAHs, although use of fast GC (discussed below) may lead to shorter analysis times [79].

Ultimately, the use of different GC columns permits the determination of PAHs that may typically coelute on one GC column. For example, chrysene and triphenylene, which coelute on a 50% phenyl methylpolysiloxane column, separate on a DB-XLB column and a liquid-crystalline column, although the liquid-crystalline column has the greater selectivity for the two isomers (Fig. 3). Other PAHs, for example benzo[*b*]- and benzo[*j*]fluoranthene, and dibenz[*a*,*c*]- and dibenz[*a*,*h*]anthracene, also separate on a liquid crystalline column [76], although benzo[*a*]- and benzo[*j*]fluoranthene coelute (Fig. 4), illustrating the advantage of using multiple columns for quantification of PAHs in environmental samples.

Multiple columns may not be an option in environmental PAH analysis because of cost or time constraints, and one column must be selected. The 50% phenyl methylpolysiloxane column usually enables separation of environmental PAHs that coelute on a 5% phenyl methylpolysiloxane column, including benzo[*b*]- and benzo[*j*]fluoranthene (Fig. 4), and dibenz[*a*,*c*]- and dibenz[*a*,*h*]anthracene, making this column the best choice for PAH separations. Benzo[*c*]chrysene, if present, may coelute with dibenz[*a*,*j*]-anthracene, however, and chrysene and triphenylene coelute (Fig. 3). As discussed in the Introduction, many of these isomers (and others) do not need to be determined individually. In such circumstances, the 5% phenyl methylpolysiloxane column (as suggested in Method TO-13A and many other test methods; Tables 1 and 2) may be used, although it is important to consider possible coelution (for example chrysene and triphenylene) when calculating concentrations. In addition, although 60 m columns and very slow temperature programming (Fig. 2) typically enable the best PAH separations, shorter columns and faster

temperature programs may be warranted when high throughput is required or site surveys are being conducted (e.g. field GC–FID), for example for only one compound, such as benzo[*a*]pyrene. Fast GC is discussed later in this paper.

Although GC is a mature technique, the development of novel stationary phases for GC analysis of PAHs continues. For example, liquid crystalline stationary phases containing crown ether groups have been developed which separate some three-ring PAHs [80]. Two high-purity all-hydrocarbon side-chain liquid-crystalline polysiloxane polymers have been synthesized by grafting all-hydrocarbon liquid-crystal monomers onto a polymethylhydrosiloxane backbone. The two polysiloxane polymers enabled enhanced separation of 21 PAHs compared with the 5% phenyl methylpolysiloxane stationary phase, although triphenylene was not included in the analysis [81]. Triphenylene coelutes with chrysene on a 5% phenyl methylpolysiloxane column (see above). Other new stationary phases have been developed for PAH separations. A mesogenic polymer was prepared from the metal complexes of 4-(dec-9′-en-1′-oxy)dithiobenzoate and polysiloxane and used as the stationary phase for ligand-exchange gas chromatographic separation of low-molecular-mass PAHs [82]. Phenanthrene and anthracene, two key low-molecular-mass environmental PAHs, were, however, only partially separated. More recently, columns containing synthetic polymer filaments have been introduced as the support material in packed capillary GC. Filaments of the heat-resistant polymer Zylon have been coated with polydimethylsiloxane and shown to be useful for the separation of some PAHs (naphthalene, fluorene, phenanthrene, pyrene, and triphenylene) [83].

Retention data

A common way of monitoring gas–liquid interactions in capillary columns and of comparing stationary phases is to examine retention data of isomers as retention indices. Retention indices are a way of normalizing solute retention relative to the retention of specific standards [84]. Different retention index systems have been based on the use of alkanes [85] or PAHs [86] as retention standards. In general, retention indices are less dependent upon chromatographic conditions than are retention times, and are a way of comparing relative behaviors on different stationary phases. In this way, the order of elution and potential for separation of specific compounds may be predicted, facilitating column selection. Relationships between gas chromatographic retention indices of PAHs have been investigated since the late 1950s, and Lee et al. [86] introduced a system based on PAHs with an increasing number of aromatic rings as retention markers. Values may be measured, although many prediction methods have been developed (discussed below). Andersson and Weis [87] have investigated the retention indices and orders of retention of a range of PAHs and fluorinated PAHs on five capillary columns of different selectivity (PB (polymethylsiloxane), DB-5 (95:5 methyl phenylsilicone), OV-1701 (5:7:88 cyanopropyl–phenyl methylsilicone), DB-17 (50:50 methyl phenylsilicone), and DB-Wax 20M (polyethylene glycol). Similarly, Escrivá et al. [88] compared separations of PAH mixtures in airborne particulate extracts on five different capillary columns. Retention indices for PAHs with molecular mass 300 and 302 have been determined using picene and benzo[*c*]picene as retention markers with a 50% phenyl methylpolysiloxane column, and picene and coronene as retention markers with a liquid-crystalline column [78]. Correlations of retention and PAH shape on the basis of length-to-breadth ratios [89, 90] were also investigated [78]. More recently, retention indices for 13 dibenzopyrene homologues (molecular mass 302) have been determined on four different stationary phases (5%, 35%, and 50% phenyl methylpolysiloxane columns and a 35% trifluoropropyl methylpolysiloxane column). Correlations of retention on each phase with eight molecular descriptors, including PAH volume and length-to-breadth ratio, were reported [91].

Saura-Calixto and Garcia-Raso presented one of the early studies on the prediction of retention indices [92]. Temperature-programmed retention indices of unsubstituted PAHs were examined in relation to different molecular descriptors (first-order valence molecular connectivity, ionization potential, length, height, and moment) for compounds of molecular mass ranging from 178 to 350 amu [93]. Temperature-programmed retention indices of 70 PAHs on a methylsilicone capillary column have been reported and applied to the analysis of fuel and fuel deposits [94]. Quantitative structure–retention relationships for predicting capillary GC retention indices of PAHs using pseudo-conjugated pi-system surface and quasi-length of carbon chain have been examined for 100 PAHs on SE-52 columns [95]. The retention indices of 17 PAHs of molecular mass 302 have been predicted using a unique model that calculates the interaction energy between solutes and a dielectric medium; this is the first report on the relationship between retention indices and the interaction between the solute and the GC column [96].

Detection of PAHs: GC–MS

Detection of PAHs in environmental samples following GC separation is most commonly accomplished by use of quadrupole electron impact (EI) mass spectrometry. In contrast with many other organic contaminants, in this impact mode most environmental PAHs yield intense molecular ions with little fragmentation [11]. GC/EI MS

Table 5 Ions reported for sixteen priority pollutant PAHs for GC/MS and GC–ion-trap MS[a]

PAH	Ion (*m*/*z*)	
	GC/MS[b,c]	GC–ion-trap MS[d]
Naphthalene	128	128
Acenaphthylene	152	153
Acenaphthene	152, 154	154
Fluorene	165, 166	165
Phenanthrene	178	178
Anthracene	178	178
Fluoranthene	202	201
Pyrene	202	201
Benz[*a*]anthracene	228	227
Chrysene	228	227
Benzo[*b*]fluoranthene	252	250
Benzo[*k*]fluoranthene	252	250
Benzo[*a*]pyrene	252	250
Benzo[*ghi*]perylene	276	277
Indeno[1,2,3-*cd*]pyrene	276	277
Dibenz[*a*,*h*]anthracene	278	277

[a] From Halaleh et al. [112]
[b] GC/MS in electron-impact mode
[c] For additional analytes (Table 3) and characteristic ions see references to test methods in Tables 1 and 2 and Refs. [24, 27]
[d] GC/MS/MS in electron-impact mode

operated in the selective ion monitoring (SIM; selected ions in Table 5) mode has advantages over full-scan mode, for example low detection limits and discrete monitoring capabilities. In general, ease of operation, and now reasonable purchase and operating costs have enabled GC/EI MS to become a popular, probably the most used, method for the determination of PAHs in laboratories worldwide. The use of multiple columns (see discussion above) that exhibit dissimilar PAH selectivity with GC/EI MS enhances this approach and addresses possible isomer coelution issues.

