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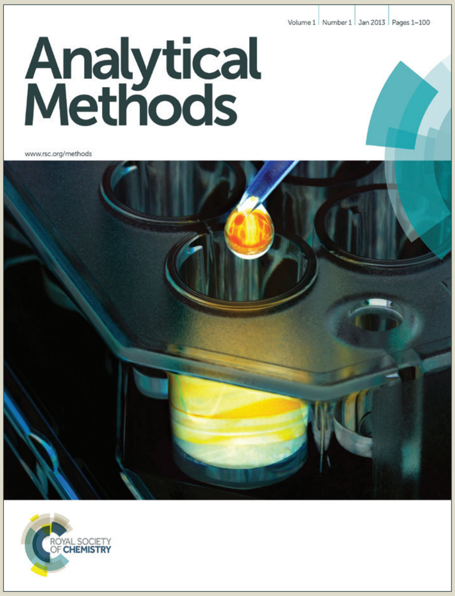

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Development and validation of a cryogen-free automatic gas chromatograph system (GC-MS/FID) for online measurements of volatile organic compounds

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Abstract

An automatic gas chromatograph system equipped with a mass spectrometer and a flame ionization detector (GC-MS/FID) was developed for online measurements of volatile organic compounds (VOCs) in the atmosphere. This system consisted of a custom-built cryogen-free cooling device that can create an ultra-low temperature of -165 °C, a two-channel sampling and pre-concentration system, and a commercial GC-MS/FID. One channel in the sampling and pre-concentration system was designated to trap C2–C5 hydrocarbons, while the other was designed to trap other VOC species. The new-developed GC-MS/FID system was then employed to measure VOCs in ambient air, and its observation data were compared with those from three well-established techniques, including an offline GC-MS/FID coupled with canister sampling, a proton transfer reaction-mass spectrometer (PTR-MS), and an online gas chromatograph system equipped with an FID and a photo ionization detector (GC-FID/PID). The online and offline GC-MS/FID measurements for alkanes, acetylene, C2–C3 alkenes, C6–C8 aromatics, and halocarbons showed good agreements. In addition, the online GC-MS/FID measurements for C6–C9 aromatics, acetone, and methacrolein+methylvinylketone (MACR+MVK) agreed well with the PTR-MS observations. Mixing ratios of C2–C7 alkanes, C3–C5 alkenes, and C6–C8 aromatics also showed good agreements between the online GC-MS/FID and GC-FID/PID techniques. These results of inter-comparison demonstrated the accuracy of online GC-MS/FID measurements for C2–C12 NMHCs, C3–C4 carbonyls, and halocarbons.

Keywords: ambient monitoring; VOCs; GC-MS/FID; inter-comparison

1 Introduction

Volatile organic compounds (VOCs) play an important role in photochemical formation of ground-level ozone (O_3) and secondary organic aerosols (SOA). VOCs can be directly emitted into the atmosphere from anthropogenic and natural sources, and some of them (e.g. carbonyls and alkyl nitrates) can also be photochemically produced from VOCs oxidation.[1] Accurate measurements for ambient VOCs are essential for top-down evaluation of VOCs emission inventories,[2] investigation of VOCs relationships with O_3 and SOA using observation-based models,[3] and indirect determination of hydroxyl radical (OH) abundances or photochemical aging of air masses.[4]

VOCs in the atmosphere include hundreds or even thousands of compounds with mixing ratios and reactivity spanning several orders of magnitude.[5] There are still challenges for VOCs measurements, especially for those species at parts per trillion (pptv) levels and/or with high reactivity. A typical VOCs analysis process at least involves two steps: sampling and instrumental analysis. Ambient air samples can be analyzed immediately upon collection by an on-line instrument at the site (i.e. the online method), or air samples can be collected and stored for a later analysis in laboratory using canister-based or adsorbent-based methods (i.e. the offline method).[6,7] The online sampling approach is especially suitable for reactive or polar species with poor stability in canisters or other containers. The detection of speciated

VOCs can be achieved by a range of instruments, such as gas chromatography (GC) with various detectors (e.g. mass spectrometer (MS), flame ionization detector (FID), photo ionization detector (PID), and electron capture detector), direct inlet MS, and some spectroscopic techniques. [6, 8, 9] Compared with the time-consuming chromatographic methods, direct inlet MS (e.g. proton-transfer reaction mass spectrometry, PTR-MS) and spectroscopic techniques (e.g. differential optical absorption spectroscopy, DOAS) can provide VOCs data with high time resolutions.[8,9] However, these instruments also some disadvantages. PTR-MS is only able to detect species with a proton affinity higher than that of water and can not distinguish isomeric/isobaric compounds.[8] DOAS measurements for ambient VOCs correspond to their average concentrations in several kilometers, and the retrieval of ground-level mixing ratios is still a challenging task.[9, 10] Additionally, the detection limits of DOAS are not low enough to measure species at pptv levels. The GC system combined with different detectors can be employed to measure a large suite of VOC species, including hydrocarbons, alcohols, carbonyls, halocarbons, and alkyl nitrates.[6] Therefore, it is still the most commonly used technique for speciated VOCs measurements nowadays.[11-13]

Besides sampling and instrumental analysis, a pre-concentration step is often required for GC-based VOCs measurements. The commonly used pre-concentration techniques include cryogenic trapping,[6, 11] sorbent enrichment,[7] and a combination of these two methods.[12-14] Liquid cryogen can create an ultra-low temperature to trap

VOCs,[6] but its supply and transportation are possibly unavailable at rural or remote sites. Therefore, online techniques for VOCs measurements in remote regions usually used solid adsorbents for the concentration of air sample.[15] However, several studies reported that the use of solid adsorbents use was prone to artifacts, such as enrichment losses of highly volatile compounds (e.g. C2 species) and desorption losses of ≥C7 components.[16-18]

The accuracy of VOCs data from field measurements can not be established by repeating experiments due to expenses and inevitable changes of atmospheric conditions.[19] The field inter-comparison of simultaneous measurements by different instruments is considered to be a useful approach to evaluate the accuracy of ambient measurement data, and are especially helpful for validating observation results obtained by new-developed techniques.[20-22]

In this paper, we described a cryogen-free automatic GC-MS/FID system for online measurements of ambient VOCs. Observation results from the custom-built online GC-MS/FID were then compared with simultaneous measurements by another three commercial techniques, including an offline GC-MS/FID coupled with canister sampling, a PTR-MS, and a GC-FID/PID, to validate the performance of this new-developed system.

2 Experimental

2.1 Development of an online GC-MS/FID system

2.1.1 Instrumentation

The online GC-MS/FID system consisted of three major components: a cryogen-free cooling device for creating ultra-low temperatures, a sampling and pre-concentration system for VOCs collection and enrichment, and a gas chromatography equipped with a MS and an FID for VOCs separation and detection.

