Development of gas chromatography-flame ionization detection system with a single column and liquid nitrogen-free for measuring atmospheric C2–C12 hydrocarbons

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ABSTRACT

A liquid nitrogen-free GC-FID system equipped with a single column has been developed for measuring atmospheric C2–C12 hydrocarbons. The system is consisted of a cooling unit, a sampling unit and a separation unit. The cooling unit is used to meet the temperature needs of the sampling unit and the separation unit. The sampling unit includes a dehydration tube and an enrichment tube. No breakthrough of the hydrocarbons was detected when the temperature of the enrichment tube was kept at -90°C and sampling volume was 400 mL. The separation unit is a small round oven attached on the cooling column. A single capillary column (OV-1, 30 m $\times$ 0.32 mm I.D.) was used to separate the hydrocarbons. An optimal program temperature ($-60 \sim 170^{\circ}\text{C}$) of the oven was achieved to efficiently separate C2–C12 hydrocarbons. There were good linear correlations ($R^2 = 0.993\text{--}0.999$) between the signals of the hydrocarbons and the enrichment amount of hydrocarbons, and the relative standard deviation (RSD) was less than 5%, and the method detection limits (MDLs) for the hydrocarbons were in the range of 0.02–0.10 ppbv for sampling volume of 400 mL. Field measurements were also conducted and more than 50 hydrocarbons from C2 to C12 were detected in Beijing city.

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1. Introduction

Volatile organic compounds (VOCs) from both anthropogenic and biogenic sources play important roles in tropospheric chemistry and their degradation in the atmosphere can form a series of harmful secondary pollutants, such as ozone [1], peroxyacetyl nitrates [2,3] and organic aerosol [4]. Knowing the concentrations and sources of VOCs with different reactivity is required to develop effective control measures for the secondary pollutants [5,6]. An important class of VOCs that contain only carbon and hydrogen, usually called non-methane hydrocarbons (NMHCs), have atmospheric mixing ratios typically ranging from below 10 pptv (parts per trillion by volume) to tens of ppbv (parts per billion by volume) [7]. For measuring such low concentrations of the atmospheric NMHCs, very sensitive instruments or instruments with the help of enrichment are needed [8].

Proton-transfer-reaction mass spectrometry (PTR-MS) has currently been found to be the most sensitive instrument to meet the request for directly measuring atmospheric NMHCs with detection limits of pptv level [9]. However, due to the low proton affinity of alkanes for the reactions with H_3O^+ ions, the PTR-MS technique only limits for measuring atmospheric alkenes, aromatic hydrocarbons and oxygenated organic compounds without distinguishing from the isomeric compounds [10,11]. In addition, the extremely expensive PTR-MS technique also limits its widely application for atmospheric NMHCs measurements. Gas chromatography equipped with flame ionization detection (GC-FID) or mass detection (GC-MS) has been widely used for measuring atmospheric NMHCs, and the isomeric compounds of NMHCs can also be quantified with the help of an efficient separation column [12–15]. To meet the detection limits of GC-FID/MS, the air samples are needed to be pre-enriched before analyzing [13,16]. Solid adsorbents and blank capillary column are usually used for pre-concentration of the air samples under extremely low temperature which is often achieved by liquid nitrogen (LN_2) [17]. However, the use of LN_2 is cumbersome (occupy a significant amount of space), complicated and a significant running cost especially at

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Table 1
Review of GC system for C2–C12 NMHC analysis.

