

Online Volatile Compound Emissions Analysis Using a Microchamber/Thermal Extractor Coupled to Proton Transfer Reaction-Mass Spectrometry

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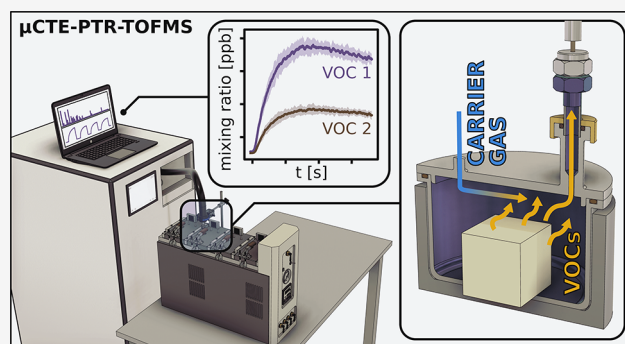
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ABSTRACT: Indoor air is a complex and dynamic mixture comprising manifold volatile organic compounds (VOCs) that may cause physiological and/or psychological discomfort, depending on the nature of exposure. This technical note presents a novel approach to analyze VOC emissions by coupling a microchamber/thermal extractor (μ -CTE) system to a proton transfer reaction-mass spectrometer (PTR-MS). This configuration provides an alternative to conventional emissions testing of small objects. The dynamic emission profiles of VOCs from a representative 3D-printed model are presented as a proof-of-concept analysis. Emission profiles are related to the target compound volatility, whereby 2-propanol and acetaldehyde exhibited the highest emissions and most rapid changes compared to the less volatile vinyl crotonate, 2-hydroxymethyl methacrylate, and mesitaldehyde, which were present at lower concentrations and showed different dynamics. Comparative measurements of the emission profiles of these compounds either with or without prior static equilibration yielded stark differences in their dynamics, albeit converging to similar values after 15 min of sampling time. Further, the utility of this system to determine the time required to capture a specific proportion of volatile emissions over the sampling period was demonstrated, with a mean duration of 8.4 ± 0.3 min to sample 50% of emissions across all compounds. This novel configuration provides a means to characterize the dynamic nature of VOC emissions from small objects and is especially suited to measuring highly volatile compounds, which can present a challenge for conventional sampling and analysis approaches. Further, it represents an opportunity for rapid, targeted emissions analyses of products to screen for potentially harmful volatiles.



INTRODUCTION

The analysis of volatile organic compound (VOC) emissions from manufactured materials represents an important aspect of exposure assessments and consumer health protection.¹ The abundance and diversity of consumer products and building materials in the modern home and workplace, together with the propensity of today's society to spend extended periods indoors, have increased the relevance of inhalation exposure to VOCs from related emissions in the indoor setting.² Although the majority of VOCs emitted in this context are benign at the concentrations typically encountered, certain compounds can elicit negative health effects when present in high amounts. Examples include formaldehyde,³ benzene,⁴ and naphthalene,⁵ among others. Consequently, screening commercial items for VOC emissions is imperative to ensure manufacturer compliance to regulated limits and thereby minimize consumer exposure to undesirable compounds.

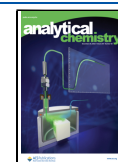
Emissions assessments are typically achieved through the use of large emissions test chambers, whereby the item under investigation is placed inside the chamber under defined conditions (temperature, humidity, air exchange rate, etc.) and

for a certain duration until a gas sample from within the chamber is withdrawn for chemical analysis.^{6,7} Although these chambers are ideal for ascertaining VOC emissions from large objects, especially building materials, their dimensions—typically several cubic meters—make them less suitable for screening smaller items or individual product components. To overcome this issue, a smaller alternative to the large emissions chambers was developed and commercialized in the form of the microchamber/thermal extractor (μ -CTE) system from Markes International Ltd. (Llantrisant, UK).⁸ The μ -CTE system has been used in various fields of application for screening VOC emissions from different objects, including construction materials⁹ and consumer products.¹⁰