2.1.1.1 Cryogen-free cooling device

The custom-built cryogen-free cooling device used a multicomponent mixed refrigerant in cascade refrigeration cycle to obtain an ultra-low cryogenic temperature of -165 °C for VOCs enrichment. The working principle for this cooling device is similar with that for a home refrigerator. In the refrigeration cycle, the compressed refrigerant was precooled in a countercurrent heat exchanger, where it liquefied. The liquid then passed through a capillary tube, dropping to a lower pressure, and evaporated such that the resulting cooled vapor precooled the incoming high-pressure fluid. As depicted in Fig. 1, this cooling device had two stages of refrigeration circulations. The first-stage circulation included a compressor (***1*** in Fig. 1), a condenser (***3***), a heat exchanger (***5***), a capillary tube (***7***), and an evaporated condenser (***10***). Refrigerant ***A*** circled with the direction of 1→3→5→7→10→5→1. The second-stage circulation included a compressor (***2***), an oil separator (***4***), a heat exchanger (***6***), an evaporated condenser (***10***), a capillary tube (***8***), and an evaporator (***9***). Refrigerant ***B*** circled with the direction of 2→4→6→10→8→9→6→2. After the heat-exchange with liquid refrigerant ***B***, the evaporator ***9*** was cooled to -165 °C and was used as the cold region for VOCs enrichment.

The most significant advantage of this cooling device is that it can create ultra-low trapping temperatures without using cryogen (e.g. liquid nitrogen), and the only requirement for its operation is three-phase electric power (380 V) which is a common method of alternating-current electric power generation, transmission, and distribution worldwide. Therefore, this device especially facilitates long-term measurements of ambient VOCs in rural or remote regions where cryogen are not available.

2.1.1.2 Sampling and pre-concentration system

A schematic of the custom-built sampling and pre-concentration system is depicted in Fig. 3. The sampling lines for ambient air and standard gases were both Teflon tubes with 1/4-inch outside diameter (OD). A 0.25-µm Teflon filter (Whatman, UK) was fitted on the front of ambient air sampling line to prevent particles into this system. A six-port stream select valve (Valve 1; Valco Instruments, Houston, TX, US) was used to direct ambient air and standard gases directed into this system. To remove ozone in ambient air, a U-tube filled with crystalline Na_2SO_3 (O_3 trap) was installed after the Valve 1. Air samples were then drawn into two parallel channels using a downstream pump (N86KTE, KNF Neuberger, France) for water removal and VOCs enrichment. Each channel was equipped with a water management trap (H_2O trap; a quartz tube with 25-cm length and 1/4-inch OD), an enrichment trap, and a mass flow controller (MFC). The enrichment trap for Channel 1 was a porous layer open tubular (PLOT) capillary column with 0.53-mm inside diameter (ID) and 25-cm length (J&W Scientific, CA, US) that was designed to trap C2–C5 hydrocarbons, while Channel 2 used a deactivated quartz capillary (25 cm, 0.32 mm ID, J&W Scientific) to trap other VOC species in air samples. A twelve-port switching valve (Valve 2, Valco Instruments) was employed to control flow pathways of carrier gas during different stages. The carrier gas for this sampling and pre-concentration system was ultra-pure helium (> 99.999% He).

2.1.1.3 Gas chromatography and detectors

A commercial gas chromatography (QP-2010S, Shimadzu, Japan) that housed two separate columns and two detectors was employed for VOCs separation and detection. A PLOT (Al_2O_3/KCl) column (15 m, 0.32 mm ID, J&W Scientific) connected with an FID was used to quantify C2–C5 hydrocarbons. A DB-624 column (30 m, 0.25 mm ID, J&W Scientific) connected with a MS was applied to analyze other VOC species (e.g. C5–C12 hydrocarbons, OVOCs, halocarbons, and alkyl nitrates). The carrier gases for these two columns were both ultra-pure helium (> 99.999%).

2.1.2 The analysis cycle for VOCs measurements

A complete analysis cycle for ambient VOC measurements by this online

GC-MS/FID system include five stages: preparation, sampling and pre-concentration, injection/GC analysis, idle/GC analysis, and back purge/GC analysis.

In the preparation stage, air samples passed through sampling line and two three-way valves V3 and V5, and vented from the sampling and pre-concentration system via the pump at a flow rate of 5.5 L min^{-1} (see the green lines and arrows in Fig. 2). The ventilation of sampling inlet using ambient air samples could reduce or avoid interferences by previous samples. In addition, temperatures for H_2O traps and enrichment traps during the preparation stage had been set at their corresponding values for sampling and pre-concentration stage.

After the 3-minute preparation stage, the in-port for Valve 1 was switched to S3, the valve V3 was closed, valves V3′, V4, V4′, and V5 were opened, and then air samples were drawn into the two parallel channels for VOCs enrichment at rates of 60 mL min^{-1} as maintained by a downstream mass flow controllers (Fig. 3a). The water management temperatures for Channel 1 and 2 were set at -50 °C and -30 °C, respectively. The temperatures of enrichment traps for both channels were set at -150 °C.

In the injection/GC-analysis stage, the downstream pump was shut down, the in-port of Valve 1 was switched to S4, Valve 2 was switched to position ***B***. The concentrated VOCs in enrichment traps were volatilized by thermal desorption at 110 °C and were injected into the GC system by Helium carrier gas (Fig. 3b).

After the 1-minute injection, GC analysis continued for VOCs separation and detection. Meanwhile, the sampling and pre-concentration system shifted to the idle condition (Fig. 3c). The in-port of Valve1 was switched to S1, meanwhile Valve 2 was switched to position ***A***. Temperatures of water management and enrichment traps gradually dropped to -165 °C.

Twenty minutes after the injection/GC-analysis stage, a 5-minute back purge for the sampling and pre-concentration system was programmed for removing residues in water management traps and cleaning sampling lines to prevent samples carryover effects. During the first 2 minutes, the water management trap and the enrichment trap for Channel 1 were both heated to 110 °C. Helium carrier gas passed through V4′, enrichment trap, CO_2 trap, water management trap, O_3 trap, V3, V3′, and V5 at a flow rate of 180 mL min^{-1}, and vented into the atmosphere using the downstream pump. During the second 2 minutes, the traps for Channel 2 were heated to 110 °C and back flushed by carrier gas. Both channels were heated and back flushed in the last minute (Fig. 3d). After the back purge stage, the sampling and pre-concentration system shifted to the idle condition again.

In a complete analysis cycle, the GC was programmed for a 32.7 min run time, with a temperature program as follows: the initial temperature was 35 °C for 3 min, then the GC oven was ramped at 6 °C min^{-1} to 180 °C, and held at 180 °C for 5 min.

