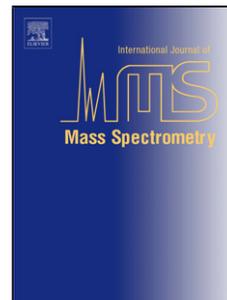


## Accepted Manuscript

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**Quantification of oxygenated polycyclic aromatic hydrocarbons in ambient aerosol samples using in-injection port thermal desorption-gas chromatography/mass spectrometry: method exploration and validation**

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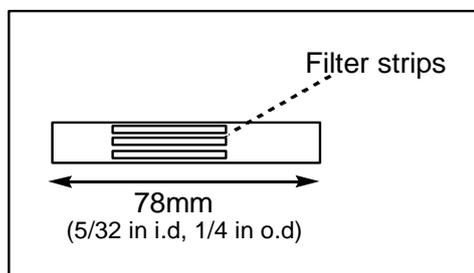
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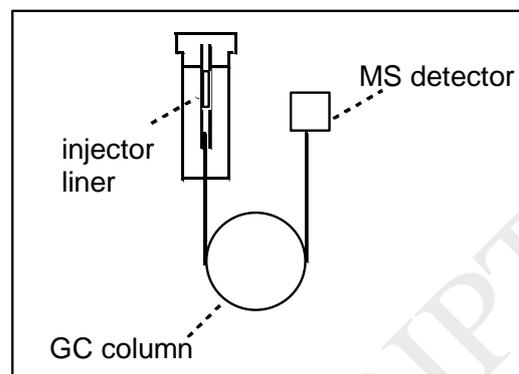
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**Graphical abstract**

An injector liner loaded with filter



Schematic diagram of the thermal extraction GC/MS system

**Highlights**

- In-injection port TD-GC/ MS was established to determine particulate oxygenated-polycyclic aromatic hydrocarbons
- It offers the lowest detection limit per sample in comparison of traditional solvent extraction approaches
- Good agreements in comparison the results with the TD and traditional SE approaches

## Abstract

In-injection port thermal desorption (TD) was evaluated for determination of particulate phase oxygenated-polycyclic aromatic hydrocarbons (O-PAHs) collected on filters coupled with a gas chromatography/mass spectrometry (GC/MS). The analytical parameters were optimized with standard testing and ambient samples. Ten of the most abundant O-PAHs in ambient air were included in the demonstration. A desorption temperature of 275 °C for 9 min was sufficient to transfer entire target compounds to the analytical system. Good linearity ( $R^2 > 0.99$ ) on the calibrations for each analyte was achieved. The limit of detection (LOD) ranged from 15 to 269 pg per sample. Method precisions, determined by replicate analyses of calibration standards and ambient samples, was less than 10% for target compounds. Comparisons were conducted on batches of 28 ambient aerosol filter samples using our TD and the traditional SE methods. Reasonably good agreement ( $R^2 = 0.98$ ) by the two methods was demonstrated for most of O-PAHs. The in-injection port TD can improve laboratory efficiency and reduce solvent-based costs for the measurement of O-PAHs.

**Keywords:** O-PAHs; thermal desorption; chemical ionization; aerosol filters; method comparison.

## 1. Introduction

Particulate oxygenated-polycyclic aromatic hydrocarbons (O-PAHs), emitted from both anthropogenic (e.g., fossil automotive fuels and coal/wood burning) [1, 2] and natural sources (e.g., fossil automotive fuels and coal/wood burning) [3-5] direct incomplete combustion processes, have toxicological significances even at much lower concentrations than those of their corresponding parent compounds [6-10]. OPAHs are stable against photo-irradiation in the atmosphere. Therefore, continuous exposure to O-PAHs are risky to human health due to their long residence time in the atmosphere [11]. Recently, OPAHs have been found to related to the generation of reactive oxygen species (ROS), which can cause severe oxidative stress and damages connected with inflammatory processes in cellular membranes, proteins and DNA in the human body [12]. An efficient and sensitive analytical method in measurement of their trace levels in atmosphere or laboratory stimulating test samples for source apportionment and health assessment are thus critical [3].