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The conventional approach for characterizing volatile emissions in chamber studies is via offline surface and bulk emissions sampling.¹¹ Using this method, compounds emitted from the product into the gaseous environment of the chamber are cumulatively extracted and preconcentrated prior to analysis, commonly achieved through use of adsorption tubes, i.e., tubes packed with adsorbent materials, such as Tenax TA. The tubes then undergo thermal desorption (TD), and the volatiles liberated through this process are transferred to an analyzer for chemical analysis, typically a gas chromatograph–mass spectrometer (GC-MS). This approach provides both qualitative and quantitative data on the type and concentration of VOCs emitted, allowing estimation of emission rates of individual compounds. Despite the strengths of this approach, it has some limitations. First, this cumulative sampling method precludes the possibility of performing continuous, i.e., online, monitoring of the emissions, since sampling is laborious, and subsequent analysis requires considerable instrumental time. Second, some compounds might undergo changes during tube storage and/or thermal desorption, thus compromising the reliability for volatiles susceptible to such effects, and for the case of some specific very volatile organic compounds (VVOs), e.g., those relevant to material emission studies, such as formaldehyde, methanol, and acetaldehyde, these are typically poorly retained by conventional sorbent tubes,¹² while others are not easy to measure using GC-MS (e.g., acetic acid, formic acid).

An alternative to offline sampling with separate analysis is an online approach whereby the target gas is sampled continuously and fed directly into the analyzer for immediate analysis in real time. In online analysis, the feed system transports the sample gas, collected at atmospheric pressure, to an ionization chamber and subsequently a mass spectrometer, which operate under vacuum. An immediate and continuous ionization of volatile constituents within the sample gas allows for their quantitative detection in real time, without the need for time-consuming sample preparation or compound pre-separation via chromatography. These techniques are often referred to as direct injection mass spectrometry (DIMS) and include atmospheric pressure chemical ionization mass spectrometry (APCI-MS), selected ion flow tube-mass spectrometry (SIFT-MS), and proton-transfer-reaction mass spectrometry (PTR-MS), among others.¹³ A particular strength of PTR-MS technology is that it can rapidly detect trace concentrations of most VOCs with high sensitivity over a broad dynamic range (at volume mixing ratios from low parts-per-trillion to low parts-per-million, i.e., ppt_v to ppm_v, respectively).^{14,15} PTR-MS is a well-established tool for VOC detection that has found footing in a broad range of applications, from environmental monitoring to medical research.¹⁶ One particular configuration of PTR-MS technology is its coupling to a time-of-flight mass spectrometer (PTR-TOFMS), which enables high frequency full mass spectral data acquisition (≤ 1 Hz) at a high resolution (>5000 $m/\Delta m$), making it ideal for detecting rapid changes of numerous compounds simultaneously.

In this work, we present a novel coupling of the μ -CTE system with a PTR-TOFMS instrument and explore the potential of this configuration to characterize VOC emissions from a model sample in real time. For the latter, we used 3D-printed resin cubes as representative test objects. Complementary sampling and analysis via the conventional approach

of TD-GC-MS were undertaken to provide compound identities for assignment to the PTR-MS mass signals.

EXPERIMENTAL SECTION

3D-Printed Samples. A 1 cm³ 3D-printed cube was selected as a representative model for these proof-of-concept analyses. The choice of using a sample with a defined size and volume allowed for simple production of replicates as reference materials. Cubes were printed from a resin (BioMed Clear, Formlabs, Somerville, MA, USA) using a stereolithography (SLA) printer (Form 3B; Formlabs). The resin is composed of bisphenol A dimethacrylate, 2-hydroxyethyl methacrylate, and urethane dimethacrylate. A series of individual cubes were 3D printed to enable the use of a new cube for each experiment and replicate. Details on the printing procedure can be found in the [Supporting Information \(SI\)](#).

Microchamber/Thermal Extractor. A μ -CTE250 system (Markes International Ltd.) consisting of four individual 114 cm³ passivated (Siltek-treated) stainless-steel chambers was used for all investigations. Each chamber was located in a heating block that allowed the samples to be heated to 40 °C. The chambers were supplied with a common flow of synthetic air that was passed through an activated charcoal filter (Supelcarb HC Hydrocarbon Trap; Supelco, Sigma-Aldrich, Co., St. Louis, MO, USA) to remove potential confounders. The flow of this gas was controlled by the corresponding supply pressure regulator and an integrated flow restrictor in the μ -CTE. This chamber purge gas acted as a carrier gas for VOCs emitted from the sample and transferred to the PTR-TOFMS instrument or through the adsorption tubes.