Range	Dryer	Trapping/Temperature (°C)	Sampling volume (mL)	DT* (°C)	GC column	GC run time (min)	Reference
C2–C8	N.R.	Glass beads/–196	1519	80	GS-Alumina PLOT column, 30 m × 0.53 mm; DB-1, 5 m × 0.53 mm, 1.0 μm; –20 ~ 200 °C	18	[17]
C2–C10	K ₂ CO ₃ –NaOH;	Tenax TA–Carbopack B/N.R.	5520 ~ 6000	300	Al ₂ O ₃ /KCl PLOT column, 50 m × 0.32 mm; HP-1, 60 m × 0.25 mm, 1.0 μm; N.R.	N.R.	[20]
C2–C12	Nafion Cooling trap	PLOT column–deactivated quartz capillary/–150	300	110	Al ₂ O ₃ /KCl PLOT column, 15 m × 0.32 mm; DB-624, 30 m × 0.25 mm, 1.0 μm; 35 ~ 180 °C	32.7	[21]
C3–C10	Cooling trap	Glass beads/–175	1500	80	CP-Al ₂ O ₃ /Na ₂ SO ₄ Plot column, 50 m × 0.53 mm, 10 μm; VF-5 ms, 60 m × 0.32 mm, 1.0 μm; 35 ~ 200 °C	24.5	[19]
C2–C9	Nafion	Carbosieve SIII–Carbopack B/–30	N.R.	350	Plot Al ₂ O ₃ /Na ₂ SO ₄ , 50 m × 0.32 mm, 5.0 μm; CP Sil 5CB, 50 m × 0.25 mm 1.0 μm; N.R.	N.R.	[22]
C3–C12	N.R.	Carboxen 1000–Carboxen 1003–Carbotrap/30	N.R.	250	PLOT column, 10 m × 0.32 mm, 8.0 μm; DB-1, 60 m × 0.32 mm, 1.0 μm; 40 ~ 200 °C	52	[23]
C2–C10	Nafion	Glass beads–Chromasorb A/–180	300	120	DB-1, 100 m × 0.25 mm, 0.5 μm; –50 ~ 250 °C	47	[13]
C2–C8	Mg(ClO ₄) ₂	Carbopack BHT/–130	1000	90	DH, 150 m × 0.25 mm, 1.0 μm; –10 ~ 200 °C	60	[24]
C2–C10	Cooling trap	Sample loop/–190	1000	80	DB-1, 90 m × 0.32 mm, 3.0 μm; –50 ~ 200 °C	67	[25]
C4–C10	N.R.	Glass beads/–165	500	200	DB-5, 60 m × 0.25 mm; –15 ~ 250 °C	33	[26]
C3–C12	Nafion	N.R./–150	25 ~ 1000	150	DB-1, 60 m × 0.32 mm, 1.0 μm; –60 ~ 250 °C	51.8	[27]
C2–C12	Cooling trap	Carbopack™ B/–90	400	100	OV-1, 30 m × 0.32 mm, 1.0 μm; –60 ~ 170 °C	31	This study

* DT = desorption temperature; N.R. = not reported.

remote locations [18]. Consequently, without the use of LN₂ for atmospheric NMHCs analysis is a preferable choice [19].

The information about GC systems developed by various laboratories is listed in Table 1. Because water component readily plugs trapping tube, extinguishes flame of FID or affects the retention time of species on some capillary columns, pre-removing water from the ambient air is very necessary for almost all GC systems. As shown in Table 1, several techniques for removal of water were adopted, e.g. drying agents of (Mg(ClO₄)₂ or K₂CO₃–NaOH), cold traps, Nafion dryer. To meet the request of detection, all GC systems equipped with enrichment techniques, including different adsorbents and capillary columns under low temperature or room temperature. Because NMHCs with few carbon numbers (such as C2 compounds) are difficult to be captured by various adsorbents under room temperature, enrichment under extremely low temperature is widely used. The low temperature for enrichment is usually achieved by LN₂ [17,24]. Other techniques for cryo-enrichment without LN₂ have also been developed, such as multi-step cooling system or Peltier cooling system [19,21,22,28]. Various capillary columns are adopted for separating NMHCs by all GC systems. To efficiently separate NMHCs with carbon numbers less than six, porous-layer open tubular (PLOT) capillary column is usually adopted for cryogen-free GC-FID. However, very strong retention of higher boiling point species on the column leads to extensive peak broadening and very lengthy analysis time. To achieve the objective for separating NMHCs with carbon number greater than five, a second capillary column is used and the NMHCs are detected by MS for the commercial GC-FID/MS [19,29], resulting in the increment of the complicity and cost of the analysis system. Single capillary column has also been found to efficiently separate

NMHCs with carbon numbers from 2 (C2) to 12 (C12), but the separation needs initial low temperature which is currently achieved by LN₂ [17,27]. Because the oven of commercial GC has relatively large volume, the consumption of LN₂ is considerable to achieve the initial temperature as low as –50 ~ –60 °C. In addition, relatively long single capillary column are usually adopted to achieve effective separation of the NMHCs, resulting in relatively long analyzing cycles of about 1.5–2.0 h [30,31].

