Technical note

Quantification of nitrated-polycyclic aromatic hydrocarbons in atmospheric aerosol samples with in-injection port thermal desorption-gas chromatography/ negative chemical ionization mass spectrometry method

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ABSTRACT

In-injection port thermal desorption (TD) was extended in determination of particulate phase nitrated-polycyclic aromatic hydrocarbons (N-PAHs) on filter samples coupled with a gas chromatography/negative ion chemical ionization-mass spectrometry (GC/NCI-MS). The experimental and analytical parameters were optimized with standard testing and ambient samples. Fourteen of the most abundant N-PAHs in ambient airs were included for their quantification. A desorption temperature of 280 °C for 10 min was sufficient to transfer entire target compounds from injection port to the analytical system. Good linearity ($R^2 > 0.995$) on the calibrations for each analyte was achieved. The limit of detections (LODs) ranged from 46.5 to 152.3 pg per filter sample, which were 4–66% better than solvent extraction (SE) approach. Method precision, repeatability and reproducibility, determined by replicate analyses of calibration standards and ambient samples, were less than 6% for target compounds. Validation of the method were conducted with two batches of a total of 30 ambient aerosol-loaded filters using our TD and the traditional SE approaches. Reasonably good agreement ($R^2 = 0.98$) by the two methods was demonstrated for most of N-PAHs, except for 9-nitrophenanthrene and 6-nitrobenzo(*a*)pyrene. The in-injection port TD can improve laboratory efficiency and reduce solvent-based costs for the measurement of N-PAHs.

1. Introduction

Particulate phase nitrated-polycyclic aromatic hydrocarbons (N-PAHs), formed either by direct incomplete combustion processes or photochemical oxidation at the presence of nitrogen oxides (NO$_x$) (Arey et al., 1986; Ovrevik et al., 2010), have toxicological significances even at much lower concentrations than those of their corresponding parent PAHs (Bandowe et al., 2014; Durant et al., 1996). Determination of their abundances in atmosphere or samples generated from laboratory stimulating tests for source apportionment and health assessment are critical (Bandowe and Meusel, 2017). An efficient and sensitive

analytical method is thus necessary for accurate quantification (Santos et al., 2016).

The most common offline method is to extract particulate matter (PM)-loaded filter with organic solvent (i.e., solvent extraction [SE]), followed by separations with chromatographic techniques such as gas chromatography (GC) and high-performance liquid chromatography (HPLC). The analytes are usually detected by a mass spectrometer (MS) or other detectors (Bandowe and Meusel, 2017). However, SE, including pressurized fluid extraction (PFE, or co-called accelerated solvent extraction, ASE), Soxhlet extraction, ultrasonication, and microwave extraction, often involves complicated pretreatment processes

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and multiple pre-concentration steps (Albinet et al., 2014; Bandowe et al., 2014; Bezabeh et al., 2003; Brichac et al., 2004; Galceran and Moyano, 1993; Ho et al., 2008a, 2011; Ho and Yu, 2002; Robbat et al., 1986; Teixeira and Garcia, 2011). Those time- and labor-consuming procedures suffer from limitations in sensitivity or selectivity (Ho et al., 2008b, 2017a; Zielinska and Samy, 2006). Large quantities of solvents used and long extraction times also introduce impurities to the extracts (Ho and Yu, 2004). SE is therefore not a desirable method for the determination of picogram (pg) to sub-pg per cubic meter of N-PAHs in PM samples.

Thermal Desorption (TD) is an alternative mean to SE by using elevated temperatures to transfer organic analytes to a GC/MS system (Chow et al., 2007; Helmig et al., 1992; Waterman et al., 2000). Helmig et al. (1990) analyzed particle bound organics by TD-GC/MS technique with modified septum cap in GC injector port. Recent years, TD-GCMS has been widely used for analysis of volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) (Bates et al., 2008; Ho et al., 2017b; Kim and Tanabe, 2016; Li and Zhu, 2017; Martins et al., 2013; Mercier et al., 2012; Provost et al., 2014). Ho and Yu (2004) developed an in-injection port TD-GCMS approach for analysis of nonpolar organic compounds of ambient aerosol samples collected on Teflon impregnated glass-fiber filters with no modification of existing GC–MS. This approach is less time-consuming than SE since no pre-analysis preparation is required. In-injection port TD not only requires small quantity of samples (0.5–5 cm^2) and short sample preparation duration (< 1 min), and also offer excellent precisions (< 10% variation) and accuracy (− 4.8–4.9%) in measurement of non-polar organic compounds (i.e., polycyclic aromatic hydrocarbons [PAHs], alkanes, hopanes, steranes and phthalates) on PM filters (Ho et al., 2008b). The target analytes are detected with electron-impact ionization (EI) in MSD. It can be adopted for a conventional GC unit without any modification and additional TD device (Sigman and Ma, 1999).

N-PAHs are two orders of magnitude sensitive to negative chemical-impact ionization (NCI) than universal EI in mass detection due to their high electronegativity with electron-withdrawing groups (Bezabeh et al., 2003; Húsková et al., 2009; Zielinska and Samy, 2006). GC/NCI-MS has been proven to be one of the most selective and sensitive methods for analyzing most common N-PAHs (Robbat et al., 1986). In early stage, Oehme et al. (1982) achieved detection limits ranged from 0.5 to 4 pg in the analysis of N-PAHs with NCI-MS operated at selected ion monitoring (SIM) mode. The objective of this work is to explore the in-injection port TD approach coupled with GC/NCI-MS to quantify N-PAHs in PM-loaded filter samples. Its feasibility was demonstrated by their precisions and detection limits, and the results from TD were also validated with those from traditional SE approach.