Online Emissions Measurements Using PTR-TOFMS.

Online measurements of volatiles emitted from the 3D-printed model samples were made using a commercial PTR-TOFMS instrument (PTR-TOF 8000; IONICON Analytik GmbH, Innsbruck, Austria), which was connected to the μ -CTE using a novel sampling interface, as depicted and described in [Figure 1](#); further details are provided in the [SI](#). All measurements were performed with the μ -CTE temperature maintained at 40 °C and a carrier gas flow of ~ 75 mL/min (with the corresponding valve opened for flushing a single microchamber); details of gas flow configurations are given in the [SI](#).

Two sampling approaches were made for emissions analysis, one that included a prior equilibration period under static conditions before online sampling/real-time analysis and the other without prior equilibration. In both approaches, a 1 cm³ cube sample was loaded into an individual preheated (40 °C) chamber, and the lid of the chamber was closed and affixed with the corresponding lever. For the first procedure with prior equilibration, the sample in the microchamber was held under static conditions, i.e., without a purge gas flow (achieved by closing the corresponding toggle valve of the μ -CTE) for 15 min, after which the purge gas was activated, and the microchamber gas was sampled dynamically with continuous analysis by PTR-TOFMS for a further 15 min. For the second procedure without prior equilibration, dynamic sampling with continuous analysis by PTR-TOFMS proceeded immediately after placing the sample in the microchamber, also for 15 min. Each sample was measured in triplicate for each configuration. Background profiles of the individual empty microchambers were measured directly before placing the cubes inside. Complementary analysis of VOC emissions were made by the conventional approach for comparison with the PTR-TOFMS analyses to provide compound identities for signal

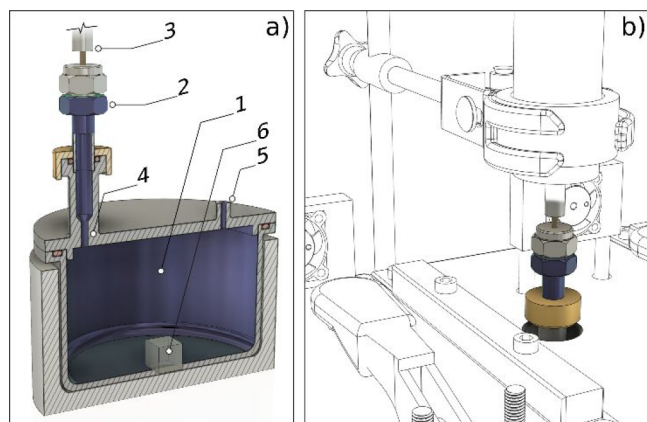


Figure 1. Schematics of the sampling interface between the μ -CTE system and the PTR-TOFMS instrument. (a) Cross-sectional oblique view of the connection to a single microchamber (1) comprising a 1/4" Sulfinert-treated port connector (2) with reducing union to accommodate the connection of a 1/8" OD tube (3) (i.e., PTR-TOFMS 1/16" sampling capillary sheathed in a 1/8" tube). The port connector is inserted into the sampling port on the lid of the microchamber (4) (where an adsorption tube is conventionally connected). The heated purge gas supply at the inlet port of the lid (5) carries volatiles from the sample (6) to the PTR-TOFMS instrument. In this projection, the purge gas enters the microchamber on the right (5) and is continuously sampled by PTR-TOFMS from the port connector union on the left (4). (b) Sketch view of the μ -CTE-PTR-TOFMS coupling, with the connection interface highlighted through coloration.

assignment purposes. These analyses were made using a comprehensive GC-MS system (TD-GC \times GC-TOFMS). Details on the respective instrument and data acquisition settings, as well as data processing procedures, are provided in the SI.

