

Assaying particle-bound polycyclic aromatic hydrocarbons from archived PM_{2.5} filters

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Abstract

Airborne particulate matter contains numerous organic species, including several polycyclic aromatic hydrocarbons (PAHs) that are known or suspected carcinogens. Existing methods for measuring airborne PAHs are complex and costly, primarily because they are designed to collect both gas-phase and particle-phase PAH constituents. Here, we report an assay for measuring particle-bound PAHs in archived filters from the network of U.S. monitoring stations for particles less than 2.5 μm in diameter (PM_{2.5}), without the need for deploying specialized samplers. PAHs are extracted from Teflon filters with dichloromethane, concentrated, and measured at trace levels using gas chromatography–mass spectrometry. Although PAHs with 3–6 aromatic rings can be assayed, results are only unambiguously accurate for compounds with 5- or 6-rings, due to variable vaporization losses of the more volatile 3- and 4-ring compounds during sampling and/or storage. The method was evaluated for sensitivity, recovery, precision, and agreement of paired air samples, using PM_{2.5} samplers locally in Chapel Hill, NC. Additionally, three sets of archived samples were analyzed from a study of PM_{2.5} in the Czech Republic. Levels of some 4-ring and all 5- and 6-ring PAHs in both the local and Czech samples were consistent with published results from investigations employing PAH-specific air samplers. This work strongly suggests that assessment of particle-bound 5- and 6-ring PAHs from archived PM_{2.5} filters is quantitatively robust. The assay may also be useful for selected 4-ring compounds, notably chrysene and benzo(a)anthracene, if PM_{2.5} filters are stored under refrigeration.

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1. Introduction

Increased risks of mortality and morbidity have been associated with levels of particulate matter (PM) in ambient air, especially for fine particles with aerodynamic diameters up to 2.5 μm (PM_{2.5}) [1–5]. The strength and consistency of these associations across studies has motivated the U.S. Environmental Protection Agency to promulgate National Ambient Air Quality Standards for PM_{2.5} and to establish an air monitoring network for PM_{2.5} at more than 1000 sites across the USA [6,7]. Air samples are collected with monitors that remove particles greater than 2.5 μm and use 47-mm Teflon filters to trap the remaining ($\leq 2.5 \mu\text{m}$) particulate mass; af-

ter weighing, the filters are archived in cold storage (usually $< 4^\circ\text{C}$) for a minimum of 1 year.

Airborne PM contains a myriad of inorganic and organic species, many of which can adversely affect human health (e.g. [8–12]). Of these constituents, the class of polycyclic aromatic hydrocarbons (PAHs) is noteworthy because it is ubiquitous and includes several potent carcinogens [13,14]. PAHs are produced by the incomplete combustion of hydrocarbons and thus are emitted to the air via engine exhausts, residential and commercial heating, carbonaceous smokes and many industrial processes that employ fuels [15–19].

More than 600 PAHs have been characterized [20]. Of these, the simplest and most volatile compound is naphthalene, which has two aromatic rings and is present almost exclusively in the gas phase (vapor pressure = 0.087 Torr). At the other extreme, the largest of the commonly occurring PAHs (5- and 6-ring) tend to be present only in the particulate phase (vapor pressure $\approx 10^{-11}$ Torr). PAHs with

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3 or 4 rings (vapor pressure $\approx 10^{-6}$ to 10^{-8} Torr) can have significant fractions in both the gas and particulate phases, depending upon the particular compound [16,21].

The mixed-phase representation of PAHs has greatly complicated measurement of these compounds in ambient air. Indeed, specialized samplers have been developed for this purpose employing glass- or quartz-fiber filters for collecting particulate-bound compounds followed by sorbents to trap gaseous compounds. After collection, filters and sorbents are extracted with solvents and analyzed by GC–MS or HPLC [15,22–24]. Additionally, experimental methods using supercritical fluid extraction, pressurized liquid extraction, etc. have been applied [25]. Although accurate and precise, these mixed-phase-PAH methods are also complex and costly; and as such their application has been limited to small studies. Yet, many of the PAHs associated with carcinogenicity and mutagenicity are 5- and 6-ring compounds that reside only in the particulate phase, notably: benzo(b) fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene, and benzo(g,h,i)perylene. Thus, it would be desirable to exploit the extensive collection of ambient PM_{2.5} samples, if possible, to measure representative carcinogenic PAHs.