The most common offline approach for O-PAHs is to extract particulate matter (PM)-loaded filter with organic solvents (i.e., solvent extraction [SE]), followed by separation with chromatographic techniques such as gas chromatography (GC) and high-performance liquid chromatography (HPLC) coupling with detection by a mass spectrometer (MS) [3]. However, SE often involves complicated pretreatment processes and multiple pre-concentration steps [13-16]. Solvent consumption varies between 40 and 100 ml per analysis [3], introducing impurities to the extracts [17]. Those time- and labor-consuming steps suffer from limitations in sensitivity or selectivity [18, 19]. Besides, the solvent selection and temperature were observed to be critical in control of the recoveries and precision significantly of SE [20]. SE is

therefore not a desirable method for the determination of picogram (pg) to sub-pg per cubic meter of O-PAHs in PM samples.

In-injection port TD is an alternative mean to SE by using elevated temperatures to transfer organic analytes to a GC/MS system [21-26]. It can be adopted for conventional GC unit without any modification and additional equipment [27]. Simply and speedily analytical protocols facilitate the in-injection port TD to be applied for nationwide monitoring scheme (e.g., STN) [28]. However, TD is still a challenge for measurement of polar compounds (e.g., with oxo-, carbonyl- and hydroxyl- groups). The attractive interaction between an electronegative atom (e.g., oxygen [O] and nitrogen [N]) and an H atom bonded to another electronegative atom leads increase of the enthalpy change of vaporization ( $\Delta_vH$ ), which is the energy required to overcome intermolecular forces in the solid or the liquid state, and individual molecules escape and enter the gas state [29, 30]. This normally leads the incomplete desorption of polar analytes from the sample matrix. In this work, we have demonstrated the feasibility on analysis of O-PAHs, which have relatively higher polarity than *n*-alkanes and parent PAHs, with the direct in-injection port TD approach. Method precisions detection limits, and method comparisons for O-PAHs analyses using in-injection port TD- GC/MS are evaluated with the traditional SE approach on standards and ambient samples.

## 2. Materials and methods

### 2.1 Chemicals

1,4-Naphthoquinone ( $\geq 99\%$ ) and 9,10-anthraquinone ( $\geq 99\%$ ) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). 9-Fluorenone ( $\geq 98\%$ ), 6H-benzo(c,d)pyren-6-one ( $\geq 98\%$ ), benzophenone-D10 ( $\geq 99\%$ ) and anthraquinone-D8

( $\geq 98\%$ ) were purchased from J&K chemical Ltd.( USA). 1-Naphthaldehyde ( $\geq 98\%$ ), 1,8-naphthalic anhydride ( $\geq 98\%$ ) and 5,12-naphthacenequinone ( $\geq 98\%$ ), were obtained from Sigma (St. Louis, MO, USA). 1,4-Chrysenequinone ( $\geq 97\%$ ) and 1-acenaphthenone ( $\geq 97\%$ ) were purchased from Tokyo Chemical Industry Co., Ltd. Benzo(a)anthracene-7,12-dione ( $\geq 98\%$ ) was obtained from AccuStandard (New Haven, CT, USA). Fluoranthene-D<sub>10</sub> ( $\geq 98\%$ ) was obtained from Supelco (St. Louis, MO, USA).

## 2.2 Testing sample

Ten target O-PAHs were diluted to working level of  $0.5 \mu\text{g mL}^{-1}$  with toluene (JT Baker, Phillipsburg, USA). A punch of  $0.526 \text{ cm}^2$  of pre-baked ( $800 \text{ }^\circ\text{C}$ , 8 h) quartz fiber-filter (QM/A,  $20.3 \times 25.4 \text{ cm}^2$ , Whatman Inc., Clifton, NJ, USA) was spiked with  $8 \mu\text{L}$  of the O-PAHs solution. One microliter of a mixture solution containing two deuterated O-PAHs (i.e., Benzophenone-D<sub>10</sub>, Anthraquinone-D<sub>8</sub>) ( $5 \mu\text{g mL}^{-1}$ ) and  $1 \mu\text{L}$  of a parent PAHs of fluoranthene-D<sub>10</sub> ( $5 \mu\text{g mL}^{-1}$ ) 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  $450 \text{ }^\circ\text{C}$  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.

## 2.3 Ambient samples

PM<sub>2.5</sub> ambient air samples were collected on pre-baked quartz fiber-filters (QM/A,

20.3×25.4 cm<sup>2</sup>, Whatman Inc.) using high-volume samplers (Graseby-Andersen, Atlanta, GA, USA) operated at a flow rate of 1.1 m<sup>3</sup> min<sup>-1</sup> for 24 h (from 10:00 to next day 09:59 local standard time). Two sets of samples 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<sup>2</sup> were obtained from a parent filter sample. The samples were then prepared into the TD tubes as the same way as the testing samples.