GC/MS is often more accurate than conventional universal detection methods, for example GC–FID, for the quantification of PAHs, because interferences from coeluting compounds are minimized by the selective nature of the detector. Removal of the more polar analytes from the extract by column chromatography (solid-phase extraction or liquid chromatography, Fig. 1) before either GC–FID or GC/MS assists in obtaining the best chromatographic conditions. GC–FID is still a useful method, and a wealth of literature is available on the use of this method for the determination of PAHs in all types of environmental sample. For example, GC–FID is a component of national standard methods for the determination of PAHs in air (Fig. 4 in Ref. [31]) and in solid waste [26]. One advantage of FID is that the response is proportional to the number of carbons so one can quantify compounds in the same isomer group even if a matched calibrant is not available. Recent examples of the use of GC–FID for determination of PAHs in environmental samples include the analysis of air particulates [97], water [98], and sediment [99, 100]. A review of analytical methods for determination of PAHs in air (gaseous and particle-associated) documents the use of GC–FID and/or GC/MS to quantify compounds collected from a variety of sampling environments [101]. In the analysis of complex matrices, such as sediment or oil, GC/MS is often used for the determination of PAHs, and GC–FID is reserved for the determination of alkanes or aliphatic compounds [102, 103]. The usefulness of GC/MS compared with GC–FID for the analysis of complex matrices such as biological organisms has been presented in terms of sensitivity and selectivity [104]. Baumard and Budzinski concluded that the observed reduction in the number of interfering peaks in GC/MS chromatograms in comparison with those obtained by use of GC–FID makes GC/MS "the preferred analytical system for PAH environmental analyses" [104]. A recent overview of developments and applications of GC/MS in the analysis of environmental samples for the determination of a range of persistent pollutants has been presented by Santos and Galceran [105]. Different mass analyzers and recent developments in field-portable GC/MS have also been examined [105].

Alternative MS modes to EI for the determination of PAHs include positive and negative chemical ionization (PCI and NCI, respectively). Conventional chemical ionization methods using methane as the reagent gas typically produce mass spectra similar to those produced by EI. NCI often produces a low yield of negative ions, and a decrease in sensitivity in NCI may be observed [11]. However, NCI with methane has been shown to be highly sensitive and selective for some isomeric PAHs. Selective detection of the molecular anions of fluoranthene over pyrene and of benzo[*a*]pyrene over benzo[*e*]pyrene has been demonstrated, and the approach has been used to determine selected PAHs and alkyl-PAHs in diesel and air particulate matter [106]. GC/MS strategies for both PCI and NCI modes with a range of reagent gases, for example methane, dimethyl ether, tetramethylsilane, ammonia, carbon dioxide, or mixtures of gases, have been reported for the determination of PAHs. Selected priority pollutant PAHs (Table 5, excluding naphthalene, acenaphthylene, acenaphthene, and fluorene) have been separated and identified on the basis of the identities and relative abundances of the ions produced by PCI using dimethyl ether as reagent gas [107]. When ammonia was used as the reagent gas, however, benzo[*ghi*]perylene and indeno[1,2,3-*cd*]pyrene were not distinguishable [107]. Many GC PCI and NCI applications for PAHs are mentioned by Yurchenko and Mölder, who used both PCI with ammonia

and methane and NCI with methane to determine PAHs in smoked fish and oil samples [108].

GC–ion-trap MS

A method for the separation and determination of PAHs using an ion-trap MS has been developed and compared with alternative GC and LC methods, including GC/MS using a quadrupole and SIM techniques and LC–fluorimetric methods. Use of the ion trap detector resulted in greater sensitivity than using GC/MS or LC–fluorimetry. This ion-trap method was designed to run simultaneously with GC–FID, enabling simultaneous qualitative identification and quantitative determination [109]. This method, because of its increased selectivity, is receiving increased attention for PAH analyses. In contrast to quadrupole instruments, there is no sensitivity advantage to be gained by limiting the number of ions detected in the ion-trap. Hence, all samples can be scanned in full-scan mode with little or no extra effort. In addition, archived sample files can be viewed later for compounds that may not have been a target at the time of analysis [11]. However, GC–ion-trap MS is not without limitations. Linearity may be a problem, because of the capacity of the ion trap. Despite this, GC–ion-trap MS has recently been used for determination of PAHs in marine environmental matrices (seawater, sediment, and mussel homogenate samples [110], estuarine sediments [111], and sewage sludge [112]). Ions reported for GC–ion-trap MS analysis of sewage sludge samples are listed in Table 5 [112]. Low-pressure GC–ion-trap MS (LPGC–ITMS) has been used for the determination of PAHs in aerosol samples from sugar cane burning, and 16 PAHs were separated in less than 13 min [113]. LPGC–ITMS has also been used for the analysis of gas and aerosol phase samples collected in the ambient air of Hasselt, Belgium [114]. In low-pressure GC, a gain in speed is obtained by operating a column under vacuum-outlet conditions rather than at atmospheric pressure. This gain in speed becomes substantial for short and/or wide-bore thick-film columns [115]. PAHs may also be determined by GC–ion-trap MS using collision-induced dissociation (CID) and electron impact (EI) [116, 117]. CID analysis has been shown to be more sensitive than EI in the analysis of used motor oil [117].

GC–time-of-flight (TOF) MS (GC–TOF-MS)

In recent years TOF-MS with GC and LC sample-introduction has become increasingly prevalent in environmental analysis [118, 119]. The unique aspect of this detection method is that accurate mass measurements and full-scan data can be acquired on short time scales. Quantitative data are also obtainable. Because of its higher mass resolving power, TOF-MS can enable better structural conformations and better signal-to-noise ratios than single quadrupole analyses, especially with complex samples [119]. When conducting surveys or discovery-based analysis for new contaminants the full spectral sensitivity of TOF-MS is an advantage over traditional scanning MS instruments where limits of sensitivity are often experienced even when scans are conducted over a narrow mass range [119]. Vreuls et al. provide a brief summary of TOF-MS and recently evaluated the spectrum storage rate, linearity of response, and detection limits of GC–TOF-MS for a range of organic contaminants, including the 16 priority pollutant PAHs, in a sediment and boiled tea [120]. Other studies of PAHs using GC–TOF-MS include the rapid analysis of PAHs in fly ash using thermal desorption directly coupled to the GC [121, 122]. Thermal desorption techniques with GC are discussed below, although the approach is also reported in combination with GC–TOF-MS. For example, thermal desorption coupled to GC–TOF-MS has recently been used for analysis of air particulate matter (≤2.5 μm) for the determination of PAHs, oxidized PAHs, *n*-alkanes, hopanes, and long-chain linear alkylbenzenes [123]. In a related study, two hundred compounds were quantified and "semi-quantified" on a daily basis by thermal desorption GC–TOF-MS with data thought to be suitable for source receptor modeling and epidemiological time series studies on the health effects of air particulate matter [124]. The authors note, however, that use of comprehensive two-dimensional GC (GC×GC) with TOF-MS enhanced the chromatographic resolution of the components of ambient air particulate matter compared with GC–TOF-MS and significantly improved the peak-identification capabilities of TOF-MS [124]. Methods that make use of multidimensional GC and GC×GC are gaining popularity, because of the benefits of enhanced separation to quantitative analysis [125, 126]. A collection of papers from the 2003 First International Symposium on Comprehensive Multidimensional Gas Chromatography reveals the wide range of multidimensional GC and GC×GC approaches for the determination of analytes, including PAHs, in environmental samples, petrochemical-related samples, cigarette smoke, fish, food, and essential oils [127]. The analysis of petrochemical and related samples by GC×GC using FID and TOF-MS as detection methods has recently been reviewed [128]. This issue contains a review of GC×GC by Gorecki [59].

GC–isotope-ratio mass spectrometry (IRMS)

Approximately a decade ago it became clear that source inputs of PAHs to the environment could be determined using carbon isotope measurements of individual PAHs [129–131]. Compound-specific carbon-isotope ($^{13}C/^{12}C$) ratios enable quantitative assessment of PAH sources in

natural environments and have been applied to source apportionment studies of PAHs in soils and sediments from marine, lacustrine, and terrestrial environments [129, 132–134]. These specialized measurements are conducted by use of GC coupled with isotope-ratio mass spectrometry (IRMS), as recently reviewed by Schmidt et al. [135] and Lima et al. [3]. In this technique, a GC is coupled to a combustion furnace and the isotopic composition of the resulting CO_2 is continuously analyzed using a magnetic sector MS. McRae et al. described the determination of the isotope ratios of specific aromatic and aliphatic hydrocarbons from coal-conversion processes [136]. GC–IRMS instruments for the determination of the isotope ratios of four elements (H, C, N, and O) are commercially available, and coupling of LC with IRMS has been attempted, although no commercial instrument is available because of the difficulties associated with the presence of a solvent mobile phase in the combustion unit [135]. Kim et al. have described a unique approach for purification of environmental extracts targeted for specific isotope analysis using column chromatography, LC, and thin-layer chromatography [134]. The GC–IRMS technique is a potential environmental forensic method at sites formerly used for gas manufacture [137].