Considering the complicity, inconveniency, high cost and relatively long analyzing cycle for atmospheric NMHCs measurements by using the current GC-FID/MS methods, the main objective of this study is to develop a convenient and non-expensive GC-FID system using a single capillary column and LN₂-free for measuring atmospheric C2–C12 NMHCs.

2. Experimental

2.1. The apparatus developed for analyzing NMHCs

The apparatus developed for analyzing NMHCs is schematically shown in Fig. 1, which mainly includes a cooling unit, a sampling unit, a separation unit, and a detection unit. The cooling unit is a special refrigerator with coolants (HFC-236, HFC-23, PFC-14 and C₂H₆) passing through a stainless steel column (designated as the cooling column), and the lowest temperature of the cooling unit can achieve –120 °C. The overall dimensions of the special refrigerator are 450 × 520 × 870 mm (*W* × *D* × *H*). The cooling column is used for cooling the sampling unit and the separation unit. The sampling unit mainly consists of an adsorption tube and a dehydration tube

Fig. 1. Schematic of the analytical system for measurement of C₂–C₁₂ hydrocarbons.

(6 mm O.D., 150 mm in length) made of poly-tetrafluoroethylene (PTFE). Both the adsorption tube and dehydration tube were evenly wrapped with resistance wire and closely connected with the cooling column, and their temperatures were measured by two PT-100 thermocouples. The separation unit is a capillary column (OV-1, 30 m × 0.32 mm I.D., film thickness: 1.0 μm) wrapped on a thin layer of resistance wire which enlaced the cooling column. The capillary column temperature is measured by a PT-100 thermocouple. All units of the GC system are fixed with their temperatures controlled by the balance of the cooling and heating. The temperature of each unit can be independently controlled; e.g., the adsorption tube can be cooled while the separation unit is heating. As illustrated in Fig. S-1, the adsorption tube is made of stainless steel tube (3 mm I.D., 120 mm long) filled with approximately 10 mg CarboxenTM B adsorbent (60/80 mesh), which is connected to the six-port valve (V1) as a loop (Fig. 1). The adsorption tube is wrapped by resistance wire, and its temperature is controlled by the balance between the cooling and heating and measured by a PT-100 thermocouple. A thin layer of conductive grease is coated on the outside of the adsorption tube to increase thermal conduction between the tube and the cooling column. The temperature of the adsorption tube can be controlled from −110 °C to 220 °C. The detection unit is a FID. To increase the analyzing sensitivity, a stream of make-up gas of N₂ was introduced into the FID.

2.2. The apparatus operation

Standard NMHCs samples or ambient air samples are driven to the adsorption tube by a micro diaphragm pump (KNF Neuberger Incorporated) at a fixed flow rate (which was exactly controlled by a mass flow controller (MFC)) at the position illustrated in Fig. 1 when the temperature of the adsorption tube is achieved a pre-set value. Once the pre-concentration was finished, the adsorption tube was quickly heated by the heating wire to be a preset high temperature (100 °C) with duration of 6 min, and the NMHCs desorbed were injected into the capillary column for separation by simultaneously turning the two six-port valves into the opposite position, and then the carrier gas of N₂ with a flow rate of 5 mL min^{−1} carried the NMHCs desorbed into the capillary column for separation. After

