Fully Automated Online Dynamic In-Tube Extraction for Continuous Sampling of Volatile Organic Compounds in Air

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ABSTRACT: Comprehensive and time-dependent information (e.g., chemical composition, concentration) of volatile organic compounds (VOCs) in atmospheric, indoor, and breath air is essential to understand the fundamental science of the atmosphere, air quality, and diseases diagnostic. Here, we introduced a fully automated online dynamic in-tube extraction (ITEX)–gas chromatography/mass spectrometry (GC/MS) method for continuous and quantitative monitoring of VOCs in air. In this approach, modified Cycle Composer software and a PAL autosampler controlled and operated the ITEX preconditioning, internal standard (ISTD) addition, air sampling, and ITEX desorption sequentially to enable full automation. Air flow passed through the ITEX with the help of an external pump, instead of plunger up–down strokes, to allow larger sampling volumes, exhaustive extraction, and consequently lower detection limits. Further, in order to evaluate the ITEX system stability and to develop the corresponding quantitative ITEX method, two laboratory-made permeation systems (for standard VOCs and ISTD) were constructed. The stability and suitability of the developed system was validated with a consecutive 19 day atmospheric air campaign under automation. By using an electrospin polycrylonitrile nanofibers packed ITEX, selective extraction of some VOCs and durability of over 1500 extraction and desorption cycles were achieved. Especially, the latter step is critically important for on-site long-term application at remote regions. This ITEX method provided 2–3 magnitudes lower quantitation limits than the headspace dynamic ITEX method and other needle trap methods. Our results proved the excellence of the fully automated online dynamic ITEX–GC/MS system for tracking VOCs in the atmospheric air.

Identification and quantitation of volatile organic compounds (VOCs) in air is essential to understand the fundamental science of the atmosphere, air quality, and disease diagnostics. Ubiquitously present VOCs in atmospheric air are reactive with atmospheric oxidants (e.g., OH, NO3, or O3) and form water-soluble organic compounds which can further promote the formation of secondary organic aerosols (SOAs) or are eliminated by wet deposition.1,2 SOAs further influence Earth’s climate by directly scattering/absorbing sunlight or acting as cloud/ice condensation nuclei which change the cloud microphysical and optical properties.3,4 In addition, some VOCs, which exist not only in outdoor but also in indoor air, have adverse health effects on humans especially at high concentration levels.5 Profiling the VOCs in air exhaled by patients has been explored for noninvasive diagnostics of cancers and benign diseases.6–8

Owing to the reactivity of VOCs and time-dependent alteration of VOC concentrations, on-site sampling and measurement of VOCs have become a trend.5,9 Full automation and uninterrupted long-term measurement are also critical aspects which are meaningful, especially for atmospheric researchers who process their studies in remote regions, e.g., boreal forests and rural areas.10,11

Typically, passive or active sampling of VOCs with an air sampler followed by thermal desorption (TD) and consequent gas chromatography/mass spectrometry (GC/MS) determination is the most frequently performed strategy. Equilibrium-based devices, solid-phase microextraction (SPME) in its diverse formats,12–15 sorbent-coated disks and membranes16 have been widely utilized as passive air samplers thanks to their easy operation and cost-effectiveness, but unfortunately with the difficulties in quantitation.16 On the contrary, active air sampling is perceived as the most accurate quantitative technique due to its exhaustive characteristic.16 Further, it is more time-efficient for gaining informative results in a period of time. A sorbent-packed trap is the conventional format of an active air sampler.17 Recently, Romano et al. employed commercial TD tubes coupled to proton-transfer reaction time-of-flight mass spectrometry (PTR-TOF-MS) for 24 h of...
measurement of biomarkers in exhaled air samples. Pawliszyn’s group has reported a series of miniaturized sorbent traps, named as needle trap (NT) devices, for air sampling. In our group, a commercial NT device was successfully used with a portable GC/MS for on-site measurement of biogenic and anthropogenic VOCs at a boreal forest. But fully automated operation of entire sampling and measurement procedures is strictly restricted to these devices. For instance, Gong et al. and Mieth et al. have reported several automated NT methods, but automation was achieved only in desorption and determination steps. In addition, Sanchez et al. designed and utilized several multilayer sorbent-packed tubes and laboratory-made configurations for online sampling and analysis of breath and environmental air. However, manual operations were still needed and the applicability of the systems for nonstop long-term measurements was not demonstrated. Another similar configuration, including a dual-adsorbent preconcentrator, has experienced the same challenge. Currently, sensors and PTR-MS have become the routine tools for air monitoring with direct and real-time measurements. But the former need the enhancement in selectivity and sensitivity and the latter in separation and identification of isomers, although greatly improved in the past decade.

