Monitoring the Liberation of Volatile Organic Compounds During Fused Deposition Modeling Three Dimensional Printing Using Solid-Phase Microextraction Coupled to Gas Chromatography/Mass Spectrometry

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Abstract

Three-dimensional (3D) printers have gained tremendous popularity and are being widely used in offices, laboratories, and private homes. Fused deposition modelling (FDM) is among the most commonly used mechanisms by desktop 3D printers in indoor settings and relies on the extrusion and deposition of heated thermoplastic filaments, resulting in the liberation of volatile organic compounds (VOCs). With the growing use of 3D printers, concerns regarding human health have risen as the exposure to VOCs may cause adverse health effects. Therefore, it is important to monitor VOC liberation during printing and to correlate it to filament composition. In this study, VOCs liberated with a desktop printer were measured by solid-phase microextraction (SPME) combined with gas chromatography/mass spectrometry (GC/MS). SPME fibers featuring sorbent coatings of varied polarity were chosen for the extraction of VOCs liberated from acrylonitrile butadiene styrene (ABS), tough polylactic acid, and copolyester+ (CPE+) filaments. It was found that for all three filaments tested, longer print times resulted in a greater number of extracted VOCs. The ABS filament liberated the most VOCs while the CPE+ filaments liberated the fewest VOCs. Through the use of hierarchical cluster analysis and principal component analysis, filaments as well as fibers could be differentiated based on the liberated VOCs. This study demonstrates that SPME is a promising tool to sample and extract VOCs liberated during 3D printing under non-equilibrium conditions and can be used to aid in tentative identification of the VOCs when coupled to gas chromatography-mass spectrometry.

Keywords: 3D printing; solid-phase microextraction; gas chromatography/mass spectrometry; environmental analysis; air sampling.

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1. Introduction

Three-dimensional (3D) printing, also referred to as additive manufacturing, rapid prototyping, or solid-freeform technology, is a process used to print 3D objects when a printer is fed by a digital file [1]. Solids are fabricated by laying down successive layers of constituent materials such as thermoplastics, resins, molten metals, glass, ceramic, and concrete [2]. 3D printing has become increasingly popular today due to its speed, ease of use, versatility, and relatively low cost. It has been employed in a number of interdisciplinary areas such as aerospace, automotive, medical, construction and architectural design [3,4]. Many 3D printing processes such as stereolithography (SLA), fused deposition modeling (FDM) [5], selective laser sintering (SLS), inkjet and polyjet printing, laminated object manufacturing (LOM) and direct printing [6] have been investigated throughout the years with some of them being commercialized.

FDM is among the most popular 3D printing methods and involves the extrusion of thermoplastic materials through a heated nozzle and deposition on a moving bed [7]. Acrylonitrile butadiene styrene (ABS), polylactic acid (PLA), copolyester (CPE), and polyvinyl alcohol are among some of the most popular thermoplastic filaments. Each filament is printed at specific nozzle and bed temperatures with optimum temperature ranges being specified by manufacturers. Generally, nozzle temperatures range from 180-270 °C but can also be as high as 500 °C [8]. During the heating and extrusion of molten filaments, physical and chemical changes occur resulting in the liberation of volatile organic compounds (VOCs) [9]. With increasing use of desktop FDM printers in indoor settings such as educational institutions, libraries, offices, and homes, concerns regarding VOC production during printing have risen as they may possess potential health risks [10,11]. Thus, monitoring the production of VOCs and their spatial distribution within the environment is crucial.

Sorbent tubes containing different sorbent materials have been used in the sampling of VOCs liberated from different filaments and combined with thermal desorption gas chromatography mass spectrometry (TD/GC/MS) for analysis [9,12,13]. However, sorbent tubes are limited by slow sample collection [14], indicating a need for alternative techniques that are more rapid. Solid-phase microextraction (SPME) is a popular sampling technique that integrates sample collection, extraction, and analyte enrichment from the sample matrix into a single step leading to significantly shortened analysis times [14]. Other advantages include its high sensitivity, minimal solvent consumption, and the capability of coupling with separation techniques such as gas chromatography (GC), high performance liquid chromatography, and capillary electrophoresis [15]. Several studies have shown applications of SPME in the sampling and analysis of air as well as the development of SPME methods for VOCs in air [16–18].

Chemometric approaches are often necessary for the statistical analysis of complex data sets obtained using SPME. Cluster heatmap analysis and principal component analysis (PCA) are among the most used approaches to process and extract useful information from multivariate datasets [19,20]. Cluster heatmap is a chemometric technique that allows visualization of a data matrix into a rectangular grid with the corresponding rows and column of the matrix being colored according to their values in the data matrix [21]. It also simultaneously depicts a hierarchical cluster structure of rows and columns in the data matrix. Hierarchical clusters represent data in the shape of binary tree where clustering of the most similar patterns is seen in a hierarchy of nested subsets [22]. Lying at the top of the nested subset will be single, all-inclusive clusters while singleton clusters lie at the bottom. PCA, on the other hand, is a technique that reduces dimensionality of large datasets by increasing their interpretability while retaining much of the information [23]. The idea behind PCA is to identify principal components (PCs) which are linear

combinations of the original variables. PCs are uncorrelated and are chosen so that the first principal component (PC1) accounts for most of the variation in the data set, the second (PC2) accounts for the next largest variation, and so on. PCA is a simple exploratory technique that is used to recognize unsupervised patterns (i.e., it does not require any prior knowledge of classes or groups to identify clusters or correlation among samples) [24].

In this study, SPME coupled with GC/MS is combined with chemometric methods to evaluate VOCs liberated during 3D printing. This study is first to employ SPME fibers as sampling devices inside a FDM 3D printer to extract VOCs while printing. Previous studies involving sorbent tubes for the extraction of VOCs during printing have been reported but very little is known regarding the use of more rapid microextraction methods, such as SPME, for these types of studies. This work seeks to unravel the capability of the microextraction platform in rapidly identifying and quantifying possibly hazardous compounds released from filaments at different temperatures. The aim of this study is to extract and detect as many VOCs as possible as they are released during FDM 3D printing in an effort to characterize various filaments based on this metric. Three commonly used FDM filaments including ABS, tough polylactic acid (TPLA) and co-polyester+ (CPE+) were chosen for the study. Three SPME fibers possessing sorbent coatings of varied polarity including polyacrylate (PA), polydimethylsiloxane (PDMS) and divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) were evaluated based on their extraction performance. The effects of print time and extraction time on the amount and number of VOCs detected was examined. Statistical analysis methods enable characterization of the filaments as well as the fibers based on the liberated VOCs. Overall, this work demonstrates that SPME combined with GC/MS is a promising approach for detecting and monitoring the release of VOCs during 3D printing.

