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# Improved GC/MS methods for measuring hourly PAH and nitro-PAH concentrations in urban particulate matter

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**Abstract**

This study presents two methods for the quantification of nitro-substituted and parent polycyclic aromatic hydrocarbons (NPAH and PAH, respectively), respectively, utilizing large volume injection gas chromatography/mass spectrometry (GC/MS). Both methods (PAH and NPAH, respectively) employed a programmed temperature vaporization injector (PTV) in solvent vent mode, optimized using standard solutions. For the PAH method, the precision of the PTV was comparable to hot splitless injection for exhibiting a percent relative standard deviation (%RSD) consistently below 8% for 100 pg injections. Compound %RSDs for the NPAH method were consistently below 5% using the PTV. Microgram quantities (30–500 μg) of particulate matter Standard Reference Materials (SRM 1649 and 1650, National Institutes of Standards and Technology) were analyzed to simulate PAH and NPAH quantification on small aerosol mass loadings. The method detection limits from this study suggest PAHs and NPAHs can be easily quantified using low-volume samplers (> 5 Lpm) on hourly timescales. In addition, this technique enabled the quantification of 12-h NPAH size distributions in the Baltimore, MD, atmosphere.


*Keywords:* Polycyclic aromatic hydrocarbons; Nitro-polycyclic aromatic hydrocarbons (nitro-PAHs); Programmed temperature vaporization (PTV); Large volume injection; Aerosol; Organic

## 1. Introduction

Understanding the evolving chemical composition of atmospheric aerosol is critical to accurately assessing aerosol sources and their potential health effects. Polycyclic aromatic hydrocarbons (PAHs) and nitro-substituted polycyclic aromatic hydrocarbons (NPAHs) are two classes of compounds implicated in the mutagenicity of ambient air (Arey et al., 1988; IARC, 1989; Gupta et al., 1996). Formed from incomplete combustion, PAH profiles have also been utilized in source apportionment studies in urban areas (Venkataraman and Friedlander, 1994; Harrison et al., 1996; Simcik et al., 1999; Larsen and Baker, 2003). NPAHs are either directly emitted from combustion sources (i.e. diesel, Paputa-Peck et al., 1983) or formed through the oxidation of parent PAHs in the atmosphere (Arey, 1998 and references therein). NPAH isomers are source specific (combustion or oxidation) and therefore NPAH fingerprints may be useful to determine primary and secondary aerosol sources (Cecinato et al., 1996).

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The observed atmospheric distributions (gas/particle and isomeric) of PAHs and NPAHs depend strongly on the temporal scale of the measurement. Measured PAH and NPAH profiles at a receptor site result from the integration of many time variable sources. These profiles are influenced by changing wind direction, oxidant concentration and source emission patterns (i.e. traffic) during the sampling period. The phase distribution (particle vs. gas) of these semi-volatile organics is governed by vapor pressure and hence temperature (Pankow, 1994). Therefore, changes in temperature during a sampling period may alter the observed gas and particle distributions during extended sampling times (Yamasaki et al., 1982; Mader and Pankow, 2000). The collected particulate matter can be exposed to elevated levels of oxidants (ozone), concurrently sampled, degrading more labile constituents (Schauer et al., 2003). Therefore, minimizing these sampling errors requires measuring PAH and NPAH concentrations on timescales relevant to temperature, wind direction and source type changes while minimizing exposure to oxidants.

In the literature, PAH and NPAH samples are typically collected using a filter/polyurethane plug (PUF) configuration (EPA Method 625; Yamasaki et al., 1982; Keller and Bidleman, 1984; Offenberg and Baker, 1999; Marino et al., 2000; Feildberg et al., 2001; Bamford and Baker, 2003). Potential artifacts associated with this technique have been discussed in detail by Turpin et al. (2000). Arguably, the most debated artifact of the filter/PUF sampler is the magnitude and correction for ad/absorption of organic gases to the filter media (i.e. quartz fiber, glass fiber or Teflon). Others have employed a denuder/filter technique for PAHs (Gundel et al., 1995; Kavouras et al., 1999; Peters et al., 2000; Possanzini et al., 2004) and NPAHs (Wilson et al., 1995; Fan et al., 1995) to minimize this artifact by scavenging gas phase organics via an annular denuder prior to the filter. This technique disturbs the gas/particle equilibrium during sampling, perhaps initiating particulate matter volatilization losses. These are collected on a second vapor sorbent after the filter. In addition, entrainment of small particles in the denuder has been observed (Volckens and Leith, 2003), further skewing the measured distribution.

Sampling times for the aforementioned studies, as well as the standard for monitoring campaigns (Integrated Atmospheric Deposition Network, IADN, Gatz et al., 1994; Sweet et al., 1996), are usually 24 h. To our knowledge, the greatest temporal resolution using standard analytical techniques for PAHs was 4 h in Baltimore, MD (Dachs and Eisenreich, 2000), and Southern California (Fraser et al., 1998) using hi-volume samplers operated at $\sim$0.5 and 0.19 $m^3 min^{-1}$, respectively. Dachs and Eisenreich (2000) evaluated the soot contribution to the PAH gas/particle partitioning coefficient ($K_p$) by modeling the evolving $K_p$ over multiple days. Fraser et al. (1998) observed PAH degradation and enhanced NPAH formation downwind during a photochemical smog episode.

In Southern California, Reisen et al. (2003) analyzed NPAHs by compositing 3.5 h segments over 5 days using a hi-volume filter/PUF sampler ($\sim$0.6 $m^3 min^{-1}$). Feildberg et al. (2001) reported selected 12-h NPAH concentrations in Denmark using flow rates $>1\ m^3 min^{-1}$. The flow rates employed in these studies are on the upper edge of commercially available instruments (see Watson and Chow (1992) for a review). Typical denuder/filter designs have a much lower flow rate (usually 0.1 $m^3 min^{-1}$ or less, Gundel et al., 1995; Volckens and Leith, 2003; URG, Chapel Hill, NC).

The temporal resolution of these compounds in ambient air is limited by the detection limits of current analytical techniques. Either collecting more sample or increasing the analytical sensitivity is required to increase the detectability of PAHs and NPAHs in ambient air. Greater sampling flow rates and the corresponding larger pressure drops may increase volatilization losses from the sampling substrate. In addition, the higher sample volumes and longer sampling times may increase the exposure of PAHs and NPAHs to oxidants. Increasing collection surface area to increase sampler flow rates without additional pressure drops may increase both gas ab/adsorption and the potential for greater matrix contamination. Therefore, increasing sample volumes using the current sampling methodology is not a promising approach to improve PAH and NPAH detection.

While numerous sensitive high-performance liquid chromatography (HPLC) methods have been published for the determination of PAHs and NPAHs (Mac Crehan et al., 1988; Li and Westerholm, 1994; Lee, 1995; Bonfanti et al., 1996), gas chromatography/mass spectrometry (GC/MS) is more commonly used due to greater separation efficiency of complex non-polar analytes. For GC analysis, the final volume of the organic extracts is usually $>100\ \mu L$. Using the conventional inlets (hot

splitless and cool on-column), only 2 μL or less of extract is applied to the column. For semi-volatile compounds (i.e. PAHs and NPAHs), concentrating extracts below this volume may increase losses of the more volatile components. Therefore, 98% of the analyte mass extracted is not introduced into the chromatographic system. With the advent of large volume injection (Vogt et al., 1979), the widely used hot splitless injection technique can be modified to load a greater portion of an extract (from 2 μL to 100s of μL). The use of large volume injection (specifically programmed temperature vaporization–large volume injection) has been increasing (see Engewald et al. (1999) for review). The commercial availability of the programmed temperature vaporization (PTV) inlet has made this injector attractive for trace-level analysis. The performance of other large volume techniques, such as cool on-column injection with solvent venting (SVE-COC) may be quickly degraded by system fouling from complex sample extracts (see Grob and Biedermann (1996) for review). Like the splitless injector, the PTV incorporates a glass sleeve that traps non-volatile contaminants, keeping them from degrading the capillary column. Zrostlikova et al. (2001) reported greater chromatographic stability (peak shape and compound response) per number of plant extracts analyzed for a suite of pesticides using the PTV in solvent vent mode as compared to a pulsed splitless and cool on-column configuration.