Quantification of PAHs

Prior to using GC for the separation of PAHs in environmental samples, samples are usually extracted with solvent, and the extracts are concentrated and cleaned up by use of normal-phase LC or solid-phase extraction procedures to remove potential interfering polar constituents (Tables 1 and 2 and Fig. 1) [4, 29, 30, 42–45]. Modern methods of sample preparation have been reviewed by Smith [138]. Schantz et al. [139] have evaluated pressurized liquid extraction (PLE) for the determination of PAHs in environmental matrices, and this issue includes a review of PLE in environmental samples [140].

Identification and quantification of individual isomers is dependent on the use of authentic standards. These may be characterized by spectroscopic methods (UV, MS, or high-resolution nuclear magnetic resonance (NMR)) or by melting point [141]. Many PAH standards are commercially available and several PAH-related solutions are available from NIST (Table 6). Schantz et al. have recently reviewed NIST SRM solutions [142].

Two solution SRMs are available that contain PAHs in either acetonitrile (SRM 1647e, 16 PAHs) or toluene (SRM 2260a, 36 aromatic hydrocarbons, primarily PAHs, Table 6). The concentrations of the 16 priority pollutant PAHs in SRM 1647e range from 1 mg kg^{-1} for anthracene to 26 mg kg^{-1} for acenaphthene. With acetonitrile as the solvent, this SRM is intended for the calibration of LC systems for PAH analyses but it can also be used to fortify aqueous samples with known concentrations of PAHs. SRM 2260a is the replacement for two previously available materials, SRM 1491 and SRM 2260, which contained the same 24 PAHs at nominal concentrations of 10 mg kg^{-1} and 70 mg kg^{-1}, respectively. SRM 2260a contains 36 aromatic hydrocarbons at concentrations that mimic the relative concentrations of PAHs found in environmental matrices. Concentrations range from 2 mg kg^{-1} for cyclopenta[*cd*]-pyrene to 12 mg kg^{-1} for phenanthrene. SRM 1491a contains 18 methyl-substituted PAHs in toluene at concentrations ranging from 1 mg kg^{-1} to 2.5 mg kg^{-1}. Several solutions are also available for the determination of nitro-substituted PAHs (Table 6).

The solutions listed in Table 6 are intended for use as calibration solutions and are typically processed and analyzed in parallel with environmental samples to generate individual response factors relative to internal standards for quantification purposes [18]. The internal standard(s) added to samples should have similar or matching chemical and physical properties relative to the target analytes, must not be present in the environment, and should elute from the GC column at a time near to that of the target analyte(s). Stable isotope-labeled internal standards are preferred to others. When labeled reagents are not available, a compound as similar as possible to the analyte should be selected (i.e. an isomer, a methyl analog, or other related compound not present in the sample). Internal standards in PAH environmental analyses are most often perdeuterated PAHs (^{2}H-labeled PAHs) [42–45, 104, 143, 144] (Table 6). Perdeuterated PAHs are resolved from parent PAHs by both LC and GC. They are components in most standard test methods (US EPA [24, 27], also see Tables 1 and 2). Fluorinated PAHs [145, 146] have also been shown to be useful. Both of these analogs may be used with either GC/MS or GC–FID. Carbon-13 labeled PAHs [147] may be used as internal standards, although only in GC/MS analysis in which the selective nature of the mass spectrometer affords the opportunity for detection of these compounds, which typically coelute with the unlabeled compounds. Use of selected ^{13}C-labeled PAHs was part of the analytical scheme for the determination of PAHs in a mussel tissue SRM [44]. Eighteen monohydroxy PAHs (OH-PAHs) containing up to four rings have been measured in human urine using ^{13}C-labeled internal standards and GC/MS (high resolution) [148]. Although many of these compounds are commercially available, ^{13}C-labeled compounds are usually more expensive than perdeuterated compounds. NIST has produced two SRM solutions containing perdeuterated PAHs (Table 6). These may be used as internal standard or surrogate solutions. Both solutions are prepared in a 96:4 (*v*/*v*) hexane–toluene,

Table 6 Solution SRMs for PAHs and substituted-PAHs[a]

SRM	Title	Constituents	Concentration range (mg kg^{-1})
1491a	Methyl-Substituted Polycyclic Aromatic Hydrocarbons in Toluene	1-methylnaphthalene, 1-methylnaphthalene, 1,2-dimethylnaphthalene, 1,6-dimethylnaphthalene, 2,6-dimethylnaphthalene, 1-methylphenanthrene, 2-methylphenanthrene, 3-methylphenanthrene, 9-methylphenanthrene, 2-methylanthracene, 1,7-dimethylphenanthrene, 1-methylfluoranthene, 3-methylfluoranthene, 1-methylpyrene, 4-methylpyrene, retene, 3-methylchrysene, 6-methylchrysene	1–2.5
1587	Nitrated PAHs (Nitro-PAHs) in Methanol	2-nitrofluorene, 9-nitroanthracene, 3-nitrofluoranthene, 1-nitropyrene, 7-nitrobenz[*a*]anthracene, 6-nitrochrysene, 6-nitrobenzo[*a*]pyrene	5–10
1596	Dinitropyrene Isomers and 1-Nitropyrene in Methylene Chloride	1-nitropyrene, 1,3-dinitropyrene, 1,6-dinitropyrene, 1,8-dinitropyrene	2–8
1647e	Priority Pollutant Polycyclic Aromatic Hydrocarbons (in Acetonitrile)	naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzo[*b*]-fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]-pyrene, benzo[*ghi*]perylene dibenz[*a*,*h*]anthracene	1–26
2260a	Aromatic Hydrocarbons in Toluene	naphthalene, biphenyl, acenaphthylene, acenaphthene, fluorene, dibenzothiophene, phenanthrene, anthracene, 4(*H*)-cyclopenta[*def*]-phenanthrene, fluoranthene, pyrene, benzo[*ghi*]fluoranthene, cyclopenta-[cd]pyrene, benzo[*c*]phenanthrene, benz[*a*]anthracene, chrysene, triphenylene, benzo[*b*]fluoranthene, benzo[*j*]fluoranthene, benzo[*k*]-fluoranthene, benzo[*a*]fluoranthene, benzo[*e*]pyrene, benzo[*a*]pyrene, perylene, indeno[1,2,3-*cd*]pyrene, benzo[*ghi*]perylene, dibenz[*a*,*h*]-anthracene, dibenz[*a*,*c*]anthracene, dibenz[*a*,*j*]anthracene, picene, benzo[*b*]-chrysene, anthanthrene, coronene, dibenzo[*a*,*h*]pyrene, dibenzo-[*b*,*k*]-fluoranthene, dibenzo[*a*,*e*]pyrene	2–12
2264	Nitro-PAHs in Methylene Chloride I	1-nitronaphthalene, 2-nitronaphthalene, 1-methyl-4-nitronaphthalene, 1-methyl-5-nitronaphthalene, 1-methyl-6-nitronaphthalene, 2-methyl-4-nitronaphthalene, 2-nitrobiphenyl, 3-nitrobiphenyl, 4-nitrobiphenyl, 5-nitroacenaphthene, 2-nitrofluorene	2–4
2265	Nitro-PAHs in Methylene Chloride II	2-nitrophenanthrene, 3-nitrophenanthrene, 9-nitrophenanthrene, 2-nitroanthracene, 2-nitrofluoranthene, 3-nitrofluoranthene, 1-nitropyrene, 2-nitropyrene, 4-nitropyrene, 6-nitrochrysene, 7-nitrobenz[*a*]anthracene, 3-nitrobenzanthrone, 1+3-nitrobenzo[*e*]pyrene, 6-nitrobenz[*a*]pyrene	2.5–5
2269	Perdeuterated PAH-I Solution in Hexane/Toluene	biphenyl-d_{10}, phenanthrene-d_{10}, fluoranthene-d_{10}, benz[*a*]anthracene-d_{12}, dibenz[*a*,*h*]anthracene- d_{14}	7–65
2270	Perdeuterated PAH-II Solution in Hexane/Toluene	naphthalene-d_8, acenaphthene-d_{10}, pyrene-d_{10}, benzo[*a*]pyrene-d_{12}, perylene-d_{12}, benzo[*ghi*]perylene-d_{12}	7–80

[a] From Schantz et al. [142]

which can be gravimetrically added to samples and/or calibration solutions.