## 2.4 Thermal desorption method

In-injection port TD coupled with GC/MS was applied to quantify of the non-polar organic compounds in the PM<sub>2.5</sub> filter samples. The detail analytical procedures have been reported in our previous publications [17, 18]. 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). Figure S1 illustrates the time events of the GC injector and column compartment throughout the whole analysis. The selected ion for each analyte was chosen on the base of characteristic fragment. The information was shown in Table S1. Calibration samples were prepared by adding standard mixture with the deuterated IS onto pre-baked blank filter punches. The spiked punches were processed and analyzed in the same way as the testing samples.

## 2.5 Solvent extraction method

A 47-mm diameter filter (17.34 cm<sup>2</sup>) were punched from the parent high-volume sample. The two deuterated O-PAHs spiked on the filter was 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 ( $22\pm 2$  °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 (99.99%, Xi'an Teda Cryogenic Equipment Co.) gas blowing. Twenty-five microliters of fluoranthene- $D_{10}$  at a concentration level of  $20\text{ ng }\mu\text{l}^{-1}$  was added in the extract solution that served as an injection IS. The final solution was mixed to 1 ml. The detail analytical procedures have been reported in previous publications [31, 32].

### 3. Results and discussion

#### 3.1 Identification and separation

The TD-GC program provided baseline resolution of the ten target analytes within a 53 min chromatographic runtime (Figure 1a) and adequate separation of the target analyzed in the  $\text{PM}_{2.5}$  sample matrix (Figure 1b). Retention times for each analyte, molecular ions, and major fragment ions used for compound identification are summarized in Table 1. The TD-GC program provides sufficient resolution of the target analytes for the purpose of individual compound quantitation.

#### 3.2 Method validation

The method was validated using a routine validation procedure that included the following parameters: linearity, limits of detection (LODs), accuracy and precision. The linearity of the method was evaluated by analyzing standard solution at seven concentrations (0.01, 0.05, 0.1, 0.2, 0.4, 0.8 and 1.0 ng). The parameters of the linear

regression equations were slope, intercept and correlation coefficient ( $R^2$ ). The LOD is defined as the minimum amount of an O-PAH that generates the minimum distinguishable signal plus three times the standard deviation of the blank signals. The accuracy and precision of analysis method were assayed by duplicate analysis of standards and ambient samples.

Good linearity with a correlation coefficient  $> 0.99$  was found for 10 individual O-PAHs. No peaks were detected for neither n-alkanes nor PAHs in the blank calibration samples. Table 1 shows that the LODs were 21.5–269.4 pg with TD approach for the O-PAHs. These numbers translate into air concentrations of 0.061–0.770  $\text{pg m}^{-3}$  if we assume a sampled air volume of 350  $\text{m}^3$ . The LOD of the target O-PAHs with SE approach are also shown in Table 1. The TD method utilized the whole sample while only a small fraction ( $\sim 0.02\%$ ) of the final solvent extract was utilized in the SE method. Since only 1% of the final extract (i.e., 1  $\mu\text{l}$  out of a final extract of 1000  $\mu\text{l}$ ) was used for SE-GC/MS, the LOD values, when expressed as nanograms per injection (or analysis), were 30–90% lower of the SE method than those by the TD-GC/MS. Table 1 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. The LODs in ng per sample by SE-GC/MS were factors of 2 to  $>52$  times higher than those in ng per sample by TD-GC/MS. SE-GC/MS may achieve lower LODs by using larger filter area or lowering the final extract volume, while the TD-GC/MS sample size is limited by the size of the injector liner.

The filter with certified standard mix was prepared to examine the accuracy. Table 2 shows the differences of seven “standard” filters from the certified values ranged from  $-5.1\%$  to  $5.8\%$ . The precision was assessed by replicate analyses of calibration standards and ambient samples. Figure 2 shows that the relative standard deviations

(RSDs) for the calibration standard mixture were 1.6–8.9% with a median RSD of 4.2% for 10 compounds. RSDs for ambient samples are affected by inhomogeneities of sample deposits as well as uncertainties in the analytical process. Six replicate analyses of ambient sample reported RSDs of 1.3–9.7% with a median RSD of 5.0% for TD-GC/MS. RSDs for all O-PAHs did not exceed 10% (Figure 2). The good reproducibility demonstrates the quantitative desorption of O-PAHs from the filter as well as the stability of the MS system.