2.2 Field measurements of VOCs by four techniques

To validate VOCs measurement data obtained by the new-developed

GC-MS/FID system, another three commercial techniques were also employed at an urban site of Beijing (the PKU site, 40.00° N, 116.31° E) to observe ambient VOCs during August to September, 2010, including (1) an offline GC-MS/FID system coupled with canister sampling, (2) a PTR-MS, and (3) an online GC-FID/PID. Canister sampling coupled with GC-MS/FID analysis is an U.S. EPA recommended offline method for VOCs measurements. The GC-FID/PID is commonly used for online measurements of hydrocarbons. PTR-MS is an acceptable method to observe aromatics and carbonyls. Detailed descriptions about the PKU site were provided by previous studies.[25-27] Briefly, the PKU site is located in the northwest of Beijing city and represents the urban atmospheric environment in Beijing.

2.2.1 Offline GC-MS/FID coupled with canister sampling

Whole air samples were instantaneously collected by pre-cleaned evacuated 3.2-L canisters, which were then returned to our lab in Peking University for VOCs analysis. Detailed analytical methods and quality assurance and quality control (QA/QC) procedures for this offline method were described by Liu et al. (2008) and Wang et al. (2010).[13, 25] Briefly, a 500-mL aliquot of air sample from each canister was concentrated using a three-stage cryofocusing pre-concentration system (Entech 7100, Entech Instruments, US), and then the vaporized VOCs were injected into a gas chromatography system (GC, HP-7890A, Hewlett Packard, US) for analysis. A PLOT (Al_2O_3/KCl) column with an FID was employed to separate and detect C2–C4 hydrocarbons. A DB-624 column with an MS (HP-5975C, Hewlett Packard, US) was used to measure C5–C12 hydrocarbons, alkyl nitrates, and halocarbons.

The online and offline GC-MS/FID systems both applied a PLOT column connected an FID to quantify light hydrocarbons and a DB-624 column equipped with a MS to measure the other VOC species. However, the sampling and pre-concentration methods for these two techniques showed significant differences: (1) the online GC-MS/FID system collected ambient air using a Teflon tube, while the offline method used canisters to sample and store whole air samples; (2) the Entech 7100 pre-concentration system for the offline system used liquid nitrogen as cryogen, while the new-developed system employed a cryogen-free cooling device to create a ultra-low temperature; (3) the Entech 7100 used three series connected traps to pre-concentrate VOCs, while the custom-built system used two parallel traps to concentrate C2–C5 NMHCs and the other VOC species separately.

2.2.2 PTR-MS

PTR-MS is a commonly used technique for online measurements of ambient VOCs.[8] Target compounds react with H_3O^+ in the drift tube of PTR-MS to form $VOC{\cdot}H^+$ which can be detected by a quadruple mass spectrometer.[8] In this study, a commercial high-sensitivity PTR-MS (Ionicon Analytik, Innsbruck, Austria) was employed to measure ambient isoprene (m/z 69), C6–C9 aromatics (m/z 79 for benzene, m/z 93 for toluene, m/z 105 for styrene, m/z 107 for C8 aromatics, and m/z

121 for C9 aromatics), methanol (m/z 33), and C2–C4 carbonyls (m/z 45 for acetaldehyde, m/z 59 for acetone, m/z 71 for methyl vinyl ketone (MVK) and methacrolein (MACR), and m/z 73 for methyl ethyl ketone (MEK)). Background signals of PTR-MS were determined by 15-min measurements for zero air every 2.5 h. A Pt-coated quartz wool converter performed at 370 °C was used to remove VOC species in ambient air to produce zero air. The method detection limits (MDL) for each compound ranged from 40 to 200 pptv. Detailed descriptions about the PTR-MS set-up and quality QA/QC procedures were provided by Yuan et al. (2012) and Chen et al. (2014).[28, 29]

2.2.3 Online GC-FID/PID system

The commercial online GC-FID/PID system (Syntech Spectra GC955 series 611/811 VOC analyzer) was used to measure non-methane hydrocarbons (NMHCs) in ambient air. This system works semi-continuously: the first step is flushing the sample tube by drawing air through it with a pump. Then the pump was switched off and a volume of 35 ml sample gas was pre-concentrated on absorbents with the help of an indirect piston system. This procedure would be repeated until enough air sample (i.e. ~220 mL for the series 811 and ~180 mL for the series 611) has been drawn. For the series 811, C2–C5 NMHCs in ambient air were pre-concentrated on Carbosieves SIII at low temperature of –5 °C. The enriched compounds were then thermally desorbed by heating (270 °C) and were purged into the separation column, which consisted of a stripper column (AT^{TM}-5, 5 m × 0.25 mm ID) and a analysis column (PLOT (Al_2O_3/Na_2SO_4), 10 m × 0.32 mm ID). The target compounds were then detected by a PID and an FID. The series 611 was applied to measure C6–C10 NMHCs. Air samples were pre-concentrated on Tenax GR at normal atmospheric temperature (~30°C). Target compounds were then desorbed at 230°C, and were brought into a stripper column (AT^{TM}-1, 2 m × 0.32 mm ID) and a analysis column (AT^{TM}-1, 28 m × 0.32 mm ID) for separation and a PID for detection. The MDLs for NMHCs ranged from 0.05 to 0.20 ppbv. Detailed descriptions about this system were provided by Xie et al. (2008) and Zhang et al. (2014).[15, 26]

2.2.4 Time resolutions of VOCs measurements

The sampling acquisition times and analysis cycle lengths for VOCs measurement by these four techniques are summarized in Table 2. The time resolution for online GC-MS/FID measurements was 60 min, and ambient air was sampled during the first 5 minutes of each hour. The entire analysis cycle length for the online GC-FID/PID was 30 min, and meanwhile the next sample was collected. The cycle length for PTR-MS was 25 s, and the integration times for most single ions were 1s, except mass 21 (0.1 s) and mass 137 (2 s).[28] To compare with online GC-MS/FID measurements, canister samples were instantaneously collected in the first 5 minutes of each hour.

3 Results and discussion

3.1 Calibrations and Quality Assurance/Quality Control (QA/QC) procedures for online GC-MS/FID system

Three cylinder standard gases of VOCs were employed to calibrate the online GC-MS/FID system. The calibrations of NMHCs and alkyl nitrates were based on a mixture standard gas of 56 NMHCs (Spectra Gases, Newark, New Jersey, US) and a laboratory-prepared alkyl nitrates standard gas provided by the Earth System Research Laboratory, National Oceanic and Atmospheric Administration (NOAA), respectively. A 63-chemicals mixture standard (Spectra Gases) was used to calibrate C2–C6 carbonyls, methanol, and halocarbons. Figure 4a and b show typical chromatograms of FID measurements for 56-NMHCs standard gas and ambient air, respectively. It can be found that peaks for target compounds (i.e. C2–C5 hydrocarbons) were separated well by the PLOT column at the setting chromatographic conditions.