2. Materials and methods

2.1. Chemicals

5-Nitroacenaphthene (≥98%), 2-nitrofluorene (≥98%), 9-nitrophenanthrene (≥99.5%), 3-nitrofluoranthene (≥99.5%), and 1,6-dinitropyrene (≥98%) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). 1-Nitronaphthalene (≥99%), 2-nitrobiphenyl (≥97%), and 2,7-dinitrofluorene (≥97%) were obtained from Ultra Scientific (North Kingstown, RI, USA). 9-Nitroanthracene, 1,3-dinitropyrene, 1,8-dinitropyrene (≥98%), 6-nitrochrysene (≥99%), and 6-nitrobenzo(a)pyrene (≥99%) were obtained from AccuStandard (New Haven, CT, USA). 1-Nitropyrene (≥99%) was obtained from Sigma (St. Louis, MO, USA). 1-Nitronaphthalene-D$_7$ (≥98%), 2-nitrofluorene-D$_9$ (≥98%), 3-nitrofluoranthene-D$_9$ (≥98%) and 6-nitrochrysene-D$_{11}$ (≥98%) were obtained from CDN Isotopes (Quebec, Canada). Fluoranthene-D$_{10}$ (≥98%) was obtained from Supelco (St. Louis, MO, USA).

2.2. Testing sample

Fourteen target N-PAHs were diluted to a working level of 0.5 μg mL^{-1} with toluene (JT Baker, Phillipsburg, USA). A punch of 0.526 cm^2 of pre-baked (800 °C, 8 h) quartz fiber-filter (QM/A, 20.3 × 25.4 cm^2, Whatman Inc., Clifton, NJ, USA) was spiked with 8 μL of the standard mixture solution. One microliter of a solution containing four deuterated N-PAHs (i.e., nitronaphthalene-D$_7$, 2-nitrofluorene-D$_9$, 3-nitrofluoranthene-D$_9$ and 6-nitrochrysene-D$_{11}$) (5 μg mL^{-1}) and 1 μL of a parent deuterated PAHs of fluoranthene-D$_{10}$ (5 μg mL^{-1}) were spiked as internal standards (IS). The punch was then cut into small pieces with a clean razor blade and inserted into a Pyrex glass tube (a diameter of 78 mm long, 4 mm i. d., and 6 mm o. d.; pre-heated at 450 °C for 6 h) with a small amount of pre-baked glass wool (Alltech, Dearfield, IL, USA). The glass wool at the two ends held the filter parts in position and prevented any contamination of the GC column. The size of the Pyrex tube was identical to a liner used in an Agilent GC 7890 injection port. The sample-loaded tube was stored in an amber tube no longer than 12 h prior to chemical analysis. All prepared amber tubes were stored at 0 °C before analysis. Detailed sample handling and precautions have been shown in our previous publications (Ho et al., 2008b, 2011; Ho and Yu, 2004).

2.3. Ambient samples

PM$_{2.5}$ ambient air samples were collected on pre-baked quartz fiber-filters (QM/A, 20.3 × 25.4 cm^2, Whatman Inc.) using high-volume samplers (Graseby-Andersen, Atlanta, GA, USA) operated at a flow rate of 1.1 m^3 min^{-1} for 24 h (from 10:00 to next day 09:59 local standard time). Two sets of samples, with 15 samples in each set, collected in Beijing and Xi'an, China were used to demonstrate the feasibility of the TD method. After sampling, the filter samples were packed in pre-baked aluminum foil and stored in a freezer at − 20 °C until chemical analysis. One or two punches of 0.526 cm^2 were obtained from a parent filter sample. The IS mixtures were spiked onto the filter punches for quantification. The samples were then prepared into the TD tubes as the same way as the testing samples. The tube was also analyzed between 12 h after spiking.

2.4. Thermal desorption method

The TD step took place in the injector port of an Agilent Technology 7890A GC coupled with a 5975C MS detector (Santa Clara, CA, USA). Fig. 1 illustrates the time events of the GC injector and column compartment throughout the whole analysis. Briefly, the GC injector temperature was lower to 50 °C, while the oven temperature was kept at 50 °C. Once the sample-loaded tube was exchanged into the injector port, the injector temperature was raised to 280 °C manually. After it reached to the set point, the GC oven program started at an initial temperature of 50 °C for 2 min, then programmed at a rate of 45 °C min^{-1} to 150 °C, held at 150 °C for 10 min and ramped to 300 °C at a rate of 5 °C min^{-1}, and finally held at the temperature of 300 °C for 5 min. The injector was operated in the splitless mode during the GC run. The GC was equipped with an HP-5MS (5% diphenyl/95% dimethylsiloxane, 30 m length x 0.25 mm diameter x 0.25 μm film thickness, Agilent Technology). Helium (He) was used as carrier gas held at a constant flow rate of 1.2 ml min^{-1}. The transfer line temperature was set at 280 °C. The MSD was operated at NCI mode using methane (CH$_4$) (Xi'an Teda Cryogenic Equipment Co., Xi'an, China) as a reagent gas at 150 °C. The quadrupole temperature was at 150 °C. A SIM mode was applied to scan the target compounds. The selected ion for each analyte was chosen on the base of its characteristic fragment. The information was shown in Table S1.