### 3.3 Method inter-comparison with PM samples

SE with subsequent liquid injection of the extract into a GC/MS is a common method that has been widely utilized in the determination of O-PAHs in aerosol-loaded filter samples. It acts as a reference to validate the TD approach for OPAHs. Ho et al. [18] demonstrated a good agreement between the TD- and SE-GC/MS for 132 non-polar organic compounds. An inter-comparison study was conducted for 28 ambient samples collected in Beijing and Xi'an, China.

The recoveries of the target analytes were determined with the SE approach (Figure S2). The average extraction recoveries ranged from 75% to 116%. The standard deviations of the recoveries ranged from 0.4 to 8.5%, demonstrating that a good stability of SE condition was applied in this study. The results of this inter-comparison (Fig. 3) show good correlations between the TD- and SE-GC/MS methods for O-PAHs ( $R^2 > 0.90$ ). The ratios of TD- to SE-GC/MS methods were 0.75–1.23 for PAHs. The deviation from unity was generally below 10%, and none exceeded 25%. Figure 3 shows scatter plots with zero-intercept slope (0.97) and good overall correlations ( $R^2 = 0.95$ ). The regression line is dominated by the O-PAHs with higher concentrations. Good comparability was found for the majority of quantified O-PAHs.

## 4. Conclusions

In summary, excellent precision and accuracy were found for 10 O-PAHs using in-injection port TD-GC/MS. Good agreement was also obtained between the TD-GC/MS and more commonly applied SE-GC/MS methods. Inter-method comparison further demonstrates the comparability of the in-injection port TD-GC/MS method in the determination of O-PAHs for aerosol filter samples. Compared with the SE method, the TD method requires much less filter material and solvent in detection of the ambient level of O-PAHs. The results in this work further demonstrate the suitability of TD in analysis of these relatively polar compounds without any pre-treatment steps required. This approach offers an effective advantage for routine analysis of the O-PAHs. Since the current one-dimensional GC offers limited chromatographic resolution for the semi-volatile PAH-derivates, TD coupled with comprehensive two-dimensional GC/MS (e.g., GCxGC-TOF/MS) would be further developed in our future work.

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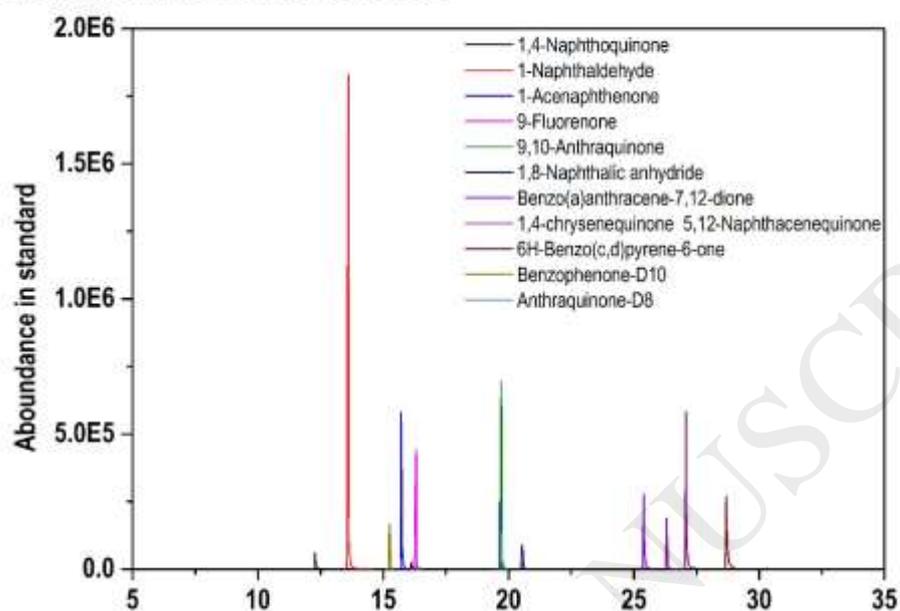
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## Figure captions