Response factors relative to internal standards are typically calculated using either a single concentration or multiple concentrations to generate calibration plots. Single concentrations are useful when determining an expected or known concentration (e.g. samples subjected to preliminary characterization or solutions for which the mass of the analyte is known from the gravimetric preparation of the solution). Calibration plots are useful when a range of concentrations is expected. Although zero or non-zero intercept models may be used, a non-zero intercept should usually be small in relation to the concentration of the analyte. Standard test methods, for example those provided by the US EPA [24, 27], typically provide approaches for quantification (Tables 1 and 2).

An essential part of excellent analytical chemistry is the appropriate use of reference materials. Reference materials are stable, homogeneous materials that are well-characterized for one or more properties and enable instrument calibration, method evaluation, or characterization of other materials. Reference materials may also be used to obtain estimates of intermethod and/or interlaboratory comparability [149]. A certified reference material (CRM) is one with properties certified by validated procedures; and is accompanied by documentation from the certifying organization that assesses the uncertainty of the property values (or its properties are traceable to such documentation)

[150]. An SRM [150] is a CRM issued by NIST (http://www.nist.gov/srm). Reviews on environmental reference materials and their use are provided in this issue by Wise et al. [40], Zeisler [151], and Ulberth [152]. Many reference materials are available for the determination of PAHs (Table 4).

Enhancements to GC for PAH analysis

Large-volume injection GC

The growing demand in trace analysis for lower detection limits has led to the development of innovative ways of introducing larger sample volumes into LC and GC systems [153]. Large-volume injection techniques have advantages in addition to improved sensitivity. For example, use of large-volume injection often reduces or eliminates the need for sample concentration (i.e. solvent evaporation), thus saving time and effort. Accuracy may also be improved, because potential losses of analytes in the concentration step are minimized [51]. If the sample extract is sufficiently clean and/or the detector selectivity high, detection limits improve in proportion to the volume injected [154]. Methods for, and applications of, large-volume injection in GC have been reviewed by Teske and Engewald [155]. Large-volume samples (30 μL to approx. 100 μL and larger) can be injected by use of several techniques, including on-column [156] and temperature-programmable approaches [154]. In the latter mode, referred to as a programmed-temperature vaporizing (PTV) injection, the inlet temperature at the time of injection is usually below the boiling point of all the analytes and the solvent and can be time-programmed during the GC runtime. Large-volume injections are usually performed in split mode, so most of the solvent vapor exits the system via the split vent [155]. During this time, the higher-boiling compounds are enriched in the insert and the analytes are subsequently transferred onto the analytical column in the splitless mode by rapid heating of the injector [155]. Retention gaps (or precolumns) are recommended to assist with sample recondensation and desolvation, and to maintain system performance by preventing contamination of the GC column with non-volatile materials or traces of water [154, 157]. Norlock et al. recently reported results obtained from the optimization of PTV-large-volume injections (up to 150 μL) for the determination of PAHs by MS [158]. Aspects investigated included detection limits, maximum total volume of injection, dependence of linearity of MS response on injection volume, and analytical repeatability [158]. Norlock et al. also investigated the determination of PAHs in air and sediment samples using their optimized method [158]. Other examples of applications in which large-volume injection methods were used include analysis of extracts from aqueous solutions [153], river water [154], soils and sediment [154, 156, 159, 160], and air particulate samples [161]. In the air particulate study, the authors note that a ten to fiftyfold increase in sensitivity was achieved with the large-volume injection technique compared with use of a 2-μL splitless injection [161]. Large-volume injection has also been used for the determination of PAHs by dual column GC [157]. Large-volume injection techniques will probably become more prevalent in environmental analysis now that commercial injectors are available in a variety of configurations (PTV, cool on-column) [154, 156, 158]. Večeřa et al. [156] constructed a large-volume injection system from common materials found in a GC laboratory; a wide-bore retention gap was placed between an on-column injector and the analytical column to enable injection of up to 80 μL [156]. Use of large-volume injection as an interface for coupling GC with other separation techniques (e.g. LC) or with sample-preparation methods (e.g. extraction) has been recently reviewed by Teske and Engewald [155].

Thermal desorption techniques with GC

Thermal desorption is a powerful technique that eliminates the need for sample extraction. Sample processing is accelerated, and potential contamination from solvents is eliminated. Initial studies of adsorption/thermal desorption have been directed toward the analysis of organic contaminants in environmental samples and volatile organic compounds in air [101]. In the early 1980s the sorbent Tenax was used for direct sampling and analysis of water for sample volumes up to several liters, and recoveries near 100% were obtained for a variety of phenols, monocyclic aromatic compounds, and selected PAHs, pesticides, phthalates, and alkanes [162, 163]. This technique was later applied to air sampling, and gaseous organic contaminants were directly sampled and analyzed by thermal-desorption GC/MS [164]. The use of adsorption/thermal desorption for PAHs is not reported extensively in the literature as a routine approach. Instead, the focus in recent years has been more on direct sample introduction via thermal desorption [123, 165–168]. In this approach, solid or liquid samples are introduced into the GC inlet with no extensive modification of the inlet. The sample is usually stored in a sample holder that is inserted into the GC inlet. The compounds are thermally desorbed directly in the liner and focused onto a cool GC column for separation and detection, usually by MS [166]. Several air particulate SRMs have been used to study the effectiveness of the desorption process [101, 166, 167]. Thermal desorption has also been coupled to GC–TOF-MS (see above) for the determination of PAHs in fly ash [121, 122] and air

particulate matter [123, 124]. Direct thermal desorption of samples via Curie point pyrolysis coupled to GC/MS has been demonstrated for determination of PAHs in soil [169], and this pyrolysis technique has been directly compared with thermal desorption GC/MS for the determination of PAHs in river sediments [170]. EPA Method 8275 [26] makes use of thermal extraction–GC/MS (Table 1).

Thermal desorption coupled with stir-bar sorptive extraction is gaining popularity. Stir-bar sorptive extraction is an extraction technique similar to SPME but larger in scale than the fibers in SPME (SPME is reviewed in this issue by Ouyang and Pawliszyn [60]) and is based on the solid phase polydimethylsiloxane. Stir-bar sorptive extraction is relatively novel, and is often used for the determination of PAHs in water (reviewed by Rawa-Adkonis et al. [171]). This extraction technique may be coupled with thermal desorption GC. The theory and practice of this technique for a wide range of organic contaminants in aqueous samples, including PAHs, has been described [172]. A recent paper describes the optimization of this method coupled with GC/MS for 35 semi-volatile organic contaminants, including PAHs, in water [173]. Method sensitivity, linearity, repeatability and reproducibility, accuracy, matrix effects, and overall uncertainty have been studied by the same group, using ISO guidelines, for validation of the method, and the accuracy of the method was also evaluated by participation in a proficiency interlaboratory test with ground, tap, and surface-water samples [174]. This method has also been applied to the analysis of seawater for the determination of PAHs [175]. Other extraction techniques coupled on-line with GC include supercritical-fluid extraction (SFE), liquid–liquid extraction, and membrane-based techniques. These approaches have recently been reviewed in several articles on coupled extraction–GC techniques [176–181].

Fast GC

Fast GC is designed to minimize analysis time without compromising chromatographic resolution; it is usually accomplished by reducing the characteristic diameter of the GC column. A major advantage of this technique is that peak width is small so the signal-to-noise ratio is larger. A disadvantage is that the stationary phase may be substantially overloaded if analytes are highly concentrated. The concepts of fast GC with packed and capillary columns has been reviewed by Cramers et al. [182]. In addition to reduced column diameter, nearly all fast GC instruments utilize short columns. A recent review by Snow [183] describes the practical implications of the use of short columns on fast GC method development, optimization, and resolution. Short, microbore columns have been shown to work well for separation of the priority pollutant PAHs [184]. Microbore (0.1 mm i.d.) columns are much more efficient than conventional 0.25 mm i.d. columns; this enables separations to be performed on shorter columns (10–20 m) and with faster analysis times [184]. Analysis times for PAHs on 20 m and 10 m columns coated with 5% phenyl methylpolysiloxane have been reduced by approximately 45% and 60%, respectively, compared with 30 m columns, with no compromise on data quality (precision and accuracy), although smaller injection volumes (0.2 μL to 0.5 μL) and injection liners (1 mm to 2 mm) were necessary to achieve optimum, reproducible chromatography [184].