Calibration standards were prepared by spiking known amounts of liquid standard mixtures and the deuterated IS onto separate pre-baked filter punches (i.e., 0.526 cm^2). A maximum filter size of 10 punches
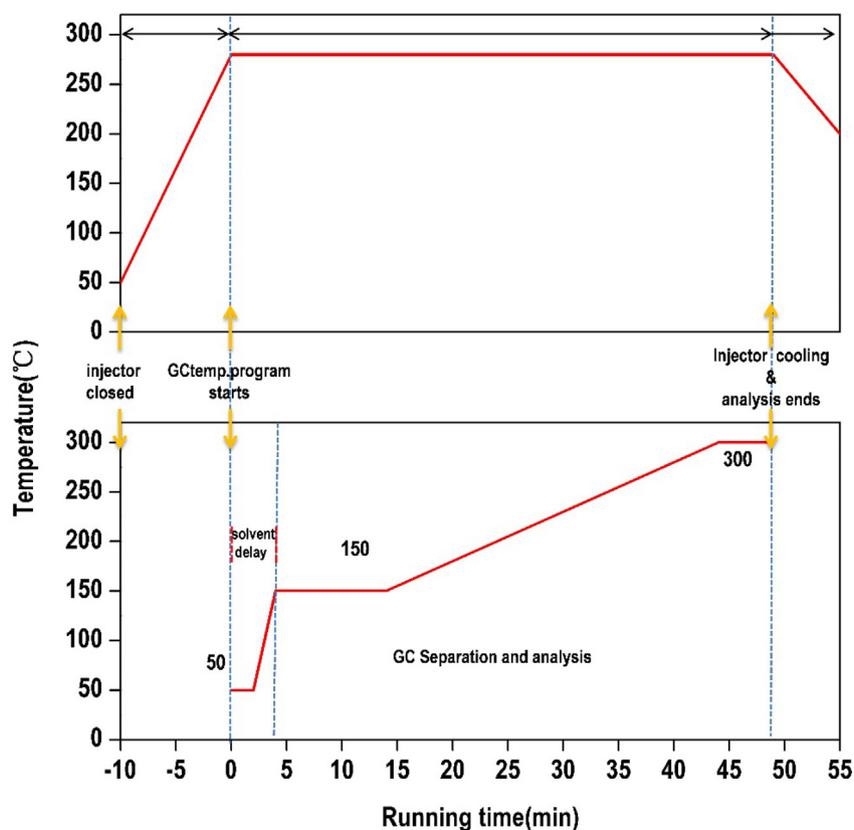
Fig. 1. Time events of the GC injector (top) and the column oven (bottom) during the TD and GC-NCI-MS method.

($5.26 \, cm^2$) were used to determine the limit of detection (LOD). The standard-spiked filters were then cut and transferred into the TD tubes in the same way as for the sample filters. The analysis of the calibration samples was conducted within 12 h after their preparation. Calibration curve of each analyst was established by plotting the peak area ratios between the analytes and fluoranthene-D_{10} versus the amounts of the analytes. All Pyrex tubes were cleaned and reused after cleaning and baking at 450 °C for 6 h.

2.5. Solvent extraction method

A 47-mm diameter filter ($17.34 \, cm^2$) was punched from the parent high-volume sample. The four deuterated N-PAHs spiked on the filter were used as recovery IS for extraction. The filter was then extracted with 5 ml of dichloromethane:methanol (3:1, v/v) (JT Baker) in an ultrasonication water bath operated at room temperature (22 ± 2 °C) for 15 min, followed by twice extractions with 5 ml dichloromethane for each of 15 min. Three portions of extracts were combined and removed from water by adding anhydrous sodium sulfate (Sigma-Aldrich). The dried extract was then concentrated to below 0.5 ml using rotary evaporator and gentle high-purity nitrogen (Xi'an Teda Cryogenic Equipment Co.) gas blowing. Twenty-five microliters of fluoranthene-D_{10} at a concentration level of $20 \, ng \, \mu l^{-1}$ was added in the extract solution that served as an injection IS. The final solution was mixed to 1 ml.

One microliter of the sample extract was injected into the GC at an injection temperature of 280 °C with an autosampler (7693, Agilent Technology). The injector was operated in a pulsed splitless mode at a pressure of 250 hPa. The liquid injection temperature program was identical as a previous study (Bezabeh et al., 2003). The initial GC oven temperature of 60 °C was held for 2 min, ramped to 150 °C at a rate of 45 °C min^{-1} and held for 10 min, and increased to 300 °C at a rate of 5 °C min^{-1} and held at the final temperature for 5 min. The target

compounds were scanned and detected by the MSD with SIM mode. The MSD was operated as the same as the condition for TD experiment. Calibration curves were established by plotting the peak area ratios (analytes/injection IS) versus the amounts of the analytes per injection. The extraction recoveries of the analytes were estimated using blank filters spiked with analytes at certain quantity. The concentrations of the spiked blank filters were calculated from the calibration curve and compared to the theoretical values to calculate the extraction recoveries.

3. Results and discussion

3.1. Optimization of the developed method

Splitless is a classic injection mode applied in TD processes to transfer entire desorbed analytes into the stationary column, particularly critical for in-injection port TD (Bezabeh et al., 2003; Ho and Yu, 2004; Ho et al., 2008b). Figure S1 compares the responses of target N-PAHs loaded samples analyzed through two types of splitless modes (i.e., regular splitless verse pulsed splitless). In comparison, higher intensities (expressed in absolute peak areas) of the analytes were seen with regular splitless. Besides, pulsed splitless often resulted in greater retention time shifts (> 0.2 min) from observations of replicate analysis. Regular splitless can offer a relatively consistent retention time for each analyte, and thus was selected in the TD application.