While standard methods rely upon glass- or quartz-fiber filters to quantitatively trap particle-bound PAHs, we evaluated Teflon filters for this purpose because they are used extensively in nationwide monitoring and are readily available following gravimetric determination of PM_{2.5}. It has been shown that various commercially available filters, including Teflon-coated glass- and quartz-fiber filters, provided comparable gravimetric results [26]. Furthermore, as early as 1983, Grosjean suggested that Teflon filters were preferable for collection of PAHs, because glass- and quartz-fiber filters

can potentially catalyze chemical reactions of PAHs with air and other oxidants [27]. More recently, Cecinato et al. [28] successfully used Teflon filter samples for assigning various organic compounds (including PAHs) into particulate size fractions. Thus, use of Teflon filters poses no apparent problems for assaying particle-bound PAHs.

Storage stability may also be of concern when using archived Teflon filters for PAH analysis. Because most specialized PAH methods seal and analyze the filters and sorbent traps together, compounds evaporating from the filter during storage merely migrate to the adsorbent and so are not lost from the assay. However, after gravimetric analysis of PM_{2.5}, Teflon filters are generally stored in Petri dishes, either refrigerated or at room temperature; under these conditions, semivolatile 3- and 4-ring PAHs can be lost. This issue has been investigated with stability tests where Teflon filters were stored at room temperature, and then analyzed up to 118 days after collection [29]. The researchers found that all PAHs from fluoranthene (4 rings) to coronene (7 rings) were recovered without observable loss.

In this paper, we describe a simple method for assaying particle bound PAHs in archived Teflon PM_{2.5} filters. The method employs solvent extraction followed by concentration and analysis by gas chromatography–mass spectrometry (GC–MS) with electron ionization and selective ion monitoring (SIM). Although we assay a set of PAHs containing from 3 to 6 rings (listed in Table 1), we focus primarily upon the 5- and 6-ring fraction containing several potent carcinogens and address the likelihood of measuring some 4-ring PAHs as well. We estimate precision and quantitation limits of the method using ambient air samples collected locally in Chapel Hill, NC. Validity is inferred by comparing levels of PAHs from these local samples, as well as

Table 1
List of PAH analytes, including some important physical and analytical parameters

Compound	SIM ion (amu)	No. of rings	Vapor pressure ^a (mm Hg)	Ret. time ^b (min)	Dwell time ^c (ms)	SIM group
Phenanthrene	178	3	6.8×10^{-4}	21.25	225	1
Anthracene	178	3	1.7×10^{-5}	21.31	225	1
d10-Anthracene	188	3	na	21.34	225	1
Fluoranthene	202	4	5.0×10^{-6}	23.85	500	2
Pyrene	202	4	2.5×10^{-6}	24.36	500	2
d10-Pyrene	212	4	na	24.40	500	2
Benz(a)anthracene ^d	228	4	2.2×10^{-8}	27.04	500	3
Chrysene ^d	228	4	6.3×10^{-7}	27.16	500	3
Benzo(b)fluoranthene ^d	252	5	5.0×10^{-7}	29.89	500	4
Benzo(k)fluoranthene ^d	252	5	9.6×10^{-11} *	29.94	500	4
Benzo(e)pyrene	252	5	5.7×10^{-9}	30.60	500	4
Benzo(a)pyrene ^d	252	5	5.6×10^{-9}	30.92	500	4
Indeno(1,2,3-c,d)pyrene ^d	276	6	$\sim 10^{-11}$	35.01	225	5
Dibenz(a,h)anthracene ^d	278	5	1.0×10^{-10}	35.06	225	5
Benzo(ghi)perylene ^d	276	6	1.0×10^{-10}	36.22	225	5

* This value can be estimated at 2.6×10^{-9} mm Hg from Piogo and Minas de Piadade [41].

^a As listed by ATSDR [16].

^b Typical retention time in minutes—varies according to column condition, age, and exact length.

^c Optimized dwell time to achieve about 2 Hz cycle time within SIM group.

^d Associated with carcinogenicity.

archived samples from the Czech Republic, with published data.

2. Experimental

2.1. Chemicals and materials

Analytical reagent grade dichloromethane was obtained from Mallinckrodt Baker Inc. (Paris, KY), internal standards (IS) [$^2\text{H}_{10}$]anthracene and [$^2\text{H}_{10}$]pyrene from Sigma-Aldrich Corp. (St Louis, MO, USA), and certified “EPA 16-PAHs” standards at 1000 or 500 ng/ml in DCM (610 PAH Calibration Mix A) were obtained from Restek Corp. (Bellefonte, PA, USA). Air sampling and preparation of blanks was carried out with 47-mm diameter, 2- μm PTFE filters (#7592-104) with a polypropylene ring circumference for stability and individual serial numbers obtained from Whatman, Inc. (Clifton, NJ, USA). Extractions and initial-volume reductions were performed in 20-ml glass vials with foil-lined caps (Kimble #58510B-20) from Fisher Scientific (Atlanta, GA, USA). Final-volume reductions and analyses were performed in autosampler vials (#5182-3454) from Agilent Technologies (Englewood, CO, USA), using ultra-pure (99.999%) nitrogen (HoloX, Norcross, GA, USA).