## a. Chromatograms separation of OPAHs



## b. Extracted ion chromatograms for ambient sample

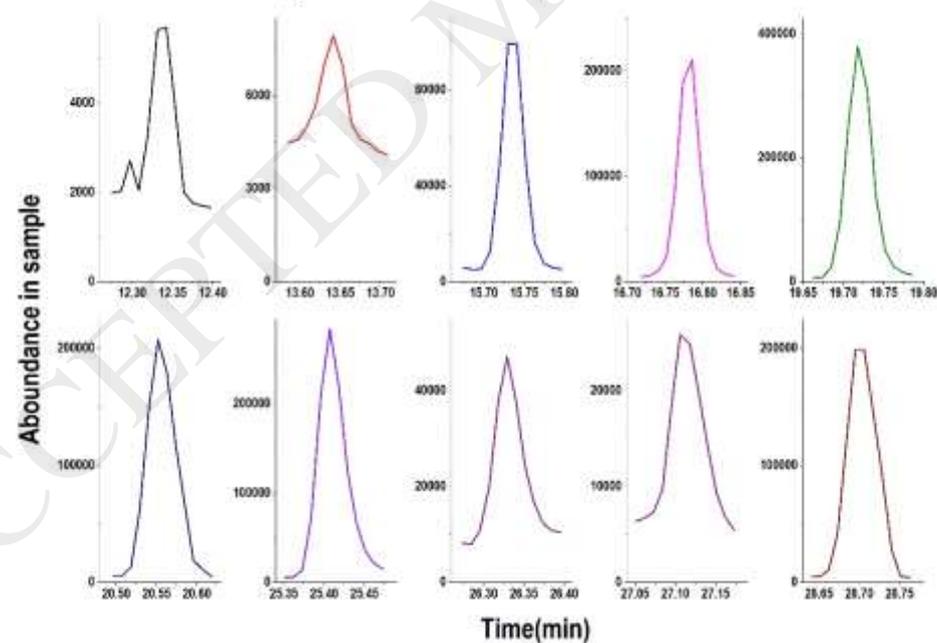


Figure 1. Selected ion chromatogram for a) standard solution for a mixture, and b) ambient PM<sub>2.5</sub> sample from Xian in winter

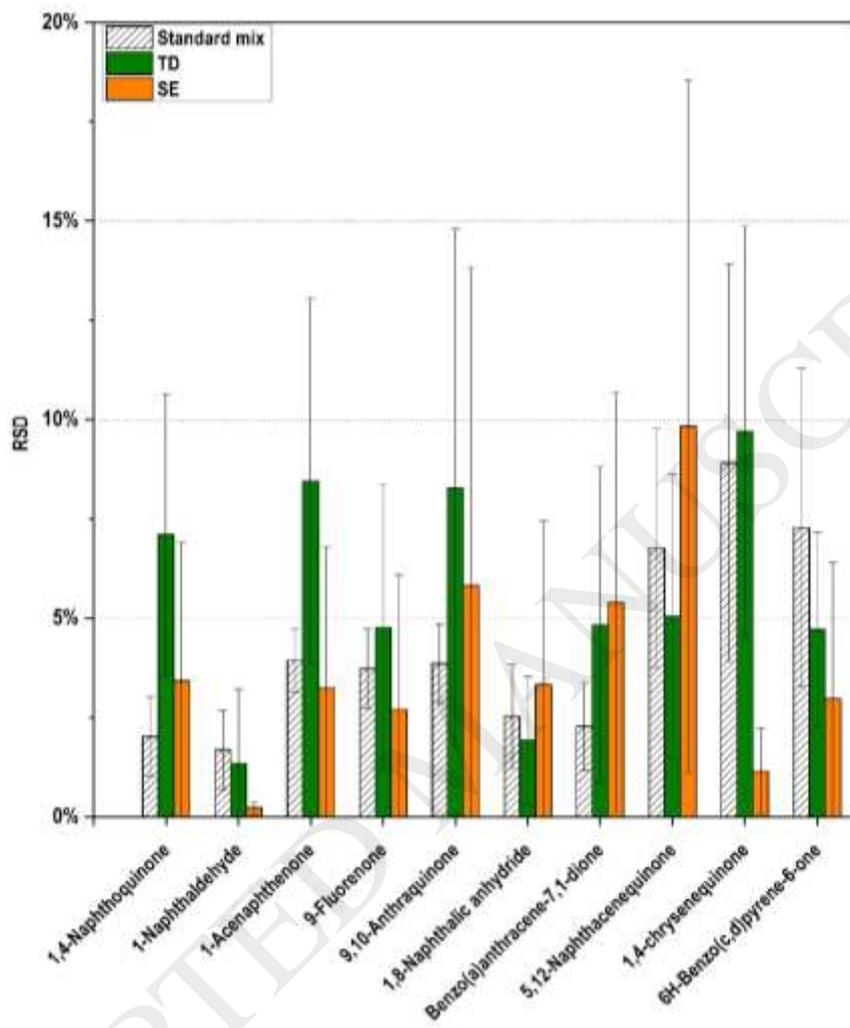


Figure 2. Relative standard deviations (RSD) of replicate analyses for ambient samples.

