Extraction of Volatile Organic Compounds Liberated Upon Filament Extrusion by 3D Pen and its Comparison with a Desktop 3D Printer Using Solid-Phase Microextraction Fiber and Arrow

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Abstract

Desktop 3D printers that operate by the fused deposition modeling (FDM) mechanism are known to release numerous hazardous volatile organic compounds (VOCs) during printing, including some with potential carcinogenic effects. Operating in a similar manner to FDM 3D printers, 3D pens have gained popularity recently from their ability to allow users to effortlessly draw in the air or create various 3D printed shapes while handling the device like a pen. In contrast to numerous modern 3D printers, 3D pens lack their own ventilation systems and are often used in settings with minimum airflow. Their operation makes users more vulnerable to VOC emissions, as the released VOCs are likely to be in the breathing zone. Consequently, monitoring VOCs released during the use of 3D pens is crucial. In this study, VOCs liberated while extruding acrylonitrile butadiene styrene (ABS) filaments from a 3D pen were measured by solid-phase microextraction (SPME) combined with gas chromatography/mass spectrometry (GC/MS). SPME was investigated using the traditional fiber and Arrow geometries with the DVB/Carbon WR/PDMS sorbent while four different brands of ABS filaments—Amazon Basics, Gizmodork, Mynt 3D, and Novamaker—were used with the 3D pen. Heatmap analysis showed differentiation among these brands based on the liberated VOCs. The nozzle temperature and printing speed were found to affect the number and amount of released VOCs. This study goes a step further and presents for the first time a comparison between 3D pen and a desktop 3D printer based on liberated VOCs. Interestingly, the findings reveal that the 3D pen releases a greater number and amount of VOCs compared to the printer. The amounts of liberated VOCs, as indicated by the corresponding chromatographic peak areas, were found to be 1.4 to 62.6 times higher for the 3D pen compared to the 3D printer when using SPME Arrow.

Keywords: 3D printing; 3D pen; volatile organic compounds (VOCs); solid-phase microextraction; gas chromatography/mass spectrometry.

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1. Introduction

Volatile organic compounds (VOCs) are compounds characterized by high vapor pressure, high mobility, low water solubility, and can originate from both natural and anthropogenic sources [1,2]. The presence of VOCs in indoor environments is closely linked to indoor air pollution, directly affecting human health since people tend to spend up to 90% of their life indoors [3,4]. Various VOCs identified as indoor pollutants, including aldehydes, ketones, aromatic compounds, alcohols, esters, olefins, and alkanes, have been found to have adverse effects on human health [5]. VOCs in indoor environments originate from diverse sources, including building materials, wallpaper, office chairs, paints and electronic equipment [6]. Moreover, as the utilization of 3D (three-dimensional) printing technologies continues to expand, they can be seen as a contributing element to indoor VOCs.

3D printing, also referred to as additive manufacturing or rapid prototyping, has been in existence for decades [7]. 3D printing is a process used to create 3D objects through depositing successive layers of constituent materials [8]. The versatility of 3D printing allows for the customization of products as per the user's specifications which has made it applicable in diverse fields, including but not limited to industries such as medicine, education, aerospace, automotive, construction, and architectural design [9,10]. As the cost of producing 3D printers has gradually decreased over time, their adoption has become widespread. Currently, a number of 3D printing techniques exist and include fused deposition modeling (FDM), stereolithography (SLA), selective laser sintering (SLS), inkjet and polyjet printing, laminated object manufacturing (LOM), and direct printing [11,12]. Among these methods, FDM stands out as one of the most widely used methods and involves the melting of thermoplastic filament in an extruder and its deposition on a moving bed to form a solid 3D object [8,13]. Although