2.2. Sample collection

Local ambient-air samples were collected at the University of North Carolina in Chapel Hill on the roof of the four-story School of Public Health. These suburban air samples were impacted by steady automobile and bus traffic as well as by an adjacent construction site. Samples were collected using MiniVol PM_{2.5} samplers (AirMetrics, Portland, OR) at a flow rate of 5 l/min from September 2002 to February 2003 for different sampling periods (from 1 up to 14 days) to achieve a wider range of particle loadings. A subset of the samples was collected in duplicate ($n = 14$ matched pairs).

Archived PM_{2.5} samples were obtained from EPA repositories in Research Triangle Park, NC, USA. They had been collected at 1 l/min with PM_{2.5} samplers (University Research Glassware, Carrboro, NC, USA) during a series of studies performed in the Czech Republic between 1991 and 1995, as described in Watts et al. [30], Lewtas et al. [31] and Williams et al. [32]. Specifically, sets of 10 filters were obtained from each of three investigations of ambient air, conducted in Prachaplice (Summer 1994) and Teplice (Winter 1993 and Summer 1994), in the Czech Republic, along with the respective PM_{2.5} masses, sampling dates, and air volumes. The summer samples from the Czech Republic had been impacted by coal and oil combustion for electricity generation and by some industrial sources; the winter samples had been additionally impacted by residential and commercial heating with coal and oil [30].

2.3. Sample processing and extraction

Teflon filters were individually excised from their polypropylene rings and placed into 20-ml extraction vials, to which was added 10 ml of dichloromethane containing internal standards ([$^2\text{H}_{10}$]anthracene and [$^2\text{H}_{10}$]pyrene, both at 4 ng/ml). Samples were capped, vortexed for 20 s, and then agitated on an orbital shaker table at 300 rpm for 90 min. After removing the Teflon filters with forceps, the extracts were reduced in volume to 1 ml under N₂. Extracts were then transferred to conical autosampler vials, further reduced under N₂ to about 50 μl , and sealed with Teflon-lined septum crimp caps. Separate external standards and reagent blanks were prepared in the same manner as experimental samples.

All glassware, tools, and syringes were rinsed with dichloromethane prior to contacting samples, extracts, or solvents. No plastic or other deformable materials contacted any samples, solvents, or extracts (with the exception of Teflon plunger tips in some syringes). Samples and extracts were stored at -20°C and were kept shielded from ambient light as much as practical during processing.

2.4. GC-MS analysis

Analysis was performed with a GC-MS system (6890N GC, 5973N MS, 7683 autoinjector, Agilent Technologies, Palo Alto, CA, USA). Two μl of each extract were injected into the GC in splitless mode using a 10 μl syringe (Hamilton Co., Reno NV) and a gooseneck injection-port liner (20074, Restek Corp. Bellefonte, PA, USA) held at 275°C with a 20 psig (240 kPa) by 2 min pulse pressure and 1.0 ml/min He flow. Two GC columns were used interchangeably; they were DB-5 60 m \times 0.25 mm i.d. \times 0.25 μm phase thickness (J&W Scientific/Agilent Technologies, Folsom, CA, USA) and RTX-5SILMS 60 m \times 0.25 mm i.d. \times 0.25 μm phase thickness (Restek Corp. Bellefonte, PA, USA). The GC oven was programmed with an initial temperature of 50°C , where it was held for 3 min, then ramped to 150°C at $25^\circ\text{C}/\text{min}$, then ramped to 300°C at $10^\circ\text{C}/\text{min}$, where it was held for 24 min. The MS was operated in SIM mode (9-min solvent delay) with optimized ion groups and dwell times to achieve a sampling rate of ~ 2 Hz and a minimum of 10 points per GC peak [33]. Molecular ions were used for quantitation. Compounds, and their respective ions, numbers of rings, vapor pressures, typical retention times, SIM groups, and dwell times are listed in order of elution in Table 1. Quantitation was based on peak areas relative to the deuterated internal standard closest in molecular weight to the analyte. To preserve sensitivity and chromatographic performance, the GC injection liner was replaced and the first few centimeters of the column were clipped when chromatographic resolution began to degrade. Additionally, we periodically backflushed the analytical column with dichloromethane to remove buildup of nonvolatile impurities.