Fig. 2a compares the responses of fourteen target N-PAHs loaded into the injector port at different temperatures. The relative differences were demonstrated by analyses of same amounts of target analytes spiked on blank filter punches which were transferred to the injector port at 40, 80 and 100 °C, in comparison with that at 50 °C. The final desorption temperature was consistently set at 280 °C. The TD durations ranged from 8.3 to 12 min as longer desorption times were required for lower initial temperatures. During the TD taken place, the analytes
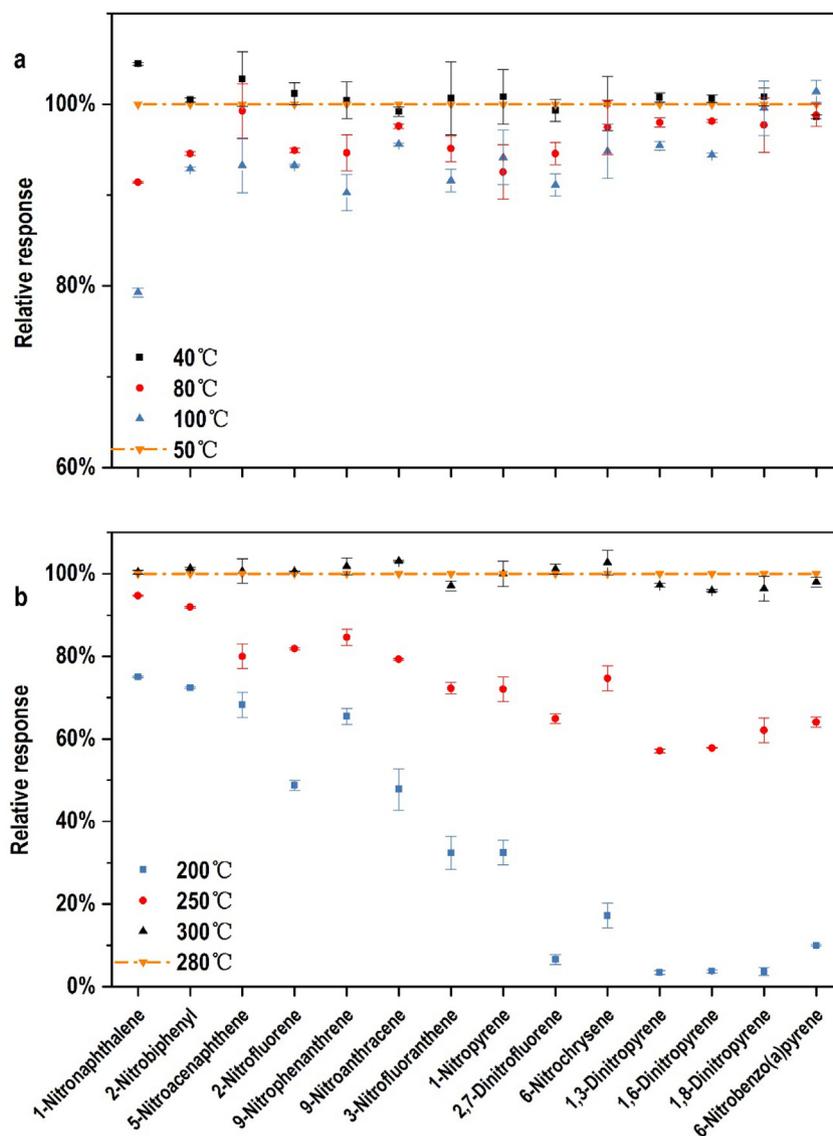
Fig. 2. Relative responses at different (a) initial sample loading injector temperatures and (b) final TD injector temperatures for N-PAHs. **Peak Identification:** 1. 1-Nitronaphthalene; 2. 2-Nitrobiphenyl; 3.5-Nitroacenaphthen-e; 4. 2-Nitrofluorene; 5. 9-Nitrophenanthrene; 6. 9-Nitroanthracene; 7. 3-Nitrofluoranthene; 8. 1-Nitropyrene; 9. 2,7-Dinitrofluorene; 10. 6-Nitrochrysene; 11. 1,3-Dinitropyrene; 12. 1,6-Dinitropyrene; 13. 1,8-Dinitropyrene; 14. 6-Nitrobenz(*a*)pyrene. IS1. 1-Nitronaphthalene-D$_7$; IS2. 2-Nitrofluorene-D$_9$; IS3. 3-Nitrofluoranthene-D$_9$; IS4. 6-Nitrochrysene-D$_{11}$.

were refocused onto column head at 50 °C. The more volatile analytes were expected to be more sensitive to the loading temperatures due to prior evaporation before closure of injector cap (~10 s). In addition, the affinity between the analytes and polymer coating on the capillary column is a controlling factor. At the lowest temperature of 40 °C, the responses of the first three eluted target N-PAHs, including, 1-nitronaphthalene (boiling point [b.p.] = 304 °C, 2-nitrobiphenyl (b.p. = 320 °C) and 5-nitroacenaphthene (b.p. = 279 °C), were 4.0%, 0.4% and 3.0%, respectively, higher than those analyzed at 50 °C. However, it typically requires extra 20 min for the injector decreased from 50 °C to 40 °C with default GC ventilation. The relative responses of 1-nitronaphthalene and 2-nitrobiphenyl dropped by 9% and 6%, and 21% and 8%, respectively, when the samples loaded at higher temperatures of 80 °C and 100 °C. The responses of those N-PAHs eluted beyond 5-nitroacenaphthene were unaffected by the examined injector temperatures, demonstrating that the loss from prior evaporation or non-effective retainment onto the column head were negligible. Based on the results, we standardize to exchange the tube inside the injector at the temperature of 50 °C for chemical analysis.

The final desorption temperature controls the completeness of analytes transferred from the filter to the analytical system. Fig. 2b shows the relative responses of target analytes desorbed at final temperatures of 200, 250, and 300 °C in comparison with that at 280 °C. The standard-containing tubes were consistently loaded in the GC injector at 50 °C. The injector took approximately 6.0, 8.0, 10.0 and 11.0 min to reach the set temperatures of 200, 250, 280 and 300 °C, respectively. Optimal temperature was selected for the maximal response of the target analytes (i.e., peak area). It is apparent that greater responses were achieved at higher desorption temperatures. The worst responses were seen at 200 °C, which were 25–97% lower than those analyzed at 280 °C. Insufficient desorption temperatures cannot completely remove the analytes from the samples subjected to their volatility and affinity to the filter matrix. This can be proved by the results that the responses were dropped only 54.4–97.0% for the less volatile N-PAHs (b.p. > 400 °C) at both of 200 °C and 250 °C, in comparison of 5.3–52.3% for more volatiles. No significant difference (< 3.0%) was seen between the results obtained at 280 and 300 °C for all target compounds. It should be noted that N-PAHs are thermolabile at high temperatures

(Albinet et al., 2014). When heated to decomposition most of NPAHs (i.e., 1-nitronaphthalene, 5-nitroacenaphthene, 1-nitropyrene, 1,6-dinitropyrene, 1,8-dinitropyrene, 6-nitrobenzo(*a*)pyrene (Lewis, 1996) and 1,3-dinitropyrene (Sciencelab.com, 2013) emit toxic fumes of nitrogen oxides. Therefore, unnecessarily high injector temperature would lead loss of analytes.

The completeness of desorption was demonstrated by re-analysis of the TD tube consequently after the first desorption. No any detectable signal for the target peaks was seen in the chromatogram. Further extension of desorption times (e.g., held at final desorption temperature before the oven temperature program starts) had no any signal increase as well. The results prove that the target compounds were entirely desorbed from the loading temperature of 50 °C–280 °C in 10 min.