the analytes were swept onto the analytical column, the temperature of the adsorbent trap was increased to 220 °C for 10 min with 60 mL N₂ min^{−1} (in a direction opposite to the sampling process) to thoroughly clean the adsorbent (bake-out). While the cleaning was completed, the power of the heating wire was turned off and the adsorption tube was cooled down by the cooling column for the next cycle. The temperature program of the capillary column used was as follows: 3 min at −60 °C, ramp at 12 °C min^{−1} to −20 °C, ramp at 6 °C min^{−1} to 30 °C, ramp at 10 °C min^{−1} to 170 °C, then hold for 2 min. The temperature of the FID is operated at 250 °C. The typical temperature variations of the adsorption tube and the capillary column during one course of operation are shown in Fig. S-2. The fast recovery of the temperatures for the adsorption tube and the separation column after heating provided precondition for analyzing atmospheric NMHCs with a frequency of 1 h.

2.3. The apparatus calibration and measurements

A standard gas mixture of 57 NMHCs in nitrogen was purchased from Linde SPECTRA Environmental Gases (Alpha, NJ), with a stated concentration of ~1 ppmv. The standard gas mixture of NMHCs was further diluted by high purity of N₂ (99.999%) by dynamic method (two flow streams controlled by two MFCs) to low concentrations (1.0–30.0 ppbv) which approached to ppbv levels of the ambient air. According to the procedure introduced in Section 2.2, different amount of NMHCs in the dilution standard gas mixture were analyzed, and linear relations between injection dose and the respond values of the GC-FID were analyzed as shown in the Section 3. Ambient air samples were also collected and analyzed by using the same procedure as those for the standard gas mixture to reveal that the apparatus developed could be applied for measuring atmospheric NMHCs. To avoid the possible loss of some NMHCs species with high reactivity, an oxidant scrubber tube filled with sodium sulfite (Na₂SO₃) was connected before the adsorption tube for removing the oxidants during sampling the ambient air, and the Na₂SO₃ trap was changed approximately every 2 days. Each target compound in the ambient air was identified by its retention time and the quantification of target NMHCs was accomplished using multi-point external standard curves.

3. Results and discussion

3.1. The separation of NMHCs

According to the operation procedure of the apparatus in Section 2.2, a diluted standard NMHCs (C2–C12) sample with concentration of ~ 30 ppbv for each species was analyzed, and the chromatogram is shown in Fig. 2 and the corresponding species numbered in the figure are listed in Table S-1. Only with the exception for the co-elution of 2-methylhexane/2,3-dimethylpentane, m-/p-xylene, and m-/p-ethyltoluene, the method developed by this study can efficiently separate the other 51 NMHCs species. The initial temperature of the OV-1 capillary column was lower, the separation of C2 compounds (ethane, ethylene and acetylene) was better, but the separation of C3 compounds (propene and propane) would become worse when the column was initially controlled below -60°C . The narrow peaks of the NMHCs in Fig. 2 also indicated that the initially low temperature (-60°C) of the OV-1 capillary column played an important role in cryofocusing the NMHCs with large carbon numbers, because the total release of the NMHCs with large carbon number on the adsorbent to the gas phase under the heating needed about 6 min.

3.2. The adsorption and thermal-desorption efficiencies of the adsorption tube

The adsorption efficiency is a key factor for reliably analyzing atmospheric NMHCs besides the separation effect of the capillary column as discussed above. The adsorption efficiency of the