2.5. Estimation of analyte concentrations, extraction efficiencies, quantitation limits, precision, and agreement

Extraction efficiencies were assessed via re-extraction and re-analysis of 26 randomly selected filters from Chapel Hill samples and blank filters. Let E_1 and E_2 represent the masses of analyte found in the first and second extractions, respectively. Under the assumption that the extraction efficiency of a given PAH was independent of a sample's analyte mass, it was estimated as the mean value of $(E_1 - E_2)/E_1$ for all observations ($n = 26$).

Because background analyte levels were usually detected in field blank filters, limits of quantitation (LOQ) were evaluated as three times the standard deviation (S.D.) of 20 field-blank analyses for each compound. The precision and agreement of paired assays were evaluated based upon the within- and between-pair variance components estimated from one-way analyses of variance (ANOVA) of the analyte levels (ng/filter) observed in 14 side-by-side filter samples collected in Chapel Hill, NC, USA. (Prior to ANOVA, data pairs were visually examined for normality and homoscedasticity). The precision of the assay for each analyte was evaluated as the coefficient of variation (CV), estimated as the square root of the within-pair variance component divided by the estimated mean for all 14 data pairs. Agreement between side-by-side samples was evaluated as the intraclass correlation coefficient (ICC), estimated as the between-pair variance component divided by the sum of within- and between-pair variance components.

Graphs and linear regressions were produced and calculated using GraphPad Prism version 3.03 (GraphPad Software, Inc., San Diego, CA, USA). ANOVA and paired t -tests

were performed using SAS for Windows version 8.02 (SAS Institute, Cary, NC, USA).

2.6. Comparisons of PAH air concentrations with other studies

Analyte masses were used, along with air volumes and masses of $PM_{2.5}$, to estimate the corresponding air concentrations (ng/m^3) and mass fractions ($ng\ PAH/mg\ PM_{2.5}$) of PAHs in samples collected in Chapel Hill and the Czech Republic. The estimated mean air concentrations from these samples, aggregated by season of collection, were compared to various published values [34–38].

3. Results and discussion

3.1. Quantitation limits and linear ranges

Analyses of blank AR grade dichloromethane exhibited detectable PAH contamination especially for the 2- and 3-ring compounds. When volumes were concentrated about 200-fold, as required by the assay, background levels were detectable even for the 4-, 5-, and 6-ring PAHs. The levels of contamination detected in blank solvent samples and filter field-blank samples varied randomly. As described above, we interpreted the LOQ for each analyte as three times the S.D. of 20 field blanks carried through the assay. The LOQ of each PAH is shown in Table 2, both as ng per filter and as ng/m^3 air, assuming a standard $24\ m^3$ air sample (volume proscribed for $PM_{2.5}$ samples). The median value of the LOQ was $0.005\ ng/m^3$ (range: 0.002–0.017). The method is sufficiently sensitive to measure these PAHs

Table 2

Average values for limits of quantitation, extraction efficiencies, precision and agreement of the PAH assay

Compound	LOQ ^a (ng/filter), $n = 20$	LOQ ^b (ng/m^3), $n = 20$	Extraction efficiency ^c (%), $n = 26$	CV ^d , $n = 14$ data pairs	ICC ^e , $n = 14$ data pairs
Phenanthrene	0.125	0.005	99.6	0.186	0.918
Anthracene	0.122	0.005	99.6	0.138	0.958
Fluoranthene	0.070	0.003	99.2	0.117	0.977
Pyrene	0.135	0.006	99.0	0.099	0.984
Benz(a)anthracene ^f	0.041	0.002	99.1	0.107	0.986
Chrysene ^f	0.065	0.003	98.4	0.027	0.999
Benzo(b)fluoranthene ^f	0.050	0.002	98.6	0.115	0.988
Benzo(k)fluoranthene ^f	0.409	0.017	98.6	0.085	0.995
Benzo(e)pyrene ^f	0.078	0.003	97.5	0.105	0.987
Benzo(a)pyrene ^f	0.048	0.002	98.6	0.157	0.972
Indeno(1,2,3-c,d)pyrene ^f	0.299	0.012	99.3	0.166	0.978
Dibenz(a,h)anthracene ^f	0.246	0.010	99.5	0.404	0.839
Benzo(ghi)perylene ^f	0.296	0.012	99.2	0.143	0.981

^a Average limit of quantitation in ng/(filter sample) based on field blanks.