With the in-injection port TD approach, the GC column head acts a cryo-focusing trap to retain the analytes before the oven temperature starts. An optimum initial oven temperature of 50 °C was found which gave the highest responses to the target analytes. Higher temperatures could result wider peak width on the chromatogram, representing that the analytes were unable to retain onto a short band in the capillary column during the TD process. An extra benefit of the initial temperature of 50 °C is that it does not require cooling of the oven with any cryogenic reagents (i.e., liquid nitrogen or carbon dioxide). It can be thus adopted on any conventional GC unit.

3.2. Characterization of the developed method

Fig. 3 shows the SIM chromatogram for a standard loaded filter sample. The fourteen target N-PAHs and the IS could be separated. Table 1 lists the calibration slopes, intercepts, and coefficients of determination (R^2) for each analyte with a range of 0.02–30 ng per analysis. The R^2 are all greater than 0.995, indicating good linearity for the responses with the TD method. The LOD is defined as the minimum

amount of a N-PAH that generates the minimum distinguishable signal plus three times the standard deviation of the blank signals. No peak was detected for all target analytes in the blank calibration samples. Therefore, we approximated the mean blank signal with the calibration line intercept and the blank signal standard deviation with the standard error for the y (peak area ratio) estimate (Ho et al., 2017b). By this approach, the LODs were calculated to be in the range of 14.1–46.2 pg per loading for N-PAHs (Table 1). Reproducibility was assessed by replicate analyses of calibration standards and ambient samples (Fig. 4). Seven replicate analyses of standard samples reported RSDs of 1.0–4.9% with a median RSD of 3.1% for the target N-PAHs. Five replicate analyses of ambient samples reported RSDs of 0.3–5.7%, with a median RSD of 2.2%. RSDs for all N-PAHs did not exceed 10% and most (> 90%) of the RSDs did not exceed 5%. The good reproducibility demonstrates the quantitative desorption of N-PAHs from the filter as well as the stability of the MS system. RSDs for ambient samples could be affected by inhomogeneities of sample deposits as well as uncertainies in the analytical process.

Table 2 compares the LODs and precisions for the common quantification methods for particulate-phase N-PAHs with either SE or TD approaches. For SE, different chromatographic separations such as GC and high-performance liquid chromatography (HPLC) were coupled with a variety of detectors such as MS (e.g., NCI, negative ion laser desorption ionization [LDI]- and multiphoton ionization [MPI]- time-of-flight [TOF]), electron capture detector (ECD), thermionic nitrogen-phosphorus detector (NPD), thermionic ionization detector (TID), or chemiluminescence detector (CLD), fluorescence detector (FD), or electrochemical detector (ED). In general, low LOD (in a range of pg to ng levels) per injection and good reproducibility (< 10%) were reported in most of the studies. However, there are many short-comings for these methods. The ECD did not respond uniformly to all N-PAH (Robbat et al., 1986). Besides, widely different responses of GC-TID
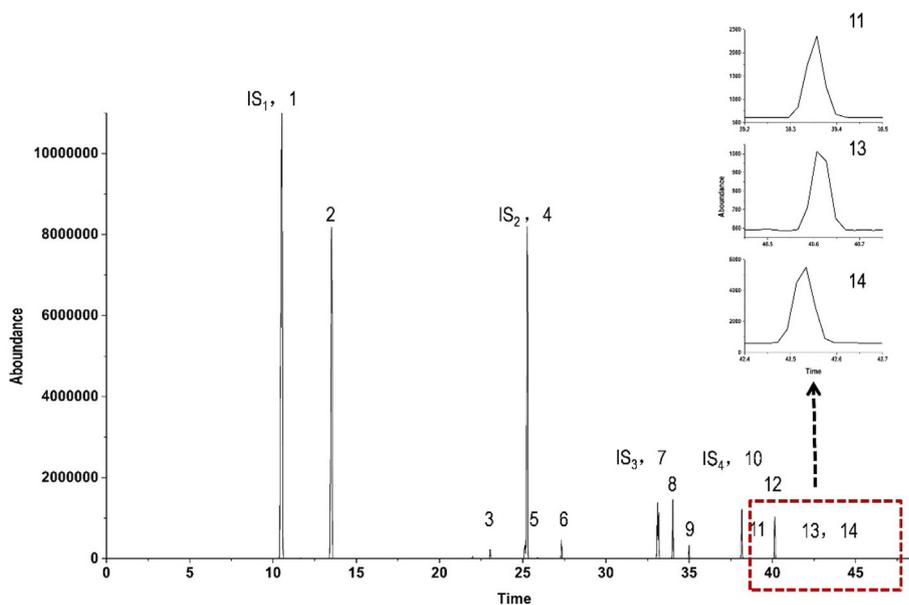
Peak Identification:
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10. 6-Nitrochrysene; 11. 1,3-Dinitropyrene; 12. 1,6-Dinitropyrene; 13. 1,8-Dinitropyrene; 14. 6-Nitrobenz(a)pyrene.
IS1. 1-Nitronaphthalene-D7; IS2. 2-Nitrofluorene-D9; IS3. 3-Nitrofluoranthene-D9;
IS4. 6-Nitrochrysene-D11.

Fig. 3. A chromatogram of target N-PAHs with TD-GC/NCI-MS method.

Table 1

Physical properties and the limits of detection (LODs) of NPAHs using the thermal desorption and the solvent extraction methods.