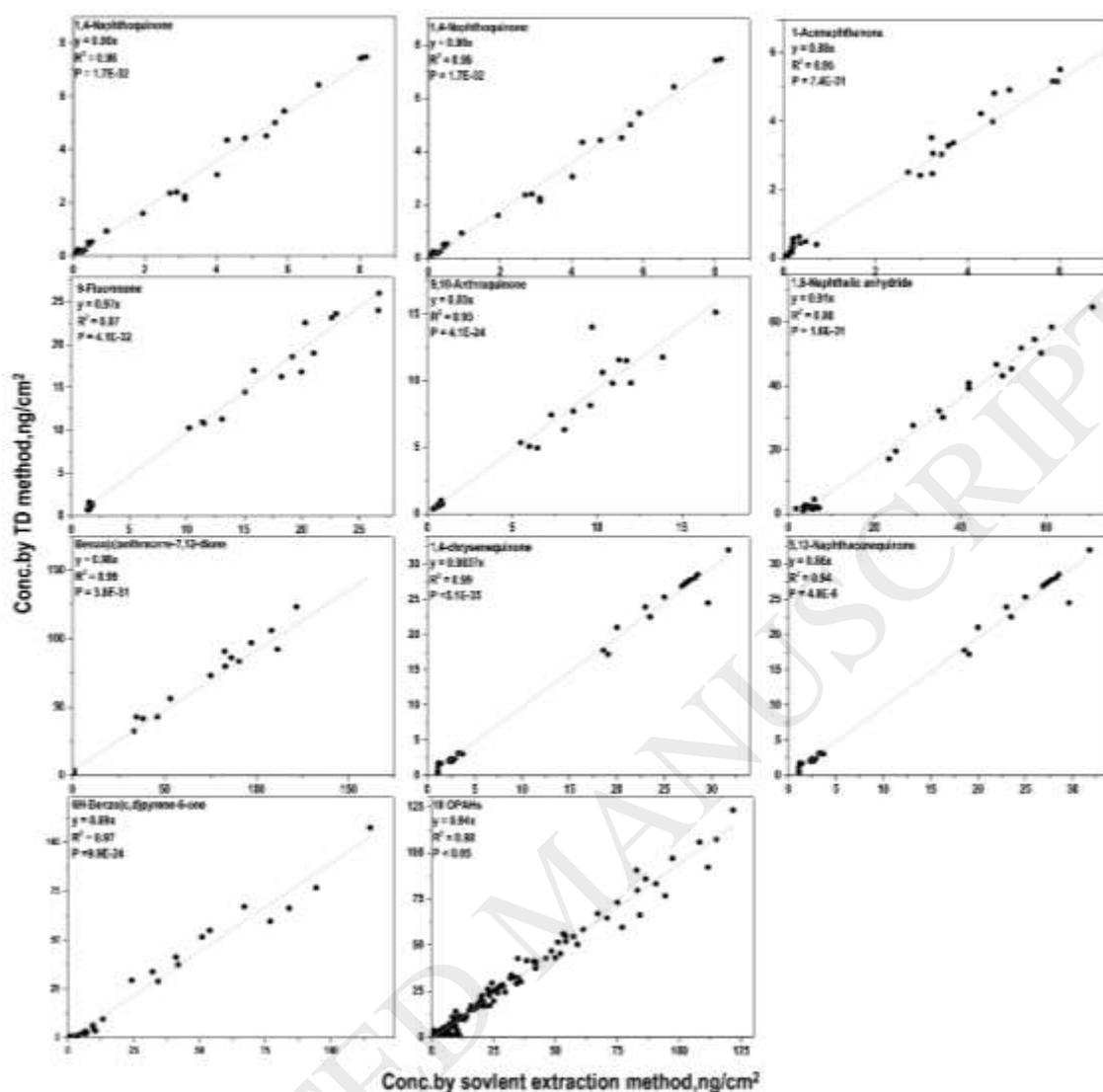


Figure 3. Comparison of 10 OPAHs for the 28 PM<sub>2.5</sub> samples collected at Beijing and Xi'an, China, determined by the in-injection port TD-GC/MS and SE-GC/MS method.