The calibration standards of multiple mixing ratios (0.5–8.0 ppbv) were generated by dynamic dilution of cylinder standard gases (~1 ppmv). The calibration curves for measured VOCs were extremely linear with correlation coefficient (*r*) greater than 0.996 and negligible intercepts. Reproducibility of the new-developed system was evaluated based on seven replicate analyses of 1-ppbv standard mixtures. The precisions for target compounds (i.e. relative standard deviations of replicate analyses) ranged from 0.8 to 6.1%. The MDL for each compound was calculated using the method recommend by EPA TO-15 (www.epa.gov/ttnamti1/files/ambient/airtox/to-15r.pdf). The MDLs for NMHCs, OVOCs, halocarbons, and alkyl nitrates were 0.002–0.021, 0.008–0.026, 0.003–0.016, and 0.001–0.003 ppbv, respectively.

The drift in MS responses was corrected based on two types of internal standards. One was the diluted commercial mixture standard (Spectra Gases), which included four chemicals, namely bromochloromethane, 1,4-diflurobenzene, chlorobenzene-d5, and 1-bromo-3-flurobenzene. The other type of internal standards were those compounds in ambient air which had stable mixing ratios during the entire measurement period.[6, 23] In this study, trichlorotrifluoroethane (CFC-113) in ambient air was selected as the internal reference compound to validate MS responses because its ambient responses are high enough to be accurately detected by MS and its ambient levels during several months can be considered to be constant (~85 pptv).[24] The smoothed CFC-113 responses were used to correct the systematic temporal drift in MS responses based on the following equation:

$$\mathrm{Response}^{c}_{\mathrm{VOC}}=\frac{\mathrm{Response}_{\mathrm{VOC}}}{\mathrm{Response}^{s}_{\mathrm{CFC\text{-}113}}}\times\mathrm{Response}^{ref}_{\mathrm{CFC\text{-}113}} \quad (1)$$

where $\mathrm{Response}_{\mathrm{VOC}}$ and $\mathrm{Response}^{c}_{\mathrm{VOC}}$ are the measured and corrected responses for target VOC species, respectively. $\mathrm{Response}^{s}_{\mathrm{CFC\text{-}113}}$ corresponds to the smoothed CFC-113 responses. $\mathrm{Response}^{ref}_{\mathrm{CFC\text{-}113}}$ is the CFC-113 response in ambient air when calibration curves were established. Ambient mixing ratios for target VOC species were then calculated based on $\text{Response}_{\text{VOC}}^{\text{c}}$ and corresponding response factors (i.e. the slope of calibration curve).

The 1-ppbv mixture standard of 56 NMHCs was analyzed once a day to check the stability of the new-developed GC-MS/FID system. Figure 5 shows temporal variations of response factors for *m*,*p*-xylene and toluene detected by MS and ethene and *i*-pentane detected by FID for daily calibrations. It should be pointed out that response factors of *m*,*p*-xylene and toluene have been corrected based on ambient responses of CFC-113. It can be found that response factors for these compounds varied within ±10%, suggesting the stability of this system.

3.2 Comparisons of ambient VOCs measurements by four techniques

3.2.1 Time series of ambient VOCs measurements

Figure 6 shows the time series of online GC-MS/FID, online GC-FID/PID, PTR-MS, and offline GC-MS/FID measurements for benzene, toluene, styrene, C8 aromatics, C9 aromatics, and isoprene in ambient air at the PKU site from August 12 to September 6, 2010. As shown in this figure, all of these techniques can track fluctuations of VOCs levels. The observations for benzene and toluene by these four systems showed good agreements, whereas measurements for isoprene, styrene, C8 and C9 aromatics showed some disagreements, which will be further discussed in the following sections.

3.2.2 Comparison between the online and offline GC-MS/FID

There are a total of 24 canister samples that were collected to compare with the online GC-MS/FID measurements for NMHCs and halocarbons. As shown in Table 3, ambient mixing ratios of alkanes, acetylene, C2–C3 alkenes, C6–C8 aromatics, and halocarbons agreed well between these two techniques, with *r* of 0.88–0.99 and linear regression slopes of 0.83–1.20. However, the offline GC-MS/FID measurements for reactive NMHCs (e.g. C4–C6 alkenes, styrene, and C9 aromatics) tended to be lower than the online GC-MS/FID observations. This was possibly due to the losses of reactive NMHCs during storage in canisters.[30, 31]

3.2.3 Comparison between the online GC-MS/FID and PTR-MS

Isoprene, C6–C9 aromatics, and C3–C4 carbonyls were measured in common by the online GC-MS/FID and PTR-MS. The PTR-MS data with high time resolution were averaged over the sampling period of online GC-MS/FID (i.e. the first 5 minutes of each hour) and then compared with the online GC-MS/FID observations. As shown in Table 3 and Fig. 7, the online GC-MS/FID and PTR-MS measurements showed good agreements for benzene, toluene, styrene, C8 aromatics, C9 aromatics, acetone, and MACR+MVK, with *r* of 0.88–0.99 and slopes of 0.80–1.29. MEK measurements by these two techniques exhibited a good correlation (*r* = 0.89), but the PTR-MS observations were 39% higher than those from the online GC-MS/FID. One possible explanation was that the MEK signals at 73 mass detected by the PTR-MS were interfered by some additional species. Methyl glyoxal was suggested to be a candidate of the ions at 73 mass.[32]

The online GC-MS/FID and PTR-MS measurements for isoprene showed a poorer correlation than other species, with *r* of 0.73 (Fig. 7b). Interestingly, mixing ratios of daytime isoprene showed a good agreement between these two techniques, with *r* of 0.88 and a linear regression slope of 0.91; however, the nighttime isoprene measurements by the PTR-MS were significantly higher than those from the online GC-MS/FID (Fig. 8). This was possibly because the PTR-MS measurements for isoprene (m/z 69) were interfered by additional species, such as furan, 2-methyl-3-buten-2-ol, cyclopentene, and pentanal.[8, 20] In this study, none of these species were measured by the online GC-MS/FID, and thus it is difficult to identify which species resulted in this disagreement. Further research is required to identify the exact interference species for nighttime isoprene measurements by PTR-MS in urban atmosphere of Beijing.

3.2.4 Comparison between the online GC-MS/FID and GC-FID/PID

There are 52 NMHC species commonly measured by the online GC-MS/FID and GC-FID/PID. The online GC-MS/FID measurements represented VOCs average levels during the first 5 minutes of each hour, while the online GC-FID/PID observations corresponded to 30-minutes average mixing ratios. In this study, the online GC-FID/PID data in the first half hour were selected to compare with the online GC-MS/FID data. It should be pointed out that this difference in sampling times of these two techniques would possibly result in some disagreements of VOCs measurements, especially when ambient VOCs levels undergoing intensive changes.