On the basis of the aforementioned context, the in-tube extraction (ITEX) technique is an excellent choice to meet the requirement in terms of the simultaneous integration of full automation, continuous air sampling and analysis, long-term sampling, and the possibility for quantitation. By coupling an autosampler to the ITEX device, full automation and uninterrupted measurement can be achieved. An ITEX device packed with a large amount of sorbent allows exhaustive sampling and quantitative analysis of VOCs. In addition, ITEX meets well the reliability and stability requirements, which are particularly important for long-term application.

Further, efficient and selective sorbent materials are desired for ITEX devices. The suitability of particulate and fibrous adsorbent as the packing materials of needle-shaped devices has been well-evaluated and demonstrated. Nanofibers with appropriate permeability and porosity are promising alternative packing sorbents for ITEX and recently organic and inorganic nanofibers have been available as directly electrospun or indirectly calcined electrospun nanofibers with additional inorganic precursors.

In this research, an online dynamic ITEX–GC/MS method was developed which integrated the air sampling and measurement steps under full automation and was applicable for long-term monitoring of VOCs without any human involvement and interruption. For this aim, the autosampler and its software were modified to allow the fully automated ITEX movements (including ITEX preconditioning, internal standard (ISTD) addition, air sampling, and desorption) in

Figure 1. Schematic of the fully automated online dynamic ITEX system consisting three steps: (1) preconditioning, (2) ISTD extraction, and (3) standard sampling. The system was employed for (a) online dynamic ITEX calibration and method development or (b) air sampling.
online dynamic sampling and GC/MS analysis. Two reliable laboratory-made permeation systems were designed and constructed for ITEX testing and method development. Further, ITEX traps packed with different fibrous and particulate adsorbents were tested in terms of extraction performance.

**EXPERIMENTAL SECTION**

**Reagents and Materials.** The details are given in the Supporting Information.

**Instruments and GC/MS Analysis.** The details are given in the Supporting Information.

**Nanofibers Preparation and ITEX Packing.** Polycrylonitrile (PAN) nanofibers were electrospun from a 5, 7.5, and 10 wt % PAN/dimethylformamide (DMF) solution (named 5%, 7.5%, and 10% PAN). For electrospinning, 2.5 mL of each solution was pushed through a stainless-steel needle with a 15 kV voltage at 0.5 mL h⁻¹ and collected on a grounded 8 in. silicon wafer. ZnO and ZIF-8/ZnO nanofibers were prepared as previously reported. First, 1 g of Zn(NO₃)₂·4H₂O in 2 mL of deionized water was mixed with 4.5 mL of DMF and 7.5 mL of a beforehand prepared 18 wt % poly(vinylpyrrolidone)/ethanol solution. The mixture was electroblown into nanofibers and calcined in air at 500 °C for 4 h, and then converted to ZIF-8/ZnO nanofibers by thermal treatment with 2-methylimidazole vapor. Porous ZnO nanofibers were prepared by annealing ZIF-8/ZnO nanofibers at 500 °C for 15 min in air. The aforementioned materials were then packed into ITEXs individually: 20 mg of deactivated silica wool, 50 mg of adsorbent; 20 mg of deactivated silica wool, and a stainless-steel spring were sequentially packed for the first time. Before extraction, each ITEX was preconditioned with nitrogen at 250 °C for 12 h.

**ITEX Selection.** Optimal ITEX sorbent material for extraction of VOCs was selected after comparing laboratory-made and commercial ITEXs under dynamic headspace extraction mode. Sample extraction, desorption, and injection were controlled and operated by the PAL Cycle Composer (CTC Analytics) and PAL RTC autosampler with the manufacturer’s original program. An amount of 5 mL of standard mixture (1 μg mL⁻¹) with 2 g of NaCl was placed in a 20 mL headspace vial. The ITEX trap was preconditioned with nitrogen for 10 min at 250 °C accompanied by the sample incubation (10 min at 40 °C). Then, the trap temperature was set to 40 °C and syringe temperature to 60 °C. Twenty strokes (defined as the number of plunger up-down movements) of 1 mL of headspace sample at a flow rate of 100 μL s⁻¹ were used. After the extraction, 1.2 mL of helium was aspirated from the injector and analytes were injected with 200 μL s⁻¹ after the trap was heated to 250 °C. Triplicate measurements were performed with each ITEX.

**Permeation Systems for Online Dynamic ITEX.** The permeation system comprised two operation modes: standard VOCs and air sampling (Figure 1). The first mode provided constant gas flow of VOCs for online dynamic ITEX calibration and method development (Figure 1a). Pure chemicals were first capped into commercial GC sample vials individually, and then placed in a metal cylinder and kept at 30 °C in an oven. A slow nitrogen flow (2 mL min⁻¹) was introduced into the metal cylinder from one end and mixed with constantly vaporized analytes and exited from the other end of the cylinder. In order to decrease the sample concentration, the sample flow was diluted by an extra nitrogen flow (6 L min⁻¹), and the combined flow was guided to the modified extraction port of the autosampler. Copper tubing was used as the sampling and connection lines due to its low memory effect for the analytes when compared to polymeric tubes. It could be completely cleaned by flushing with nitrogen for a few hours. The sampling line length was shorter than 1 m in order to reduce the adsorption. The second mode was for air sampling, and the total diluted standard flow from the permeation system was replaced by an air flow (Figure 1b).