The main limitation of fast GC is the speed of detector response. Fast GC is therefore limited mainly to GC–FID, GC–ECD, and GC–TOF-MS. An ion-trap MS GC method (LPGC–ITMS, see above) that is considered “fast” has also been reported; 16 PAHs are separated in approximately 13 min [113, 114]. However, much shorter analysis times are possible. Up to 16 PAHs have been shown to elute from 1 m and 5 m 5% phenyl methylpolysiloxane columns in approximately 3 min with fast oven-temperature programming and GC–FID [185]. While pairs of peaks were not completely resolved, chromatography coupled to MS in the selected-ion-monitoring mode enabled spectrometric resolution of the isomers if enough points per peak were acquired. The best resolution is, in fact, obtained by combining fast GC with either selective sampling techniques or selective detectors [182, 183]. The use of MS is often necessary for positive identification of solutes. This is particularly important in ultra-fast GC, in which very-high-speed temperature or pressure programming is used, because this results in reduced reproducibility of retention data [182]. In addition, because peak widths decrease substantially with increasing analysis speed, TOF-MS or spatial-array detection may be necessary to complete fast scans over large mass ranges [182].

Fast GC/MS has recently been reviewed [186], and five main approaches to the technique were discussed:

1. short, microbore capillary GC columns;
2. fast temperature programming;
3. low-pressure GC/MS;
4. use of a supersonic molecular beam for MS at high GC carrier gas flow; and
5. pressure-tunable GC×GC.

Topic 4, supersonic GC/MS, has been reviewed by Fialkov et al., and the use of this approach for rapid elution of pyrene and higher-molecular-mass PAHs has been described [79]. Fast GC/MS coupled with on-line thermal desorption has been used by Münchmeyer et al. for analysis of particle-associated PAHs formed in combustion processes [187]. This group designed a unique system that made use of a dilution method and filter tape sampling for the collection of particles in combustion effluents. Results were

obtained in minutes at the ppb level for particle-associated PAHs. The analytical system was tested at oil combustion plants, coke ovens, and with diesel engine emissions [187]. A membrane inlet system was used for the MS [187]. In this technique, which is applied mainly to the analysis of VOCs [56], organic compounds are separated from water or air by a thin membrane (typically polydimethylsiloxane) installed between the sample and the ion source of a mass spectrometer. Organic compounds dissolve in and diffuse through the membrane then flow, via evaporation, into the ion source. Ketola et al. have written comprehensive review of environmental applications of membrane-introduction MS [188]. An advantage of membrane-inlet MS is that the method is fast, because the separation step is eliminated. However, its use for the determination of PAHs has not been widely reported.

As manufacturers respond to the need of the analytical community to reduce analysis times, techniques such as fast GC and membrane-introduction MS will probably become more prevalent in the PAH literature. The development of computer programs to predict temperature and pressure programs to enhance fast GC results will also foster growth in this area [51].

LC–GC approaches

Coupled liquid chromatography–gas chromatography (LC–GC) is a powerful technique that combines the best features of both techniques and is ideal for analysis of complex samples [179, 189, 190]. When using LC–GC, the whole sample is typically injected into the liquid chromatograph and subsequently analyzed by GC. In this way, several milliliters of eluent are introduced into the GC, affording excellent sensitivity and low detection limits. LC–GC methods have been reported for analysis of PAHs in atmospheric particles. Shimmo et al. have reviewed the use of LC–GC/MS coupled with on-line SFE as the extraction technique [191, 192]. Christensen et al. have reported an LC–GC/MS method for determination of PAHs in particulate matter from ambient air and diesel exhaust emissions with a limit of detection of approximately 1 pg per sample for individual compounds [193]. The method was examined using SRMs 1649a Urban Dust and 2975 Diesel Particulate Matter (Industrial Forklift). More recently, an LC–GC/MS method has been described for determination of dibenzopyrenes in diesel and air particulate materials; air and diesel particulate matter SRMs were used as control materials [194].

Concluding remarks

Interest in the determination of PAHs in environmental samples is motivated by their biological activity and the possible adverse health effects of this class of compounds. The oil and gas industries are also interested in the determination of PAHs, as also the space research community for analysis of meteorites and planetary materials. Gas chromatographic techniques have enabled researchers to measure and monitor PAHs in environmental, biological, and food-related samples. The development of new or enhanced GC techniques, for example GC–TOF-MS, has afforded scientists the opportunity to meet the ever increasing demands for the determination of PAHs with greater sensitivity, selectivity, and speed. As environmental forensic applications increase, sophisticated GC techniques, for example GC–IRMS, will probably be reported more often for the determination of the stable isotope ratios of individual PAHs in environmental matrices. Enhancements to GC for determination of PAHs can also be expected to be a continuing topic of research, with the objective of meeting the evolutionary measurement and monitoring needs associated with this class of compound in relation to ecological and human health effects.

Disclaimer Commercial equipment, instruments, or materials are identified in this paper to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

References

1. Harvey RG (1997) Polycyclic aromatic hydrocarbons, 1st edn. Wiley–VCH, New York
2. Howsam M, Jones KC (1998) Sources of PAHs in the environment. In: Neilson AH (ed) The handbook of environmental chemistry, vol 3.1: PAHs and related compounds—chemistry. Springer, Berlin Heidelberg New York, pp 137–174
3. Lima ALC, Farrington JW, Reddy CM (2005) Environ Forensics 6:109–131
4. US Department of Health and Human Services (1995) Toxicological profile for polycyclic aromatic hydrocarbons, agency for toxic substances and disease registry. US Department of Health and Human Services, Atlanta, GA, http://www.atsdr.cdc.gov/toxprofiles/tp69.pdf Cited 7-28-0006
5. Simoneit BRT (1998) In: Neilson AH (ed) The handbook of environmental chemistry, vol 3.1: PAHs and related compounds—chemistry. Springer, Berlin Heidelberg New York, pp 175–221
6. Lemieux PM, Lutes CC, Santoianni DA (2004) Prog Energy Combust 30:1–32
7. Wilcke W (2000) J Plant Nutr Soil Sci 163:229–248
8. Zolotov MY, Shock EL (2000) J Geophys Res—Solid Earth 105:539–559
9. Yamanaka T, Mizota C, Murae T, Hashimoto J (1999) Geochem J 33:355–367
10. Neilson AH (1998) PAHs and related compounds—biology. Springer, Berlin Heidelberg New York
11. de Boer J, Law RJ (2003) J Chromatogr A 1000:223–251
12. Roose P, Brinkman UAT (2005) Trends Anal Chem 24:897–926
13. Herod AA (1998) In: Neilson AH (ed) The handbook of environmental chemistry, vol 3.1: PAHs and related com-