The PTV can be configured to inject large volumes of liquid depending on the volume of the inlet liner (usually $<250\,\mu L$) or in sequential injections of smaller volumes. During the injection time, the cool inlet sleeve is purged to remove solvent. The initial injector temperature is set below the carrier solvent boiling point and optimized to retain (cold trapping) the compounds of interest. The solvent is then evacuated through the open split vent. Once the solvent is removed, the split valve is closed. Then the inlet is rapidly heated (up to $700\,^{\circ}C\,min^{-1}$) to a final temperature, desorbing analytes to the column. Typical conditions for optimizing the PTV injection parameters are outlined in the literature (Mol et al., 1996; Engewald et al., 1999; Grob and Biedermann, 1996).

Previously, this technique has been used to quantify numerous classes of compounds in a variety of matrices (see Teske and Engewald (2002) for review). Norlock et al. (2002) evaluated the PTV for PAH analysis in air and sediment samples. Although this work was extensive using standards, sediment and ambient air collected in Chicago, IL, matrix effects were not evaluated. In this study, we present optimized methods for PAH and NPAH quantification in ambient aerosol. These methods outline an efficient way to increase the analytical sensitivity and temporal resolution by utilizing a greater percentage of the extract (mass of analyte extracted) through large volume injection. Matrix effects are evaluated using Standard Reference Materials (National Institutes of Standards and Technology (NIST), Gaithersburg, MD) and an example of the benefits of increased temporal resolution is presented in our analysis of the diurnal size distribution of NPAHs in the Baltimore, MD, atmosphere. The goal of this study is to develop an analytical method capable of $pg\,m^{-3}$ detection limits and a precision of 20% for measuring PAHs and NPAHs in ambient aerosol samples with 1-h resolution.

## 2. Materials and methods

### 2.1. Standards

The 42 PAHs used in this study were supplied by Ultra Scientific (North Kingstown, RI). Two deuterium-labeled PAH solutions, internal and surrogate standards, were also made using neat standards from Ultra Scientific in hexane. Nitro-PAH standards were acquired from AccuStandard (New Haven, CT) in concentrated solutions ($\sim 100\,mg\,mL^{-1}$ in toluene) except for 2-nitrofluoranthene and 2-nitropyrene which were supplied by Chiron (Trondheim, Norway) and Chemsyn Science Laboratories (Lenexa, KS), respectively. The internal standard solution components (3-nitrofluoranthene-$d_9$, 6-nitrochrysene-$d_{11}$, 2-nitrofluorene-$d_9$ and 5-nitroacenaphthene-$d_9$) were purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA). The surrogate solution components were acquired from C/D/N isotopes (Pointe-Claire, Quebec, Canada, nitronaphthalene-$d_7$) and Cambridge Isotope Laboratories, Inc. (9-nitroanthracene-$d_9$ and 1-nitropyrene-$d_9$).

### 2.2. Standard reference materials and ambient particulate matter

Size-resolved aerosol was collected at the Baltimore PM2.5 Supersite during April 2002. The Berner low-pressure impactor collected five particle size cuts (0.04–0.14, 0.14–0.49, 0.49–1.7, 1.7–6,

6–20 μm) at 80 Lpm. Non-greased foils ashed at 450 °C for 4 h and tared to 0.1 μg prior to deployment. The particle laden foils were prepared in the same manner as the SRM outlined below.

Urban Dust and Diesel Particulate Matter Standard Reference Materials (SRM 1649a and SRM 1650a, respectively) were obtained from NIST (Gaithersburg, MD). Microgram quantities were transferred to 20-mL test tubes via tared foil (pre-rinsed with DCM) sonicated for 30 min in dichloromethane (DCM) and stored at −20 °C for 48 h. Prior to adding DCM, PAH (naphthalene-$d_8$, fluorene-$d_8$, fluoranthene-$d_{10}$, perylene-$d_{12}$) and NPAH (1-nitronaphthalene-$d_7$, 9-nitroanthracene-$d_9$ and 1-nitropyrene-$d_9$) surrogates were added.

The PAH extracts were filtered, concentrated under $N_2$ (Turbovap II, Zymark, Hopkinton, MA) to ~200 μL and analyzed. PAH internal standard containing acenaphthene-$d_{10}$, phenanthrene-$d_{10}$, benz[*a*]anthracene-$d_{12}$, benzo[*a*]pyrene-$d_{12}$ and benzo[*g,h,i*]perylene-$d_{12}$ were added to each sample just prior to analysis. Further purification was required for NPAHs using additional clean-up steps previously reported (Bamford et al., 2003) with minor modifications. After PAH analysis, each extract was eluted through an aminopropyl SPE cartridge (Sep-Pak, Waters, Milford, MA) using 40 mL of a 20% DCM/hexane solution, concentrated under $N_2$ and exchanged to hexane. Normal phase LC was then employed for the final clean-up step using a 5 μm, 9.6 mm × 30 cm Chromegabond amino/cyano column (ES Industries, West Berlin, NJ) using 20% DCM/hexane as the mobile phase. After concentration, NPAH internal standards were added just prior to analysis.

### 2.3. Instrumental parameters

An Agilent (Palo Alto, CA) 6890/5973 gas chromatograph/mass spectrometer equipped with a standard split/splitless and a PTV (Gerstel, Mülheim an der Ruhr, Germany) inlet was employed in the analysis. The instrument was configured for electron ionization (EI) for PAH analysis with a source temperature of 230 °C. Negative chemical ionization (NCI) using methane ionization gas (40 ml min$^{-1}$) and a source temperature of 200 °C was employed for NPAHs. The instrument was tuned to factory specifications and selective ion monitoring was used in both MS configurations. Molecular ions were used in PAH and NPAH quantification. A 0.25 mm × 30 m × 0.25 μm DB-5 ms (Agilent Technologies, Palo Alto, CA) capillary column was used in the PAH quantification. The initial oven temperature (40 °C) was ramped to 280 °C at 10 °C min$^{-1}$, then ramped at 5 °C min$^{-1}$ to 310 °C and held for 10 min. NPAHs were resolved using a 0.25 mm × 30 m × 0.25 μm DB-17 ms capillary column. The oven temperature program for NPAH analysis was 40 °C (held 1.7 min) ramped to 150 °C at 20 °C min$^{-1}$, held for 10 min, then to 220 °C at 10 °C min$^{-1}$, held for 10 min and finally ramped to 310 °C and held for 15 min.

For PAHs, the hot splitless injector was configured for 2 μL injections at 250 °C. The oven was held at 40 °C for 1.0 min. The PTV injector was configured for 10 injections of 5 μL at 45 °C held for 1.2 min then ramped to 250 °C at 600 °C min$^{-1}$ holding the oven at 40 °C for 1.6 min. During the injection process, the inlet was held at 5 psi with a purge flow of 50 mL min$^{-1}$. For NPAH analysis, the PTV was configured to perform ten 5 μL injections venting at 100 mL min$^{-1}$ at 2 psi for 1.10 min. At 1.2 min, the PTV was ramped at 600 °C min$^{-1}$ to 280 °C.