The permeation system for the ISTD was similar to the above-described system (Figure 1a). In a GC vial insert tube, 10 mg of decafluorobiphenyl was capped and placed in a 20 mL headspace vial. A nitrogen flow (216 mL min⁻¹) was introduced to flush the vaporized ISTD (at 40 °C) to the ISTD extraction port (see Movie 1).

**Online Dynamic ITEX Procedures for Air Sampling.** The controlling software, PAL Cycle Composer, was modified to allow its operation with two different extraction steps, first with the ISTD, and then with air sample. The PAL autosampler was modified to allow dynamic sampling. A laboratory-made mechanical switch was used to automatically open and close (with an electronic controller) the gas valves used to select between air sampling and nitrogen flow (Figure 1a). The ISTD addition step was processed before sampling by 1 stroke (1 mL with 100 μL s⁻¹ aspirating speed) from the ISTD extraction port. Then, the ITEX was moved to the air/standard sampling port. The atmospheric air was introduced to the sampling port from a lab window by the corrugated aluminum ducting hose (i.d. 10 cm) which was purchased from a local hardware store at Helsinki, Finland. The tube was placed under the sampling port, and the ITEX needle penetrated the tube during air sampling. At the same time, the plunger of the ITEX syringe was lifted up and positioned above the side hole of the syringe by the software. Then, the mechanical switch triggered the electronic controller to close the nitrogen line and open the line to the air pump (ASF Thomas Industries GmbH, Germany), and air started to pass continuously through the adsorbent due to the vacuum made by the membrane pump connected to the end of the gas line of the ITEX. Trap and syringe temperatures during the sampling were 30 and 40 °C, respectively. After sampling and closing the line to the air pump, helium (800 μL) was aspirated from the GC inlet and analytes were desorbed (240 °C) and injected into GC/MS by moving the plunger down (100 μL s⁻¹). After desorption, the nitrogen line was opened for ITEX preconditioning. Sampling was done at 200 mL min⁻¹ for 90 min in the campaign in July 2018 and indoor air sampling, 200 mL min⁻¹ for 10 min in the exhaled air sampling, and 56 mL min⁻¹ for 30 min in the campaign in November 2018, respectively.

**RESULTS AND DISCUSSION**

The applicability of laboratory-made inorganic and organic nanofibers and commercial particulate adsorbents was first compared for the extraction of VOCs with a wide range of chemical properties. Then, a fully automated, fast, and convenient online dynamic ITEX method was developed with laboratory-made permeation systems and electronic ITEX flow controller, modified software, and autosampler. The stability and applicability of the developed method was validated with atmospheric air sampling. After optimization,
the whole approach was applied for quantitative monitoring of VOCs in atmospheric air.

**Selection of the Packing Material for ITEX.** VOCs contained in the atmosphere have a wide range of polarity, volatility, and molecular mass at trace-level concentrations. Thus, a proper packing material for the ITEX device to allow air to easily flow through and efficiently capture VOCs with selectivity, if required, has become a key point. The permeability of commercial (Tenax TA, Tenax GR, Tenax TA/Carbosieve S-III, Carbosieve S-III, and Carboxen 1000) and laboratory-made (10% PAN, ZnO, porous ZnO, and ZIF-8/ZnO nanofibers) sorbents (Figure 2) in ITEX were tested for the extraction of selected template compounds (Table S-1). The ITEX tube, packed with polymeric PAN nanofibers (PAN-ITEX), exhibited the best extraction affinity to most analytes (Figure 3a), mainly due to the amine and imide group rich surface of PAN nanofibers. However, ZnO-ITEX had excellent affinity and selectivity toward amines and hydrocarbons but extracted only slightly other types of compounds (Figure 3a). ZnO nanofibers gained extra specific surface area after annealing (porous ZnO nanofibers) and resulted in better extraction performance toward all the analytes, being still weaker compared to PAN nanofibers. Among the laboratory-made nanofibers, ZIF-8/ZnO nanofibers demonstrated the lowest interactivity with template VOCs due to their inaccessible cavities (~1 nm) and lack of analytes containing a benzene ring for π−π interaction with them. Between ZnO and ZIF-8/ZnO nanofibers, the former exhibited better porosity compared to the latter (Figure 2), which resulted in their higher extraction capacity. As a conclusion, surface functional groups in the nanofibers played a major role in determining the extraction affinity toward the selected VOCs studied. Further, the viscosity of the PAN/DMF solution decided the morphologies of PAN nanofibers (Figure S-1) and thereby the extraction performance (Figure 3b).