pounds—chemistry. Springer, Berlin Heidelberg New York, pp 271–323
14. Andersson JT (2001) In: Kleiböhmer W (ed) Environmental analysis. handbook of analytical separations. Elsevier Science, Amsterdam, The Netherlands, pp 75–98
15. Leotz-Gartziandia E, Tatry V, Carlier P (2000) Polycycl Aromat Compd 20:245–258
16. Zielinska B, Sagebiel J, McDonald JD, Whitney K, Lawson DR (2004) J Air Waste Manage 54:1138–1150
17. Fetzer JC (1989) In: Vo-Dinh T (ed) Chemical analysis of polycyclic aromatic compounds. Chemical analysis. Wiley, New York, pp 59–109
18. Poster DL, Sander LC, Wise SA (1998) In: Hutzinger O (ed) The handbook of environmental chemistry, vol 3 Part I, PAHs and related compounds. Springer, Berlin Heidelberg New York, pp 77–135
19. Lee HK (2001) In: Kleiböhmer W (ed) Environmental analysis. handbook of analytical separations. Elsevier Science, Amsterdam, The Netherlands, pp 39–74
20. US Environmental Protection Agency (1990) Methods for the determination of organic compounds in drinking water supplement I, EPA/600/4-90/020, National Technical Information Service, PB91-146027, Washington D.C., http://www.epa.gov/safewater/methods/methods.html Cited 7-28-0006
21. US Environmental Protection Agency (1995) Methods for the determination of organic compounds in drinking water-supplement III, EPA/600/R-95-131, National Technical Information Service, PB95-261616, Washington D.C., http://www.epa.gov/safewater/methods/methods.html Cited 7-28-0006
22. US Environmental Protection Agency (1982) Determination of polynuclear aromatic hydrocarbons in industrial and municipal wastewaters, EPA 600/4-82-025, National Technical Information Service, PB82-258799, Springfield, VA, http://www.ntis.gov Cited 7-28-0006
23. US Environmental Protection Agency (2005) Method 610-polynuclear aromatic hydrocarbons, PART 136 guidelines establishing test procedures for the analysis of pollutants; appendix A: methods for organic chemical analysis of municipal and industrial wastewater, 40CFR136.1, US Environmental Protection Agency, Washington D.C., http://www.epa.gov/waterscience/methods/guide/610.pdf Cited 7-28-0006
24. US Environmental Protection Agency (2005) Method 625-base/neutrals and acids, PART 136 guidelines establishing test procedures for the analysis of pollutants; appendix A: methods for organic chemical analysis of municipal and industrial wastewater, 40CFR136.1, US Environmental Protection Agency, Washington D.C., http://www.epa.gov/waterscience/methods/guide/610.pdf Cited 7-28-0005
25. US Environmental Protection Agency (2005) Method 1625 revision B - semivolatile organic compounds by isotope dilution GC–MS, PART 136 guidelines establishing test procedures for the analysis of pollutants; appendix A: methods for organic chemical analysis of municipal and industrial wastewater, 40CFR136.1, US Environmental Protection Agency, Washington D.C., http://www.epa.gov/waterscience/methods/guide/1625.pdf Cited 7-28-0006
26. US Environmental Protection Agency (1980) Test methods for evaluating solid waste, physical/chemical methods, SW-846, US Environmental Protection Agency, Washington D.C., http://www.epa.gov/epaoswer/hazwaste/test/main.htm Cited 7-28-2006
27. US Environmental Protection Agency (1999) Compendium method TO-13A: determination of polycyclic aromatic hydrocarbons (PAHs) in ambient air using gas chromatography/mass spectrometry (GC–MS), compendium of methods for the determination of toxic organic compounds in ambient air, second edition, EPA/625/R-96/010b, US Environmental Protection Agency, Cincinnati, OH, http://www.epa.gov/ttn/amtic/airtox.html Cited 7-28-0006
28. US Environmental Protection Agency (1993) Methods for sampling and analyzing contaminants in fish and shellfish tissue, guidance for assessing chemical contaminant data for use in fish advisories. volume 1: fish Sampling and analysis - third edition, EPA 823-B-00-007, US Environmental Protection Agency, Office of Water, Washington, D.C., http://www.epa.gov/waterscience/fishadvice/volume1/index.html Cited 7-28-0006
29. National Ocean Service (1998) Sampling and analytical methods of the national status and trends program mussel watch project: 1993-1996 Update, NOS ORCA 130, National Ocean and Atmospheric Administration, Coastal Monitoring and Bioeffects Assessment Division, Office of Ocean Resources Conservation and Assessment, National Ocean Service, Silver Spring, MD, http://www.ccma.nos.noaa.gov/publications/tm130.pdf Cited 7-28-0006
30. National Ocean and Atmospheric Administration (1993) Sampling and analytical methods of the national status and trends program national benthic surveillance and mussel watch projects 1984–1992. Volume IV. Comprehensive descriptions of trace organic analytical methods., NOS ORCA 71, National Ocean and Atmospheric Administration, Silver Spring, MD, http://www.ccma.nos.noaa.gov/publications/tm71v4.pdf Cited 7-28-0006
31. European Commission (2001) Ambient air pollution by polycyclic aromatic hydrocarbons (PAH). Position Paper, Prepared by the European Commission Working Group on Polycyclic Aromatic Hydrocarbons, Office of Official Publications of the European Communities, Luxembourg, http://europa.eu.int/comm/environment/air/pdf/pp_pah.pdf; http://ec.europa.eu/environment/air/pdf/annex_pah.pdf Cited 7-28-0006
32. World Health Organization (1998) Selected non-heterocyclic polycyclic aromatic hydrocarbons, environmental health criteria, 202, United Nations Environment Programme, International Labour Organisation, World Health Organization, Geneva, http://www.inchem.org/documents/ehc/ehc/ehc202.htm Cited 7-28-0006
33. Siemiatycki J, Richardson L, Straif K, Latreille B, Lakhani R, Campbell S, Rousseau M, Boffetta P (2004) Environ Health Perspect 112:1447–1459
34. Wenborn MJ, Coleman PJ, Passant NR, Lymberidi E, Sully J, and Weir RA (1999) Speciated PAH inventory for the UK, AEAT-3512/REMC/20459131/Issue 1, AEA Technology Environment, UK Department of the Environment, Transport, and the Regions, United Kingdom, http://www.airquality.co.uk/archive/reports/cat08/0512011419_REPFIN_all_nov.pdf Cited 7-28-0006
35. Field RA, Perez Ballesta P, Baeza Caracena A, Nikolova I, Connolly R, Cao N, Gerboles M, Buzica D, Amantini L, Lagler F, Borowiak A, Marelli L, De Santi G, De Seager E (2005) Population exposure to air pollutants in Europe, methodological strategy and basic results, EUR 21810, European Commission, Joint Research Centre, Institute for Environment and Sustainability, Ispra, Italy, http://ies.jrc.cec.eu.int/fileadmin/Documentation/Reports/Emissions_and_Health/EUR/PEOPLE-_final_report.pdf Cited 7-26-0006
36. Menichini E, Belladonna V, Bergoglio F, Gabrieli C, Ceccanti M, Rossi I, Cellini L, Corradetti E, Grechi D, Tricarico V, Rosa M, Zemello C, Spiazzi A, Stella A, Valerio F, Trevisani GR, Villalta R (2006) Polycycl Aromat Compd 26:79–92
37. US Environmental Protection Agency (1997) The Great Lakes Binational Toxics Strategy, US Environmental Protection Agency, http://www.epa.gov/glnpo/p2/bnsintro.html Cited 7-28-0006
38. US Environmental Protection Agency (2005) The Great Lakes Binational Toxics Strategy. Assessment of Level 1 Substances,