## 3. Results

### 3.1. Reproducibility

#### 3.1.1. PAHs

The reproducibility of the split/splitless and PTV injectors is shown in Table 1. For each injector, a standard containing 43 PAHs and nine perdeuterated PAHs (five internal standards and four surrogates) was used to test the reproducibility of each injector ($N = 7$). A similar mass (~100 pg) of each analyte was introduced into the chromatographic system. The mean percent relative standard deviation (%RSD) after normalizing the PAHs to their respective internal standards was 2.6% ranging 0.6% to 9.5% (fluorene-$d_{10}$ and 3-methylcholanthrene, respectively). Using the PTV, naphthalene-$d_8$ exhibited the largest variability (13%) while the %RSD for acenaphthene was the lowest (0.4%). The variability of the low-molecular-weight PAHs was higher using the PTV whereas the largest %RSD using the splitless injector was found for the high-molecular-weight PAHs. Although internal standard normalization increased precision, significant variability was found for naphthalene-$d_8$ using the PTV. Due to the solvent venting during multiple injections, compounds with elevated vapor pressures may purge with the carrier solvent (Mol et al.,

Table 1
Injector precision; 2 μL hot splitless (SL) and 50 μL PTV in solvent vent mode

| | PAHs[a] | SL %RSD[c] norm | PTV %RSD norm | | NPAHs[b] | PTV %RSD norm |
|---|---|---|---|---|---|---|
| I.S.[d] | Acenaphthene-$d_{10}$ | | | I.S. | 5-nitroacenaphthene-$d_9$ | |
| Surr[e] | Naphthalene-$d_8$ | 3.5 | 13 | | 1-nitronaphthalene | 4.2 |
| | Naphthalene | 3.2 | 11 | | 2-nitronaphthalene | 6.5 |
| | Azulene | 2.2 | 7.0 | | 2-nitrobiphenyl | 2.2 |
| | 2-methylnaphthalene | 1.6 | 4.2 | | 3-nitrobiphenyl | 2.3 |
| | 1-methylnaphthalene | 1.8 | 7.3 | | 4-nitrobiphenyl | 3.3 |
| | Acenapthylene | 1.0 | 4.9 | | 1,3-dinitronaphthalene | 3.8 |
| | Biphenyl | 1.5 | 2.1 | | 1,5-dinitronaphthalene | 3.1 |
| | Acenaphthene | 0.9 | 0.4 | | 5-nitroacenapthene | 2.2 |
| I.S. | Phenanthrene-$d_{10}$ | | | I.S. | 2-nitrofluorene-$d_9$ | |
| Surr | Fluorene-$d_{10}$ | 0.6 | 3.3 | | 2-nitrofluorene | 1.3 |
| | Fluorene | 2.4 | 5.0 | | 2,2'-dinitrobiphenyl | 3.1 |
| | Phenanthrene | 0.9 | 0.4 | | 9-nitroanthracene | 1.3 |
| | Anthracene | 3.1 | 1.8 | | 2-nitroanthracene | 1.3 |
| | 1-methylfluorene | 2.4 | 4.1 | | 9-nitrophenanthrene | 1.7 |
| | 4,5-methylenephenanthrene | 3.0 | 2.0 | | 3-nitrophenanthrene | 4.7 |
| | 2-methylphenanthrene | 2.4 | 2.2 | | 4-nitrophenanthrene | 1.5 |
| | 2-methylanthracene | 5.9 | 3.9 | | | |
| | 1-methylanthracene | 6.4 | 5.3 | I.S. | 3-nitrofluoranthene-$d_9$ | |
| | 1-methylphenanthrene | 4.1 | 3.4 | | 2-nitrofluoranthene | 1.4 |
| | 9-methylanthracene | 7.0 | 5.4 | | 3-nitrofluoranthene | 1.6 |
| | | | | | 1-nitropyrene | 1.4 |
| I.S. | Benz[*a*]anthracene-$d_{12}$ | | | | 2-nitropyrene | 2.1 |
| Surr | Fluoranthene-$d_{10}$ | 4.4 | 10.2 | | 2,7-dinitrofluorene | 4.7 |
| | Fluoranthene | 5.5 | 11 | | | |
| | Pyrene | 4.4 | 9.8 | I.S. | 6-nitrochysene-$d_{11}$ | |
| | 9,10-dimethylanthracene | 4.9 | 8.2 | | 7-nitro[*a*]anthracene | 1.4 |
| | Benzo[*a*]fluorene | 3.7 | 7.6 | | 6-nitrochysene | 0.8 |
| | Benzo[*b*]fluorene | 4.2 | 7.8 | | 1,3-dinitropyrene | 2.4 |
| | Benz[*a*]anthracene | 0.7 | 1.8 | | 1,6-dinitropyrene | 1.4 |
| | Chrysene + triphenylene | 4.5 | 9.2 | | 9,10-dinitroanthracene | 4.7 |
| | Napthacene | 2.2 | 10 | | 1,8-dinitropyrene | 3.7 |
| | 3-methylcholanthrene | 9.5 | 7.7 | | 6-nitrobenzo[*a*]pyrene | 6.5 |
| | | | | | 1-nitrobenzo[*e*]pyrene | 1.5 |
| I.S. | Benzo[*a*]pyrene-$d_{12}$ | | | | 3-nitrobenzo[*e*]pyrene | 1.8 |
| Surr | Perylene-$d_{12}$ | 1.2 | 7.8 | | 1-nitro- and 3-nitro- | |
| | Benzo[*b*]fluoranthene | 1.5 | 5.6 | | benzo[*a*]pyrene | 5.5 |
| | Benzo[*k*]fluoranthene | 4.1 | 5.2 | | | |
| | Benzo[*a*]pyrene | 2.4 | 4.0 | | | |
| | Benzo[*e*]pyrene | 3.7 | 3.3 | | | |
| | Perylene | 1.1 | 2.8 | | | |
| | Dimethylbenz[*a*]anthracene | 2.4 | 6.1 | | | |
| I.S. | Benzo[*g,h,i*]perylene-$d_{12}$ | | | | | |
| | Indeno[1,2,3-*c,d*]pyrene | 2.2 | 6.0 | | | |
| | Benzo[*g,h,i*]perylene | 1.6 | 2.3 | | | |
| | Anthanthrene | 2.3 | 6.8 | | | |
| | Dibenz[*a,h* + *a,c*]anthracene | 2.2 | 4.6 | | | |
| | Coronene | 3.8 | 8.1 | | | |

[a]100 pg per analyte.
[b]1000 pg per analyte.
[c]Relative standard deviation of internal standard normalized responses.
[d]Internal standard.
[e]Surrogate standard.

1996; Bosboom et al., 1996), resulting in greater variability for low-molecular-weight compounds. The elevated precision for internal standard normalized acenapthene is due to the use of acenaphthene-$d_{10}$ as the internal standard for that window.

### 3.1.2. NPAHs

Recent studies utilize cool on-column injection for GC analysis of NPAHs (Bamford et al., 2003; Bamford and Baker, 2003) due to degradation artifacts using hot splitless injections. However, column degradation and contamination associated with loading large volumes of sample matrix limit the use of cool on-column injection for this application. For the NPAH evaluation, a standard solution containing 30 NPAHs and four perdeuterated NPAHs ($\sim$20 ng mL$^{-1}$) was employed. The injection volume was 50 μL, introducing $\sim$1 ng of each NPAH into the chromatographic system. The %RSDs for NPAHs were similar to and often better than those of the PAHs (Table 1). The geometric mean %RSD for the normalized area counts was 2.4%, ranging 0.8% (6-nitrochrysene) to 6.5% (2-nitronaphthalene and 6-nitrobenzo[*a*]pyrene), with no apparent trend with vapor pressure. The mass used in this analysis is approximately 1000-fold greater than the method detection limits presented below. Therefore, the precision reported here is applicable to NPAH analysis where concentrations are well above reporting limits.