Compared to five commercial ITEX sorbent materials, 10% PAN-ITEX exhibited better extraction affinity to alcohols, aldehydes, and ketones and comparable with Tenax TA-ITEX toward sulfides (Figure 3c). The latter had an exceptional selectivity toward amines. Carbosieve S-III and Carboxen 1000 ITEXs had the worst extraction affinity to template VOCs. Multilayer ITEXs packed with Tenax TA and Carbosieve S-III were the most universal commercial ITEXs and showed similar extraction coverage to 10% PAN-ITEX. After considering the ITEX permeability, extraction coverage, and capacity to the studied VOCs, 10% PAN-ITEX was selected for further studies.

**Reusability and Reproducibility of 10% PAN-ITEX.** Since the 10% PAN-ITEX device was constructed for long-term nonstop measurements, its reusability affected the lifetime of the whole system in use. Because the 10% PAN-ITEX had an excellent extraction affinity to alcohols, aldehydes, nitriles, and sulfides, therefore, a few analytes from each group were selected for the experiments in this section (Figure S-2). The 10% PAN-ITEX could be used for over 1500 extraction and desorption cycles, which indicated its suitability for long-term air monitoring. On the other hand, the excellent reproducibility of 10% PAN-ITEX [average relative standard deviation (RSD) of 15 compounds in terms of peak area was 9.7%] (Figure S-2) decreased the need for calibration renewal if the ITEX used happened to be accidently broken and the replacement with a new one was needed.

**Tests for the Permeation and ITEX Systems.** Prior to ITEX method development, the applicability of permeation systems for standard VOCs and ISTD was validated with 14 model compounds (Table S-2), which are widely distributed in the atmosphere in Helsinki, and ISTD decafluorobiphenyl, which (1) does not exist in the atmosphere, (2) does not cause any interferences to analysis results, (3) is not reactive with other analytes, (4) can easily be adsorbed by 10% PAN-ITEX, and (5) has a different retention time with that of other compounds.

First, the 10% PAN-ITEX was used to extract VOCs from the standard permeation system for 0.5, 1, 2, 5, 10, 15, 20, 30, 45, and 60 min. For triplicate measurements with each extraction time, RSDs ranged from 0.26% to 3.2% for 14 compounds, which revealed that the permeation system provided constant VOCs contained gas flow and very good reproducibility.
repeatability of the 10% PAN-ITEX device. The ISTD permeation system showed excellent repeatability with an RSD of only 2.1% (22 extractions), which ensures the accurate and equivalent ISTD addition in the ITEX before every sampling cycle.

The reliability and stability of the fully automated online dynamic ITEX system for a long-term application was then tested by performing a consecutive 19 day campaign from the 12th to 30th of July, 2018 at Kumpula Campus, University of Helsinki, Helsinki, Finland. Totally 207 sampling and measurements cycles were successfully processed without any interruption. If needed, this system could be used for a longer campaign. Previous studies which were based upon NT, sorption tube, and TD tube devices coupled to GC/MS or PTR-TOF-MS only provided semiautomated methods. In addition, multi-TD devices were needed in order to achieve high-throughput analysis, which is not likely to guarantee the excellent result repeatability and reproducibility. During the campaign, concentration alterations of representative α-pinene, δ-3-carene, and p-cymene are shown in Figure 4, and those of the rest of the 11 VOCs of interest are in Figure S-3. Three representative chromatograms are shown in Figure S-4a.

The feasibility of the developed system was further evaluated by sampling indoor and exhaled air. Most of the VOCs detected from the indoor air were also found in the atmospheric air due to the ventilation system of the building which filled outdoor air into the laboratory. So, it is logical that the components of the indoor and outdoor air are partly the same. Furthermore, some other VOCs which are commonly used in chemistry laboratories were also detected, such as ethyl acetate and toluene.
acetate, chloroform, and pyridine. The successful analysis of the exhaled air indicated the system suitability for sampling of high-humidity air (Figure S-4b).