2. Experimental

2.1 Materials

Three FDM filaments, namely, ABS, TPLA and CPE+ were examined in this study. All filaments were purchased from Dynamism Inc. (Chicago, IL, USA) and used as received. SPME fibers (1 cm long) were employed for the extraction of VOCs liberated during 3D printing and included PA (film thickness of 85 μm), PDMS (film thickness of 30 μm) and DVB/CAR/PDMS (film thickness of 50/30 μm). All fibers were provided as gifts by Millipore-Sigma (Bellefonte, PA, USA). A 3D PrintPro 3 air filtration system was purchased from BOFA Americas, Inc. (Staunton, IL, USA).

2.2 Methods

2.2.1 3D printing of a representative model

An Ultimaker 3 printer (Geldermalsen, Netherlands) was employed throughout the study. An important aspect of this study is the relatively closed system that was used to house the 3D printer. As illustrated in Figure S1, the printer was open at the top; however, an air filtration (vent) system featuring an opening at the back was added which served the purpose as a cover. In all experiments employing SPME, the printer was assigned to print a tray (see Figure 1) using a design that was obtained as open-source code from Thingiverse.com. All extractions were carried out using time-courses of 1 hour, 2 hours and 4 hours by printing the tray with a particular filament using the default printer settings given by Ultimaker Cura (Geldermalsen, Netherlands) software. For the ABS filament, extractions were also carried out using a print time of 10 hours. Table 1 shows the printing conditions used for each filament. The size and mass of all printed objects is shown in Table S1.

2.2.2 SPME procedures

The PA, PDMS and DVB/CAR/PDMS fibers were conditioned prior to use according to the manufacturer's guidelines. For extraction of VOCs, the SPME fiber was placed inside the 3D printer using a SPME holder with the fiber initially retracted inside the holder, as shown in Figure S2. When printing was commenced, the fiber was exposed to the liberated VOCs for the time-course of the extraction. Throughout all extractions, the vent system covered the top of the printer but was not activated (see Figure S1). In this series of experiments, only one fiber was placed in the printer. Prior to analysis of a specific filament using SPME, a series of extractions were obtained from the background of the system (i.e., no printing was performed) using each fiber. Initially, the print bed and print nozzle were held at room temperature (~ 21°C) and were then heated to temperatures specific for each filament, as shown in Table 1. Finally, only the print bed was heated.

Extractions were carried out at three different periods of time (1 hour, 2 hours, 4 hours) using each filament. For each time period, triplicate extractions were performed with each fiber. A detailed scheme demonstrating the extraction processes employed in the study is shown in Figure S3. After completing all extractions using a particular 3D printing filament, a new print nozzle was used to prevent contamination and subsequently fed with another filament. Prior to printing with a new type of filament, the 3D printer was vented by activating the vent system for one hour with the 3D printer door left open. The vent system was then removed from the top of the printer for an additional one hour. The walls of the printer were cleaned with a Kimwipe (Kimberly-Clark, Irving, Texas, USA), followed by cleaning of the print bed with isopropanol. The door of the printer was then closed, and the vent system replaced on top of the printer and activated for one additional hour. Extractions from the background of the system were performed for two hours at

room temperature (~ 21 °C) to ensure that the background was free of characteristic peaks generated from the previous filament.

2.2.3 GC/MS analysis

VOCs extracted by each SPME fiber were desorbed, separated, and detected using an Agilent Technologies 7890B gas chromatograph (Agilent Technologies, Santa Clara, USA) coupled to a 5977A mass spectrometer (Agilent Technologies) controlled by Mass Hunter software. A Rtx-5MS capillary column (30 m x 0.25 mm and 0.25 μm film thickness) from Restek Corporation (Bellefonte, PA, USA) was used for all separations. Helium was used as carrier gas at a constant rate of 1 mL/min. After extraction, the fiber was inserted into the GC inlet maintained at 250 °C and operated in splitless mode where desorption was performed for 4 minutes. These inlet conditions were maintained for all three fibers. During GC analysis, the oven temperature was initiated at 40 °C and was held for 5 min, and then ramped to 180 °C at a rate of 10 °C/min and held for 5 min. Another ramp was then used at a rate of 10 °C/min to 270 °C followed by a ramp of 20 °C/min to 300 °C, and finally held for 10 min. The total separation time for each run was 44.5 min. The ion source was set to a temperature of 230 °C and operated in electron ionization mode using an ionization energy of 70 eV. Mass spectra were acquired in full scan mode using a scan range from 45-300 m/z.

2.2.4 Statistical analysis of data

All chromatograms were analyzed to determine the probable VOCs liberated from the filament that yielded a signal-to-noise ratio of 3 and above (based on peak height). The signal-to-noise ratio was calculated by dividing the height of the peak by the calculated peak-to-peak noise. Statistical analyses including heatmap and PCA were performed on the obtained data using XLSTAT

software, version 2022.1.1 (Addinsoft, New York, USA). A confidence interval of 95 % was employed in PCA score plots.

3. Results and discussion

The purpose of this study was to monitor VOC production during 3D printing with respect to time from various FDM printing materials using commercial SPME fibers possessing different sorbent coating chemistries. The choice of filaments was made based on the print nozzle temperatures specific to each filament in an effort to examine a possible relationship between the number of VOCs extracted and print nozzle temperature. As shown in Table 1, the TPLA and CPE+ filaments possessed the lowest and highest nozzle temperatures, respectively. SPME fibers possessing the PA, PDMS and DVB/CAR/PDMS sorbent coatings of varying polarity (polar, non-polar and bipolar, respectively) were chosen to maximize the extraction of VOCs. For compounds possessing lower molecular weight, adsorbent-type fiber coatings are preferred [25]. The DVB/CAR/PDMS sorbent coating can typically extract analytes possessing a wide range of molecular weights through an adsorption-type mechanism owing to its two different layers, namely, a layer of DVB-PDMS coated over a layer of Carboxen-PDMS [26]. For higher molecular weight analytes, absorbent-type coatings are preferred [27]. For this purpose, the polar PA and non-polar PDMS sorbent coatings were also employed as both can extract analytes by an absorption-type mechanism [28].