adsorption tube was tested at -70°C , -80°C and -90°C under the same apparatus operation conditions, e.g., the same diluted standard mixture of ~ 30 ppbv for each NMHC, the same thermal-desorption temperature of 100°C , and the same temperature program of the OV-1 column. Because the NMHCs with carbon number greater than six could be easily captured by the adsorption tube even under room temperature, only the results of chromatogram for the NMHCs with carbon number less than six are comparably shown in Fig. S-3. It is evident that the peak heights of C3–C6 NMHCs have no significant change at the three different adsorption temperatures, however, remarkable loss of C2 NMHCs (ethylene, acetylene, and ethane) was observed under -70°C in comparison with those under -80°C and -90°C . The proportions of the peak heights of C2 NMHCs to those of larger NMHCs were almost kept constants when the pre-concentration was conducted under -80°C and -90°C , indicating that C2 NMHCs could be efficiently captured by the adsorption tube under temperature below -80°C . Although the multi-absorbents (several absorbents in series) can efficiently capture NMHCs under relatively high temperature which can be easily achieved by Peltier cooling system, extremely high desorption temperature is usually needed (e.g. 310°C) for completely releasing NMHCs, which would result in broaden peaks [28]. In addition, complex separation procedures for the method of multi-absorbents were usually adopted for efficiently separating NMHCs, e.g., combination of a PLOT capillary column and a secondary capillary column [20,22], or initial low separation temperature achieved by LN_2 [17]. In this study, a multistage adsorbent trap (filled with Carboxen 1000 and CarboxenTM B) was also tested for enrichment NMHCs under -50°C , although no breakthrough was found, the peaks of C2 compounds evidently broadened. Therefore, considering both the efficiency and convenience for enrichment and separation of NMHCs, the refrigerator used in the GC system for both enrichment and separation of NMHCs was a preferable choice.

In addition to the influence of temperature on the adsorption efficiency, the contacting time between the adsorbent filled in the adsorption tube and the gas samples may also affect the adsorption efficiency. Fig. S-4 illustrates the chromatogram of a standard sample pre-concentrated on the adsorption tube with flow rates of 20, 40, and 50 mL min^{-1} , respectively. The variation of each NMHC peak under the three flow rates was within the standard deviation of the standard air sample collected at a fixed flow rate. Because the fast sampling rate can save time for the same sampling volume, which can make sure enough time for a whole analyzing period of air sample within 1 h, a sampling rate of 50 mL min^{-1} was recommended.

The thermal-desorption without bake-out was first carried out at 200°C . Although no residue of the NMHCs was found in the second run with high purity N_2 enrichment, remarkable temperature elevation of the cooling column was found, which could cause much longer time for recovering the adsorption tube temperature to be -90°C for the next sampling. Therefore, the efficiency of the thermal-desorption was tested under low temperature with duration of 6 min. As shown in Fig. S-5, remarkable residue of the larger NMHCs was found under thermal-desorption temperatures of 50°C and 80°C , but no residue under 100°C . The less duration of the thermal-desorption is, the less influence of the heating for thermal-desorption on the cooling column is. Therefore, the residue after the thermal-desorption at 100°C was further checked with different durations. As shown in Fig. S-6, no residue could be detected when the thermal duration lasted 6 min. The optimal condition for the thermal-desorption is then recommended at 100°C with duration of 6 min.

The NMHCs adsorbed on the adsorbent can't be liberated immediately as the adsorbent is heated during the thermal-desorption process, and hence the peaks of the NMHCs would become broaden

Fig. 2. Chromatograms of the standard mixture of 57 NMHCs (the corresponding species of the numbers is listed in Table S-1).

when injection by turning the two six-port valves (Fig. 1) was conducted at the same time of beginning thermal-desorption. However, longer time delay before injection would result in evident loss (diffusion or chemical decomposition) of the NMHCs, especially for the C2 NMHCs and isoprene. As shown in Fig. S-7, the optimal injection time was recommended at 5 s after the beginning of the thermal-desorption.

3.3. Removal of water

Although the capillary column OV-1 used in this study isn't sensitive to water for the NMHCs separation in comparison with the PLOT capillary column, considering water vapor in the ambient air can easily plug the adsorption tube, removal of water from the ambient air is still necessary for actual measurements [32]. Drying agents of CaCl_2 and Na_2SO_4 were initially tested for removing water, but severe loss of the NMHCs with carbon number greater than eight was found. Therefore, drying trap (dehydration tube) with low temperature was designed for removing water, and the influence of the dry trap at three temperatures (-20 , -40 and -60°C) on the recovery of NMHCs signals is illustrated in Fig. S-8. In comparison with the chromatogram conducted without the drying trap, remarkable loss of the NMHCs with carbon number greater than eight was also found when temperature of the drying trap was kept at -60°C , while only modest loss of C12 NMHC (n-dodecane) was found when temperature of the drying trap was kept at -20°C and -40°C . However, the adsorption tube was frequently jammed under extremely high relative humidity (RH, raining days) when the temperature of the drying trap was kept at -20°C . No jam of the adsorption tube under -40°C occurred for the ambient air samples collected nine times (each 600 mL) in a rainy day, and hence the drying trap at -40°C was recommended for removing water from the ambient air samples.