## 3.2. Mass transfer efficiency

### 3.2.1. PAHs

The major advantage to the PTV is the ability to introduce a larger volume (larger fraction) of sample onto the column, thus increasing sensitivity. We evaluated the relative mass transfer efficiency of each PAHs from the injection port to the column using the hot splitless and the PTV in solvent vent mode (Fig. 1). If both injectors transfer analytes equally, the ratio of the mean detector response from injections of equal masses using the PTV and splitless (PTV/SL response) injectors should equal one. The lighter PAHs (naphthalene to acenapthene) have ratios less than one with naphthalene exhibiting a response ratio of 0.5. The response ratios are greater than 1 for mid-to high-molecular-weight PAHs (166–300 amu, fluorene and coronene, respectively), with an apparent increase in the response ratio with decreasing vapor pressure from fluorene to benzo[*b*]fluorene. For PAHs larger than fluorene, the injector response ratio (PTV/SL) is consistently 4–5.

The lighter PAHs naphthalene to acenaphthene (128 and 154, respectively) are apparently better transferred using the splitless injector. The loss of low-molecular-weight PAHs in the PTV is due to co-venting the more volatile PAHs with the solvent (Mol et al., 1996; Bosboom et al., 1996). This also corresponds to the lower precision observed for the low-molecular-weight PAHs. A splitless or possibly a large volume cool on-column injection may remedy co-venting losses of lighter PAHs (Bosboom et al., 1996). PTV parameters such as the initial temperature and carrier (keeper) solvent may also be altered to compensate for volatiles losses (Mol et al., 1996).

Particulate matter contains minimal concentrations of the lightest PAHs. The increase in sensitivity using the PTV for PAHs with four rings or more (benz[*a*]anthracene to coronene) cannot be accounted for by the variability in replicate runs. One explanation is the smaller volume of the PTV multi-baffled liner compared to the single gooseneck splitless injector liner. The smaller liner volume results in large carrier gas velocities. The smaller liner volume results in larger carrier gas velocities, less active sites on the liner surface and less exposure to elevated temperatures that may degrade analytes (Zrostlikova et al., 2001), thus better transfer of PAH mass to the chromatographic column. This problem may be easily solved using a different liner in the splitless injector with a volume comparable to the PTV. But possible degradation of high-molecular-weight PAHs may also be attributed to thermal degradation in the hot splitless injector as observed for NPAHs (see below).

### 3.2.2. NPAHs

To evaluate the mass transfer efficiency of NPAHs using the PTV, three PTV inlet heating configurations were tested; hot splitless (280 °C), temperature programmed splitless (initial temperature of 40 °C, ramped 600 °C min$^{-1}$ to 280 °C in splitless mode) and solvent vent (initial temperature of 40 °C, held 1.0 min, then 600 °C min$^{-1}$ to 280 °C at 2 psi with a purge flow of 100mL min$^{-1}$). The initial oven time was held for 1.06 min at 40 °C for each injector configuration. A 2-μL injection volume was used for each mode to eliminate any solvent effects in the hot and programmed temperature splitless modes. The response for the hot splitless mode is consistently lower than the

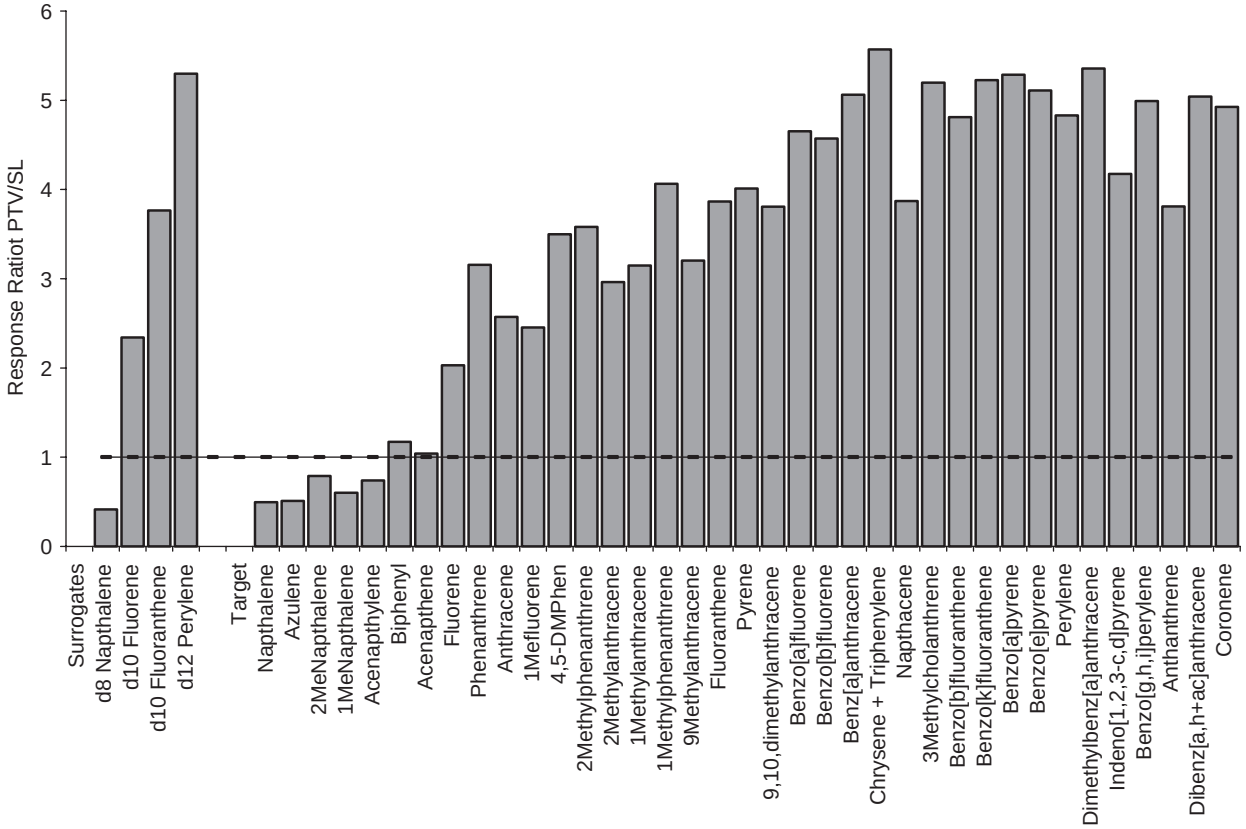


Fig. 1. PAH 100 pg response comparison; PTV (50 μL injected), hot splitless (SL, 2 μL injected).

temperature programmed modes, indicating thermal degradation of NPAHs in the injection port (Fig. 2). The dinitro-substituted PAHs are not detectable in the constant temperature mode (10 ng injected). This illustrates the degradation of more labile NPAHs in a constant temperature splitless injector. The programmed temperature solvent vent and splitless mode responses agree well. In the solvent vent and temperature programmed splitless modes, a similar replicate precision was observed for all NPAHs with no apparent co-venting of the lighter NPAHs (mononitronaphthalenes) in the solvent vent mode.

As described above, the PTV uses multiple injections to load larger sample volumes to the inlet while venting the solvent. Therefore to test the NPAH trapping efficiency, or losses of analytes, during the multiple injections the PTV was configured to inject 2 and 10 μL (2 times 5 μL each) of the NPAH standard containing ~10 ng of each analyte. The area count ratio 10 μL/2 μL injections (Fig. 3) exhibited no losses of NPAHs with respect to vent time. In fact, a greater relative sensitivity (10 μL area counts/2 μL area counts $>5$) was achieved with the increased mass loadings using the 10 μL injection. Therefore, we conclude that there are no significant losses of NPAHs during the sequential injections.