Before placing the fibers in the printer for extraction, chromatograms of fiber bleed were obtained by desorbing the conditioned fibers in the GC inlet for 4 minutes at 250 °C using a temperature program described in section 2.2.3. Peaks originating from column bleed using the same temperature program were obtained from a separate chromatogram. With these two chromatograms, analytes originating from the GC column's stationary phase and SPME sorbent

196 coating bleed could be differentiated from those extracted during printing. Initially, a series of
197 background extractions (when no printing was performed) were carried out, as discussed in section
198 2.2.2. Chromatograms corresponding to extractions performed when the print bed and print nozzle
199 were held at room temperature were found to be similar to those obtained from the fiber blank. On
200 the other hand, chromatograms corresponding to extractions performed when the print bed and
201 print nozzle were heated to temperatures specific for each filament were similar to those obtained
202 when only the print bed was heated, indicating that heating the build plate within the 3D printer
203 was also responsible for liberating VOCs. Since the build plate has considerable surface area
204 compared to the print nozzle and thermal energy generated from the hot build plate can also heat
205 the adjacent plastic walls and the rubber belts within the printer, they all represent possible sources
206 of VOCs. Thus, prior to extraction using each fiber, a background extraction was also performed
207 by raising the build plate temperature to 80 °C. Chromatograms of background extractions carried
208 out at 60 °C (build plate temperature for printing TPLA), 80 °C (build plate temperature for
209 printing ABS), and 107 °C (build plate temperature for printing CPE+) were found to be similar
210 (data not shown). Thus, a temperature of 80 °C was chosen as it was the approximate average build
211 plate temperature corresponding to the three filaments, as shown in Table 1.

212 After each extraction, the fiber was then desorbed in the GC inlet. A representative total ion
213 chromatogram obtained by SPME-GC/MS using the three fiber sorbent coatings with the ABS
214 filament for four hours is shown in Figure 2. Chromatograms obtained from printing with TPLA
215 and CPE+ filaments for four hours are shown in Figures S4 and S5, respectively. To identify
216 probable peaks corresponding to liberated VOCs for a particular filament, chromatograms
217 obtained after extraction were compared to chromatograms from background extraction, fiber
218 blank, and column blank. To determine whether a peak from the chromatogram originated from

the filament, the signal-to-noise ratio was determined by calculating the peak-to-peak noise and then dividing the height of the peak by the noise, with a signal-to-noise ratio of 3 being designated as the limit of detection [29]. Therefore, any peak not present in any of the blanks and possessing a signal-to-noise ratio of 3 and above was considered as a probable VOC originating from a particular filament. Figure 2 shows all of the detected peaks originating from ABS filament when four hour extractions were carried out using the PA, PDMS and DVB/CAR/PDMS fibers. Peaks are indicated by their corresponding numbers as shown in Table 2.

3.1 Mitigation of contamination issues within the 3D printer system

Contamination is a formidable challenge in air sampling and can lead to potential bias from the surrounding atmosphere [30,31]. Thus, it was necessary in this study to carefully assess all possible sources of contamination. Within the 3D printing system, contamination was observed after printing with a particular filament followed by transitioning to another filament. Upon completing extractions with a particular filament, a two hour extraction was performed from the background of the system at room temperature (~ 21 °C). The corresponding chromatogram revealed the presence of probable VOC peaks that were detected from the previous filament, indicating contamination of the system by previously liberated VOCs. In an attempt to eliminate all sources of contamination, venting and cleaning of the printer was carried out, as described in section 2.2.2. Upon meticulous cleaning, background extractions were carried out until no remnant peaks were detected in the chromatograms, and it was found that this procedure was able to remove background contamination for all three filaments. When a new filament was fed into the print nozzle, it was observed that some VOCs originating from the previous filament were detected in the corresponding chromatogram, indicative of the print nozzle being a major source of

241 contamination. To eliminate this, three separate print nozzles were employed for each of the tested
242 filaments to avoid subjecting contaminating compounds into subsequent analyses.

243 **3.2 Liberation of VOCs from printer filaments as a function of time**

244 To determine the number of VOCs released during printing as a function of time, extractions
245 were performed during printing using time-courses of 1 hour, 2 hours, and 4 hours. Upon
246 increasing the printing time, it was observed that the peak areas of probable VOCs increased with
247 the appearance of additional peaks in the chromatogram. The 3D printer system used in this study
248 is not controlled as it has an opening at the back, as shown in Figure S1. Since VOCs are constantly
249 leaving the system from the opening, it is assumed that equilibrium is not attained under the
250 conditions employed in this study [34,35]. The detection of additional peaks can be attributed to
251 the accumulation of VOCs within the contained system.

252 Figure 3 shows a comparison of probable VOCs and their corresponding peak areas obtained
253 upon analyzing corresponding chromatograms pertaining to extractions performed while printing
254 with the ABS filament. Table S2 shows the peaks detected for the ABS filament using the PA fiber
255 at three different extraction times. A total of 15 probable VOCs were detected when performing a
256 one hour extraction. When the extraction time was lengthened to two hours, an additional four
257 peaks were detected. Further increasing the extraction time to four hours resulted in the detection
258 of 20 total probable VOCs, as shown in Figure 2(A). Using the PDMS fiber, a total of 17, 21, and
259 22 probable VOCs were detected when extractions were carried out for one, two and four hours,
260 respectively, as shown in Table S3. Figure 2(B) shows all probable VOCs detected for four hour
261 extraction using the PDMS fiber. For the DVB/CAR/PDMS fiber, the number of peaks detected
262 was found to be 16, 24, and 28 for extraction times of one, two, and four hours, respectively (see
263 Table S4). Probable VOCs detected using the DVB/CAR/PDMS fiber are shown in Figure 2(C).

For all three of the fibers tested, an increase in peak areas for the probable VOCs was observed when the extraction time was lengthened. A total of 34 VOCs were detected for the ABS filament, out of which 28 VOCs were unique to the ABS filament (5 VOCs were common with the TPLA filament while one VOC was common to the CPE+ filament).

A comparison of VOCs and their obtained peak areas for extractions carried out at one, two and four hours while printing with TPLA filament is shown in Figure 4. For this filament, one and two hour extractions yielded 6 peaks while the four hour extraction provided an additional 4 peaks using the PA fiber, as shown in Table S5. With the PDMS fiber, the number of peaks detected for extraction times of one, two and four hours were 9, 10 and 12, respectively (see Table S6). Finally, Table S7 shows that the DVB/CAR/PDMS fiber was able to extract 9 probable VOCs at an extraction time of one hour, 15 probable VOCs at 2 hours and an additional VOC (for a total of 16) at four hours. All probable VOCs detected for the TPLA filament using PA, PDMS and DVB/CAR/PDMS fibers at extraction times of four hours are shown in Figure S4(A), S4(B) and S4(C), respectively. In case of the TPLA filament, a total of 23 VOCs were detected out of which 5 VOCs were common with the ABS filament.