RESULTS AND DISCUSSION

Proof-of-Concept Analysis. Using our novel μ -CTE-PTR-TOFMS configuration, we detected and followed 12 m/z traces that were associated with the dynamic emissions of at

least 13 compounds from the 3D-printed cube samples at 40 °C; five representative compounds are presented and discussed in this paper, with the profiles of all 13 compounds provided in the SI. The overall small number of compounds detected reflects the properties of the resin-constructed sample, whereby the BioMed Clear resin is produced in compliance with biocompatibility end points, as stated by the manufacturer, including ISO 18562-3:2017 that requires low VOC emissions within specific thresholds.¹⁷

Detection of compounds by PTR-TOFMS is based on characteristic m/z signals, with the protonated molecule often a dominant (or sole) product of the soft proton-transfer reaction.¹⁴ Nevertheless, molecular fragmentation or interference from isomeric compounds cannot be ruled out. Consequently, unequivocal compound identification is seldom possible in nontargeted PTR-TOFMS analysis without a complementary GC-MS screening to identify compounds and aid m/z signal assignments, as reported previously.^{18,19} Accordingly, the TD-GC \times GC-TOFMS data were drawn upon here for assigning compounds to the PTR-TOFMS m/z signals, which was achieved for nine of the traces (including two isomers associated with one trace); for the remaining three traces, only their elemental compositions could be determined, thus each of these might be associated with more than one compound.

A selection of five VOC signatures of varying volatility, thus representative of the different emission patterns observed across the 13 compounds detected, was made to appraise and illustrate the performance of the new configuration. Selected compounds were 2-propanol (m/z 43.035), acetaldehyde (m/z 45.033), vinyl crotonate (m/z 113.056), 2-hydroxyethyl methacrylate (2-HEMA; m/z 131.065), and mesitaldehyde (m/z 149.096). This technical note aims to present a proof-of-concept analysis of this novel sampling approach, which is relevant to characterizing the emissions from a broad range of materials or products, thus an appraisal of the origins of the compounds specific to the 3D-printed resin sample is not given here, but will be reported in a companion paper.

Dynamic Profiles after Prior Equilibration: Comparison with Conventional Analysis. The dynamic emissions

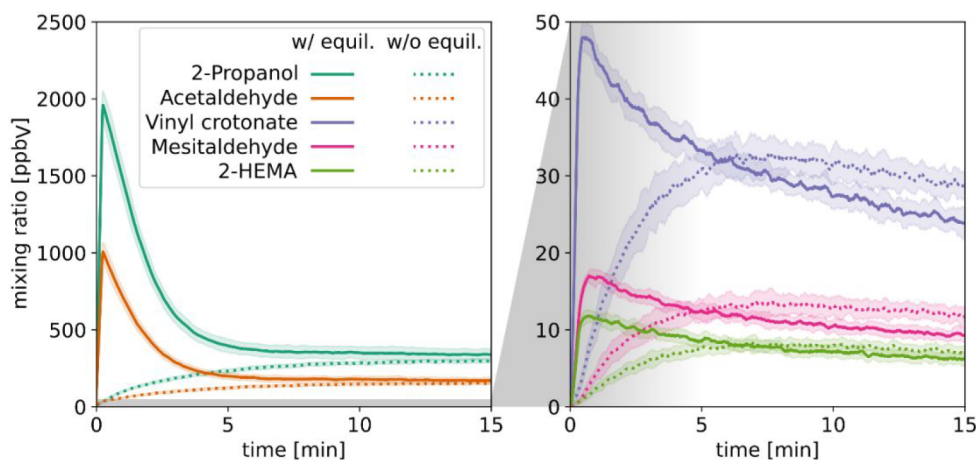


Figure 2. Dynamic profiles of five representative compounds emitted from the resin-based sample, as analyzed by PTR-TOFMS. The plots depict the profiles of the compounds under two conditions, either with a prior 15 min equilibration of the sample in the microchamber under static conditions (w/equil.; solid traces) or without prior equilibration (w/o equil.; dotted traces). Traces represent mean abundances ($n = 3$), with shaded areas denoting corresponding standard deviations. Subplots on the right have been magnified for clarity of the lower concentrations observed for the different compounds and conditions. 2-HEMA: 2-hydroxyethyl methacrylate.