FDM was initially designed and applied as an industrial quality process utilizing larger machines, its evolution now spans the broadest range of smaller and more affordable machines, contributing to its growing popularity [14]. Owing to their low cost and increased popularity, FDM printers have been increasingly used in indoor settings such as homes, offices, libraries, and educational institutions [15–17]. Numerous studies have documented the release of VOCs during the printing process with desktop FDM printers, using widely employed thermoplastic filaments such as acrylonitrile butadiene styrene (ABS), polylactic acid (PLA), copolyester (CPE), nylon, among others [18–21]. Some reported VOCs are known carcinogens (benzene), potential carcinogens (styrene, ethylbenzene), and irritants (methyl methacrylate) while others including toluene, xylene, caprolactam, lactide, aldehydes, ketones, alcohols, and acids may have other potential health concerns [16,22]. Indoor settings in non-work or residential environments may not necessarily have ventilation systems as robust as those in occupational workplaces, potentially making people more vulnerable to the released VOCs.

Like FDM 3D printers, 3D pens are also employed indoors. 3D pens are handheld devices that operate by essentially the same mechanism of printing as FDM 3D printers and allow users to draw objects in the air, turning their doodles and designs into tangible, physical objects. Particularly popular among children, 3D pens utilize similar thermoplastic filaments and emit potentially hazardous fumes (i.e., VOCs) during filament extrusion to create various objects [23]. So far, only one study has reported the emission of organic vapors from 3D pens specifically in the form of total volatile organic compound (TVOC) rather than individual VOCs [24]. The primary focus of the study revolved around examining emission rates and yields of different elements alongside TVOC. In a 3D printer, the extruder nozzle's movement is automated, whereas with a 3D pen, the operator (often a child) manually controls the movement. Consequently, the distance between the nozzle and the operator is likely to be shorter than the length of the operator's arm, resulting in VOC generation that likely is within the children's breathing zone [24]. Respiratory defense mechanisms of children against gaseous pollution are generally not fully developed, and their higher volume of air intake per body weight makes them more susceptible to these emissions [25,26]. Therefore, it is essential to monitor VOCs that are emitted during their use.

The most widespread technique used for measuring VOCs liberated from different 3D printing filaments is the collection of VOCs in sorbent tubes, followed by their desorption into a gas chromatographic (GC) inlet and analysis by mass spectrometry (MS) [18–21]. Rather recently, solid-phase microextraction (SPME) was employed for the preconcentration of VOCs liberated during printing using different thermoplastic filaments and combined with gas chromatography mass spectrometry (GC/MS) analysis [16,22]. SPME using the traditional fiber geometry, was employed for the first time as a sampling device inside a FDM 3D printer to extract VOCs while printing [22]. Jaroslav, Minář, et al., reported the use of SPME in Arrow geometry for the same purpose [16]. SPME is a widely used sampling technique that has numerous advantages, such as substantially reduced analysis times as it consolidates sample collection, extraction, and analyte enrichment from the sample matrix into a single step while also possessing minimal solvent consumption, and high sensitivity [27,28]. The fiber and Arrow are two different geometries of SPME which largely differ from each other in terms of their respective dimensions. As the name implies, SPME Arrow features an arrow-shaped tip and is characterized by increased phase length, phase volume, and phase area, which can address some of the limitations of traditional SPME fibers that include limited mechanical robustness and small extraction phase volumes [29]. As a result, it often delivers enhanced sensitivity.

In this work, SPME in both geometries (Fiber and Arrow) is used to evaluate VOCs liberated during filament extrusion from a 3D pen and enables a comparison to be made to filament extrusion from a desktop 3D printer. This study is the first to compare the amount and number of VOCs produced from 3D pen and 3D printer during extrusion/printing. It is also the first study to compare the performance of SPME fiber and Arrow with regards to VOCs liberated during the extrusion of filament from the 3D pen. The aim of this study was to design an extraction system that can extract/preconcentrate VOCs released during filament extrusion from a 3D pen and subsequently compare the VOCs with those released during filament extrusion with a FDM 3D printer. Four different brands of ABS filament, namely, Amazon Basics, Gizmodork, Novamaker and Mynt 3D were chosen for the study and are differentiated from each other based on the VOCs detected. The effects of nozzle temperature and print speed of the 3D pen on the amount and number of VOCs detected were examined. A comparison between 3D pen and printer revealed that the 3D pen releases a greater number and amount of VOCs compared to the 3D printer.