### 3.3. Evaluation of method

The advantages of using the PTV in solvent vent mode for PAHs and NPAH are 2-fold. In addition to loading a larger fraction of the extract to the chromatographic system, the PTV in solvent vent mode apparently allows for a more efficient transfer of analyte mass to the GC as compared to the conventional hot splitless configuration. To test the applicability of this method for atmospheric particulate matter, a series of SRMs were quantified for PAHs and NPAHs. Microgram quantities of Diesel Particulate Matter and Urban Dust (SRM 1650 and 1649a, respectively) were analyzed using standard extraction and purification techniques described above. Using these two SRMs as surrogate matrices, we can assess the potential use of the PTV to

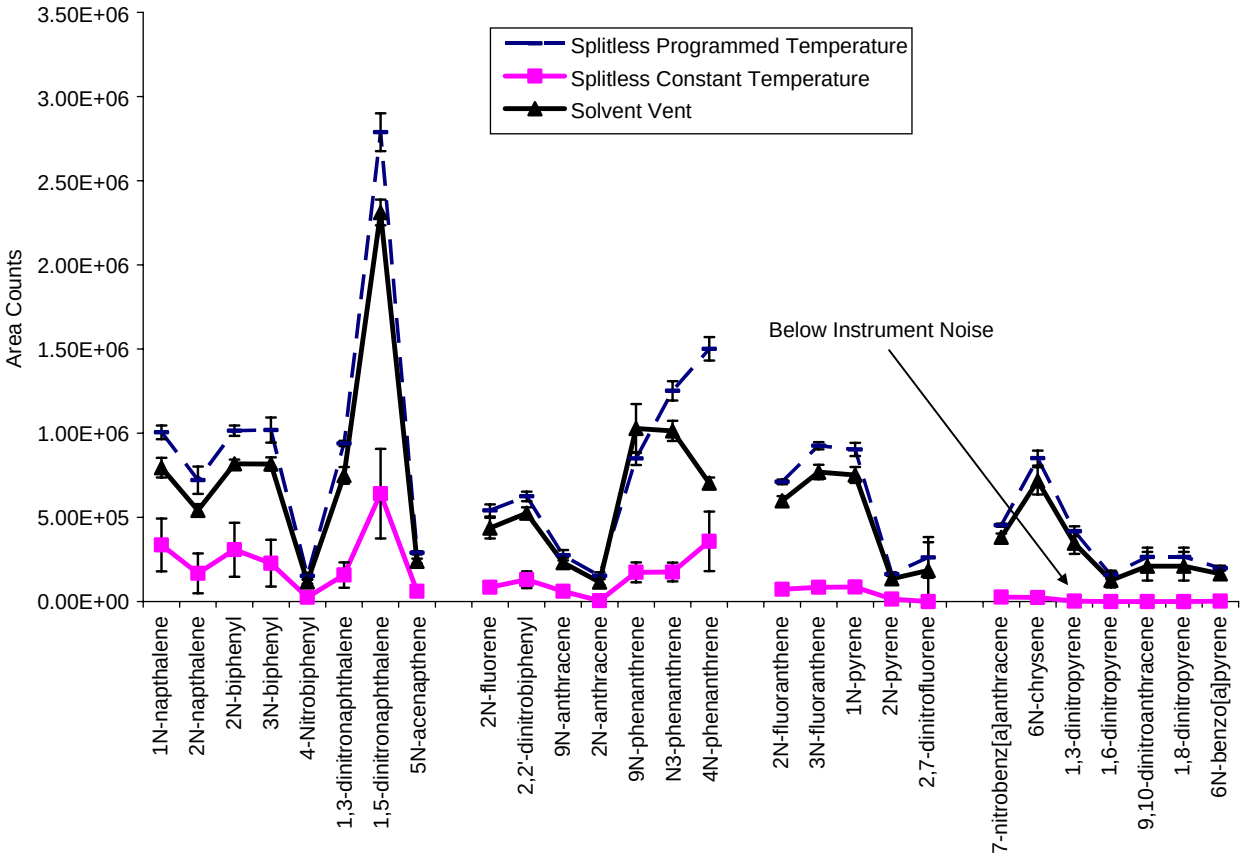


Fig. 2. NPAH mean area counts for solvent vent, hot splitless (SLC) and temperature programmed splitless (SLT).

quantify PAHs and NPAHs in ambient particulate matter on hourly timescales or better.

### 3.3.1. PAHs

Triplicate analyses of SRM 1649 and 1650 (~80 μg and 30 μg, respectively) were performed (Table 2). The geometric mean %RSD of the analysis was 22% and 6.5% for 1649a and 1650, respectively. The Urban Dust SRM PAH concentrations (Certificate of Analysis, 2001) were consistent with the certified values with the exception of the lightest PAHs quantified in this study. Fluoranthene, pyrene, benz[*a*]anthracene, benzo[*b*]- and benzo[*k*]fluoranthene, benzo[*e*]pyrene, perylene, indeno[1,2,3-*c,d*]pyrene, benzo[*g,h,i*]perylene were within 1–2 standard deviations (from this study) of the certified values. Phenanthrene, anthracene, 2-methylphenanthrene, 1-methylphenanthrene and fluorene were consistently 5–10-fold above reported values, of which the latter three are not certified concentrations. All of these compounds were quantified using the same internal standard (phenanthrene-$d_{10}$), suggesting possible matrix interference.

The Diesel Particulate Matter SRM (Certificate of Analysis, 2000) results for PAHs were more consistent, exhibiting a geometric mean %RSD of 6.5%. Similar to SRM 1649, the most volatile PAHs (phenanthrene, anthracene, 1-methylphenanthrene and 2-methylphenanthene) were 1.4–7.6-fold above reported values, with phenanthrene as the only certified concentration. Fluoranthene, pyrene, benz[*a*]anthracene, indeno[1,2,3-*cd*]pyrene, benzo[*g,h,i*]-perylene and coronene were all within 1–2 standard deviations of reported values. The PAHs with molecular weight of 252 were greater than two standard deviations above reported values. Benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[a]pyrene were 1.2-, 1.5- and 2.7-fold above certified values. Benzo[e]pyrene and perylene were 5-and 17-fold, respectively, above certified values. For the majority of PAHs, the certification process of this SRM employs GC/MS and liquid chromatography with fluorescence detection (LC-FL). The