Mixing ratios of C2–C7 straight-chain alkanes, C4–C5 branched alkanes, most of C2–C4 alkenes, isoprene, and C6–C8 aromatics showed good agreements between these two techniques, with *r* of 0.80–0.96 and slopes of 0.75–1.23. However, the online GC-FID/PID measurements for some cycloalkanes and alkenes tended to be higher than the online GC-FID/MSD observations (Table 3). Since the online GC-FID/PID identified target compounds based on their retention times, and thus the co-elution of target compounds with other species would result in positive biases for specific VOC measurements.[33]

3.3 Advantages of this new-developed GC-MS/FID system

The advantages of the online GC-MS/FID system include: (1) the cryogen-free cooling device can create an ultra-low temperature of -165 °C with the only requirement of electric power (380 V), and thus this system especially facilitates VOCs measurements in rural or remote regions where liquid cryogens are not readily available; (2) the pre-concentration traps eliminate the use of solid adsorbents for VOCs enrichment which could be a potential source of artifacts; (3) the sampling and pre-concentration system employs two independent channels to measure a wide variety of compounds; (4) Teflon lines and joints are used for this system to prevent the losses of polar compounds (e.g. aldehydes and alcohols); (5) this system can be easily constructed and connected to any existing GC system with great flexibility.

4 Conclusions

An online GC-MS/FID system was developed to measure a variety of VOC species in ambient air, such as C2–C12 hydrocarbons, C3–C6 carbonyls, methanol, halocarbons, and alkyl nitrates. The heart of this system was a custom-built cryogen-free cooling device which can create an ultra-low temperature of -165 °C. C2–C5 hydrocarbons in air samples were pre-concentrated at a PLOT column trap, followed by the FID detection. The other VOC species were enriched by a deactivated quartz capillary trap and were quantified by the MS. Based on current mixture standards, this new-developed system quantified 110 ambient volatile organic compounds with precisions ranging from 0.8 to 6.1%. The method detection limits for NMHCs, OVOCs, halocarbons, and alkyl nitrates were 0.002–0.021, 0.008–0.026, 0.003–0.016, and 0.001–0.003 ppbv, respectively. Simultaneous measurements for ambient VOCs by the online GC-MS/FID and three well-established techniques were conducted to validate VOCs data obtained by this new-developed system. Mixing ratios of alkanes, acetylene, C2–C3 alkenes, C6–C8 aromatics, and halocarbons measured by the online GC-MS/FID showed good agreements with those observed by the offline GC-MS/FID. The online GC-MS/FID measurements for aromatics and carbonyls also showed good agreements with PTR-MS observations. By comparing with these well-established techniques, the performance of this new-developed GC-MS/FID system to measure C2–C12 hydrocarbons, C3–C4 carbonyls, and halocarbons was validated.

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Tables

Table 1 Target compounds and configurations for two parallel channels of custom-built online GC-MS/FID system.

Channel	Channel 1	Channel 2
Target compounds	C2–C5 NMHCs	C5–C12 NMHCs, OVOCs, halocarbons, and alkyl nitrates etc.
Water management traps	quartz tube (25 cm, 1/4 inch OD)	
Enrichment traps	PLOT (Al_2O_3/KCl) column (25 cm, 0.53 mm ID)	deactivated quartz capillary (25 cm, 0.53 mm ID)
Separation columns	PLOT (Al_2O_3/KCl) (15 m, 0.32 mm ID)	DB-624 (30 m, 0.25 mm ID)
Detectors	FID	MS

Table 2 Sampling acquisition times and cycle lengths for four VOCs measurement instruments.

Instrument	Sample acqisition time	Cycle length	Coverage percent [b]
online GC-MS/FID	5 min	60 min	--
online GC-FID/PID	20–30 min	30 min	50%
offline GC-MS/FID	~1–2 min	60 min	100%
PTR-MS	1 s [a]	25 s	8%

[a] PTR-MS single ion intergration time;

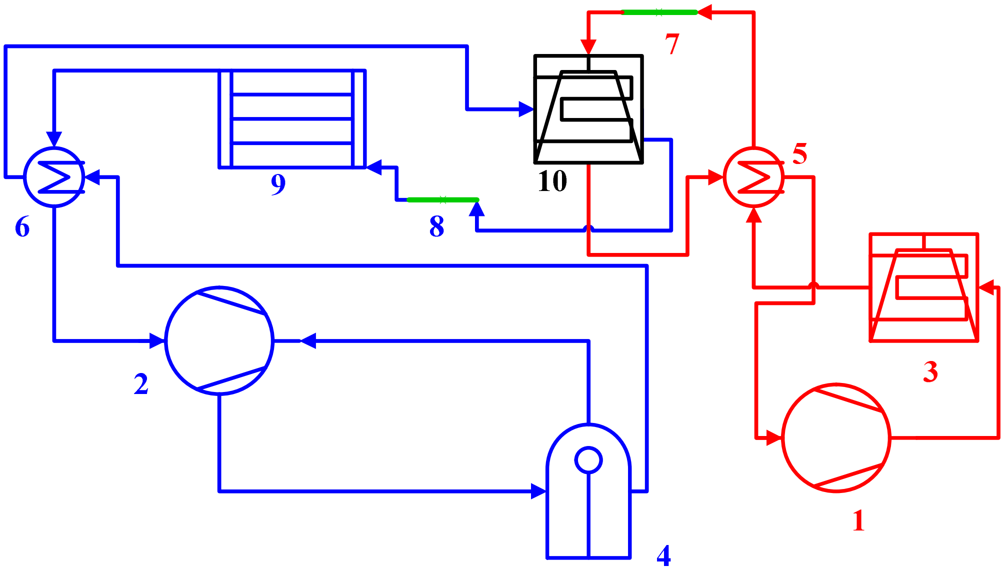
[b] The coverage percent means the percentage of measurement data that used in correlation analysis between observations by this instrument and the online GC-MS/FID system.

Table 3 Linear regression analysis results for ambient VOCs measurements by the online GC-MS/FID with those measured by offline GC-MS/FID, online GC-FID/PID, and PTR-MS.