NPAHs	M.W.	Quan. Ion	Thermal desorption						Solvent extraction					
			RT	Slope	Intercept	R^2	LOD[a]	LOD[b]	RT	Slope	Intercept	R^2	LOD[c]	LOD[d]
							(pg per loading)	(pg per sample)					(pg per injection)	(pg per sample)
1-Nitronaphthalene	173.17	173	10.48	2.077	−0.044	1.000	32.5	107.1	10.53	2.315	−0.052	0.998	79.1	228.1
2-Nitrobiphenyl	199.22	199	13.50	1.821	−0.178	0.998	28.7	94.6	13.46	1.777	−0.031	0.999	64.5	186.0
5-Nitroacenaphthene	199.22	199	23.04	0.026	0.000	0.995	20.3	66.9	23.03	0.026	0.000	0.997	54.8	158.0
2-Nitrofluorene	211.2	211	25.25	1.017	−0.478	0.998	16.7	55.1	25.2	0.945	−0.021	0.998	20.7	59.7
9-Nitrophenanthrene	223.23	223	25.9	0.029	0.000	0.999	29.6	97.6	25.88	0.040	0.000	1.000	41.9	120.8
9-Nitroanthracene	223.23	223	27.32	0.305	−0.063	0.996	30.5	100.5	27.4	0.241	−0.002	0.999	50.3	145.0
3-Nitrofluoranthene	247.25	247	33.15	0.484	−0.044	0.997	29.6	97.6	33.47	0.453	0.002	1.000	53.2	153.4
1-Nitropyrene	247.25	247	34.01	0.831	−0.110	1.000	26.4	87.0	34.35	0.658	−0.004	0.999	52.0	149.9
2,7-Dinitrofluorene	256.21	256	34.99	0.379	−0.032	1.000	30.3	99.9	35.44	1.079	−0.016	0.999	50.3	145.0
6-Nitrochrysene	273.29	273	38.23	0.02	−0.002	0.998	18.7	61.6	38.88	0.030	0.000	0.997	50.3	145.0
1,3-Dinitropyrene	292.26	292	39.36	0.003	0.000	0.997	14.1	46.5	40.09	0.008	−0.001	0.992	18.1	52.2
1,6-Dinitropyrene	292.26	292	40.12	0.038	−0.003	0.999	23.4	77.1	40.93	0.039	−0.008	0.999	79.6	229.5
1,8-Dinitropyrene	292.26	292	40.61	0.002	0.000	1.000	31.1	102.5	41.46	0.005	−0.002	0.997	68.4	197.2
6-Nitrobenzo(a)pyrene	297.31	297	42.53	0.003	0.000	0.995	46.2	152.3	43.55	0.004	0.000	0.998	55.0	158.6

[a] The LOD (pg per loading) in the thermal desorption method was based on a maximum punch size of $5.26\,cm^2$.

[b] The LOD (pg per sample) in the thermal desorption method was based on a sample filter in $17.34\,cm^2$.

[c] The LOD (pg per injection) in the solvent extraction method.

[d] The LOD (pg per sample) in the solvent extraction method was based on a sample size ($17.34\,cm^2$) of a pre-analysis filter extract of 0.05 ml. An aliquot of 1 µl was injected for each injection.
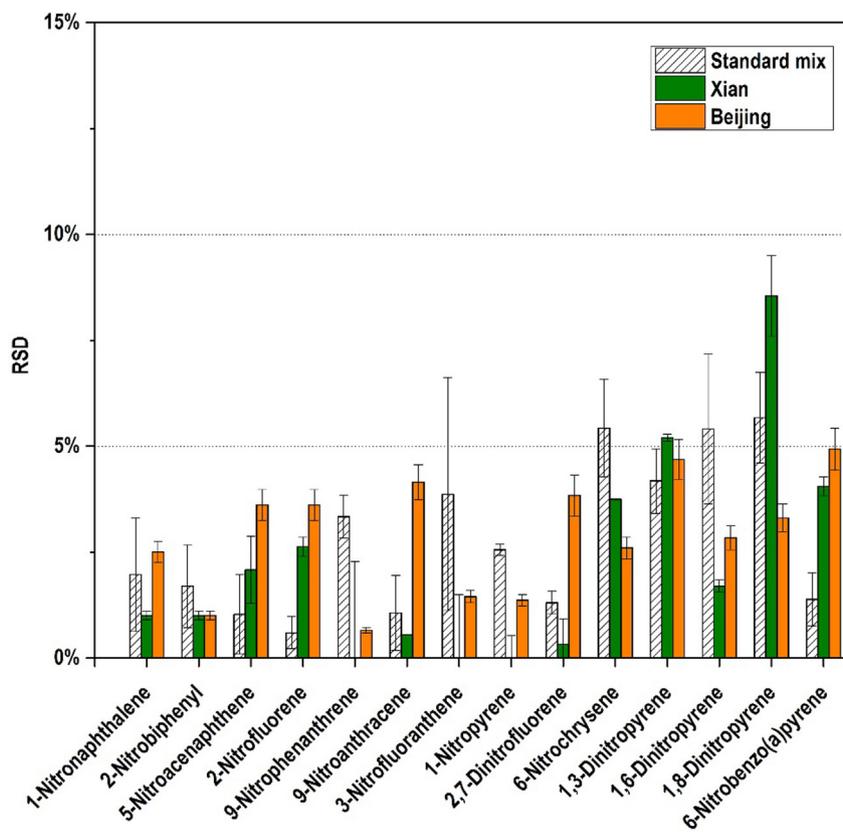
Fig. 4. Relative standard deviations (RSD) of replicate analyses for ambient samples.

between nitro compounds and the possibility of interferences pose analytical problem (White et al., 1984). The inability to distinguish between isomers with the LDI- or MPI-TOF/MS methods has forced the tentative assignment of N-PAH peaks without selective quantification. Both HPLC methods with either CLD or FD require a pre-treatment step of reduction for the N-PAH to the corresponding amino-PAH. In addition, the sensitivity of HPLC-MS is often not optimal for N-PAH analysis compared with those analyzed with GC/MS. It is worth to note that the in-injection port TD-GC/NCI-MS method offers the lowest LODs in term of mass per samples. The requirement of the smallest quantity of sample also advances comprehensive chemical analysis.

Table 2
Comparison of common analytical methods for quantification of N-PAHs.