2. Experimental

2.1 Materials

Four different brands of ABS filaments, namely, Mynt3D, Amazon Basics, Novamaker and Gizmodork were purchased from Amazon (Seattle, WA, USA). Mynt3D, Amazon Basics, and Novamaker filaments were purchased with a diameter of 1.75 mm while Gizmodork filament was purchased with diameters of 1.75 mm and 2.85 mm. A SPME fiber containing the DVB/Carbon WR/PDMS sorbent coating (film thickness of 80 μm) and the same sorbent in SPME Arrow geometry (film thickness of 120 μm) were employed for the extraction of VOCs released during filament extrusion using the 3D pen, as well as while printing with a FDM 3D printer. The SPME fiber and Arrow devices were obtained from Restek Corporation (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 Experimental setup for 3D pen and parameters of 3D printing

A Mynt3D printing pen (3D pen pro), purchased from Amazon was employed throughout the study. Initially, the 3D pen was placed on a build plate of an Ultimaker 3 printer for preliminary studies and then placed in an Ultimaker S3 FDM printer (Geldermalsen, Netherlands) for subsequent studies where the printers served as a housing for the 3D pen, as shown in Fig. S1. Two videos demonstrating the printing of filament by the 3D pen inside the desktop printer and placement of extraction devices are provided as Supporting Information. Both printers were open at the top to accommodate an air filtration (vent) system featuring an opening at the back and served as a cover to enclose the printer, as reported in a previous study [22]. The 3D pen was then fed with filament of a particular brand and VOCs released during the extrusion step for each filament were extracted by the SPME fiber and Arrow and then subjected to GC/MS analysis. Studies of the released VOCs were performed by extruding the filaments at different nozzle temperatures and speed settings of the 3D pen. The temperature at which the filament was extruded from the nozzle of the 3D pen was dictated by the type of filament used, as the manufacturer recommends specific nozzle temperatures based on the filament type. For the ABS filament, the recommended nozzle temperature for extrusion is 210 °C; however, extrusion was also carried out at 230 °C [30]. Slow, medium, and fast speed settings were used with the 3D pen. However, the manufacturer recommends using the 3D pen at its fastest speed setting [30].

For 3D printing, an Ultimaker S3 printer was used to print a tray, as described in a previous study [22], under two different conditions using a nozzle temperature of 230 °C. For the first condition, printing parameters recommended by Ultimaker Cura (Geldermalsen, Netherlands) software were used in which printing was carried out for 90 minutes. In the second condition, printing was performed for 69 minutes using settings closely resembling the slowest speed setting of the 3D pen. Using both conditions, an object (tray) of similar mass was printed. Table S1 shows the printing parameters used in both conditions for the 3D pen and 3D printer, mass of object printed by the printer, mass of filament extruded by the 3D pen, and rate of extrusion.

2.2.2 Extraction of VOCs using SPME

Prior to use, the DVB/Carbon WR/PDMS SPME fiber and SPME Arrow devices were conditioned according to manufacturer's specifications. To extract VOCs released during extrusion from the 3D pen for each filament, the SPME fiber and Arrow with their holders were sequentially placed inside the Ultimaker 3 3D printer at a position shown in Fig. S1. Additionally, extrusion of Gizmodork filament was also carried out using the 3D pen placed inside the Ultimaker S3 printer. When commencing extrusion of filament from the 3D pen, the fiber or Arrow was exposed to facilitate extraction of the liberated VOCs throughout the entire duration of the extrusion process. Prior to filament extrusion, extractions of the background were performed by exposing the fiber or Arrow inside the printer at room temperature for an equivalent time as the extrusion process. Experiments were initially conducted under varied conditions, including nozzle temperatures of 210 °C and 230 °C, as well as using fast, medium and slow speed settings of the 3D pen. Gizmodork filament was employed for these experiments, while keeping the mass of extruded filament similar using the SPME fiber. The mass of filament extruded and rate of extrusion at the two nozzle temperatures and three speed settings are shown in Table 1a and 1b, respectively. Experiments were subsequently carried out with the SPME fiber and Arrow devices while extruding each brand of the ABS filament for 6 minutes at the recommended nozzle temperature (210 °C) and speed setting (fast) of the 3D pen. The SPME fiber was first employed for the extraction of VOCs released upon extrusion of a particular brand of filament. Following extraction using the SPME fiber, the SPME Arrow device was used for the extraction of VOCs from the same brand of filament. Upon completion of extrusion/extraction using a particular brand of filament, a new print nozzle was used and fed with filament from another brand to avoid contamination.