Species	offline GC-MS/FID n=24			online GC-FID/PID n=548			PTR-MS n=548		
	r	slope	intercept	*r*	slope	intercept	*r*	slope	intercept
ethane	0.95	0.97	-0.13	0.94	1.22	-0.47	--	--	--
propane	0.98	1.08	-0.01	0.96	1.12	-0.39	--	--	--
i-butane	0.97	1.10	-0.04	0.94	1.06	-0.23	--	--	--
n-butane	0.92	1.05	0.11	0.91	1.02	-0.25	--	--	--
i-pentane	0.97	0.98	0.05	0.91	1.00	-0.12	--	--	--
n-pentane	0.99	1.02	-0.09	0.93	1.02	-0.06	--	--	--
n-hexane	0.98	1.04	-0.07	0.91	1.13	0.02	--	--	--
n-heptane	0.97	1.04	0.03	0.92	0.88	-0.04	--	--	--
n-octane	0.97	0.87	-0.01	0.57	1.05	-0.04	--	--	--
n-nonane	0.93	0.83	0.00	0.42	0.20	-0.01	--	--	--
acetylene	0.96	1.17	0.12	--	--	--	--	--	--
ethene	0.97	0.88	0.28	0.91	2.07	0.08	--	--	--
propene	0.98	0.78	0.06	0.94	1.13	0.09	--	--	--
trans-2-butene	0.64	0.66	-0.04	0.50	2.16	-0.15	--	--	--
1-butene	0.95	0.73	-0.07	0.88	1.11	-0.03	--	--	--
cis-2-butene	0.54	0.62	-0.05	0.80	1.23	0.01	--	--	--
1,3-butadiene	0.75	0.62	-0.01	--	--	--	--	--	--
1-pentene	0.72	0.75	-0.01	0.72	6.36	-0.17	--	--	--
trans-2-pentene	0.53	0.44	0.01	0.64	1.22	0.02	--	--	--
cis-2-pentene	0.59	0.45	0.00	0.59	1.34	0.01	--	--	--
1-hexene	0.67	0.68	-0.01	--	--	--	--	--	--
isoprene	0.83	0.63	-0.09	0.87	1.07	0.10	0.73	0.79	0.26
benzene	0.99	0.98	-0.12	0.96	0.95	0.12	0.96	0.80	0.07
toluene	0.98	1.02	-0.23	0.91	0.97	-0.03	0.99	0.94	0.05
ethylbenzene	0.99	0.94	-0.10	0.92	0.73	-0.08	--	--	--
m,p-xylene	0.97	0.90	-0.02	0.93	0.75	0.06	--	--	--
o-xylene	0.93	0.84	-0.04	0.88	0.70	-0.12	--	--	--
styrene	0.87	0.55	-0.04	0.80	0.29	-0.03	0.88	0.93	0.02
i-propylbenzene	0.86	0.85	0.00	0.63	0.45	-0.01	--	--	--
n-propylbenzene	0.90	0.86	-0.01	0.82	0.51	-0.01	--	--	--
m-ethyltoluene	0.82	0.70	0.00	0.53	0.57	0.00	--	--	--
p-ethyltoluene	0.73	0.73	0.00	0.66	0.45	0.01	--	--	--
1,3,5-trimethylbenzene	0.72	0.49	0.00	0.59	0.28	-0.01	--	--	--
o-ethyltoluene	0.77	0.72	0.00	0.63	0.54	-0.01	--	--	--
1,2,4-trimethylbenzene	0.91	0.58	0.00	0.90	0.41	-0.03	--	--	--
1,2,3-trimethylbenzene	0.85	0.56	0.00	0.63	0.74	-0.04	--	--	--
C8 Aromatics	--	--	--	--	--	--	0.98	0.87	0.09
C9 Aromatics	--	--	--	--	--	--	0.96	0.99	0.12
acetone	--	--	--	--	--	--	0.90	1.29	-0.44
MEK [a]	--	--	--	--	--	--	0.89	1.39	-0.18
MACR+MVK [a]	--	--	--	--	--	--	0.93	0.83	0.15
CH_2Cl_2	0.91	0.89	0.02	--	--	--	--	--	--
$CHCl_3$	0.90	1.03	0.00	--	--	--	--	--	--
C_2HCl_3	0.88	1.10	0.00	--	--	--	--	--	--
C_2Cl_4	0.89	0.83	0.00	--	--	--	--	--	--

[a] MEK: methylethylketone; MACR: methacrolein; MVK: methylvinylketone.

500 **Figures**



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503 Fig. 1 Schematic of the cryogen-free cooling device. 1 and 2: compressor; 3:

504 condenser; 4: oil-separator; 5 and 6: heat-exchanger; 7 and 8: capillary tube; 9:

505 evaporator; 10: evaporated condenser. The first and second stage circulation systems

506 are illustrated by red and blue lines, respectively.

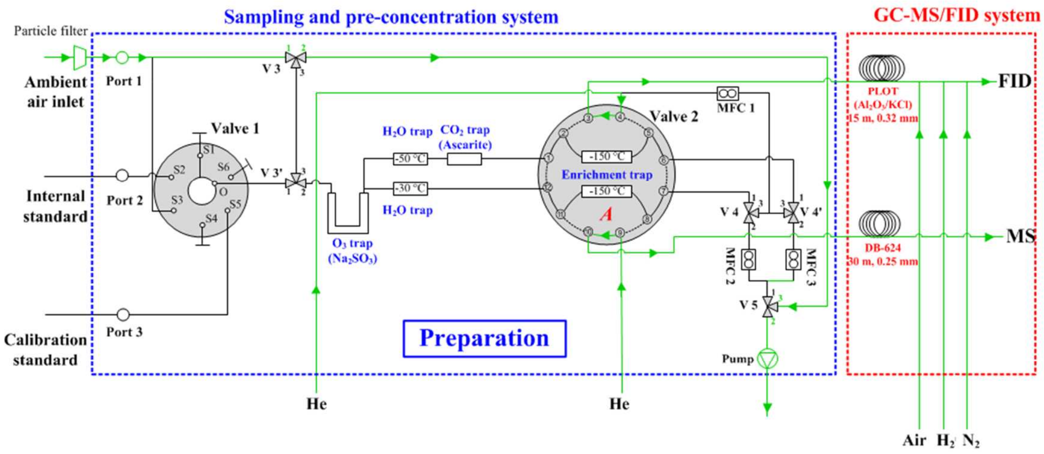

Fig. 2 Schematic of the custom-built automatic GC-MS/FID system for online VOCs measurements. The green lines and arrows illustrate flow paths of carrier gases during preparation stage.