Table 1. Physical properties and the limits of detection (LODs) of OPAHs using the

OPAHs	M. W	Q u a n. l o n	Thermal desorption						Solvent extraction					
			R T	S l o p e	I n t e r c e p t	R <sup>2</sup>	LO D <sup>a</sup> (pg per	LO D <sup>b</sup> (pg per	R T	S l o p e	I n t e r c e p t	R <sup>2</sup>	LOD <sup>c</sup> (pg per	LOD <sup>d</sup> (pg per
1,4-	15	15	12	0.	-	0	156	514	1	0.	0.00	0.	24.5	245
1-	15	15	13	0.	-	0	21.	707	1	2.	0.00	0.	28.5	285
1-	16	16	15	0.	0.0	0	222	731	2	0.	0.00	0.	22.7	227
9-Fluorenone	18	18	16	0.	-	0	215	708	2	0.	0.00	0.	20.7	207
9,10-	20	20	19	0.	0.0	0	34.	111	2	2.	0.00	0.	25.0	250
1,8-Naphthalic	19	19	20	0.	-	0	269	886	3	0.	0.00	0.	15.5	155
Benzo(a)anthrac	25	23	25	0.	-	0	25.	835	3	0.	0.00	0.	43.9	439
1,4-	25	25	26	0.	-	0	72.	237	3	0.	0.00	0.	32.1	321
5,12-	25	25	27	0.	-	0	61.	202	3	0.	0.00	0.	27.0	270
6H-	25	25	28	0.	-	0	106	351	4	0.	0.00	0.	30.0	300

thermal desorption and the solvent extraction methods.

<sup>a</sup> The LOD (pg per sample) in the thermal desorption method was based on a filter punch size of 0.52 cm<sup>2</sup>.

<sup>b</sup> The LOD (pg per sample) in the thermal desorption method was based on a sample filter in 17.34 cm<sup>2</sup>.

<sup>c</sup> The LOD (pg per injection) in the solvent extraction.

<sup>d</sup> The LOD (pg per sample) in the solvent extraction method was based on a sample size (17.34 cm<sup>2</sup>) of a pre-analysis filter extract of 1.0 ml. An aliquot of 1 µl was injected for each injection.

Table 2. Concentrations of “standard” filter with standard mix determined by the in-injection port TD-GC/MS method

ng	Filter 1	Filter 2	Filter 3	Filter 4	Filter 5	Filter 6	Filter 7	Mean	SD	Certified value	Relative difference
1,4-Naphthoquinone	0.106	0.108	0.103	0.108	0.107	0.104	0.106	0.106	0.002	0.100	5.84%
1-Naphthaldehyde	0.423	0.428	0.423	0.426	0.409	0.432	0.421	0.423	0.007	0.420	0.76%
1-Acenaphthenone	0.204	0.196	0.201	0.199	0.186	0.187	0.184	0.194	0.008	0.200	-3.05%
9-Fluorenone	0.192	0.186	0.193	0.187	0.176	0.192	0.194	0.189	0.007	0.200	-5.69%
9,10-Anthraquinone	0.304	0.306	0.302	0.283	0.276	0.291	0.295	0.294	0.011	0.300	-2.08%
1,8-Naphthalic	0.213	0.212	0.192	0.190	0.189	0.185	0.192	0.196	0.011	0.200	-1.96%
Benzo(a)anthracene	0.061	0.057	0.059	0.062	0.061	0.052	0.062	0.059	0.004	0.060	-1.50%
Benzo(a)anthracene-7,10-dione	0.063	0.066	0.063	0.075	0.057	0.063	0.081	0.067	0.008	0.070	-4.83%
1,4-chrysenoquinone	0.180	0.186	0.174	0.210	0.182	0.193	0.243	0.195	0.024	0.200	-2.37%
5,12-Naphthacenequinone	0.144	0.140	0.150	0.153	0.148	0.149	0.154	0.148	0.005	0.150	-1.18%
6H-Benzo(c,d)pyrene-6-one	0.189	0.193	0.187	0.185	0.196	0.186	0.192	0.190	0.004	0.200	-5.14%