**Optimization of the Extraction and Desorption Conditions.** Air flow rate in active sampler affects the sample throughput and also the extraction yield. Three flow rates, 35, 56, and 200 mL min⁻¹, were evaluated with 10% PAN-ITEX. The flow rates >200 or <35 mL min⁻¹ were not considered because they either risk the tightness of the sorbent bed or lead to lower method sensitivity. Model compounds, toluene, δ-3-carene, and nonanal, represented the high-, medium-, and low-volatility compounds, respectively. The breakthrough time at different flow rates was derived from the bending point in each curve. With the highest flow rate, breakthrough happened fast when sampling medium to high volatility VOCs (Figure 5, parts a and b) because high air velocity in the ITEX tube (1) increased longitudinal dispersion of analytes in the sorbent bed and (2) decreased interaction time between analytes and sorbent. With slower flow rates of 56 and 35 mL min⁻¹, breakthrough occurred at 30 and 40 min for toluene, 30 and 40 min for δ-3-carene, and 30 and 50 min for nonanal, respectively. So, a flow rate below 56 mL min⁻¹ and sampling time less than 30 min was the safest combination to eliminate analyte losses during air sampling and to maintain quantitative conditions. Further, the retention of ISTD in the ITEX tube should also be considered. ISTD started to flow out almost immediately with the flow rate of 200 mL min⁻¹. With flow rates of 56 and 35 mL min⁻¹, the ISTD was retained about 30 and almost 90 min, respectively (Figure 5d). Furthermore, total sampling volume and time will affect the sensitivity and sampling throughput of the ITEX method. After considering the quantitation, sensitivity, and time resolution of the ITEX method, sampling at 56 mL min⁻¹ for 30 min was performed during a campaign in November 2018. The optimal flow rate (56 mL min⁻¹) and total sampling volume (1.68 L) in this study were similar to those of commercial adsorbent-packed tubes and sorption traps but much larger than that of NT devices. Concentrations of three model compounds in these tests were higher than those in the atmospheric air during the campaign, which makes breakthrough even less likely to occur. Further, triplicate measurements were performed for each flow rate with each sampling time. Due to the small RSD values (≤5.9%), error bars are invisible in Figure 5. This is why the original data is also listed in Table S-4.

The following five parameters, ITEX trap temperature, syringe temperature, desorption temperature, desorption volume, and injection speed of desorption gas, can be adjusted in the PAL Cycle Composer, were evaluated to clarify their effect on extraction yield and carryover.

Most of the compounds showed optimal extraction yields at 30 °C (lowest possible temperature of the ITEX), which can be easily explained by thermodynamic theory (Figure S-5a). The ITEX syringe temperature had a similar effect as the ITEX trap temperature on the extraction yield (i.e., higher temperatures decreased the extraction yield) (Figure S-5b). In order to avoid the water condensation in the syringe needle during the sampling, the syringe temperature was therefore slightly higher than the trap temperature (40 °C). Desorption temperature had a positive influence on the extraction yield for most of the compounds (Figure S-5c). Because the PAN nanofibers were thermally stable up to 285 °C (Figure S-6), and in order to increase the reusability of PAN-ITEX, 240 °C was selected as the optimal desorption temperature. When the helium volume used for desorption was increased from 200 to 800 μL (Figure S-5d), extraction yield increased to the highest level. No changes were observed with higher desorption gas volumes. Injection speed had no obvious effect on extraction yield, and 100 μL s⁻¹ was selected after taking desorption time and plunger lifetime into consideration (Figure S-5e).

In summary, the following optimal conditions were selected: ITEX flow rate, 56 mL min⁻¹; extraction time, 30 min; ITEX trap temperature, 30 °C; syringe temperature, 40 °C; desorption temperature, 240 °C; desorption volume, 800 μL; injection speed, 100 μL s⁻¹.

**Method Validation.** For validation of the developed online dynamic ITEX–GC/MS method, the concentrations of the analytes in the permeation system were calculated from eq 1:

\[
\text{conc} = \frac{M_i - M_2}{V}
\]

where \(M_i\) and \(M_2\) are the masses of a standard VOC vial before and after a certain time of permeation and \(V\) is the total gas volume flowed through the system between the M1 and M2 mass measurements. Liquid syringe injection of the same mass
of compound as collected by the ITEX from the permeation system confirmed the accuracy of the calculated analyte concentration in the permeation system (an example is shown in Figure S-7). The small gap between them was caused by the unstable VOCs gas flow at the beginning and was negligible after the permeation system was given several days to stabilize. Further, the linear range, method limit of quantitation (LOQ), and linearity of the developed method were determined (Table 1).