profiles of five selected compounds are shown as composite plots for both configurations, i.e., with/without prior equilibration, in Figure 2; further details on the emissions patterns of all 13 compounds detected are provided in the SI. Focusing first on the measurements carried out after the initial 15 min equilibration period under static conditions (*w/ equilibration*), all compounds were observed to exhibit similar profiles, with an initial peak (concentration maximum) that tailed off over the course of the analyses. This clearly depicts the situation of concentration build-up during prior equilibration under static conditions, followed by an abrupt depletion of compounds in the headspace of the microchamber as the latter is purged with gas at the start of and throughout dynamic sampling and analysis.

Considering the compounds on an individual basis, 2-propanol and acetaldehyde, which are the most highly concentrated of the five selected compounds, exhibited rapid depletions, leveling off toward steady state within approximately 5 min of the start of analysis. By comparison, the remaining three compounds, vinyl crotonate, mesitaldehyde, and 2-HEMA, exhibited slower depletions and did not reach steady state within the 15 min analysis period. These differing profiles reflect differences in the volatilities of the compounds, whereby the former two are highly volatile (respective boiling points of 2-propanol and acetaldehyde of 82 and 20 °C),²⁰ which therefore reach steady state at a faster rate than the latter three compounds (respective boiling points of vinyl crotonate, mesitaldehyde, and 2-HEMA of 134, 239, and 250 °C).²⁰ A potential influence from interactions between the individual volatiles and the resin matrix itself cannot be inferred from the data but is expected to only negligibly affect the overall emission rates.

The analyses performed after prior equilibration represent the situation during conventional sampling, when a similar equilibration period is made prior to trapping the contents of the sample headspace gas in the microchamber onto an adsorbent tube, with subsequent analysis by GC-MS. Figure 3 depicts two individual compounds with correspondingly high and low volatilities under these conditions (left-side plots), which provide insights into the concentration profiles encountered by the tubes during sampling. A quantitative appraisal of these conditions is indicated by the numerals I and II: these respectively represent the durations required to sample the first and last 50% of the headspace concentrations accumulated over this 15 min period. (The dynamic profiles of all five representative compounds are depicted in Figure S1 in the Supporting Information.) As is evident from Figure 3 and Figure S1, the more highly volatile 2-propanol and acetaldehyde are sampled quicker (3.9 and 4.0 min, respectively, for the first 50% sampled) than the remaining, less volatile compounds, with equivalent sampling requiring 6.3 min for both vinyl crotonate and 2-HEMA and 6.4 min for mesitaldehyde; these sampling times are more than 2 min (>50%) longer than for 2-propanol or acetaldehyde. Accordingly, the higher volatility compounds can be considered to reach their steady state after a shorter period than the lesser volatile compounds. Notably, an equilibrium is not reached after 15 min sampling time for the latter compounds. As a matter of note, the presence of 2-propanol is associated with residual amounts of this compound from the washing process of the 3D-printed sample, as reported in the Supporting Information.

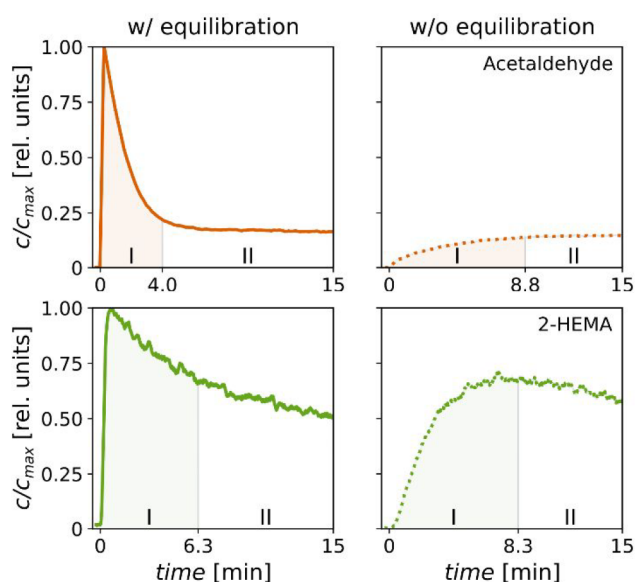


Figure 3. Dynamic profiles of acetaldehyde and 2-hydroxyethyl methacrylate (2-HEMA) concentrations relative to their peak maxima (c_{\max}), either with prior 15 min equilibration under static conditions (*w/ equilibration*: left) or without equilibration (*w/o equilibration*, right). Note that the *w/ equilibration* c_{\max} value was applied for normalization of the *w/o equilibration* data to enable a direct comparison between the two conditions.