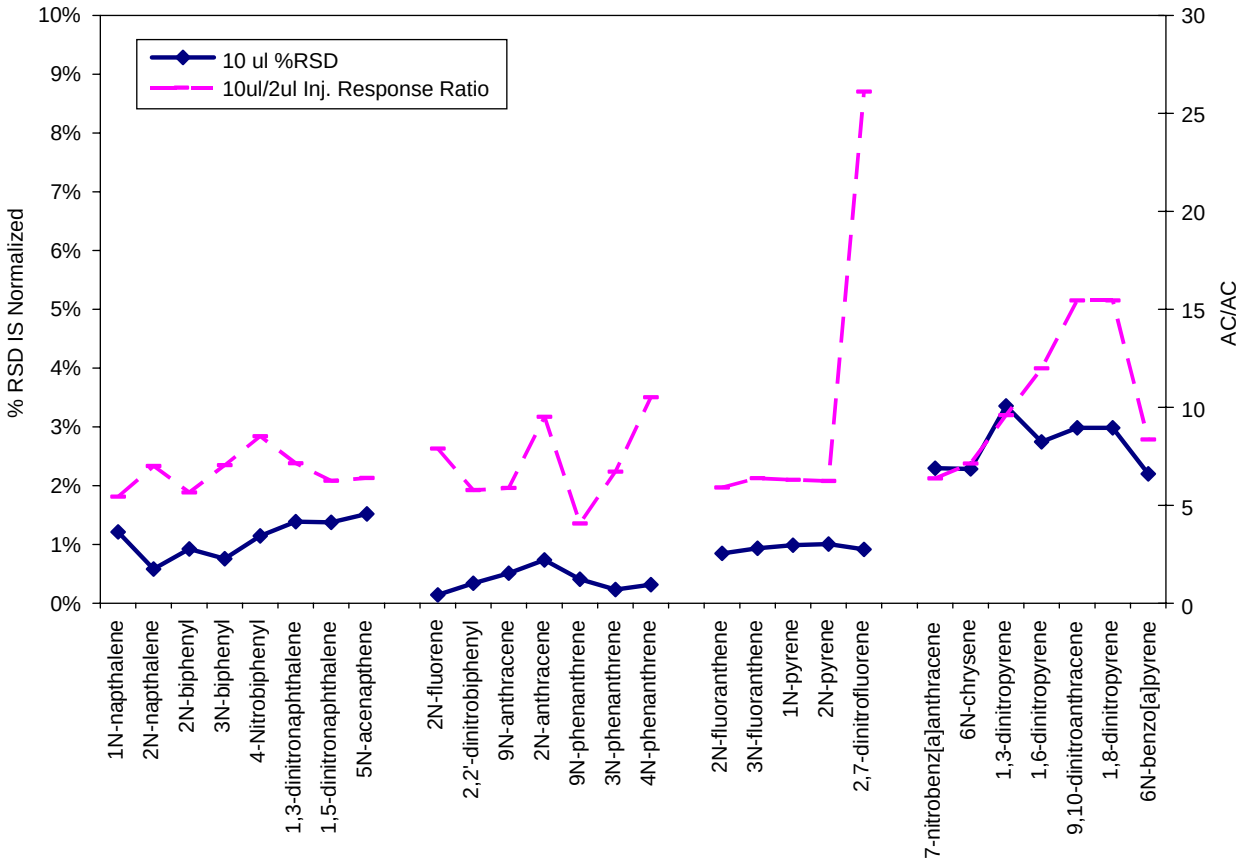


Fig. 3. PTV solvent vent mode NPAH trapping efficiency for 2 and 10 μL injections.

latter two, certified values did not include a LC-FL method. Therefore, injection-port-related matrix affects may be causing the greater discrepancy in these two compounds which are more pronounced in the Diesel SRM than the Urban Dust SRM.

The SRM values from this study agreed well with certified values for the majority of PAHs analyzed. The explanation for the elevated recoveries of the lightest PAHs in SRM 1649 is unclear at this time. Therefore, the current method is not recommended for the lightest PAHs in ambient particulate matter.

### 3.3.2. NPAHs

NPAH concentrations in the SRMs are orders of magnitude lower than PAHs (Bamford et al., 2003). To ensure the detectability of these compounds while retaining low particle mass, larger SRM masses (compared to the PAH analysis) were extracted (500 and 200 μg, respectively). These masses are considerably less than the 50–100 mg extracted by Bamford et al. (2003) analyzed using cool on-column (2 μL) injection. The geometric mean of the %RSDs for the triplicate analysis was 9.8% and 14% for 1650 and 1649, respectively. Poor reproducibility was found for 2-nitrofluorene (95 %RSD) due to low concentration in SRM 1649a (very close to the analytical detection limits). This high uncertainty is consistent with the below detection values reported by Bamford et al. (2003). Unlike the PAH results, there was no vapor pressure specific trend in NPAH recoveries. This is most likely due to the lower vapor pressures of nitro-substituted PAHs relative to the parent PAHs. With the exception of 9-nitroanthracene, our results for both SRMs were consistently below values previously reported (Bamford et al., 2003). The lower concentrations found in this study may be due to matrix-induced thermal degradation of the NPAHs during the thermal desorption step or to incomplete extraction. Values previously reported below detection limits were quantifiable using this method (2-nitrobiphenyl and 2-nitrofluorene for 1649 and 1-nitrobenzo[*e*]pyrene for 1650).

Table 2
PAH SRM comparison using the PTV

| | 1650 certified | 1650[a] this study | 1649 certified | 1649[b] this study |
|---|---|---|---|---|
| Fluorene | | | *0.23(0.05) | 8.3(1.3) |
| Phenanthrene | 68.4(8.5) | 120[c](24)[d] | 4.14(0.37) | 20(4.0) |
| Anthracene | *1.5(0.06) | 11(3.1) | 0.432(0.082) | 2.4(0.54) |
| 2-methylphenanthrene | *70(4) | 108(17) | *0.73(0.12) | 11(2.5) |
| 1-methylphenanthrene | *34(7) | 48(10) | *0.37(0.04) | 4.3(0.7) |
| Fluoranthene | 49.9(2.7) | 48(16) | 6.45(0.18) | 5.6(0.7) |
| Pyrene | 47.5(2.7) | 46(2.9) | 5.29(0.25) | 5.3(1.2) |
| Benz[*a*]anthracene | 6.33(0.77) | 7.3(0.3) | 2.208(0.073) | 2.0(0.5) |
| Chrysene + triphenylene | 26 | 15(0.8) | 4.406 | 2.4(0.4) |
| Benzo[*b*]fluoranthene | 8.81(0.60) | 7.0(0.2) | 6.45(0.64) | 5.0(0.7) |
| Benzo[*k*]fluoranthene | 2.64(0.31) | 4.1(0.4) | 1.913(0.031) | 2.3(0.5) |
| Benzo[*a*]pyrene | 1.33(0.35) | 3.6(0.04) | 2.509(0.087) | 1.7(0.3) |
| Benzo[*e*]pyrene | 7.44(0.53) | 42(5.5) | 3.09(0.19) | 6.6(2.2) |
| Perylene | 0.16(0.04) | 2.8(0.6) | 0.646(0.075) | 0.54(0.3) |
| Indeno[1,2,3-*c,d*]pyrene | 5.62(0.53) | 6.8(0.2) | 3.18(0.72) | 4.8(0.9) |
| Benzo[*g,h,i*]perylene | 6.5(0.94) | 5.0(0.2) | 4.01(0.91) | 3.7(0.6) |
| Coronene | *2(0.1) | 1.8(0.3) | NR[e] | 3.4(0.2) |

[a]Approximately 80 μg extracted and analyzed.
[b]Approximately 30 μg extracted and analyzed.
[c]Geometric mean μg/g ($N = 3$).
[d]1 Standard deviation.
[e]Not reported.
*Not certified reference value.

The dinitropyrenes were not detected in the SRMs (Table 3). During our analysis, we found these compounds to be very sensitive to matrix-induced degradation in the inlet. The relative response of the dinitropyrenes decreased dramatically (>2-fold) in the standard solution quantified after the above-mentioned SRMs ($N = 6$). Therefore, we conclude the dinitropyrenes are not reliably quantified in SRMs and ambient aerosols using the current instrumental setup.

### 3.4. Method implications

The goal of this study is to develop an analytical method for trace level analysis of PAHs and NPAHs suited for hourly quantification of PAHs and NPAHs. The maximum mass of SRM employed was 500 μg. Assuming a particulate matter concentration of 50 $\mu g\,m^{-3}$ of Urban Dust SRM, this corresponds to approximately 10 $m^3$ of air sampled. A collection rate of 0.5 $m^3\,min^{-1}$ would achieve this mass of particulate material in 20 min. Therefore, the sampling time intervals can be in the order of minutes rather than hours or days.

Instrumental detection limits (IDLs) were developed from foil blanks concurrently analyzed with the SRMs (Table 4). These values correspond to the instrument noise multiplied by 3 for each compound. This represents the lower limit of detection of PAHs and NPAHs. The IDLs for NPAHs are consistently 1–2 orders of magnitude below PAHs. Due to the ubiquitous nature of PAHs, method detection limits (MDLs) are usually determined from the greater of the instrument noise and/or contamination. Bamford et al. (1999) reported a minimum detection limit for PAHs of 1 $pg\,m^{-3}$ using 12 h (0.5 $m^3\,min^{-1}$ flow) corresponding to a minimum detection mass of ~400 pg. A similar value can be calculated from the flow and MDLs presented by Halsall et al. (1997) in their study of PAHs in the Artic (Dunai) atmosphere. Larger monitoring programs such as the IADN report similar detection (1–9 $pg\,m^{-3}$ for ~600 $m^3$ sampled) limits for PAHs using GC/MS analysis.