Figure 5 shows a comparison of probable VOCs and their corresponding peak areas when extractions were carried out using the CPE+ filament. When the DVB/CAR/PDMS fiber was employed at an extraction time of one hour, only two peaks were detected while no probable VOCs were detected using the PA and PDMS fibers, as seen in Table S8. Four VOCs were detected when the extraction was performed at four hours, as shown in Figure S5(C), while 3 VOCs were detected at an extraction time of two hours using the DVB/CAR/PDMS fiber. Only 1 and 2 peaks (see Figure S5(A)) were observed using the PA fiber at extraction times of two and four hours, respectively, while only one VOC was detected at extraction times of two and four hours using the

PDMS fiber, as shown in Figure S5(B). Out of 6 VOCs detected for CPE+ filament, 4 were extracted only by the DVB/CAR/PDMS fiber, 1 was extracted only by the PA fiber while 1 was extracted only by PA and PDMS fibers.

In case of all three filaments, it was observed that some VOCs were extracted by all three fibers, some were extracted by only two fibers while some were only extracted by specific sorbent coatings, as can be seen in Figures 2, S4 and S5. Extractions at each time-course using each filament and fiber were carried out in triplicate. Though the 3D printing system was open at the back, each triplicate extraction showed good reproducibility in terms of peak areas of the detected VOCs. Relative standard deviations of triplicate measurements did not exceed 22% with most of the replicates being in the range of 15%, which is acceptable given the openness of the system [32].

3.3 Tentative identification of liberated VOCs

Tentative identification of VOCs was performed by matching the obtained mass spectra with the NIST mass spectral library for those that yielded a match factor equal to or greater than 80 [5,33]. Table 2 shows the list of identified VOCs for the corresponding filament and retention times. Of the 34 VOCs detected for the ABS filament, 5 VOCs were tentatively identified, as shown in Figure S6. The following VOCs and their corresponding retention times were identified: hexamethyl cyclotrisiloxane (7.0 mins); 2-Oxepanone (13.6 mins); 1,1'-(1,3-propanediyl)-bis-benzene (20.7 mins); 2-[1-(4-Cyano-1,2,3,4-tetrahydronaphthyl)]propanenitrile (27.0 mins); 3-[1-(4-Cyano-1,2,3,4-tetrahydronaphthyl)]propanenitrile (28.5 mins). The latter two compounds are isomers of the styrene-acrylonitrile (SAN) trimer and are known to be degradation or synthesis by-products of ABS and are potentially genotoxic [33,34]. An additional compound liberated from the ABS filament was identified as styrene, a potential carcinogen [35], at a retention time of 8.5

mins. Identification of styrene was further confirmed by matching the retention time with that of a standard, as shown in Figure S7. A VOC released from the TPLA filament at a retention time of 3.6 mins was identified as methyl methacrylate (see Figure S8), a known irritant [36]. In the case of CPE+ filament, a VOC at a retention time of 5.8 mins was identified as 2,4-dimethyl-3-pentanone, as shown in Figure S9.

When desorbing VOCs from SPME fibers, VOCs are not only desorbed but are also accompanied by background components originating from the fiber when exposed to elevated temperatures. This resulted in increased noise and may also affect peak purity. Additionally, many of the peaks are analyzed at levels near the detection limit. Captured VOCs are possibly the degradation products of the filaments, which may not appear in the NIST database. For these reasons, only a few compounds reached the 80% similarity or above criteria for proper identification.

3.4 Statistical differentiation of SPME extraction performance for VOCs originating from different filaments

Based on the data gathered in this study, it was observed that the number of probable VOCs liberated by each filament was not a function of print nozzle temperature, but rather was characteristic to each filament. For each filament, the number of VOCs detected varied, as shown in Table 2. These results allowed differentiation of the filaments into three different categories based on the number of VOCs detected. Though the print nozzle temperature employed during the printing of CPE+ was the highest, it liberated the fewest number of VOCs. Comparison of fibers based on the extracted VOCs is complicated by the fact some of the VOCs were extracted by all three fibers, while some were extracted by only one or two fibers, especially in case of ABS and TPLA filaments. If data were used directly from the chromatograms in Figures 2 and S4 to classify

each fiber in terms of VOC extraction efficiency, peak areas of each peak would need to be compared individually. To make the results easy to visualize in one plot, cluster heatmap analysis was utilized [37] where peaks were compared based on their peak area. Only 6 peaks were detected for the CPE+ filament, which was fewer compared with the VOCs detected for the ABS and TPLA filaments. Out of 6 detected peaks, 4 were extracted only by the DVB/CAR/PDMS fiber indicating that it was better at extracting VOCs originating from the CPE+ filament. For these reasons, statistical differentiation of SPME extraction performance was carried out only for VOCs originating from ABS and TPLA filaments.

The dataset obtained from the four hour extraction using the two filaments yielded 53 probable VOCs, and this was subjected to statistical analyses. Six different filament-fiber combinations were possible, as two filaments were used for printing and three fibers were employed for extraction; the filament-fiber combinations are denoted by ABS_CAR, ABS_PA, ABS_PDMS, TPLA_CAR, TPLA_PA and TPLA_PDMS, as shown in Figure 6. These combinations were considered as samples while VOCs (retention times) were considered as variables allowing for the samples to be compared based on the peak areas of corresponding VOCs for statistical analyses.

Hierarchical cluster analysis (HCA) was performed where features (probable VOC peaks) and individuals or samples (filament-fiber combination) were clustered independently [38]. To visually perceive differences between the samples, a heatmap was generated where samples lie on horizontal axis (top) and VOCs on vertical axis (right). As shown in Figure 6, heat map analysis of six different samples resulted in a dendrogram featuring four different clusters where tentatively identified compounds are indicated by the symbol, '*' adjacent to their retention times. Two main clusters can be observed for the ABS and TPLA filaments, and each cluster can be further divided into two different sub-clusters to permit differentiation of the fibers. It can be observed that the

DVB/CAR/PDMS fiber resides as a different cluster from the PA and PDMS fibers for the ABS as well as TPLA filament, indicative of the different selectivity offered by the DVB/CAR/PDMS fiber. Colors of the cells within the heatmap provide information about the samples [21]. Cells featuring a darker yellow color indicate the highest peak area for a given VOC, whereas the blue color designates decreased peak area and a VOC that was not detected in a particular sample. For any given filament, the darker yellow color of the cells indicates that a particular fiber is better at extracting the corresponding VOCs (denoted by retention time). For instance, styrene at retention time of 8.5 mins is extracted only by the DVB/CAR/PDMS fiber and the corresponding darker yellow color is observed only under the ABS_CAR region. Similarly, one isomer of the SAN trimer at a retention time of 28.5 mins is better extracted by the PA and PDMS fibers. The darker yellow region corresponding to the DVB/CAR/PDMS fiber suggests that it is better at extracting early eluting VOCs while the PA and PDMS fibers are better at extracting later eluting VOCs based on retention times. Using the heatmap, differentiation between the fibers and their observed selectivity for various VOCs could be achieved. Additionally, the heatmap showed clear differentiation between the filaments indicating that the released VOCs were also a function of filament composition.