3D printing with the Ultimaker S3 printer was carried out using Gizmodork filament (2.85 mm) under two different conditions for 69 and 90 minutes. For VOC extraction, the DVB/Carbon WR/PDMS SPME Arrow was placed inside the printer and exposed for the entire duration of printing. The SPME Arrow was placed in the same position within the printer as the 3D pen experiment while extruding the Gizmodork filament (1.75 mm). Prior to extraction of VOCs, extractions of the background were performed using the SPME Arrow by raising the build plate temperature of the printer to 100 °C, following a previously reported procedure [22], for the same duration as printing under two conditions. For all extractions involving the 3D pen and 3D printer, the vent system remained positioned over the top of the printer but was not activated. However, in between each extrusion (using 3D pen) and each printing (using 3D printer) step, the vent system was activated for 45 min (approximate length of the separation) to achieve good reproducibility in peak areas of the extracted VOCs.

2.2.3 GC/MS analysis

An Agilent Technologies 7890B gas chromatograph (Agilent Technologies, Santa Clara, USA) coupled to a 5977A mass spectrometer (Agilent Technologies) controlled by Mass Hunter software was used for the desorption, separation, and detection of VOCs extracted by the DVB/Carbon WR/PDMS SPME fiber and Arrow devices. A Restek PAL SPME Arrow conversion kit specific for an Agilent 7890 split/splitless Injector (Restek Corporation, Bellefonte, PA, USA) was used to modify the GC inlet. For all separations, a Rxi-5MS capillary column with dimensions of 30 m x 0.25 mm and a 0.25 μm film thickness, obtained from Restek Corporation, was employed. Separations were carried out using helium at a constant flow rate of 1 mL/min. Desorption of the VOCs was performed in splitless mode for 4 min by inserting the fiber or the Arrow devices into the GC inlet maintained at 250 °C and 270 °C, respectively. The separation method for the extracted VOCs was carried out using the previously reported method [22], where the oven temperature was initially held at 40 °C for 5 min, then ramped at a rate of 10 °C/min to 180 °C and held for 5 min. Subsequently, a ramp of 10 °C/min up to 270 °C, followed by a 20 °C/min ramp up to 300 °C with a hold of 10 minutes, was employed resulting in a total separation time 44.5 min for each run. Electron ionization was performed at 70 eV with a scan a range of 45 to 300 m/z. The source and transfer line temperatures were held at 230 °C and 280 °C, respectively. In order to calculate retention index (RI) values, a solution of alkane standards ranging from C_6-C_{24} was prepared in dichloromethane at a concentration of 100 ppm each. RI values were then calculated using the Van den Dool and Kratz relationship [31,32]. VOC identification was performed by matching the mass spectra of VOCs with the NIST mass spectral library as well as matching their calculated RI values with the RI values reported in NIST chemistry webbook [33]. A VOC was considered tentatively identified when the match score of the candidate exceeded 800 and the difference between the calculated and reported RI value was within a range of ± 30 units [34,35].

2.2.4 Statistical analysis

Analysis of the chromatograms was conducted to determine the probable VOC peaks released during extrusion from the 3D pen as well as when printing with the 3D printer. Peaks having a signal-to-noise ratio of 3 and above were considered as detected VOCs. The signal-to-noise ratio was determined by dividing the height of the peak by the calculated peak-to-peak noise, as reported in a previous study [22]. A comparison of different brands of ABS filament based on the liberated VOCs was statistically performed via a heatmap analysis using XLSTAT software, version 2023.1.6 (Addinsoft, New York, USA).