Analytes selected for method validation were those representative compounds that existed in atmospheric air in November 2018. Five out of nine compounds were quantified because toluene, p-xylene, and 1,2,3-trimethylbenzene represented the aromatic compounds with one, two and three methyl groups, respectively. Benzaldehyde and acetophenone represented the aldehyde group and ketone group, respectively. Calibration curves, six data points (N = 3), of the compounds were obtained by 10% PAN-ITEX extraction of individual analytes from the standard permeation system using different extraction times. The concentrations of toluene, p-xylene, 1,2,3-trimethylbenzene, benzaldehyde, and acetophenone used for method validation were 70, 65, 192, 290, and 61 pg L$^{-1}$, respectively. LOQ (air concentration) was calculated by 10 times the signal-to-noise ratio. Because of the large volume sampling, the developed method exhibited exceptional sensitivity which is 2–3 magnitudes better than with dynamic headspace ITEX methods and dynamic NT methods (Table S-5). The method sensitivity is also comparable with that of sorbent tubes, which need 4 times more adsorbent material than the laboratory-made ITEX (Table S-5). Further, LOQs reached the requirement for quantitation of natural or anthropogenic VOCs in atmospheric air. RSDs of calibration curves for all the analytes were below 7.6% dedicating the good precision of the developed method, being comparable to those of other ITEX methods. All calibration curves showed good linearity with correlation coefficients from 0.9914 to 0.9989. Total analysis time was only 55 min for each sample.

**Atmospheric Air Monitoring.** Quantitative monitoring of VOCs in atmospheric air was carried out from the 12th to 19th of November, 2018 (Kumpula Campus, University of Helsinki, Helsinki, Finland), and 189 sampling and measurement cycles were successfully performed. The weather information shown in Figure S-8b was collected from Finnish Meteorological Institute Web site (http://en.ilmatieteenlaitos.fi/past-30-day-weather).

Amounts of hydrocarbons, toluene, p-xylene, and 1,2,3-trimethylbenzene regularly varied from daytime to nighttime.

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**Table 1. Analytical Performance of the Online Dynamic 10% PAN-ITEX–GC/MS Method**

| analyte                  | LOQ (pg L$^{-1}$) | linear range (pg L$^{-1}$) | correlation coefficient ($R^2$) |
|--------------------------|------------------|--------------------------|-------------------------------|
| toluene                  | 25               | 30–1990                  | 0.9951                        |
| p-xylene                 | 25               | 30–2720                  | 0.9989                        |
| benzaldehyde             | 120              | 120–19400                | 0.9959                        |
| acetophenone             | 120              | 120–10100                | 0.9914                        |
| 1,2,3-trimethylbenzene   | 80               | 80–19200                 | 0.9970                        |

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**Figure 6.** Variation of VOC concentrations in atmospheric air of Kumpula Campus: (a) toluene, (b) p-xylene, (c) 1,2,3-trimethylbenzene, (d) benzaldehyde, and (e) acetophenone in November 2018, using the 10% PAN-ITEX–GC/MS method.
which was attributed to high human activities (Figure 6a–c and Figure S-4c). Their concentrations ranged from 0.07 to 1.3, 0.13–2.2, and 0.03–1.1 ng L⁻¹, respectively (Figure 6a–c), which were in the same concentration magnitude as reported in the literature. However, all of them were at a low concentration level in the rainy days and several days after that because of the cleaning effect of rain in the atmospheric air. In this research, benzaldehyde exhibited relatively constant concentration during the campaign (5.3–14.1 ng L⁻¹) due to its long lifetime (74 h) in the atmosphere with OH radicals (5.3 × 10⁹ molecules cm⁻³) (Figure 6d). Acetophenone is generated by HOOH photoformation of phenol, and its concentration was 2.7–7.5 ng L⁻¹ (Figure 6e). Interestingly, phenol was also detected in this research (not quantified). Ethylbenzene, o-xylene, and 1,2,4-trimethylbenzene were identified as well and shown in Figure S-4c.

**CONCLUSIONS**

In this study, a fully automated online dynamic ITEX–GC/MS system was developed for the monitoring of atmospheric air. The VOCs in the air were identified and quantified. The combination of modified autosampler software, additional membrane pump, and modified sampler platform enabled the automated online dynamic sampling and analysis. The ITEX device packed with electrospray 10% PAN nanofibers showed (1) good permeability due to the uniform diameter of fibers, (2) the highest extraction affinity toward a wide range of VOCs compared to other laboratory-made and commercial ITEX materials thanks to the rich surface functional groups of the packing material, and (3) long lifetime. These advantages are meaningful in a long-term application of the monitoring system as they allow reliable sampling/extraction and time-saving operation without any need to frequently replace the extraction device. Laboratory-made standard VOCs and ISTD permeation systems allowed reliable calibration and quantitation. Liquid standard injection could be also used for the ITEX calibration. The developed and validated method was automated and stable, and it gave picogram per liter level limits of quantitation for the VOCs studied. The system has a great potential for continuous on-site monitoring of VOCs in air for all year round at the remote regions. Stations for Measuring Ecosystem–Atmosphere Relations (SMEAR) (https://www.atm.helsinki.fi/SMEAR/index.php), e.g., provide well-constructed laboratories, equipment, electricity, and carrier gas, etc., for measurements. By coupling this system with fast separation and detection instruments (e.g., fast GC/MS), higher time resolution of measurements can be achieved.

**ASSOCIATED CONTENT**

 Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.analchem.9b01668.