Results from the heatmap were corroborated by a score plot obtained from PCA, another chemometric approach shown in Figure 7. A total of four groups were obtained from the PCA plot which shows separation of filaments as well as fibers. F1 and F2 together account for a total variance of 64.43%, where F1 divides samples into two different groups providing separation between the ABS and TPLA filaments. Principal component F2 also divides samples into two other groups, providing further differentiation between fibers. The PA and PDMS fibers are clustered into one group while the DVB/CAR/PDMS fiber resides in a different group. Ellipses

represent the 95% confidence interval, and each ellipse color represents a group while each point inside the ellipse represents data obtained from triplicate extractions.

Conclusions

SPME was employed in this study to extract VOCs produced when printing with three commonly used FDM filaments. Meticulous cleaning of the 3D printing system and the need to perform background extractions were key aspects identified to avoid contamination when moving from one filament to another. It was found that the ABS filament yielded the most VOCs for which a total of 34 VOCs were detected, while only 6 VOCs were detected for the CPE+ filament. Despite the fact that the extractions were not performed under equilibrium conditions, a few potentially hazardous compounds, such as styrene, SAN trimer and methyl methacrylate could be tentatively identified using this approach. With the aid of chemometric approaches, filaments could be differentiated based on liberated VOCs indicating that the released VOCs are function of filament composition. Distinction between SPME fibers could also be established where the DVB/CAR/PDMS fiber was found to extract a greater number of early eluting compounds while the PA and PDMS fibers showed similar extraction profiles and were better at extracting relatively later eluting compounds.

The SPME approach can be broadened to other less common FDM filaments, as well as materials used in other printing mechanisms (i.e., SLA and digital light processing). While SPME has been demonstrated as a promising tool for the extraction of volatile compounds released during printing, approaches that can accommodate larger volumes of air samples can also be used in the future to collect more volatiles in an attempt to achieve exhaustive extraction and aid in identifying liberated VOCs at trace levels. Furthermore, results from this study are pertinent to the open volume within the 3D printer; a future goal is to monitor the spatial distribution of VOCs liberated

from an open printer by positioning SPME fibers at different locations in an enclosed room where printing is performed.

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528 **Table 1:** 3D printing conditions employed in this study when printing with ABS, TPLA and
529 CPE+ filaments.

Filament	Color	Print nozzle temperature (°C)	Print bed temperature (°C)	Layer height (mm)	Print speed (mm/s)
ABS	white	230	80	0.1	55
TPLA	black	210	60	0.1	45
CPE+	transparent	265	107	0.1	40

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Table 2. Probable VOC peaks detected for the ABS, TPLA and CPE+ filaments for a four hour extraction using the PA, PDMS and DVB/CAR/PDMS (CAR) fibers. Peaks are denoted by their retention times. Tentatively identified compounds are listed along with their % probability match and the detected peaks are marked with the symbol "**X**".

Peaks	RT (min)	Tentatively identified compounds with their % probability match	ABS			TPLA			CPE+		
			PA	PDMS	CAR	PA	PDMS	CAR	PA	PDMS	CAR
1	3.6	Methyl methacrylate (87)						X			
2	5.5										X
3	5.8	2,4-dimethyl-3-pentanone (80)									X
4	7.0	hexamethyl cyclotrisiloxane (81)			X						
5	7.8				X						
6	8.5				X						
7	8.7										X
8	9.4				X						
9	9.6							X			
10	10.7					X					
11	10.6		X	X	X						
12	13.4					X	X	X			
13	13.6	2-Oxepanone (89)			X						
14	14.1					X	X	X			
15	15.3							X			
16	16.5						X				
17	16.7								X		
18	17.0							X			
19	17.5										X
20	17.6		X	X	X						
21	17.7					X	X	X			
22	18.0		X	X	X						
23	18.1						X	X			
24	18.4		X	X	X		X	X			
25	18.6		X		X						
26	18.8							X			
27	19.6					X		X			
28	20.2							X			
29	20.7	1,1'-(1,3-propanediyl)-bis-benzene (94)	X		X						
30	21.1		X	X	X						
31	21.2				X						
32	21.4				X						
33	21.6					X	X				
34	21.9		X	X							

35	**22.6**		**X**	**X**	**X**						
36	**22.7**		**X**	**X**	**X**	**X**	**X**	**X**			
37	**23.1**				**X**						
38	**23.5**							**X**			
39	**23.9**				**X**						
40	**24.5**		**X**	**X**	**X**	**X**	**X**	**X**			
41	**24.9**		**X**		**X**	**X**					
42	**25.3**		**X**	**X**							
43	**26.0**		**X**	**X**	**X**						
44	**26.6**		**X**	**X**	**X**						
45	**27.0**	**2-[1-(4-Cyano-1,2,3,4-tetrahydronaphthyl)]propanenitrile (80)**	**X**	**X**	**X**						
46	**27.1**		**X**	**X**	**X**						
47	**27.3**		**X**	**X**	**X**						
48	**27.4**					**X**	**X**				
49	**27.8**						**X**	**X**			
50	**28.5**	**3-[1-(4-Cyano-1,2,3,4-tetrahydronaphthyl)]propanenitrile (84)**	**X**	**X**	**X**						
51	**28.8**		**X**	**X**	**X**						
52	**30.9**		**X**	**X**	**X**						
53	**31.0**		**X**	**X**	**X**						
54	**31.1**					**X**					
55	**31.8**			**X**							
56	**31.8**						**X**				
57	**31.9**			**X**							
58	**34.7**			**X**					**X**	**X**	

536

Figure 1. Photograph of the model that was printed with a four hour print time using the three test filaments in this study. The model in this figure was printed with the ABS filament and measures 53.6 x 61.9 x 25.0 mm. Masses of models varied depending on the printing time and the filament used.