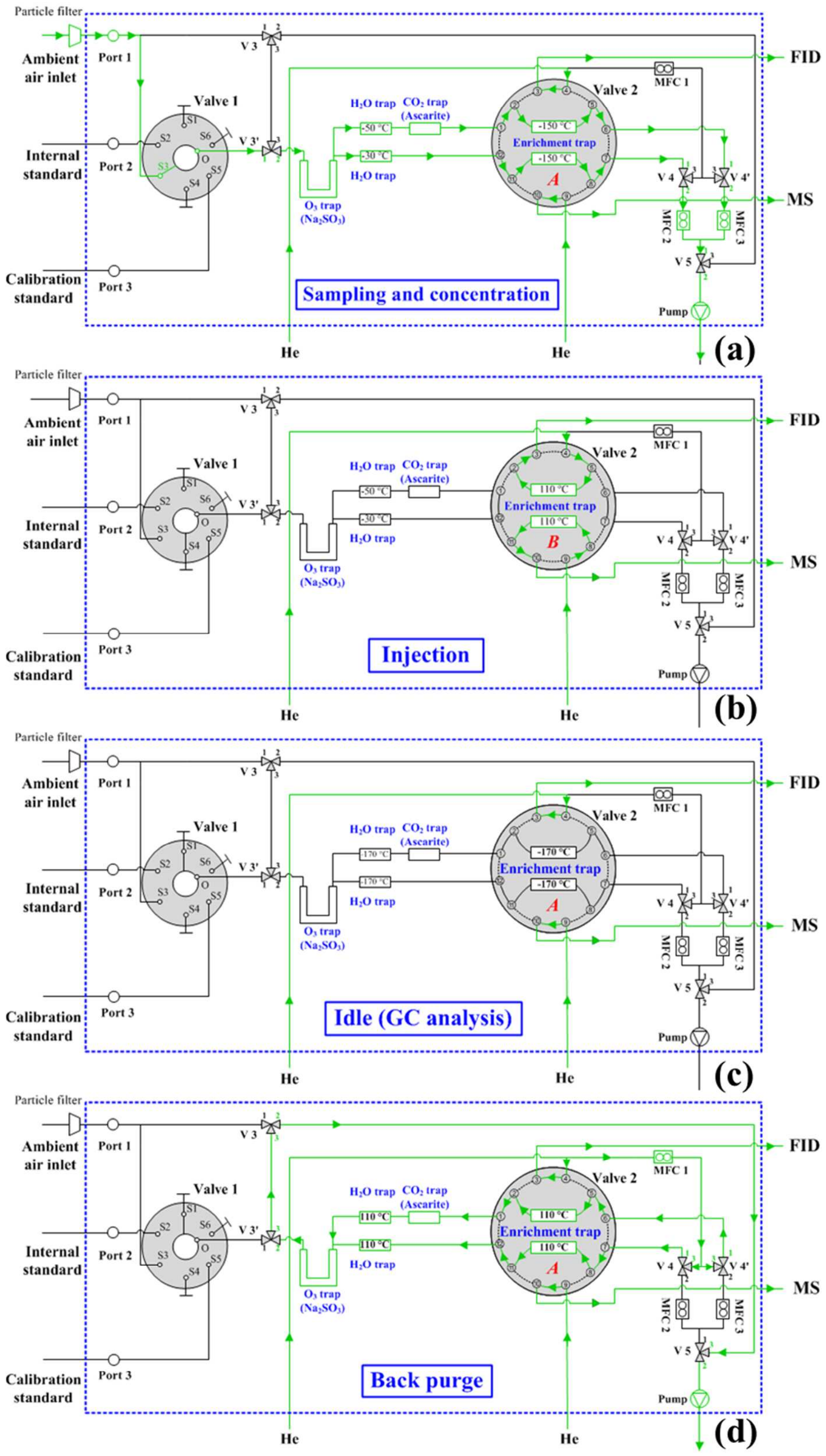

Fig. 3 Schematic of the sampling and pre-concentration system. The flow paths of carrier gase during (a) sampling and pre-concentration, (b) injection, (c) idle (GC analysis), and (d) back purge stages are illustrated by green lines and arrows.

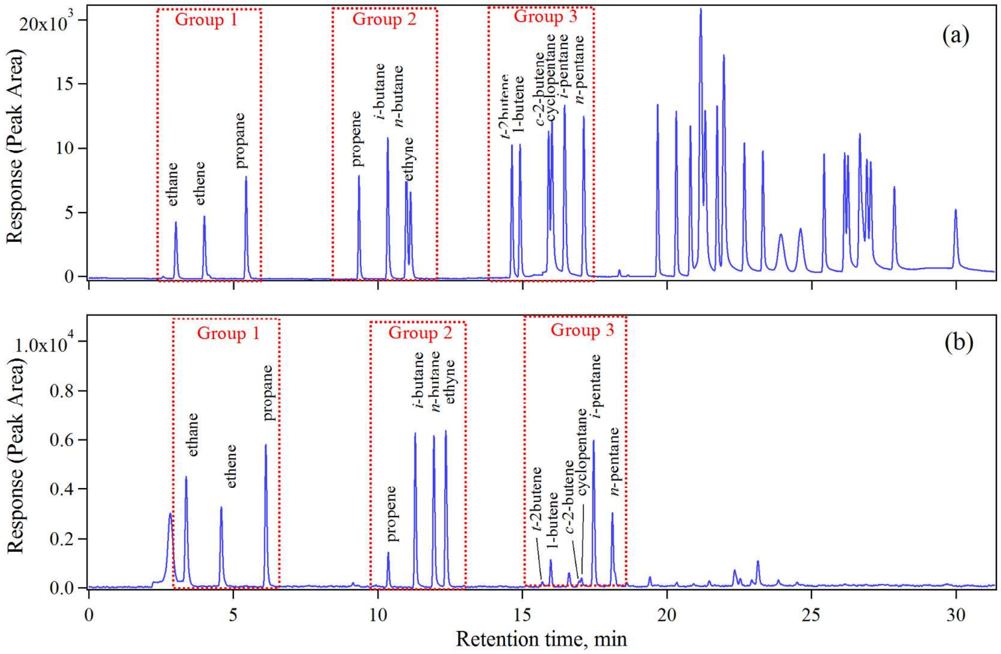

Fig. 4 Typical chromatograms of FID measurements for (a) a calibration run of 56-NMHCs mixture standard and (b) a typical ambient air sample.

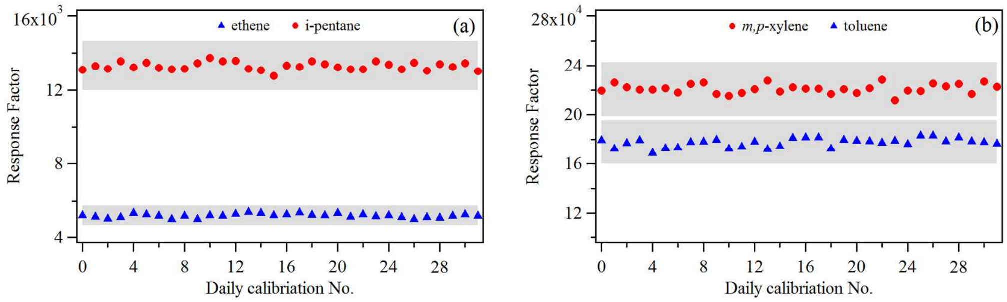

Fig. 5 Response factors of (a) *m*,*p*-xylene and toluene detected by MS and (b) ethene and *i*-pentane detected by FID for daily calibrations. Response factors of *m*,*p*-xylene and toluene have been corrected based on measured responses of CFC-113 in ambient air. The gray areas represent ±10% uncertainty range.