Additional experimental details, additional characterization data of nanofibers, original data of the reproducibility test of 10% PAN-ITEX, VOCs variation during the campaign in July 2018, chromatograms of atmospheric air (July and November 2018) and exhaled air by the 10% PAN-ITEX–GC/MS method, additional extraction and desorption optimization data of 10% PAN-ITEX, comparison of liquid and ITEX injection of 120 ng of 2-ethyl-1-hexanol, weather information during the two campaigns, VOCs for the ITEX selection experiment, VOCs for the permeation system testing, VOCs detected from indoor air, optimization data of the sampling flow rate of 10% PAN-ITEX, and comparison of the method developed with other sorbent trap-based methods for the determination of VOCs (PDF)

**Web-Enhanced Feature**

A movie showing internal standard addition, air sampling, and desorption is available in the online version of the paper.

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**Author Contributions**

The manuscript was written through contributions of all authors.

**Notes**

The authors declare no competing financial interest.

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**REFERENCES**

(1) Laathawornkitkul, J.; Taylor, J. E.; Paul, N. D.; Hewitt, C. N. New Phytol. 2009, 183 (1), 27–51.
(2) Zaemann, P. J.; Atkinson, R. Chem. Soc. Rev. 2012, 41 (19), 6582–6605.
(3) Mahowald, N. Science 2011, 334 (6057), 794–796.
(4) Armet, A.; Harrison, S. P.; Zaehe, S.; Tsigaridis, K.; Menon, S.; Bartlein, P. J.; Feichter, J.; Korhola, A.; Kulmala, M.; O’Donnell, D.; Schurgers, G.; Sorvari, S.; Vesala, T. Nat. Geosci. 2010, 3 (8), 525.
(5) Krol, S.; Zabiegala, B.; Namiesnik, J. TrAC, Trends Anal. Chem. 2010, 29 (9), 1092–1100.
(6) Ahmed, W. M.; Lawal, O.; Nijsten, T. M.; Goodacre, R.; Fowler, S. J. ACS Infect. Dis. 2017, 3 (10), 695–710.
(7) Altomare, D. F.; Di Lena, M.; Porcelli, F.; Trizio, L.; Travaglio, E.; Tutino, M.; Dragonieri, S.; Memeo, V.; De Gennaro, G. Br. J. Surg. 2013, 100 (1), 144–150.
(8) Hakim, M.; Broza, Y. Y.; Barash, O.; Peled, N.; Phillips, M.; Amann, A.; Haick, H. Chem. Rev. 2012, 112 (11), 5949–5966.
(9) Ouyang, G.; Pawliszyn, J. Trends Anal. Chem. 2006, 25 (7), 692–703.
(10) Taipele, R.; Ruuskanen, T. M.; Rinne, J.; Kajos, M. K.; Hakola, H.; Pohja, T.; Kulmala, M. Atmos. Chem. Phys. 2008, 8 (22), 6681–6698.
(11) Jordan, C.; Fritz, E.; Hagan, T.; Sive, B.; Frinak, E.; Haase, K.; Cottrell, L.; Buckley, S.; Talbot, R. Atmos. Chem. Phys. 2009, 9 (14), 4677–4697.
(12) Barreira, L. M.; Duporté, G.; Parshintsev, J.; Hartonen, K.; Jussila, M.; Aalto, J.; Bäck, J.; Kulmala, M.; Riekkola, M.-L. Boreal Environ. Res. 2017, 22, 393–413.
(13) Barreira, L. M. F.; Parshintsev, J.; Kärkkäinen, N.; Hartonen, K.; Jussila, M.; Kajos, M.; Kulmala, M.; Riekkola, M.-L. Atmos. Environ. 2015, 115, 214–222.

(14) Feijo Barreira, L. M.; Duporté, G.; Rönkkö, T.; Parshintsev, J.; Hartonen, K.; Hyrsky, L.; Heikkinen, E.; Jussila, M.; Kulmala, M.; Riekkola, M.-L. Atmos. Meas. Tech. 2018, 11 (2), 881–893.

(15) OuYang, G.; Pawliszyn, J. Anal. Bioanal. Chem. 2006, 386 (4), 1059–1073.

(16) Melymuk, L.; Bohlin, P.; Sänka, O. e.; Pozo, K.; Klánová, J. Environ. Sci. Technol. 2014, 48 (24), 14077–14091.

(17) Demeester, K.; Dewulf, J.; De Witte, B.; Van Langenhove, H. J. Chromatogr. A 2007, 1153 (1–2), 130–144.

(18) Romano, A.; Doran, S.; Belluomo, I.; Hanna, G. B. Anal. Chem. 2018, 90 (17), 10204–10210.