Overall, sampling only the first 50% of the built-up headspace concentrations might be sufficient in many applications, depending on the target compound(s), especially if concentrations are high. Taking the emission profile of acetaldehyde as an example (Figure 3), the 15 min sampling time could be curtailed to 4 min, as over 50% of the emissions are captured within this period. Consequently, the novel configuration presented here could be used as a screening approach to appraise initial concentrations after equilibration and thereby determine suitable—and reduced—adsorption tube sampling times, which in some cases have been reported to be up to 30 min.²¹

Despite the overall low number of VOCs emitted from the 3D-printed sample, one compound is especially noteworthy of discussion, namely, acetaldehyde. Due to its low molecular weight and highly volatile nature, acetaldehyde cannot be easily analyzed by TD-GC-MS. As was observed here, the dynamic emission profile of acetaldehyde was well characterized via the real-time analyses of this novel configuration; by comparison, this compound was not detected in the complementary analyses via TD-GC-MS. Consequently, this highlights a key benefit of the presented method, which allows emissions of highly volatile compounds to be characterized.

Dynamic Profiles without Prior Equilibration: A Novel Approach for Real-Time Emissions Analysis. The dynamic emissions profiles of the compounds in the absence of prior equilibration (*w/o equilibration*) are depicted in the composite plots of Figure 2 alongside the former sampling approach. Two key features are evident from these plots that differentiate the two procedures. First, the concentration maxima for all compounds are lower than with prior equilibration. This reflects the dynamic conditions of this approach, whereby partitioning of VOCs from the sample matrix to the headspace gas of the microchamber acts in competition with the removal rate from the headspace gas

through continuous purging/sampling. Here, similar to the previous conditions (*w/equilibration*), compound abundances in the microchamber headspace move toward steady state, albeit from an initial low abundance. In this situation, the low volatility compounds increase toward steady state at a faster rate than the high volatility compounds due to their lower emission rates. On the other hand, the data indicate that steady state conditions were not reached in the three lower volatility compounds, which attain their maxima between 5 and 10 min before slowly tailing off toward steady state. By comparison, the two high volatility compounds appear to reach steady state within approximately 10 min, owing to their faster emission rates.

The emissions profiles characterized under these dynamic conditions provide additional insights into the underlying processes during equilibration, i.e., before sampling via the adsorbent tubes, albeit in a slightly modified manner due to continuous headspace depletion through dynamic sampling compared with static equilibration. Nevertheless, an estimation of the period required to sample the first 50% of emissions within the 15 min period can be similarly made using these dynamic plots, as indicated in Figure 3 and Figure S1. A notable observation under these conditions is that the duration to capture the first 50% of emissions over the 15 min sampling period was similar for all compounds, with a mean value of 8.4 ± 0.4 min but with slightly shorter periods for less volatile compounds, for the reasons described above. As such, volatility plays only a secondary role in this context.

Notably, although not demonstrated here, the dynamic data delivered by this configuration offer the possibility to estimate emission rates of individual compounds from samples under investigation, which is currently mostly achieved using larger emission chambers.²² The present novel configuration allows for time-efficient monitoring of emissions from 3D-printed objects due to the small size of the microchambers, as well as the real-time quantification of emitted compounds, with optional preconcentration through short equilibration.

Comparing Profiles with and without Prior Equilibration. A comparison of the profiles with and without equilibration (left vs right plots of Figure 3; see also Figure S1) indicate that the concentrations of the individual compounds are similar at the end of the 15 min sampling period, irrespective of the use of a prior equilibration period. Further, in the case of the highly volatile compounds, steady state is reached in both sampling modes.