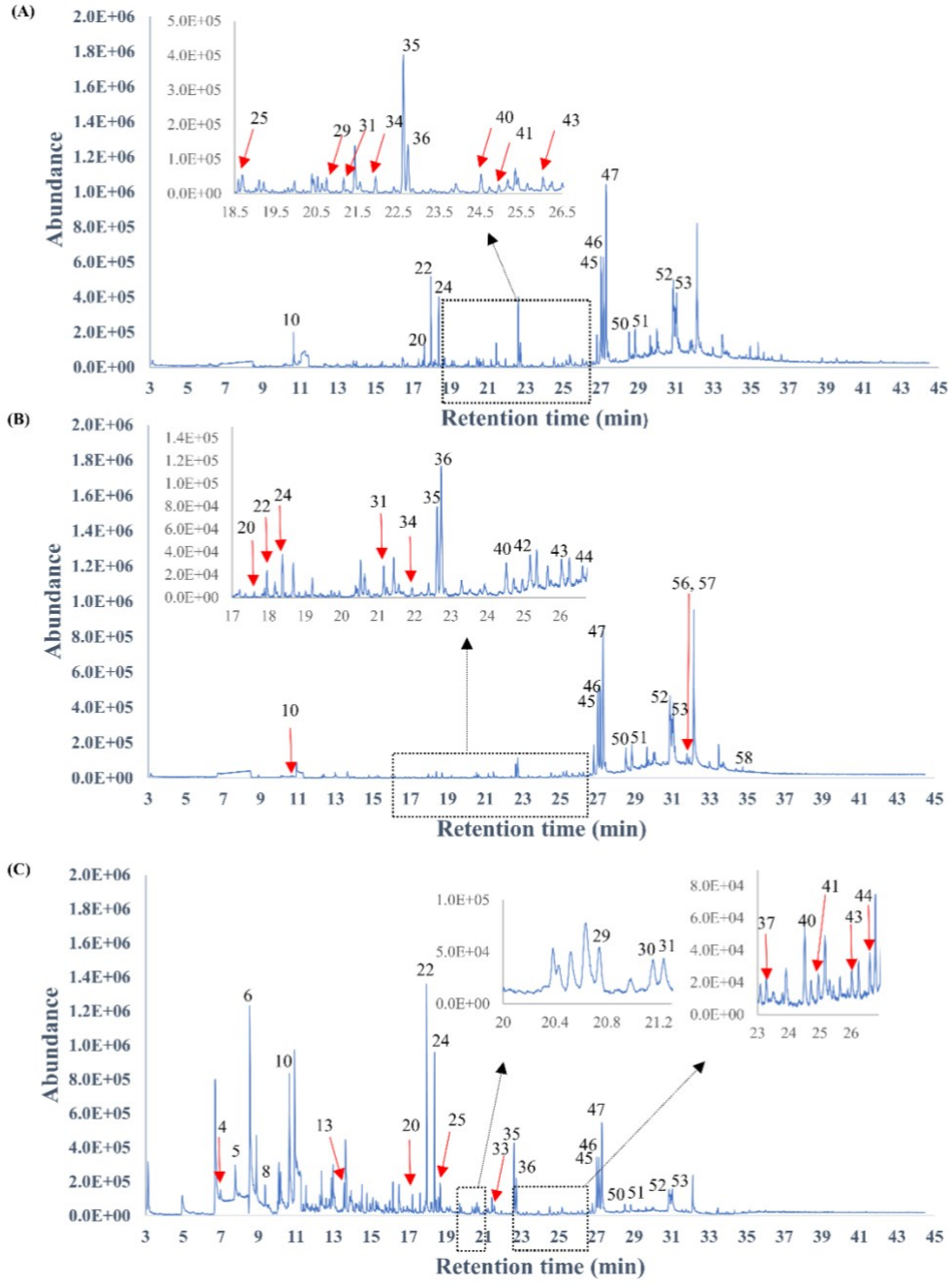
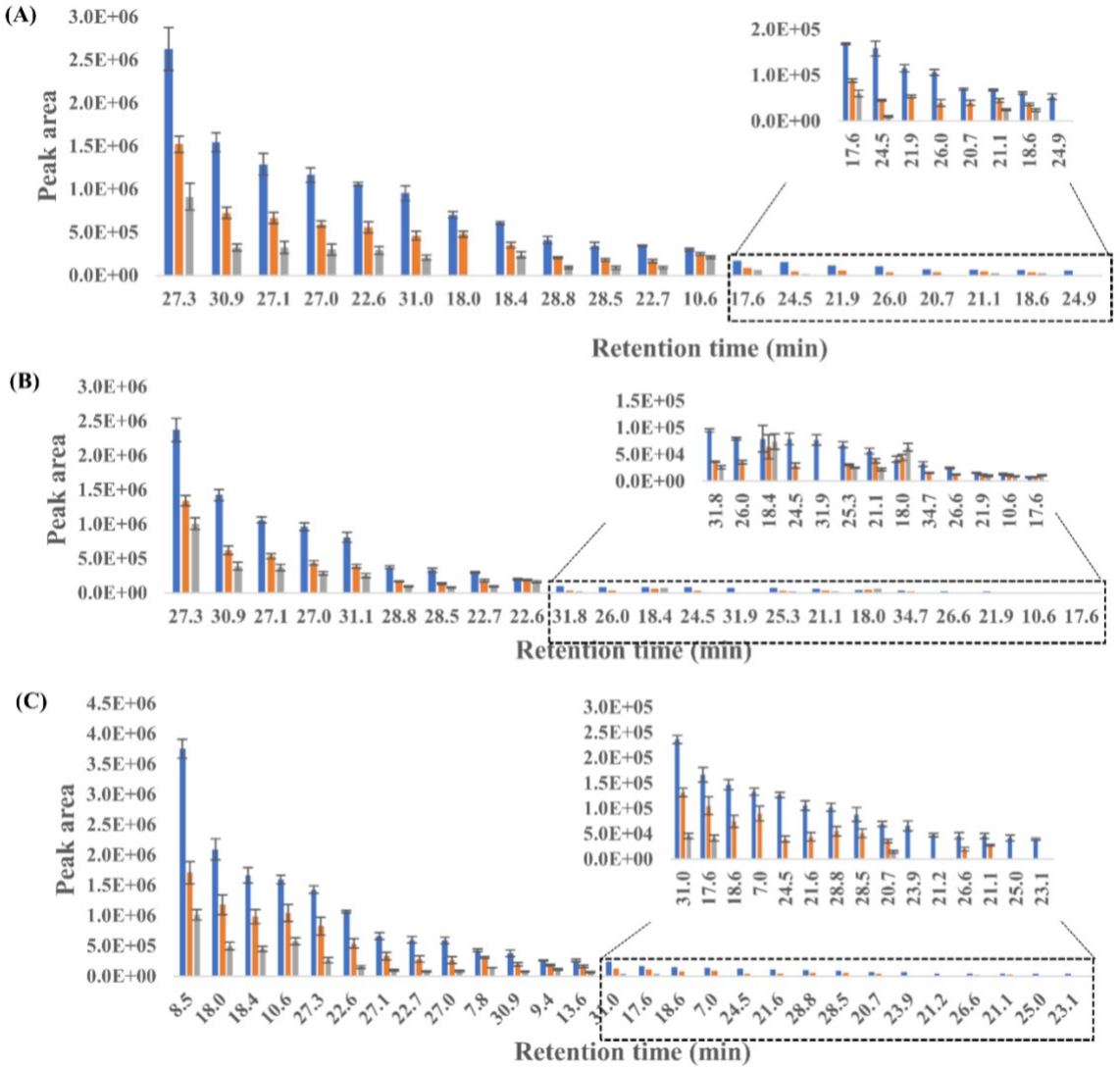