^b Average limit of quantitation in ng/m^3 assuming a standard $24\ m^3$ air sample.

^c Average extraction efficiency derived from repeated extractions.

^d Coefficient of variation.

^e Intraclass correlation coefficient.

^f Associated with carcinogenicity.

in samples of suburban/rural air where PAHs are typically present at concentrations of 0.04–0.33 ng/m³ [34].

Using synthetic standards, the analytical method demonstrated linearity of response up to 5 ng for a given analyte after which there was a very slight second-order effect. For “Minivol” samplers operating at about 6.6–7.2 m³ per day, or standard PM_{2.5} samplers operating at about 24 m³ per day, this linear range corresponds to air concentrations up to about 19 or 5.2 ng/m³, respectively. According to the literature, urban/industrial areas in Brazil, Italy, and the Czech Republic may approach these levels [36–39], but in the USA, mean PAH levels rarely exceed 2 ng/m³ [34,35]. In the unlikely event that levels past the linear range are encountered, the sample extract could be diluted and reanalyzed or the calibration curve could be modified; for example, for the winter Czech samples, we anticipated high levels and adjusted for them during the volume reduction step prior to performing analyses.

Although we used 10-ml extraction volumes in this study, we could use smaller volumes due to the small mass of the 47-mm Teflon filters (6.7 mg). This would reduce the background (blank) levels and thus enhance sensitivity.

3.2. Extraction efficiencies

Throughout the analyses, samples were selected at random, re-extracted and re-analyzed to estimate the extraction efficiency of individual PAHs. As shown in Table 2, the mean amount of each PAH recovered during the first extraction was always close to 100% (range: 98.4–99.6). Thus, we chose not to perform quantitative adjustments of PAH levels based upon extraction efficiencies.

3.3. Precision and agreement

We evaluated the reproducibility of the total method using 14 side-by-side pairs of air samples collected in Chapel Hill, NC. The precision of the method, as indicated by the CV (Table 2), had a median value of 11.7% (range: 2.65–40.4%) for the individual analytes in our investigation. The precision was much worse for dibenz(a,h)anthracene (CV = 40.4%) than for the other PAHs, probably due to the very low and erratic ambient concentrations of this compound in the Chapel Hill samples.

The agreement of the 14 pairs of air samples was estimated with ICC values (Table 2) obtained via one-way ANOVA of the data. The median ICC value was 0.981 (range: 0.839–0.999). With the exception of dibenz(a,h)anthracene (ICC = 0.839) and the volatile constituent, anthracene (ICC = 0.918), all estimated ICC values were close to 1.00 indicating excellent agreement of the methodology for air samples collected at a given site and time. This conclusion is supported by the combined scatterplot of the data pairs for the 5- and 6-ring PAHs, shown in Fig. 1, where all observations are close to a 45° line representing strict equality. Scatterplots relating difference vs. mean for each data

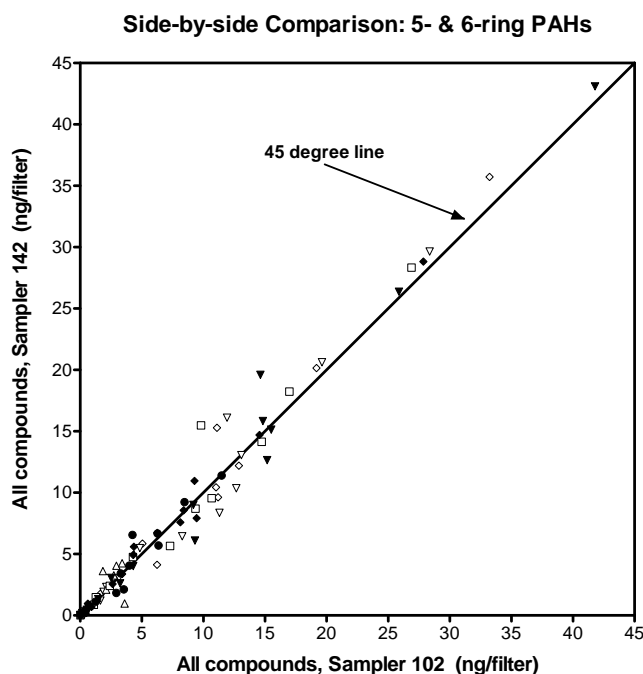


Fig. 1. Scatterplot of 14 side-by-side comparisons of duplicate sampling at Chapel Hill for all 5- and 6-ring PAH analytes (see Table 1). The 45° line indicates perfect agreement.

pair showed random and homogeneous scatter about zero, indicating no lack of fit of the one-way ANOVA model (not shown).