3.4. The relationship between the GC-FID signals and injection doses

According to the operation conditions optimized in Sections 3.2 and 3.3, the relationship between the GC-FID signals and injection doses was investigated by enrichment of fixed amount (100 mL for each) standard samples with concentrations of 1.0, 2.5, 4.5, 6.0, 9.0, 18.0 and 30.0 ppbv which were prepared by dynamic dilution of the original standard gas mixture in N_2 . As listed in Table S-1, the linear correlation coefficient (R^2) for each NMHC is greater than 0.993, usually greater than 0.999 for most NMHCs, indicating that the GC-FID signals are linearly in proportion to the injection doses. The relative standard deviations (RSD) of 0.30–4.39% (Table S-1) for the NMHCs were also obtained based on quadruplicate measurements. The method detection limits (MDLs) of 0.02–0.10 ppbv for the NMHCs (Table S-1) were roughly estimated based on the signal to noise ratio of three and enrichment volume of 400 mL.

The breakthrough volume of the adsorption tube was also checked by a diluted standard gas mixture of 4 ppbv prepared by dilution of the original standard gas mixture in N_2 . As shown in Fig. 3, only with the exception for ethane, good linear relationship between the GC-FID signals and enrichment volume was found for all NMHCs when the sampling volume was less than 700 mL. As mentioned above, a good linear relation ($R^2 = 0.9991$, Table S-1) between the GC-FID signals and the concentrations (1.0–30.0 ppbv) for ethane had been found with enriching volume of 100 mL, and hence the evident bias from the linear responds for ethane under large volume enrichment was ascribed to volume breakthrough. To certify the viewpoint, additional experiments were conducted: NMHCs were comparably analyzed for enrichment of 50 mL the standard gas mixture with each species of ~ 4.0 ppbv by purging

Fig. 3. Peak areas resulting from increasing sampling volumes of a standard gas mixture of ~ 4 ppbv. The values in the brackets are the linear correlation coefficient (R^2), R^2 for ethane is derived from the sampling volume of less than 400 mL.

Fig. 4. Chromatograms of an ambient air sample from the RCEES station (upper chromatogram: 0–17.5 min; lower chromatogram: 17.5–31.0 min). Numbers refer to the substances presented in Table S-1.

with different volume of high purity nitrogen under -90°C , and evident loss of ethane was also found when the purging volume was greater than 400 mL (Fig. S-9).

3.5. Ambient air measurements

The atmospheric concentrations of the NMHCs on the roof (the eighth floor, about 20 m above the earth surface) of

Fig. 5. Diurnal concentrations of isoprene and BTEX at the RCEES station, September 16–21, 2014.

Fig. 6. The atmospheric concentrations of benzene (a) and toluene (b) comparably measured by the PTR-TOF-MS and GC-FID at the RCEES station, March 18–23, 2015.

Environmental technology building of Research Center for Eco-Environmental Sciences (RCEES) were measured for 5 consecutive days from 9:00 am to 10:00 pm (Beijing time) in September 2014 and March 2015. As shown in Fig. 4 of a typical chromatogram of the air sample (400 mL enrichment), only with the exception for *cis*-2-butene, 56 NMHCs could be identified by comparison with the retention times of the standard gas mixture. Of the identified NMHCs, only five NMHCs (*n*-butane, 2-methylpentane, *n*-hexane, 3-methylhexane and *n*-octane) were interfered by unknown compounds, and the remaining NMHCs elute in isolated peaks with the exception for the co-elution of 2-methylhexane/2,3-dimethylpentane, *m*-*p*-xylene, and *m*-*p*-ethyltoluene.