US Environmental Protection Agency, Washington D.C., http://www.epa.gov/glnpo/bns/level1/index.html Cited 7-28-0006
39. US Environmental Protection Agency (1999) The Great Lakes Binational Toxics Strategy. Draft Report on Level 2 Substances in the Binational Toxics Strategy, US Environmental Protection Agency, Washington D.C., http://www.epa.gov/glnpo/bns/levelii/leviisubsus.html Cited 7-28-0006
40. Wise SA, Poster DL, Kucklick JR, Keller JM, Vander Pol SS, Sander LC, Schantz MM (2006) Anal Bioanal Chem, this issue
41. Wise SA, Hilpert LR, Byrd GD, May WE (1990) Polycycl Aromat Compd 1:81–98
42. Poster DL, Benner BA Jr, Schantz MM, Sander LC, Vangel MG, Wise SA (2003) Polycycl Aromat Compd 23:113–139
43. Poster DL, Lopez de Alda MJ, Schantz MM, Sander LC, Vangel MG, Wise SA (2003) Polycycl Aromat Compd 23:141–191
44. Poster DL, Kucklick JR, Lopez de Alda MJ, Porter BJ, Pugh RS, Schantz MM, Wise SA (2004) Anal Bioanal Chem 378: 1213–1231
45. Wise SA, Poster DL, Schantz MM, Kucklick JR, Sander LC, Lopez de Alda MJ, Schubert P, Parris RM, Porter BJ (2004) Anal Bioanal Chem 378:1251–1264
46. Piñeiro-Iglesias M, Grueiro-Noche G, López-Mahía P, Muniategui-Lorenzo S, Prada-Rodríguez D (2004) Sci Total Environ 334–335:377–384
47. Wise SA, Chesler SN, Hertz HS, Hilpert LR, May WE (1977) Anal Chem 49:2306–2310
48. Wise SA, Sander LC, May WE (1993) J Chromatogr 642:329–349
49. Wise SA, Benner BA Jr, Liu H, Byrd GD, Colmsjö A (1988) Anal Chem 60:630–637
50. Wise SA, Deissler A, Sander LC (1993) Polycycl Aromat Compd 3:169–184
51. Jennings W, Mittlefehldt E, Stremple P (1997) Analytical gas chromatography, 2nd edn. Academic Press, San Diego
52. Onuska FI, Karasek FW (1984) Open tubular column gas chromatography in environmental sciences. Plenum Press, New York
53. (2006) ASTM standard practice for packed column gas chromatography, E 260–96, ASTM International, West Conshohocken, PA, http://www.astm.org Cited 7-26-0006
54. (2005) ASTM standard practice for installing fused silica open tubular capillary columns in gas chromatographs, E 1510-95, ASTM International, West Conshohocken, PA, http://www.astm.org Cited 7-26-0006
55. Santos FJ, Galceran MT (2002) Trends Anal Chem 21:672–685
56. Huybrechts T, Dewulf J, Van Langenhove H (2003) J Chromatogr A 1000:283–297
57. Biziuk M (2001) Anal Lett 34:1517–1528
58. Wang D (2006) Anal Bioanal Chem, this issue
59. Gorecki T (2006) Anal Bioanal Chem, this issue
60. Ouyang GL, Pawliszyn J (2006) Anal Bioanal Chem, this issue
61. Budzinski H (2006) Anal Bioanal Chem, this issue
62. Zielinska B (2006) Anal Bioanal Chem, this issue
63. Andersson JT, Hegazi AH, Roberz B (2006) Anal Bioanal Chem, this issue
64. 50 years of gas chromatography (2002) In: Brinkman UAT, Janssen HG (eds) Trends Anal Chem 21:545–708
65. Berezkin VG, Viktorova EN (2003) J Chromatogr A 985:3–10
66. Trevelin WR, Vidal LH, Landgraf MD, Silva ICE, Rezende MOO (1992) Anal Chim Acta 268:67–71
67. Brindle ID, Li XF (1990) J Chromatogr 498:11–24
68. DeVeaux RD, Szelewski M (1989) J Chromatogr Sci 27:513–518
69. Grob K, Grob K Jr (1974) J Chromatogr 94:53–64
70. Grob K, Grob G (1969) J Chromatogr Sci 7:584–586
71. Wise SA, Sander LC, Chang H, Markides KE, Lee ML (1988) Chromatographia 25:473–480
72. Sander LC, Schneider M, Woolley C, Wise SA (1994) J Microcolumn Sep 6:115–125
73. Wise SA, Benner BA Jr, Lopez de Alda MJ, Porter BJ, Poster DL, Sander LC, Schantz MM (2000) Polycycl Aromat Compd 19:297–313
74. Wise SA, Schantz MM, Poster DL, Lopez de Alda MJ, Sander LC (2000) In: Barceló D (ed) Sample handling and trace analysis of pollutants: techniques, applications and quality assurance. Elsevier Science, Amsterdam, The Netherlands, pp 649–687
75. Wise SA (2002) Polycycl Aromat Compd 22:197–230
76. Wise SA, Schantz MM, Benner BA Jr, Hays MJ, Schiller SB (1995) Anal Chem 67:1171–1178
77. Naikwadi KP, Wadgaonkar PP (1998) J Chromatogr A 811:97–103
78. Schubert P, Schantz MM, Sander LC, Wise SA (2003) Anal Chem 75:234–246
79. Fialkov AB, Gordin A, Amirav A (2003) J Chromatogr A 991:217–240
80. Fu R, Jing P, Gu J, Huang Z, Chen Y (1993) Anal Chem 65:2141–2144
81. Lee WS, Chang-Chien GP (1998) Anal Chem 70:4094–4099
82. Liu CY, Hu CC, Yang CL (1997) J Chromatogr A 773:199–208
83. Saito Y, Tahara A, Imaizumi M, Takeichi T, Wada H, Jinno K (2003) Anal Chem 75:5525–5531
84. Popl M, Dolansky V, Mostecky J (1976) J Chromatogr 117:117–127
85. Kovats E (1958) Helv Chim Acta 41:1915–1932
86. Lee ML, Vassilaros DL, White CM, Novotny M (1979) Anal Chem 51:768–774
87. Andersson JT, Weis U (1994) J Chromatogr A 659:151–161
88. Escrivá C, Viana E, Moltó JC, Picó Y, Mañes J (1994) J Chromatogr A 676:375–388
89. Radecki A, Lamparczyk H, Kaliszan R (1979) Chromatographia 12:595–599
90. Wise SA, Bonnett WJ, Guenther FR, May WE (1981) J Chromatogr Sci 19:457–465
91. Sauvain JJ, Vu Duc T (2004) J Sep Sci 27:78–88
92. Saura-Calixto F, Garcia-Raso A (1984) Int J Environ Anal Chem 17:279–292
93. Bemgård A, Colmsjö A, Wrangskog K (1994) Anal Chem 66:4288–4294
94. Elizalde-Gonzalez MP, Hutfliess M, Hedden K (1996) J High Resolut Chromatogr 19:345–352
95. Kang JJ, Cao CZ, Li ZL (1998) J Chromatogr A 799:361–367
96. Engkvist O, Borowski P, Bemgård A, Karlström G, Lindh R, Colmsjö A (1996) J Chem Inf Comput Sci 36:1153–1161
97. Lung SCC, Wu MJ, Lin CC (2004) J Expos Anal Environ Epidemiol 14:529–535
98. Bagheri H, Mohammadi A (2003) J Chromatogr A 1015:23–30
99. Hyötyläinen T, Oikari A (1999) Sci Total Environ 244:97–105
100. Jaouen-Madoulet A, Abarnou A, Le AM (1996) J Chromatogr A 886:153–173
101. Aragón P, Atienza J, Climent MD (2000) Crit Rev Anal Chem 30:121–151
102. Russell M, Webster L, Walsham P, Packer G, Dalgarno EJ, McIntosh AD, Moffat CF (2005) Marine Pollut Bull 50:638–651
103. Meniconi MDG, Gabardo IT, Carneiro MER, Barbanti SM, da Silva GC, Massone CG (2002) Environ Forensics 3:303–321
104. Baumard P, Budzinski H (1997) Analusis 25:246–252
105. Santos FJ, Galceran MT (2003) J Chromatogr A 1000:125–151
106. Hilpert LR (1987) Biomed Environ Mass Spectrom 14:383–394
107. Riahi K, Sellier N (1998) Chromatographia 47:309–312
108. Yurchenko S, Mölder U (2005) J Food Compos Anal 18:857–869
109. Castello G, Gerbino TC (1993) J Chromatogr 642:351–357
110. Filipkowska A, Lubecki L, Kowalewska G (2005) Anal Chim Acta 547:243–254