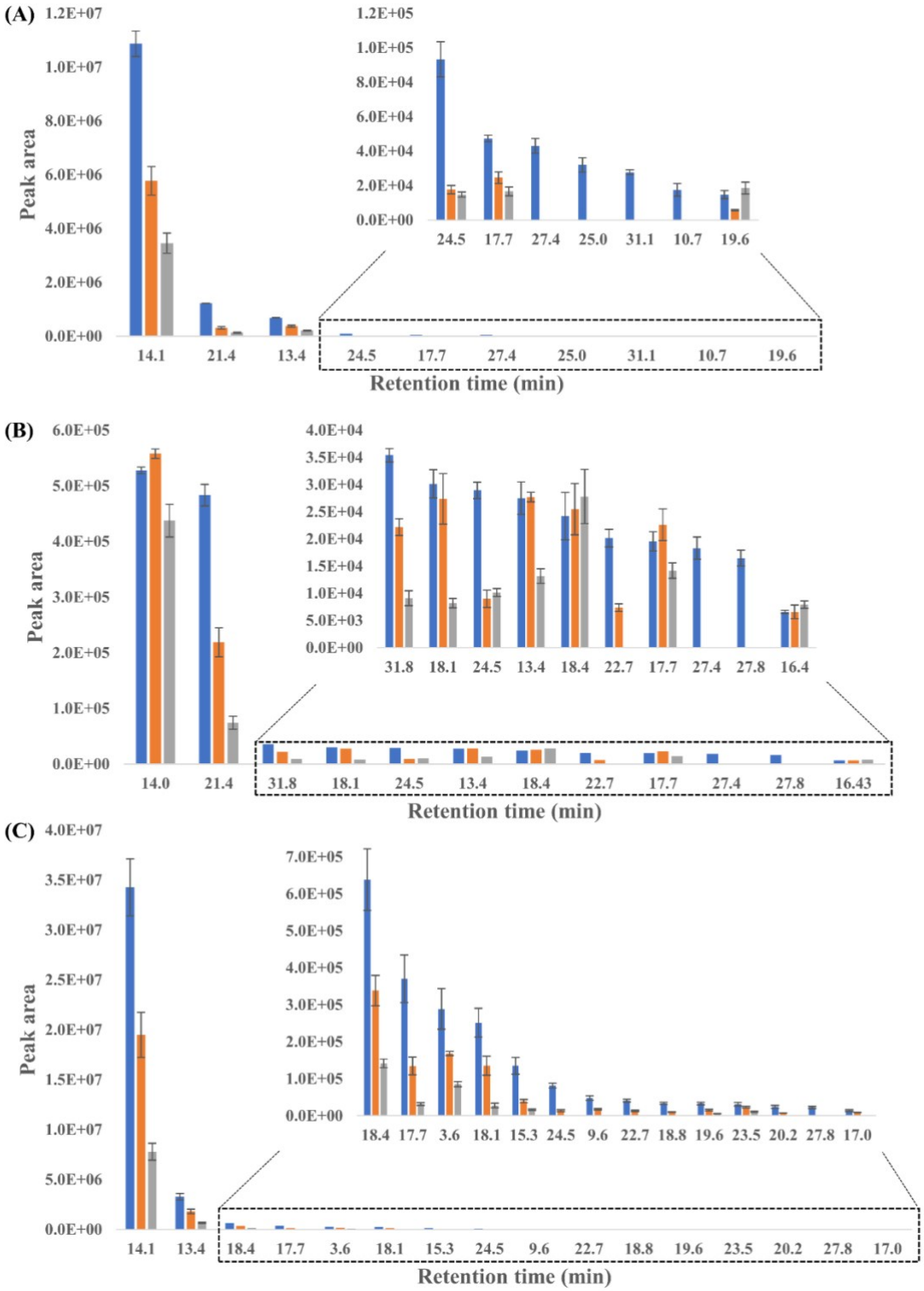