Using similar IDL calculations to this study (3 × s the noise), others have found NPAH detection limits in orders of magnitude above those presented in Table 4. Bonfanti et al. (1996) found IDLs ranging 1–700 pg for 1-nitropyrene and 2-nitrobiphenyl, respectively, using particle beam LC-MS in NCI mode. Jinhui and Lee (2001) employed a derivatization technique to increase their NPAH

Table 3
NPAH SRM comparison using PTV

| | 1650 Bamford et al., 2003 | 1650[a] This study | 1649 Bamford et al. | 1649[b] This study |
|---|---|---|---|---|
| 1-nitronaphthalene | 86.4 | 56[c](21)[d] | 6.8 | 8.4(1.6) |
| 2-nitronaphthalene | 238 | 116(2.9) | 10 | 12(1.7) |
| 2-nitrobiphenyl | 15.3 | 6.8(0.6) | <5 | 2.5(1.4) |
| 3-nitrobiphenyl | 58.1 | 35(6.0) | 3.6 | 4.7(1.0) |
| 4-nitrobiphenyl | | 78(16) | | 5.5(3.5) |
| 1,3-dinitronaphthalene | | | | |
| 1,5-dinitronaphthalene | | | | |
| 5-nitroacenapthene | 37 | 46(5.5) | 3.1 | 4.2(3.1) |
| 2-nitrofluorene | 46.2 | 44(3.3) | <2 | 2.6(3.4) |
| 2,2'-dinitrobiphenyl | | | | |
| 9-nitroanthracene | 6080 | 13000(350) | 35.9 | 70(11) |
| 2-nitroanthracene | | 1400(50) | | 14(2.8) |
| 9-nitrophenanthrene | 510 | 320(21) | 1.7 | 2.1(0.6) |
| 3-nitrophenanthrene | 4350 | 2040(79) | 0.47 | 1.6($N = 1$[e]) |
| 4-nitrophenanthrene | | | | |
| 2-nitrofluoranthene | 201 | 230(9.0) | 282 | 190(16) |
| 3-nitrofluoranthene | 65.2 | 54(3.8) | 4.5 | 1.9(0.15) |
| 1-nitropyrene | 18330 | 16000(1200) | 71.5 | 40(3.6) |
| 2-nitropyrene | | | 24.4 | 7.0(0.1) |
| 2,7-dinitrofluorene | | | | |
| 7-nitro[*a*]anthracene | 995 | 390(48) | 35.1 | 15(2.0) |
| 6-nitrochysene | 44.4 | 36(3.4) | 4.4 | 2.5(0.6) |
| 1,3-dinitropyrene | | | | |
| 1,6-dinitropyrene | | | | |
| 9,10-dinitroanthracene | | | | |
| 1,8-dinitropyrene | | | | |
| 6-nitrobenzo[*a*]pyrene | 1442 | 970(300) | | |
| 1-nitrobenzo[*e*]pyrene | <10 | 13 | | |
| 3-nitrobenzo[*e*]pyrene | 89 | 70($N = 1$) | | |
| 1-nitro- and 3-nitro-benzo[*a*]pyrene | | | | |

[a]Approximately 200 μg extracted. See text for specifics.
[b]Approximately 500 μg extracted.
[c]Geometric mean ng/g ($N = 3$).
[d]1 standard deviation ($N = 3$).
[e]Above detection limits in 1 sample.

sensitivity using a GC-electron capture detector as opposed to GC/MS (30 and 150 pg, respectively). This method utilized a hot splitless injector possibly contributing to the high (compared to this study) IDLs reported. Feildberg et al. (2001) used a temperature programmed injector and ion trap GC/NCI for NPAH analysis in Denmark. The IDLs for 9-nitroanthracene (35 pg), 2-nitrofluoranthene (20 pg), 3-nitrofluoranthene (22), 1-nitropyrene (24 pg) and 2-nitropyrene (22 pg) are also in orders of magnitude above the method presented here. Bamford et al. (2003) developed method detection limits using 3 times the blank values using cool on-column injection GC/NCI. From the mean volume (1400 $m^3$) collected and the MDL range (0.001–0.12 pg $m^{-3}$), we can estimate an IDL (including possible interferences) ranging 1.4–170 pg. This is still 5–10 times above the majority of the NPAH IDLs presented here.

From the IDLs presented in this study, an upper limit of the temporal resolution of PAHs and NPAHs has been calculated for a variety of samplers (Table 5). For this conservative comparison, a method detection limit was calculated as 10 × the IDL for benzo[*a*]pyrene and 1-nitropyrene. Mean July 2003 concentrations in Baltimore, MD,

Table 4
Instrumental detection limits for PAHs and NPAHs

| PAHs | IDL (pg)[a] | NPAHs | IDL (pg) |
|---|---|---|---|
| Naphthalene | 9.8 | 1-nitronaphthalene | 0.51 |
| Azulene | 23 | 2-nitronaphthalene | 0.79 |
| 2-methylnaphthalene | 2.7 | 2-nitrobiphenyl | 0.57 |
| 1-methylnaphthalene | 9.6 | 3-nitrobiphenyl | 0.26 |
| Acenapthylene | 7.6 | 4-nitrobiphenyl | 2.4 |
| Biphenyl | 1.8 | 1,3-dinitronaphthalene | 0.57 |
| Acenaphthene | 4.4 | 1,5-dinitronaphthalene | 0.23 |
| | | 5-nitroacenapthene | 0.71 |
| Fluorene | 7.4 | | |
| Phenanthrene | 40 | 2-nitrofluorene | 0.15 |
| Anthracene | 24 | 2,2'-dinitrobiphenyl | 0.27 |
| 1-methylfluorene | 9.2 | 9-nitroanthracene | 0.88 |
| 4,5-methylenephenanthrene | 10 | 2-nitroanthracene | 1.0 |
| 2-methylphenanthrene | 12 | 9-nitrophenanthrene | 0.19 |
| 2-methylanthracene | 19 | 3-nitrophenanthrene | 0.11 |
| 1-methylanthracene | 25 | 4-nitrophenanthrene | 0.13 |
| 1-methylphenanthrene | 20 | | |
| 9-methylanthracene | 22 | 2-nitrofluoranthene | 0.27 |
| | | 3-nitrofluoranthene | 0.16 |
| Fluoranthene | 25 | 1-nitropyrene | 0.17 |
| Pyrene | 11 | 2-nitropyrene | 1.8 |
| 9,10-dimethylanthracene | 33 | 2,7-dinitrofluorene | 0.16 |
| Benzo[*a*]fluorene | 6.0 | | |
| Benzo[*b*]fluorene | 26 | 7-nitro[*a*]anthracene | 0.30 |
| Benz[*a*]anthracene | 5.0 | 6-nitrochysene | 0.09 |
| Chrysene + triphenylene | 2.3 | 1,3-dinitropyrene | 0.53 |
| Napthacene | 24 | 1,6-dinitropyrene | 2.85 |
| 3-methylcholanthrene | 12 | 9,10-dinitroanthracene | 2.1 |
| | | 1,8-dinitropyrene | 1.7 |
| Benzo[*b*]fluoranthene | 11 | 6-nitrobenzo[*a*]pyrene | 0.65 |
| Benzo[*k*]fluoranthene | 7.7 | 1-nitrobenzo[*e*]pyrene | 1.1 |
| Benzo[*a*]pyrene | 8.2 | 3-nitrobenzo[*e*]pyrene | 1.8 |
| Benzo[*e*]pyrene | 28 | 1-nitro- and 3-nitro- | |
| Perylene | 3.3 | benzo[*a*]pyrene | 12 |
| Dimethylbenz[*a*]anthracene | 30 | | |
| Indeno[1,2,3-*c,d*]pyrene | 5.4 | | |
| Benzo[*g,h,i*]perylene | 1.7 | | |
| Anthanthrene | 1.5 | | |
| Diben[*a,h* + *a,c*]anthracene | 0.44 | | |
| Coronene | 4.4 | | |

[a]Three times the instrument noise.

from Bamford and Baker (2003) were chosen as representative ambient concentrations. The lower limit of sampling frequency for 1-nitropyrene ranges 0.4 min (hi-vol) to 42 min for a personal sampler. The sampling time required for detecting benzo[*a*]-pyrene is approximately half that of 1-nitropyrene.