Although the precision of the current method is quite reasonable, incremental improvements might be achieved by the choice and amount of internal standards used. Deuterated 3- and 4-ring compounds (rather than isotopically labeled 5- and 6-ring compounds) were originally chosen as internal standards to avoid interference from impurities and/or peak broadening. Adding [²H₁₂]benzo(e)pyrene as internal standard might better reflect the behavior of the 5- and 6-ring PAHs. Also, because U.S. samples usually contain relatively small amounts of all analytes, 10 or 20 ng per sample should be appropriate rather than the 40 ng used in the current investigation.

3.4. Validity of the method—comparison of the present results with published studies

The question of validity is difficult to address because it requires a “gold standard” for comparison of methods. At this early stage of development, we can only offer evidence from other studies to suggest that results from our assay of Teflon filters provide reasonable estimates of ambient PAH concentrations in a given geographical area.

First, we compared PAH levels from our investigation of air samples from Chapel Hill, NC with published levels from other U.S. municipalities, based upon more standard PAH (filter + sorbent) methods. Table 3 shows mean winter concentrations (ng/m³) for Chapel Hill, NC

Table 3

Comparison of average PAH levels measured in Chapel Hill, NC to average published values from other municipalities (ng/m³)

Compound	This study, Chapel Hill, NC, Winter 2002/2003, <i>n</i> = 26	Other studies				
		Sandy Hook ^a , NJ, 1-year avg 1997/1998, <i>n</i> = 85	New Bruns ^a , NJ, 1-year avg 1997/1998, <i>n</i> = 85	Los Angeles ^b , CA, 2-year avg 2000/2001, <i>n</i> = 61	Rome Italy ^c , 5-year avg 1993/1998, <i>n</i> = 608	Sao Paulo ^d , Brazil, Spring 2/1994–5/1994, <i>n</i> = 22
Phenanthrene	0.082	4.88	9.06	na	na	na
Anthracene	0.016	0.11	0.22	na	na	na
Fluoranthene	0.089	1.09	2.11	na	na	8.0
Pyrene	0.086	0.48	0.83	na	na	12.7
Benzo(a)anthracene ^e	0.058	0.04	0.10	na	0.82	4.3
Chrysene ^e	0.117	0.09	0.19	na	na	7.0
Benzo(b)fluoranthene ^e	0.248	na	na	0.15	na	na
Benzo(k)fluoranthene ^e	0.137	na	na	0.06	na	na
Benzo(b+k)fluoranthene	0.385	0.12	0.33	0.21	2.95	12.8
Benzo(e)pyrene	0.210	na	na	na	1.53	2.7
Benzo(a)pyrene ^e	0.087	0.04	0.13	0.10	1.38	2.8
Indeno(1,2,3-,d)pyrene ^e	0.167	0.10	0.20	0.21	1.51	3.2
Dibenz(a,h)anthracene ^e	0.040	0.01	0.04	0.03	0.22	0.20
Benzo(ghi)perylene ^e	0.188	0.08	0.21	0.44	na	3.0

na: not available.

^a From Gigliotti et al. [34].^b From CARB, [35].^c From Menichini et al. [36].^d From DeMartinis et al. [37].^e Associated with carcinogenicity.

(10/2002 to 2/2003), as well as data from New Brunswick and Sandy Hook, NJ (10/1997 to 10/1998) [34], and Los Angeles, CA (calendar years 2001, 2002) [35]. As expected, we found that the more volatile 3- and 4-ring PAHs, i.e., phenanthrene, anthracene, fluoranthene, and pyrene were appreciably under-represented in the Chapel Hill data, compared to the other data, because we did not use sorbents. However, for the 4- to 6-ring PAHs from benzo(a)anthracene through benzo(ghi)perylene, we see that our data are bracketed by those from the two NJ sites, and were essentially equivalent to the yearly mean levels in Los Angeles. Also, we note that the internal patterns were consistent; that is, dibenz(a,h)anthracene was consistently about 10–20% of indeno(1,2,3-c,d)pyrene and about 7–20% of benzo(ghi)perylene, and benzo(a)pyrene was consistently about a third of the summed benzo(k)fluoranthene and benzo(b)fluoranthene isomers. This preliminary evidence suggests that the methodology is likely to be valid for benzo(a)anthracene through benzo(ghi)perylene of the target analytes. For contrast, Table 3 also includes results of measurements from downtown Rome, Italy [36] and Sao Paulo, Brazil [37] where the air is impacted by some of the busiest motor vehicle traffic in the world. Clearly the air levels of particle-bound PAHs in those two cities were many-fold greater than those in the USA; however, the general PAH patterns are similar.