111. Kucklick JR, Sivertsen SK, Sanders M, Scott GI (1997) J Exp Mar Biol Ecol 213:13–29
112. Helaleh MIH, Al Omair A, Nisar A, Gevao B (2005) J Chromatogr A 1083:153–160
113. Godoi AFL, Ravindra K, Godoi RHM, Andrade SJ, Santiago-Silva M, Van Vaeck L, van Grieken R (2004) J Chromatogr A 1027:49–53
114. Ravindra K, Godoi AF, Bencs L, van Grieken R (2006) J Chromatogr A 1114:278–281
115. Joos PE, Godoi AFL, De Jong R, De Zeeuw J, van Grieken R (2003) J Chromatogr A 985:191–196
116. Mosi AA, Cullen WR, Eigendorf GK (1997) J Mass Spectrom 32:864–874
117. Pyle SM, Betowski LD, Marcus AB, Winnik W, Brittain RD (1997) J Am Soc Mass Spectrom 8:183–190
118. Koester CJ (2005) Anal Chem 77:3737–3754
119. Ferrer I, Thurman EM (2003) Trends Anal Chem 22:750–756
120. Vreuls RJJ, Dallüge J, Brinkman UAT (1999) J Microcolumn Sep 11:663–675
121. Zou DZ, Liu KL, Pan WP, Riley JT, Xu YQ (2003) J Chromatogr Sci 41:245–250
122. Liu KL, Heltsley R, Zou DH, Pan WP, Riley JT (2002) Energy Fuel 16:330–337
123. Schnelle-Kreis J, Sklorz M, Peters A, Cyrys J, Zimmermann R (2005) Atmos Environ 39:7702–7714
124. Schnelle-Kreis J, Welthagen W, Sklorz M, Zimmermann R (2005) J Sep Sci 28:1648–1657
125. Marriott PJ, Haglund P, Ong RCY (2003) Clin Chim Acta 328:1–19
126. Dallüge J, Beens J, Brinkman UAT (2003) J Chromatogr A 1000:69–108
127. (2003) Papers from the First International Symposium of Comprehensive Multidimensional Gas Chromatography, Volendam, The Netherlands. J Chromatogr A 1019
128. von Mühlen C, Zina CA, Caramão EB, Marriott PJ (2006) J Chromatogr A 1105:39–50
129. O'Malley VP, Abrajano TA, Hellou J (1996) Environ Sci Technol 30:634–639
130. O'Malley VP, Abrajano TA, Hellou J (1994) Org Geochem 21:809–822
131. O'Malley VP, Stark A, Abrajano TA, Hellou J, Winsor L (1996) Polycycl Aromat Compd 9:93–100
132. McRae C, Sun CG, McMillan CF, Snape CE, Fallick AE (2000) Polycycl Aromat Compd 20:97–109
133. Stark A, Abrajano T, Hellou J, Metcalf-Smith JL (2003) Org Geochem 34:225–237
134. Kim M, Kennicutt MCI, Qian Y (2005) Environ Sci Technol 39:6770–6776
135. Schmidt TC, Zwank L, Elsner M, Berg M, Meckenstock RU, Haderlein SB (2004) Anal Bioanal Chem 378:283–300
136. McRae C, Snape CE, Fallick AE (1998) Analyst 123:1519–1523
137. Saber DL, Mauro D, Sirivedhin T (2005) J Ind Microbiol Biotech 32:665–668
138. Smith RM (2003) J Chromatogr A 1000:3–27
139. Schantz MM, Nichols JJ, Wise SA (1997) Anal Chem 69:4210–4219
140. Schantz MM (2006) Anal Bioanal Chem, this issue
141. Seidel A, Frank H, Behnke A, Schneider D, Jacob J (2004) Polycycl Aromat Compd 24:759–771
142. Schantz MM, Brown Thomas JM, Poster DL, Sander LC, Wise SA (2006) Am Lab (in press)
143. Poster DL, Lopez de Alda MJ, Wise SA, Chuang JC, Mumford JL (2000) Polycycl Aromat Compd 20:79–95
144. Diletti G, Scortichini G, Scarpone R, Gatti G, Torreti L, Migliorati G (2005) J Chromatogr A 1062:247–254
145. Andersson JT, Weis U (1994) J Chromatogr A 659:151–161
146. Poster DL, Schantz MM, Stapleton HM, Wise SA, Johansen JE (2005) Determination of PAHs and selected methyl-PAHs in environmental standard reference materials using fluorinated PAHs as internal standards. Proceedings of Dioxin 2005/ISPAC 20, Toronto, ON, August 2005
147. Boden AR, Reiner EJ (2004) Polycycl Aromat Compd 24: 309–323
148. Smith CJ, Walcott CJ, Huang WL, Maggio V, Grainger J, Patterson DG (2002) J Chromatogr B 778:157–164
149. Schantz MM, Wise SA, Lewtas J (2005) Intercomparison program for organic speciation in PM2.5 air particulate matter: description and results for trials I and II, NISTIR 7229. National Institute of Standards and Technology, Gaithersburg, MD
150. May W, Parris R, Beck C, Fassett J, Greenberg R, Guenther F, Kramer G, Wise S, Gills T, Colbert J, Gettings R, MacDonald B (2000) Definitions of terms and modes used at NIST for value-assignment of reference materials for chemical measurements, NIST Special Publication 260–136. US Government Printing Office, Gaithersburg, MD, http://www.cstl.nist.gov/nist839/NIST_special_publications.htm Cited 7-28-0006
151. Zeisler R (2006) Anal Bioanal Chem, this issue
152. Ulberth F (2006) Anal Bioanal Chem, this issue
153. Staniewski J, Janssen HG, Cramers CA, Rijks JA (1992) J Microcolumn Sep 4:331–338
154. Mol HGJ, Althuizen M, Janssen HG, Cramers CA, Brinkman UAT (1996) J High Resolut Chromatogr 19:69–79
155. Teske J, Engewald W (2002) Trends Anal Chem 21:584–593
156. Večeřa Z, Bartošíková A, Sklenskã J, Mikuška P (2005) Chromatographia 61:197–200
157. Cavagnino D, Magni P, Zilioli G, Trestianu S (2003) J Chromatogr A 1019:211–220
158. Norlock FM, Jang JK, Zou QM, Schoonover TM, Li A (2002) J Air Waste Manage 52:19–26
159. Ramos L, Vreuls JJ, Brinkman UAT (2000) J Chromatogr A 891:275–286
160. Slobodník J, Ramalho S, van Baar BLM, Louter AJH, Brinkman UAT (2000) Chemosphere 41:1469–1478
161. Yusà V, Quintas G, Pardo O, Pastor A, de la Guardia M (2006) Talanta 69:807–815
162. Pankow JF, Isabelle LM, Asher WE (1984) Environ Sci Technol 18:310–318
163. Pankow JF, Ligocki MP, Rosen ME, Isabelle LM, Hart KM (1988) Anal Chem 60:40–47
164. Hart KM, Isabelle LM, Pankow JF (1992) Environ Sci Technol 26:1048–1052
165. Hays MD, Smith ND, Kinsey J, Dong Y, Kariher P (2003) J Aerosol Sci 34:1061–1084
166. Falkovich AH, Rudich Y (2001) Environ Sci Technol 35:2326–2333
167. Waterman D, Horsfield B, Leistner F, Hall K, Smith S (2000) Anal Chem 72:3563–3567
168. Ho SSH, Yu JZ (2004) J Chromatogr A 1059:121–129
169. Buco S, Moragues M, Doumenq P, Noor A, Mille G (2004) J Chromatogr A 1026:223–229
170. Faure P, Landais P (2001) J Anal Appl Pyrolysis 57:187–202
171. Rawa-Adkonis M, Wolska L, Namiesnik J (2006) Crit Rev Anal Chem 36:63–72
172. Baltussen E, Sandra P, David F, Cramers C (1999) J Microcolumn Sep 11:737–747
173. León VM, Llorca-Pórcel J, Álvarez B, Cobollo MA, Muñoz S, Valor I (2003) J Chromatogr A 999:91–101
174. León VM, Llorca-Pórcel J, Álvarez B, Cobollo MA, Muñoz S, Valor I (2006) Anal Chim Acta 558:261–266
175. Roy G, Vuillemin R, Guyomarch J (2005) Talanta 66:540–546

176. Goosens EC, De Jong D, De Jong GJ, Brinkman UAT (1998) Chromatographia 47:313–345
177. Lopez-Avila V (1999) Crit Rev Anal Chem 29:195–230
178. Barman BN, Cebolla VL, Membrado L (2000) Crit Rev Anal Chem 30:75–120
179. Hyötyläinen T, Riekkola ML (2004) Anal Bioanal Chem 378:1962–1981
180. Ramos L, Ramos JJ, Brinkman UAT (2005) Anal Bioanal Chem 381:119–140
181. Richardson SD (2000) Anal Chem 72:4477–4496
182. Cramers CA, Janssen HG, van Deursen MM, Leclercq PA (1999) J Chromatogr A 856:315–329
183. Snow NH (2004) J Liq Chromatogr Relat Technol 27:1317–1330
184. Boden AR, Ladwig GE, Reiner EJ (2002) Polycycl Aromat Compd 22:301–310
185. Reed GL, Clark-Baker K, McNair HM (1999) J Chromatogr Sci 37:300–305
186. Mastovska K, Lehotay SJ (2003) J Chromatogr A 1000:153–180
187. Münchmeyer W, Walte A, Matz G (1996) Polycycl Aromat Compd 9:299–306
188. Ketola RA, Kotiaho T, Cisper ME, Allen TM (2002) J Mass Spectrom 37:457–476
189. Hyötyläinen T, Riekkola ML (2004) Anal Bioanal Chem 378:1936–1938
190. Hyötyläinen T, Riekkola ML (2003) J Chromatogr A 1000:357–384
191. Shimmo M, Anttila P, Hartonen K, Hyötyläinen T, Paatero J, Kulmala M, Riekkola ML (2004) J Chromatogr A 1022: 151–159
192. Shimmo M, Jantti J, Aalto P, Hartonen K, Hyötyläinen T, Kulmala M, Riekkola ML (2004) Anal Bioanal Chem 378:1982–1990
193. Christensen A, Östman C, Westerholm R (2005) Anal Bioanal Chem 381:1206–1216
194. Bergvall C, Westerholm R (2006) Anal Bioanal Chem 384:438–447
195. Muir GD (ed) (1977) Hazards in the chemical laboratory, 2nd edn. The Chemical Society, London