This method has been recently employed to measure 12 h NPAH size distributions in Baltimore, MD, using a Berner low-pressure impactor with a flow of 80 Lpm (Crimmins and Baker, 2006). Fig. 4 depicts a mean size distribution of 1-nitropyrene and 2-nitrofluoranthene for two consecutive day and night samples collected in April 2002. For all samples, 2-nitrofluoranthene and 1-nitropyrene were above detection limits (0.34 and 0.10 pg $m^{-3}$) in the four smallest size cuts of the impactor ($<6.0\,\mu m$). The concentration in the accumulation mode (0.14–0.49 μm) was greater than 2 orders of magnitude above the MDLs accounting for the largest particle mass (~500 μg) and concentration of 2-nitrofluoranthene (48–77 pg $m^{-3}$). A similar trend was found for 1-nitropyrene with the exception of

Table 5
Lower limit of sampling times using conventional instruments and PTV-GC/MS

| | Sampling times (min) | | | | | |
|---|---|---|---|---|---|---|
| | MDL[a] (pg) | Typical concentration[b] ($pg\,m^{-3}$) | Hi-vol ($0.5\,m^3\,min^{-1}$) | Denuder ($0.05\,m^3\,min^{-1}$) | Impactors[c] ($0.08\,m^3\,min^{-1}$) | Personal[d] sampler (5 Lpm) |
| 1-nitropyrene | 1.7 | 8 | 0.42 | 4.2 | 2.6 | 42 |
| Benzo[*a*]pyrene | 80 | 80 | 0.20 | 2.0 | 1.3 | 20 |

[a]Method detection limit from this study.
[b]Mean summer concentration, Bamford and Baker (2003).
[c]This study.
[d]Personal sampler, TSI incorporated, Shoreview, MN.

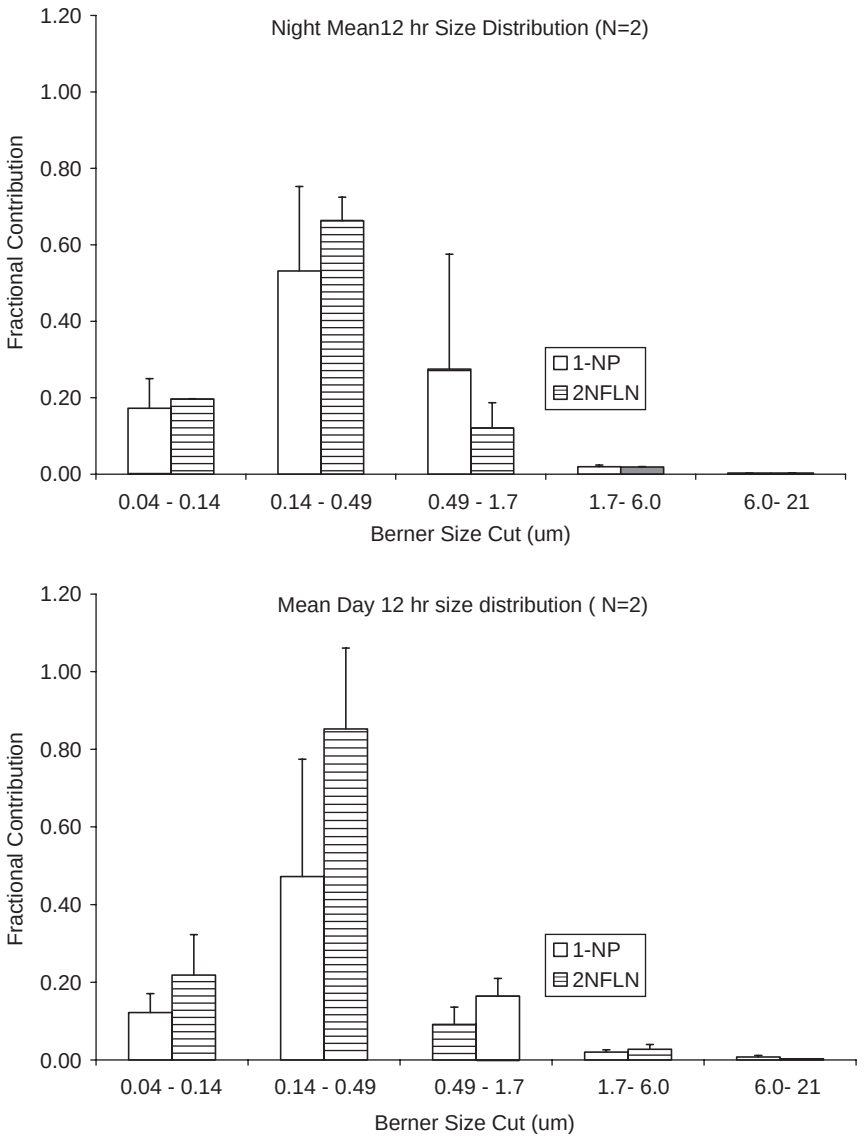


Fig. 4. Mean size distribution of 1-nitropyrene and 2-nitrofluoranthene April 2002.

one night sample where the stage 3 (0.49–1.7 μm) concentration was greatest (13 pg $m^{-3}$). During the day, approximately 83% of the total 2-nitrofluranthene concentration was associated with the greatest particle surface area (i.e. accumulation mode, 0.14–0.49 μm) whereas 1-nitropyrene was more evenly distributed among the smallest 3 particle size classes collected. To our knowledge, this is the first reported size distribution of NPAH on timescales less than a day. Using this method, we were able to quantify NPAHs consistently from $<300$ μg (extracted per stage) of ambient particulate matter mass.

## 4. Conclusions

Enhanced temporal resolution of air toxics such as PAHs and NPAHs is critical to understanding their sources and behavior in the ambient atmosphere. We present a large volume injection technique for the quantification of both classes of compounds. The programmed temperature vaporization large-volume injection techniques have similar precision as the standard hot splitless injection, while enhancing the sensitivity per mass injected up to 5-fold for PAHs. The methods were verified using microgram quantities of Standard Reference Materials. The dinitro-substituted PAHs were not quantifiable using this technique, possibly due to matrix-induced degradation.

The significance of the increased analytical sensitivity (temporal resolution) is demonstrated by the diurnal NPAH size distribution presented here. Using this method, we were able to present the first reported diurnal NPAH size distribution in ambient particulate matter. Further application of this injection technique will undoubtedly increase our knowledge and certainty (lower artifacts) of the phase distribution, sources, photochemistry and inevitably the real-time health effects associated with PAH and NPAHs in the ambient atmosphere. From the detection limits presented in this study, commercially available sampling equipment may be employed to better elucidate PAH and NPAH behavior on timescales of minutes.

In a broader sense, this technique provides a gentler sample introduction technique able to efficiently and consistently increase the method sensitivity of these compounds by orders of magnitude using commercially available sampling equipment. This increased sensitivity corresponds to greater temporal resolution, hence, minimizes potential artifacts associated with extended sampling times. In the future, this injection technique should be further evaluated for other non-polar and polar organic tracers analyzed by GC. Encompassing these tracers along with PAHs and NPAHs will undoubtedly broaden our understanding particulate organic carbon sources, photochemistry and potential health effects.

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