Our second comparison contrasts results from our current assay of archived Teflon filters from the Czech Republic with measurements made with (filter + sorbent) PAH monitors at similar locations and times. Before we received the Teflon filter samples, they had been stored for about 10 years

at room temperature. Results from our analyses of these archived filters are summarized in Table 4 along with results of more standard PAH methods reported by Lenicek et al. [38]. We note that the time frames are not identical; the reported averages from Lenicek are across 6 month sampling blocks whereas our analyses of archived filters are from one or two months in the middle of summer or the middle of winter. As expected, the mean levels from our study substantially underestimated levels of the volatile 3- and 4-ring PAHs but were consistent for the 5- and 6-ring PAHs from a given municipality and season of the year. We further note that losses of the more volatile PAHs were not complete; we distinctly observed the same pattern of higher wintertime over summertime levels even after the long (room temperature) storage period.

The potential use of Teflon filters for measurement of the 4-ring PAHs (especially the carcinogens, chrysene and benzo(a)anthracene) is further supported by a recent study in California by Eiguren-Fernandez et al. [21]. From their data, we find that the average gas/particle phase partitions for chrysene and benzo(a)anthracene were very low, at 0.3 and 0.5%, respectively, indicating that these compounds were present at essentially 100% in the particulate phase of Los Angeles air, where the average temperatures were fairly high. This indicates that the observed losses of the 4-ring PAHs in our Czech samples probably occurred during the 10 years of room-temperature storage rather than during air sampling. If this were the case, then the refrigerated storage of samples, as mandated in EPA's PM_{2.5} monitoring program [40], should be sufficient to preserve chrysene and benzo(a)anthracene on the filters prior to analysis.

Table 4
Comparison of air concentrations (ng/m³) from archived Czech filters with some related published values

Compound	This study—archived Czech samples			Czech Republic Data—Lenicek et al. [38]			
Compound	This study—archived Czech samples			Czech Republic Data—Lenicek et al. [38]			
	Prachat. Summer 5/1994–7/1994, <i>n</i> = 10	Teplice Winter 1/1993–2/1993, <i>n</i> = 10	Teplice Summer 7/1994–8/1994, <i>n</i> = 10	Prachat. Winter 10/1993–3/1994, <i>n</i> = 154	Prachat. Summer 5/1994–9/1994, <i>n</i> = 178	Teplice Winter 10/1993–3/1994, <i>n</i> = 205	Teplice Summer 5/1994–9/1994, <i>n</i> = 180
Phenanthrene	0.04	0.56	0.03	2.81	0.20	2.25	0.14
Anthracene	nd	0.07	nd	0.52	0.04	0.31	0.03
Fluoranthene	0.07	0.96	0.05	6.21	0.50	7.79	0.48
Pyrene	0.06	0.92	0.04	6.53	0.63	8.58	0.62
Benz(a)anthracene ^a	0.04	2.51	0.03	3.33	0.71	5.80	0.33
Chrysene ^a	0.04	2.02	0.03	4.32	0.40	7.47	0.48
Benzo(b)fluoranthene ^a	0.17	11.69	0.11	4.39	0.39	6.18	0.66
Benzo(k)fluoranthene ^a	0.07	4.75	0.09	2.23	0.36	4.02	0.90
Benzo(e)pyrene	0.22	8.49	0.09	2.85	0.44	4.74	0.55
benzo(a)pyrene ^a	0.12	11.11	0.12	3.68	0.41	6.05	0.57
Indeno(1,2,3-c,d)pyrene ^a	0.34	12.18	0.49	2.29	0.49	6.02	0.87
Dibenz(a,h)anthracene ^a	0.05	2.09	0.21	0.10	0.12	2.11	0.25
Benzo(ghi)perylene ^a	0.51	10.60	0.72	2.93	0.48	5.33	0.70
“c-PAHs” ^b	1.30	54.44	1.76	18.47	2.69	34.45	4.50

nd: not detected.

^a Associated with carcinogenicity.

^b Sum of 5- and 6-ring carcinogens plus chrysene, defined by Lenicek et al. [38].