Figure 2. Total ion chromatogram obtained by SPME-GC-MS after extracting VOCs using the (A) PA, (B) PDMS, and (C) DVB/CAR/PDMS fibers while printing with ABS filament for four hours with a temperature program described in section 2.2.3. The detected peaks are denoted by the corresponding peak number, as shown in Table 2. A total of 20, 22 and 28 VOCs were detected using PA, PDMS and DVB/CAR/PDMS fibers, respectively.



548 **Figure 3.** Bar graph showing a comparison of detected chromatographic peaks based on their
549 peak areas for extractions carried out at one (■), two (■), and four (■) hours while printing with
550 the ABS filament using the (A) PA, (B) PDMS, and (C) DVB/CAR/PDMS SPME fibers.
551 Triplicate extractions were performed for each time period using each fiber.

552



553 **Figure 4.** Comparison of extraction times of one (■), two (■), and four (■) hours in terms of peak
554 areas of VOCs detected for the TPLA filament using the (A) PA, (B) PDMS, and (C)
555 DVB/CAR/PDMS fibers. Extractions at each time period using each fiber were performed in
556 triplicate.

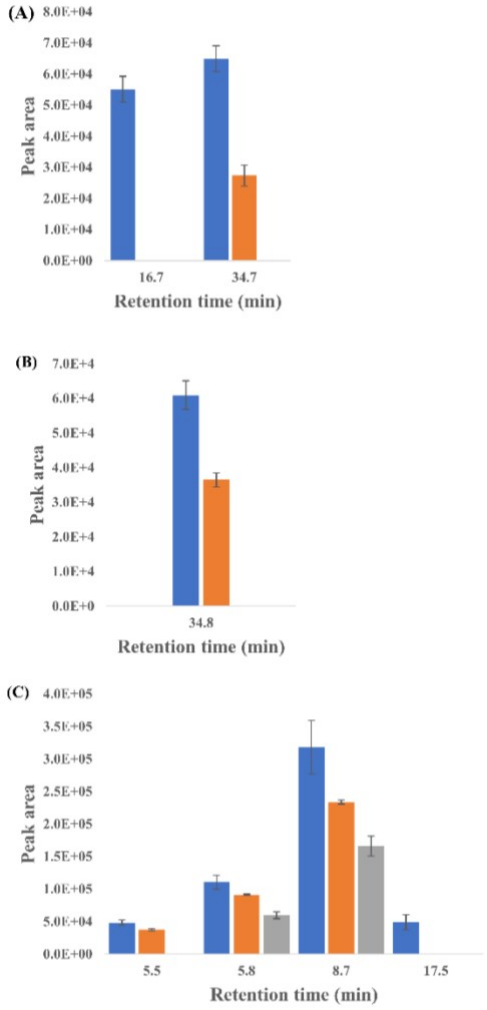


Figure 5. Comparison of peak areas of detected VOCs obtained after performing extractions at three different time periods of one (■), two (■), and four (■) hours using the (A) PA, (B) PDMS, and (C) DVB/CAR/PDMS fibers while printing with the CPE+ filament. Extractions using three time periods were carried out in triplicate.

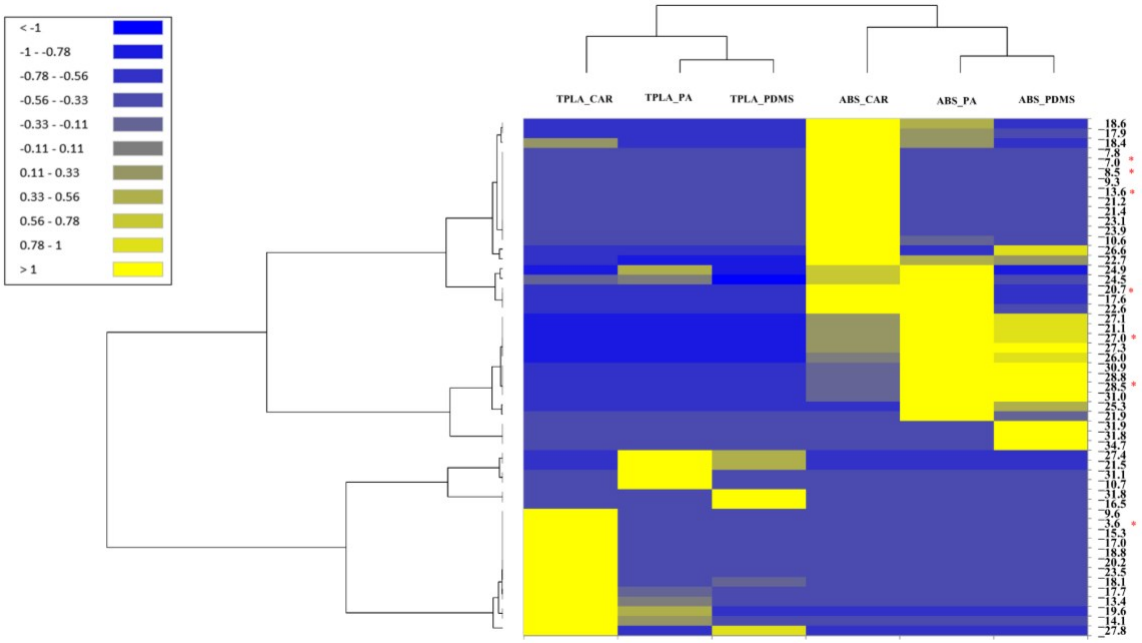
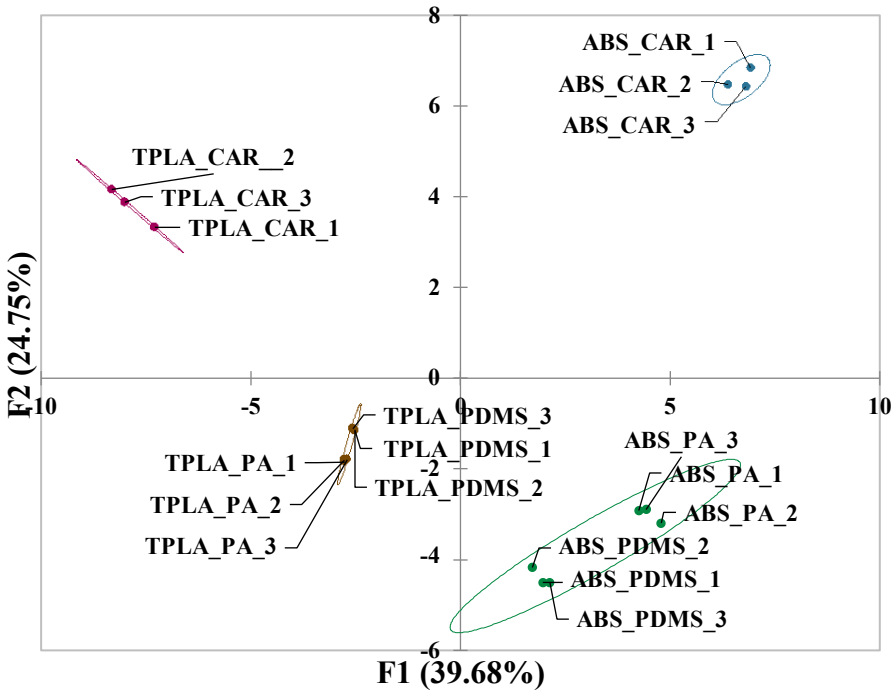


Figure 6. Heat map of hierarchical clustering analysis (HCA) for VOCs detected when performing extractions using the PA, PDMS and DVB/CAR/PDMS (denoted as CAR) fibers for four hours while printing with ABS and TPLA filaments. The labels ABS_CAR, ABS_PA, ABS_PDMS, TPLA_CAR, TPLA_PA and TPLA_PDMS represent the filament-fiber combinations. Cells are colored based on peak areas of the detected VOCs. The darker yellow color indicates the highest obtained peak area for a particular VOC with a specific filament-fiber combination while the darker blue color indicates that the corresponding VOC was not detected. Tentatively identified compounds are indicated by the symbol, '*'.



570 **Figure 7**. Principal component analysis (PCA) of VOCs detected from four hour extractions
571 while printing with ABS and TPLA filaments using PA, PDMS and DVB/CAR/PDMS (denoted
572 as CAR) fibers. The filament-fiber combinations are denoted as ABS_CAR, ABS_PA,
573 ABS_PDMS, TPLA_CAR, TPLA_PA and TPLA_PDMS. Ellipses represent the 95% confidence
574 interval and each ellipse color represents a group. Triplicate measurements were performed for
575 each fiber-filament combination.