(19) Lord, H. L.; Zhan, W.; Pawliszyn, J. Anal. Chem. Acta 2010, 677 (1), 3–18.

(20) Barreira, L. M. F.; Xue, Y.; Duporte, G.; Parshintsev, J.; Hartonen, K.; Jussila, M.; Kulmala, M.; Riekkola, M.-L. Atmos. Meas. Tech. 2016, 9, 3661–3671.

(21) Gong, Y.; Eom, I.-Y.; Lou, D.-W.; Hein, D.; Pawliszyn, J. Anal. Chem. 2008, 80 (19), 7275–7282.

(22) Mieth, M.; Kischkel, S.; Schubert, J. K.; Hein, D.; Miekisch, W. Anal. Chem. 2009, 81 (14), 5851–5857.

(23) Mieth, M.; Schubert, J. K.; Grüger, T.; Sabel, B.; Kischkel, S.; Fuchs, P.; Hein, D.; Zimmermann, R.; Miekisch, W. Anal. Chem. 2010, 82 (6), 2541–2551.

(24) Alonso, M.; Castellanos, M.; Martín, J.; Sanchez, J. M. J. Chromatogr. B: Anal. Technol. Biomed. Life Sci. 2009, 877 (14–15), 1472–1478.

(25) Sanchez, J. M.; Sacks, R. D. Anal. Chem. 2003, 75 (10), 2231–2236.

(26) Sanchez, J. M.; Sacks, R. D. J. A. c. Anal. Chem. 2003, 75 (4), 978–985.

(27) Sanchez, J. M.; Sacks, R. D. J. Sep. Sci. 2005, 28 (1), 22–30.

(28) Sanchez, J. M.; Sacks, R. D. Anal. Chem. 2006, 78 (9), 3046–3054.

(29) Lu, C.-J.; Zellers, E. T. Anal. Chem. 2001, 73 (14), 3449–3457.

(30) Lu, C. J.; Zellers, E. T. Analyst 2002, 127 (8), 1061–1068.

(31) Wenger, O. S. Chem. Rev. 2013, 113 (5), 3686–3733.

(32) Majchrzak, T.; Wojnowski, W.; Lubinska-Szczygel, M.; Róžańska, A.; Namieśnik, J.; Dymerski, T. Anal. Chim. Acta 2018, 1035, 1–13.

(33) Lorenzo-Parodi, N.; Kaziur, W.; Stojanović, N.; Joehmann, M. A.; Schmidt, T. C. TrAC, Trends Anal. Chem. 2019, 113, 321–331.

(34) Saito, Y.; Ueta, I.; Ogawa, M.; Abe, A.; Yogo, K.; Shirai, S.; Jinn, K. Anal. Bioanal. Chem. 2009, 393 (3), 861–869.

(35) Xue, J.; Xie, J.; Liu, W.; Xia, Y. Acc. Chem. Res. 2017, 50 (8), 1976–1987.

(36) Holopainen, J.; Heikkilä, M. J.; Salmi, L. D.; Ainassari, K.; Ritala, M. Microporous Mesoporous Mater. 2018, 267, 212–220.

(37) Wang, T.; Kumar, S. J. Appl. Polym. Sci. 2006, 102 (2), 1023–1029.

(38) Hellén, H.; Tykkä, T.; Hakola, H. Atmos. Environ. 2012, 59, 59–66.

(39) Laurens, J.; Rohwer, E. R. J. High Resolut. Chromatogr. 1997, 20 (2), 119–121.

(40) Hellén, H.; Hakola, H.; Laurila, T.; Hiltunen, V.; Koskentalo, T. Sci. Total Environ. 2002, 298 (1–3), 55–64.

(41) Lou, D.-W.; Lee, X.; Pawliszyn, J. J. Chromatogr. A 2008, 1201 (2), 228–234.

(42) Joehmann, M. A.; Yuan, X.; Schilling, B.; Schmidt, T. C. J. Chromatogr. A 2008, 1179 (2), 96–105.

(43) Hüffer, T.; Osorio, X. L.; Joehmann, M. A.; Schilling, B.; Schmidt, T. C. Anal. Bioanal. Chem. 2013, 405 (26), 8387–8395.

(44) Rantala, P.; Järvi, L.; Taipale, R.; Laurila, T. K.; Patokuski, J.; Kajos, M. K.; Kurppa, M.; Haapanala, S.; Siivola, E.; Petjä, T.; Ruuskanen, T. M.; Rinne, J. Atmos. Chem. Phys. 2016, 16 (12), 7981–8007.

(45) Hellén, H.; Hakola, H.; Reissell, A.; Ruuskanen, T. Atmos. Chem. Phys. 2004, 4 (7), 1771–1780.

(46) Anastasio, C.; Faust, B. C.; Rao, C. J. Environ. Sci. Technol. 1997, 31 (1), 218–232.