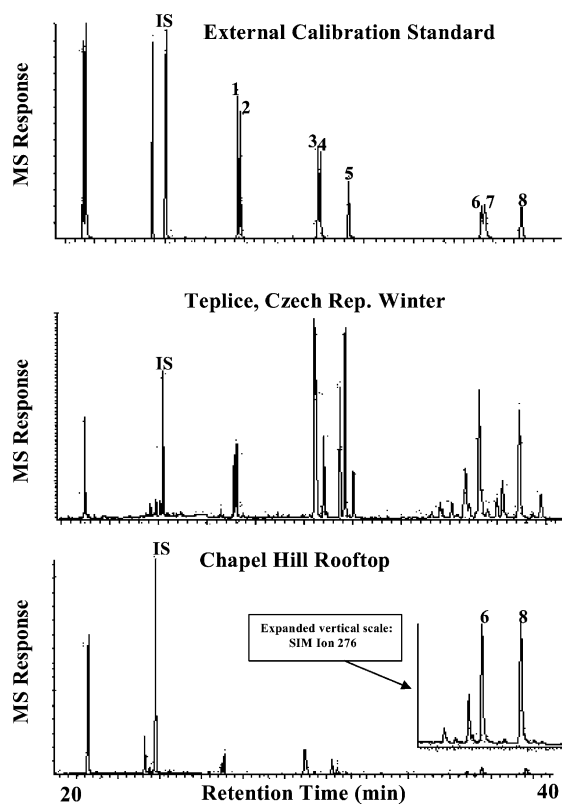


Fig. 2. Representative chromatograms of GC-MS SIM analyses of PAH analytes. Top: chromatogram of an external calibration standard containing 4.0 ng/ml per compound. IS denotes [$^{2}\text{H}_{10}$]pyrene; numbered peaks are (1) benz(a)anthracene, (2) chrysene, (3) benzo(b)fluoranthene, (4) benzo(k)fluoranthene, (5) benzo(a)pyrene, (6) indeno(1,2,3-cd)pyrene, (7) dibenz(a,h)anthracene and (8) benzo(g,h,i)perylene. Middle: chromatogram of a sample from Teplice, Czech Republic (winter 1993), with ambient PAH concentrations ranging from 1 to 13 ng/m³. Bottom: chromatogram of a sample from Chapel Hill (winter 2003), with ambient PAH concentrations ranging from 0.05 to 0.47 ng/m³. Insert is a vertically expanded profile of SIM ion 276 showing trace level peaks of two 6-ring PAHs at about 0.32 ng/m³.

3.5. Chromatographic performance

The analytical protocol yielded excellent PAH separation and peak shape under optimal conditions when the MS source, injection liner, and column were all clean. Because some inorganic and non-volatile materials are introduced with each injection, we observed gradual chromatographic degradation (peak tailing and broadening), as well as a reduction in high mass response. We found that routine maintenance after 30–40 injections was sufficient to preserve adequate sensitivity and resolution for trace level analyses. Fig. 2 shows some representative chromatograms including a moderate-level Chapel Hill sample, a high-level Czech Republic sample, and an external calibration standard. Internal standards and some prominent PAHs are indicated. Note that the benzo(b)fluoranthene and benzo(k)fluoranthene isomers are resolved in the standard; however in air samples we had to estimate quantities of these compounds from their known positions and observation of chromatographic shoulders to

avoid including the area between them represented by the “j” isomer. The close time elution of dibenz(a,h)anthracene and indeno(1,2,3-cd)pyrene is unimportant because they have different quantitation masses (276 and 278, respectively).

4. Conclusions

From these preliminary data, we conclude that samples of PM_{2.5} filters yield precise results for levels of particle-bound 5- and 6-ring PAHs in ambient air that are consistent with those from studies employing more standard (filter+sorbent) PAH-collection methods and larger sample volumes. In addition, we expect that when filters are stored under refrigeration, the method will also be sufficiently robust to quantitatively recover selected 4-ring PAHs, notably the carcinogens chrysene and benz(a)anthracene, that are of particular interest. This conjecture will require further experimental confirmation.

Our method demonstrated sufficient sensitivity to measure PAHs using low air volumes (6.6 m³) in suburban air (Chapel Hill, NC, USA) and sufficient dynamic range for applications using high air volumes (24 m³) in highly polluted air (Teplice, Czech Republic in winter). Levels of particle-bound 5- and 6-ring PAHs appear to be stable for many years on PM_{2.5} (Teflon) filters at room temperature, as indicated by the quantitative results observed for the archived Czech samples. We conclude that the PM_{2.5} filters, collected on a routine basis and archived for one year in cold storage, should be quite suitable for measuring all 5- and 6-ring PAHs. This methodology provides a simple, straightforward procedure for retrospectively determining particle-bound PAHs from the 200,000 or so archived PM_{2.5} filters routinely collected every year in the USA.

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