Extraction Approach	Analytical Methods	Numbers of Target N-PAHs	LOD (pg/per injection)	LOD (ng/per sample)	Precision	Sample Area Required (cm²)	Reference
Solvent Extraction	GC-ECD	7	30	15[b]	5.2%	N.A.	(Xu and Lee, 2000; Zielinska and Samy, 2006)
	GC-TID	2	3–25	1.5–12.5[b]	N.A.	N.A.	(White et al., 1984)
	GC-CLD	10	7–25	3.5–12.5[b]	2.5–8.6%	N.A.	(Yu et al., 1984)
	GC/MPI/TOF-MS	3	0.2–0.3	0.014–0.021	N.A.	1.5–11.34	(Tang et al., 2015)
	LDI-TOF-MS	4	250–620	250–6200[b]	N.A.	N.A.	(Lin et al., 2015)
	HPLC/FD	3	68–629	1.4–12.6	N.A.	40.8	(Brichac et al., 2004)
	HPLC/ED	3	307–1618	15–80	5%	25	(Galceran and Moyano, 1993)
	HPLC/ED-FD	4	1.0–2.2	0.05–0.1[b]	N.A.	7	(Kuo et al., 2003)
	HPLC/CLD	3	0.07–0.10	0.035–0.050[b]	N.A.	N.A.	(Hayakawa et al., 1991)
	HPLC/MS	13	1–700	0.05–35[b]	N.A.	N.A.	(Bonfanti et al., 1996)
	GC x GC/TOF-MS	18	N.A.[a]	N.A.	6.4–47.4%	N.A.	(Manzano et al., 2013)
	GC/NCI-MS	32	0.02–8.82	0.002–0.882	N.A.	6.2–11.3	(Albinet et al., 2014)
Thermal Desorption	GC/NCI-MS	14	14.1–46.2	0.05–0.152	0.3–5.7%	0.53–5.26	This study

[a] No information is shown in the publication.
[b] Due to no information on the filter size used, the LOD (ng per sample) was estimated on a sample size of a 47 mm filter extract of 1.0 ml. An aliquot of 2 μl was injected for each injection.
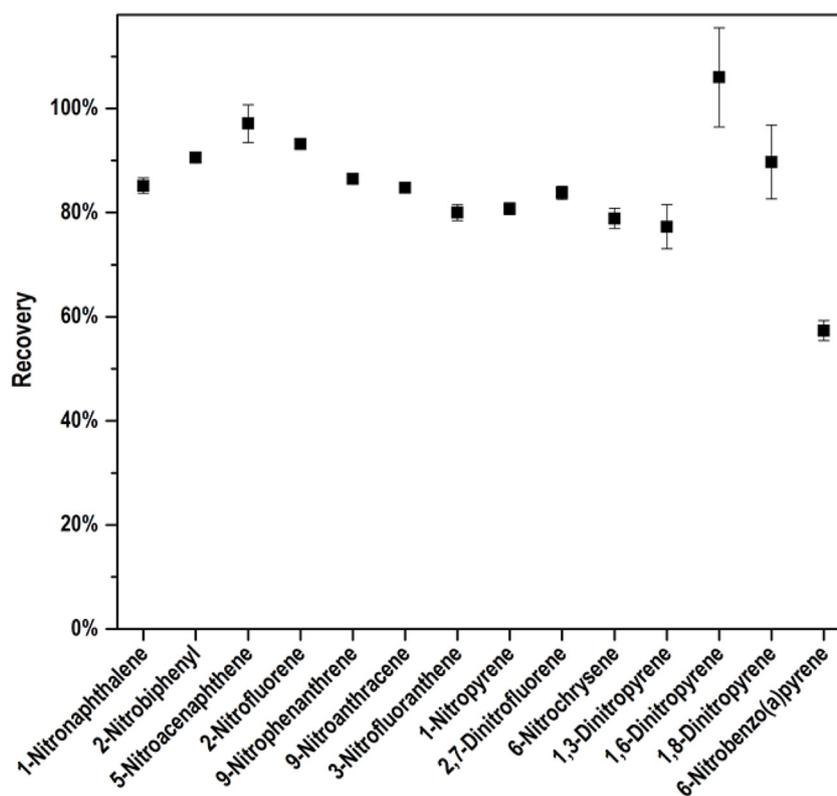
Fig. 5. Solvent extraction recoveries for the N-PAHs.

3.3. Characterization of solvent extraction method

SE with subsequent liquid injection of the extract into a GC/NCI-MS is a common method that has been widely utilized in the determination of N-PAHs in aerosol-loaded filter samples (Zielinska and Samy, 2006). It acts as a reference to validate the newly developed TD approach for N-PAHs. The LOD of the target N-PAHs with SE approach was shown in Table 1. The LOD values, when expressed as nanograms per injection (or analysis), are on average at the same level in the SE method and those in the TD method. Besides, the TD method utilized the whole sample while only a small fraction (~4%) of the final solvent extract was utilized in the SE method. Table 1 also compares the LODs in terms of ng per sample, which are better indicators for the minimal amounts of analytes necessary for quantification in each method. Under the conditions specified in the experimental procedure, the TD method provides LODs (pg per sample) that were 4–66% better for the target N-PAHs than did the SE method.

The recoveries of the target analytes were determined with the SE approach (Fig. 5). The average extraction recoveries ranged from 77% to 106%, except 6-nitrobenzo(*a*)pyrene (57%). This highest MW N-PAHs could be less prone to the extraction solvent system. The standard deviations of the recoveries ranged from 0.4 to 9.5%, demonstrating that a good stability of SE condition was achieved in this study.