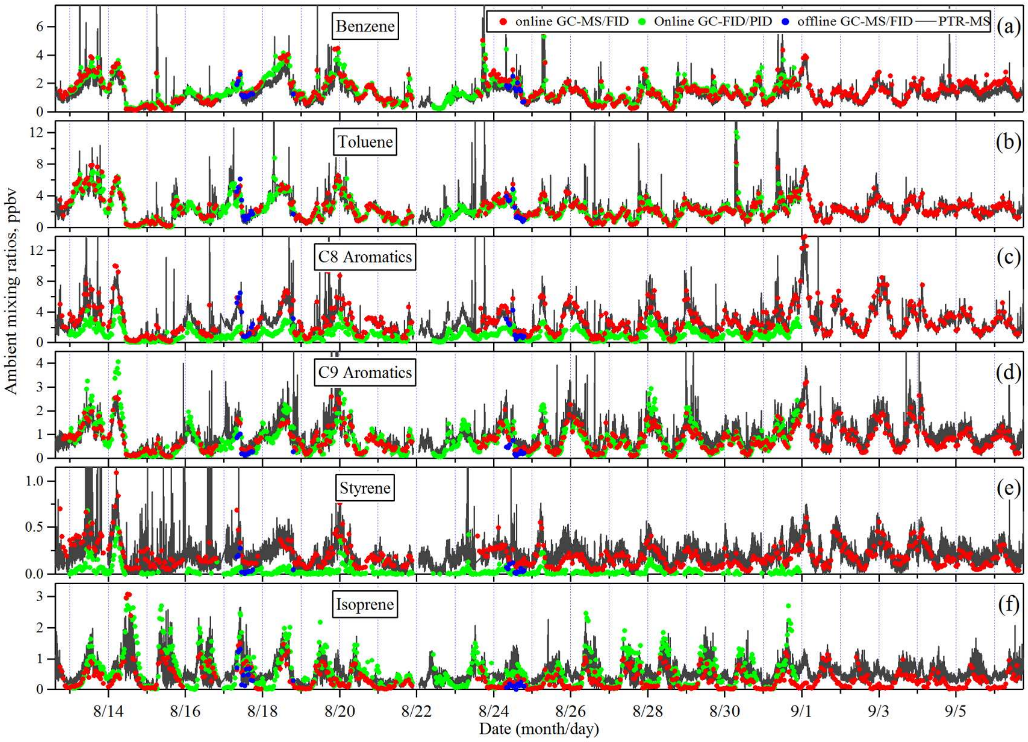

Fig. 6 Time series of (a) benzene, (b) toluene, (c) C8 aromatics, (d) C9 aromatics, (e) styrene, and (f) isoprene mixing ratios measured by online GC-MS/FID (red dots), online GC-FID/PID (green dots), PTR-MS (grey lines), and offline GC-MS/FID (blues dots) at the PKU site from August 12 to September 6, 2010.

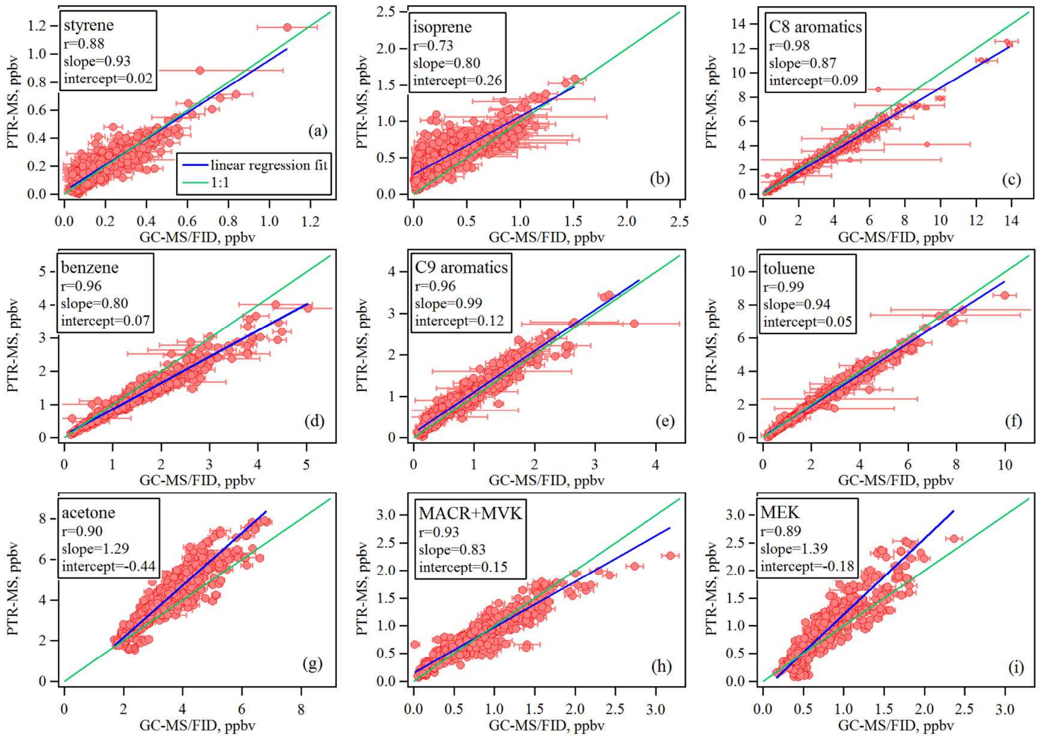

Fig. 7 Scatter plots of the PTR-MS and online GC-MS/FID measurements for (a) styrene, (b) isoprene, (c) C8 aromatics, (d) benzene, (e) C9 aromatics, (f) toluene, (g) acetone, (h) MACR+MVK, and (i) MEK. Each filled circle represents one data point. The error bars correspond to the standard deviations for 5-min averages of PTR-MS data. The blue and green lines correspond to the linear regression fit for all data points and the 1:1 relationship, respectively.

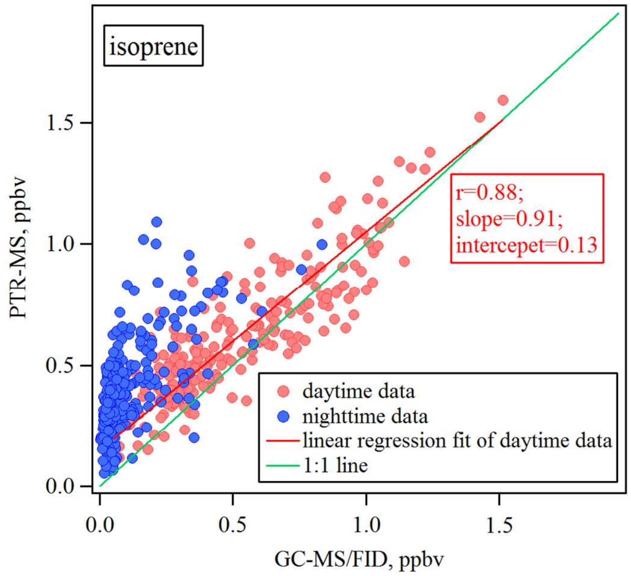

Fig. 8 Scatter plots of isoprene measurements by PTR-MS and online GC-MS/FID. The blue and red filled circles represent isoprene mixing ratios during nighttime (19:00–07:00) and daytime (08:00–18:00), respectively. The red and green lines correspond to the linear regression fit for daytime isoprene and 1:1 relationship, respectively.

Graphical Abstract

An cryogen-free automatic gas chromatograph system was developed for online measurements of volatile organic compounds in the atmosphere.