A notable observation in comparing the two approaches is the difference in total emissions sampled, whereby the concentrations for sampling after equilibration are more than twice as high as in the absence of equilibration. A comparison of the accumulated concentrations over the entire 15 min period (integrated curves) for both approaches yielded ratios of 2.26 and 2.14 for 2-propanol and acetaldehyde, respectively. This phenomenon is of relevance using this novel sampling approach, whereby the multiple microchambers housed in the μ -CTE system (four in the present case) allow for staggered analysis in succession: in this case, it would be viable to overlap the equilibration stages of consecutive measurements, thereby allowing for equivalent emissions loadings within a shorter period compared to full dynamic sampling.

In the case of the less volatile compounds, the ratios for the accumulated concentrations for both approaches ranged between 1.04 and 1.20; consequently, the advantage offered by the 15 min prior equilibration period is greatly diminished.

On the other hand, sampling the more highly volatile VOCs after equilibration through use of all four microchambers via the online approach might shorten the overall time of sequential measurements due to the shorter equilibration period required. This offers the ability to preconcentrate emissions at lower concentrations while maintaining the dynamic nature of the emissions, which is in contrast to conventional sampling and analysis that deliver only a single snapshot covering the entire accumulation period.^{22,23}

CONCLUSIONS

A novel coupling of a microchamber/thermal extractor system with a real-time proton transfer reaction time-of-flight mass spectrometer instrument was explored as a method to characterize the dynamic emissions of volatile compounds from a model sample. Analyses of the dynamic volatile emissions from 3D-printed cube samples were made directly, either with a prior equilibration period under static conditions or without equilibration. Complementary sampling and analysis using conventional thermal desorption–gas chromatography–mass spectrometry were made to aid identification of the detected compounds. The presented configuration employs commercial instruments with only minor adaptations, yet offers several benefits to conventional emissions analyses. Emission profiles can be obtained in real time, instead of receiving only infrequent snapshots of accumulated emissions, as for sampling onto adsorption tubes. Further, this online approach enables the sensitive detection and reliable quantitation of high volatility compounds, which are either poorly retained on adsorption tubes or cannot be easily analyzed offline by gas chromatography–mass spectrometry. A caveat of this new procedure is the limitation in compound identification, which is inherent to real-time mass spectrometry. Ultimately, when considering that the goal in such analyses is to assess consumer products for potentially harmful compounds, a complementary approach of using the novel online system as a quantitative screening and emission rate estimate method, with conventional offline configuration for unambiguous confirmation of the chemical structures and identities of compounds, represents a promising workflow in consumer protection endeavors. This approach might be particularly favorable for regulatory authorities as a high-throughput method to assess for the presence of hazardous volatiles emitted from recalled products, allowing for uncritical products to be rapidly identified and cleared for release back onto the market, and for products exhibiting such emissions to subsequently undergo further scrutiny through the conventional, more comprehensive analyses.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.analchem.2c03454>.

3D-printing procedure specifications, experimental details on PTR-MS sampling configuration, flow and analytical parameters, as well as information about conventional TD-GC \times GC-MS sampling and data analysis, dynamic profiles of 12 *m/z* traces associated with nine identified and three unattributed compounds, and comments on the technical configuration (PDF)

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Author Contributions

J.B. conceptualized the analytical configuration, with modifications by W.W. All authors designed the experiments. Y.L.P. and W.W. executed the measurements and processed the data. All authors contributed to data interpretation and writing this paper. All authors have given approval to this final version. Y.L.P. and W.W. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

2-HEMA; 2-hydroxyethyl methacrylate; GC × GC; comprehensive two-dimensional gas chromatography; MS; mass spectrometry; ppm_v; parts-per-million by volume; ppb_v; parts-per-billion by volume; ppt_v; parts-per-trillion by volume; PEEK; polyether ether ketone; PFA; perfluoroalkoxy; PTFE; polytetrafluoroethylene; PTR; proton transfer reaction; RI; retention index; SLA; stereolithography (printer); TD; thermal desorption; TOF; time-of-flight (mass spectrometry); VOC; volatile organic compound; μ -CTE; microchamber/thermal extractor

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