3.4. Application of the method to natural samples and validation of the method

Fig. 6 compares the amounts of N-PAHs quantified by the SE- and
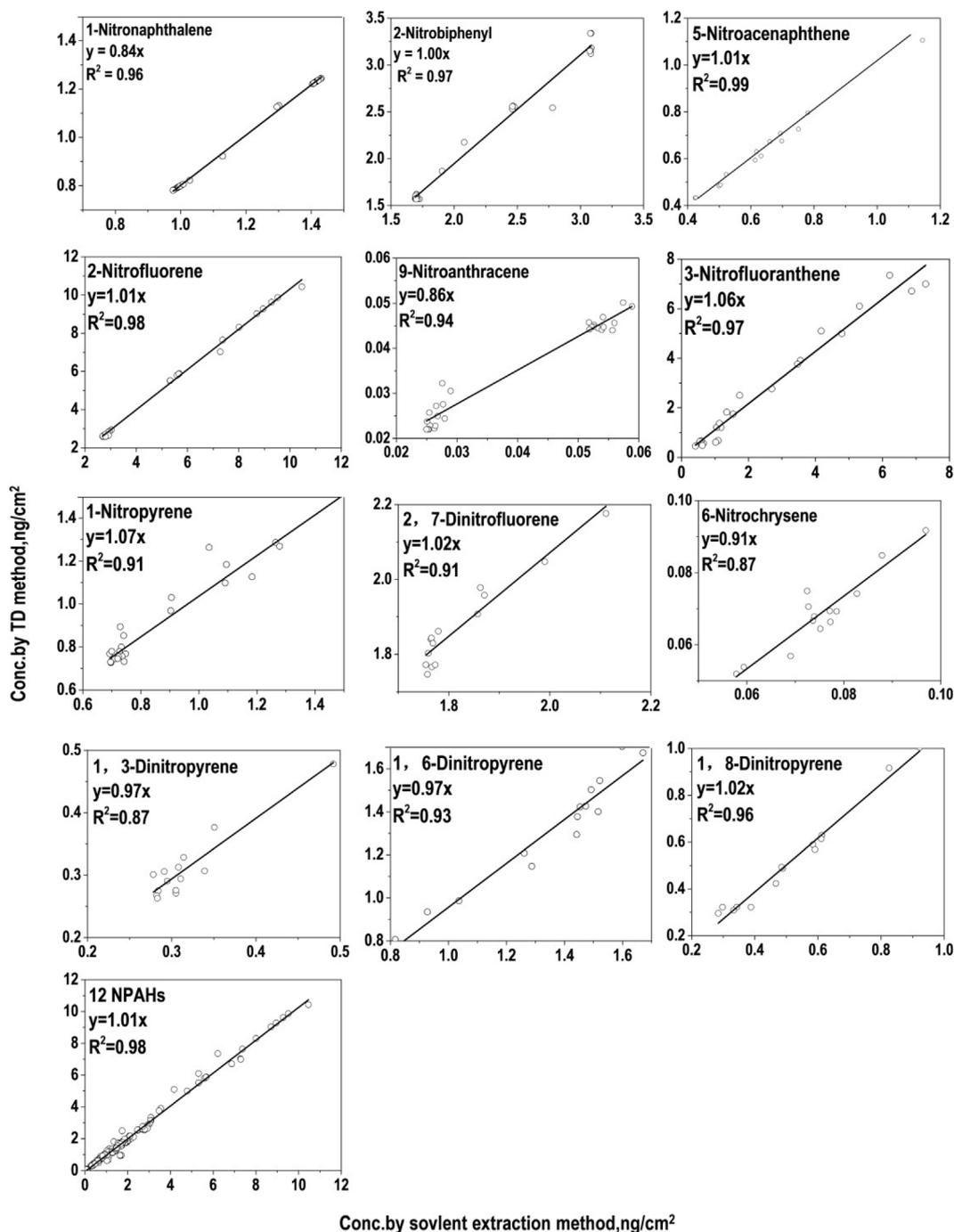
Fig. 6. Comparison of the concentrations of target NPAHs for the ambient filter samples quantified with the SE and TD method.

the TD-GC/MS methods with the two batches of PM$_{2.5}$ samples collected in Beijing and Xi'an, China. Good correlations were found between the two methods for 12 N-PAHs ($R^2 > 0.98$), except 9-nitrophenanthrene and 6-nitrobenzo(a)pyrene. The concentrations determined by the new TD-GC-NCI-MS method in the two batches of ambient samples has been shown in Table S2. A few of target analytes including 2,7-dinitrofluorene, 6-nitrochrysene, 1,3-dinitropyrene, 1,6-dinitropyrene, 1,8-dinitropyrene, and 6-nitrobenzo(a)pyrene were not detected in many samples with SE, but could be quantified by TD due to its improved sensitivity. These samples were excluded in the comparison. Besides, three dinitropyrenes (i.e., 1,3-dinitropyrene, 1,6-dinitropyrene, and 1,8-dinitropyrene) are rare to be measured because of their relatively low abundances in the atmospheres and weaker

chromatographic responses in common analytical methods (Durant et al., 1996, 1998). As a result, their validations could not be conducted for the whole sets of samples. Among the N-PAHs for which a comparison was possible, the ratio of the concentration measured by the TD to that by the SE was calculated in a range of 0.62–1.37. Such a reasonably good level of agreement between the two methods serves to demonstrate the feasibility of the TD method.

However, 9-nitrophenanthrene and 6-nitrobenzo(a)pyrene did not show a clear analyte-dependence in the comparisons. The TD method reported the concentrations of these two N-PAHs 237–402 times higher than those measured with the SE method in analysis of the ambient samples. One possible cause is that the peaks of 9-nitrophenanthrene and 6-nitrobenzo(a)pyrene overlapped with nitroanthracene isomers

(m/z = 223), and nitrobenz(a)pyrene and nitrobenz(e)pyrene isomers (m/z = 297), respectively, in the TD analysis. These potential influencers have identical fragment ions under NCI and eluted at close RTs using the TD oven temperature program with the target analytes. Besides, other organics (i.e., unresolved carbon matrices) non-selectively desorbed from the filter samples may also contribute to the overlapping. We tried adjusting the oven temperature ramping program, but no any improvement was obtained. Further adjustment or advancement is necessary to achieve the goal for their validation.

4. Conclusions

This study demonstrates the feasibility of determination of particulate-phase N-PAHs using in-injection port TD-GC/NCI-MS method. This approach offers a quick-easy-effective advantage for routine analysis of the N-PAHs. With the optimal analytical parameters, the TD method showed low LODs and good precisions in quantification of the N-PAHs by evaluating its performances with standards and ambient samples. Potential overlapping issues cause uncertainties in measurement of 9-nitrophenanthrene and 6-nitrobenzo(a)pyrene with the TD method. More speculation is thus needed.

Acknowledgment

Appendix A. Supplementary data

Supplementary data related to this chapter can be found at https://doi.org/10.1016/j.atmosenv.2018.08.049.

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