The mean concentrations and standard deviations ($n = 70$) of the identified NMHCs during the measurement period (September 2014) are listed in Table S-1. The total concentration of the identified NMHCs in September 2014 in Beijing was 52.21 ± 14.18 ppbv, and alkanes accounted for the largest percentage (60.2%), followed by aromatic (18.8%) and alkenes (14.8%), which were similar with the results of Mao et al. who reported that the concentration of the total NMHCs in Beijing was 68.0 ± 34.5 ppbv with alkanes accounting for 57.1% at a height of 32 m [26]. Several field measurements in Beijing also revealed that atmospheric alkanes contributed the largest percentage (>50%) to total NMHCs, followed by aromatics (21–32%) and alkenes (9–24%) [33]. The typical diurnal variations

of isoprene (representative of biogenic emissions) and BTEX (representative of anthropogenic emissions) are illustrated in Fig. 5. The distinct diurnal variation of isoprene with high concentrations appeared in daytime and minimal values after sunset well reflected that atmospheric isoprene is dominated by biogenic emission in Beijing [33]. The relatively high concentrations of BTEX during morning and evening rush hours were ascribed to emissions from automobile exhaust [34,35]. The average *B/T* value of 0.62 (wt./wt.) obtained in this study were well within the reported range of vehicle emission. To further verify the reliability of the GC system developed by this study, a comparison between a PTR-TOF-MS and the GC system (enrichment of 100 mL) was conducted for 5 days in March, 2015. As illustrated in Fig. 6, good agreement was found between the two techniques for measuring both benzene and toluene.

Atmospheric aerosol pollution is currently serious in China, and could be simultaneously collected on the adsorption tube and hence may affect on NMHCs measurements. The possible influence of atmospheric aerosol could be excluded based on above field measurements and additional calibration experiments during the field measurements. The distinct diurnal variation of isoprene, the reliable ratio of benzene to toluene, and the good agreement of benzene and toluene measured by the PTR-TOF-MS and the GC system developed by this study providing convincing evidences

that atmospheric aerosol had negligible influence on the measurements of NMHCs, at least for benzene, toluene and isoprene. Additional calibration experiments were conducted every day after the field measurements, and the variation of the response value of each NMHCs was within the uncertainty (<5%) of the quadruplicate measurements before the field measurements. Organics in atmospheric aerosol are usually semi-volatile and non-volatile, even if the semi-volatile organics could be released from the absorption tube under 100 °C, they would have relative long retention time because retention time of NMHCs on the separation column was found to be positively correlated with their boiling points. In addition, the ambient air was sampled in the absorption tube after the air passing through an ozone trap packed with Na₂SO₃ and quartz wool, and hence most aerosols in the air were suspected to be removed by the ozone trap before entering the absorption tube. In order to avoid possible effect of semi-volatile organic compounds in the aerosol on the next analytical cycle, the temperature of the absorption tube was increased to 220 °C with 60 mL min⁻¹ N₂ to thoroughly clean the adsorbent after each sampling.

3.6. The potential for analyzing oxygenated organic compounds

An air sample of 400 mL was collected in a room just after coating the inner wall, and analyzed by using the GC system developed by this study. As shown in Fig. S-10, several characteristically strong peaks can be found in comparison with those of the ambient air samples. These strong peaks were identified to be the signals of oxygenated organic compounds which are widely used as solvent in various dopes, such as methanol, ethanol and 1-butanol. Although the ascription of some strong peaks was not identified in this study, the GC system developed has the potential for measuring both the NMHCs and oxygenated organic compounds.

4. Conclusions

A LN₂-free/single-column GC-FID system for measuring atmospheric C₂–C₁₂ NMHCs has been developed in this study. Compared with currently available GC-FID methods, operation of this GC-FID method is much more convenient and economic due to a single capillary column used for separation and LN₂-free for enrichment. A series of tests revealed that the GC-FID method could effectively separate C₂–C₁₂ NMHCs with good linear responds, small relative standard deviations, and low detection limits. The reliability of the GC-FID system for measuring atmospheric NMHCs also verified by the field measurements and field comparison with the PTR-TOF-MS conducted in Beijing.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chroma.2015.11.060>.

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