3. Results and discussions

The aim of this study was to extract VOCs released during filament extrusion from a 3D pen using both traditional SPME (SPME fiber) and SPME Arrow devices, and to subsequently compare the detected VOCs with those detected during filament extrusion using a desktop 3D printer. Like FDM 3D printers, 3D pens can be used with different types of FDM filaments [24]. The choice of filament (ABS) and sorbent coating (DVB/Carbon WR/PDMS) for this study was made based on findings from a previous study [22], where it was found that the ABS filament liberated the most VOCs and the DVB/Carbon WR/PDMS sorbent extracted a greater number and wider range of VOCs. The DVB/Carbon WR/PDMS sorbent coating is a bipolar sorbent which extracts analytes through an adsorption mechanism [36]. Four different brands of ABS filament were investigated in this study in an effort to ascertain whether different VOCs are released depending on the filament brand.

Chromatograms demonstrating fiber/Arrow bleed (fiber/Arrow blank), column bleed (column blank), and well as an extraction of background were obtained using a similar procedure to that previously reported [22]. Background extractions for the 3D pen and 3D printing experiments were carried out as described in Section 2.2.2. Chromatograms from these experiments were then compared with chromatograms obtained from the extraction of VOCs during extrusion/printing to identify probable VOC peaks for a particular brand of filament. Peaks absent from the fiber/Arrow blank, column blank and background chromatogram and exhibiting a signal-to-noise ratio of 3 and above were considered as probable VOCs.

3.1 Effect of 3D pen printing parameters on VOC liberation

When extruding with the 3D pen, the only features that can be controlled are the nozzle temperature and extrusion speed. Varying the extrusion speed changes either the mass of filament extruded over a particular period of time or can change the time required to extrude a particular mass of filament. In this study, attempts were made to study the effect of print speed and nozzle temperature on the number and amount of individual VOCs extracted while keeping the mass of extruded filament constant (see Table 1). The ABS filament of Gizmodork brand was used as a control filament for extrusion as it was available in sizes compatible with the 3D pen (1.75 mm) as well as the 3D printer (2.85 mm) while DVB/Carbon WR/PDMS fiber was used for the extraction of liberated VOCs.

3.1.1 Effect of 3D pen nozzle temperature

Nozzle temperature is an important printing parameter which allows for smooth filament extrusion. If the filament is not heated to an adequate temperature, it may lead to either non-uniform extrusion or the material may not be extruded at all from the nozzle. In order to study the effect of nozzle temperature on VOC liberation, extrusion of Gizmodork filament was carried out at 210 °C (manufacturer recommended temperature) and 230 °C (temperature at which printing was carried out using the desktop 3D printer) for 6 minutes (details provided in Section 3.2) at the fast speed setting of the 3D pen. Triplicate extractions were performed using the DVB/Carbon WR/PDMS fiber at each nozzle temperature. A comparison of VOCs and their corresponding peak areas extracted with the SPME fiber for Gizmodork filament at nozzle temperatures of 210 °C and 230 °C is shown in Fig. 1. Fifteen (15) VOCs were detected at a nozzle temperature of 210 °C, while an additional VOC at a retention time of 18.6 min (i.e., total of 16 VOCs) was detected at a nozzle temperature of 230 °C. As depicted in Fig. 1, elevating the nozzle temperature led to an increased amount of liberated VOCs (based on peak areas) where the peak areas increased by 1.3 to 2.2 times.

3.1.2 Effect of printing speed

In this study, the 3D pen was operated under three speed settings (i.e., fast, medium and slow) in order to examine the effect of printing speed on released VOCs at a nozzle temperature of 210 °C. Extrusion was conducted in triplicate for each speed setting. However, extrusion at the slow speed setting proved challenging due to the 3D pen's inability to self-feed the filament with the same force as observed in the fast and medium speed settings, occasionally impeding extrusion from the nozzle. Consequently, manual assistance was required at times to push the filament into the feeder, resulting in variations in the time required to extrude the same mass of filament in each instance. As a result, the extrusion time was reported as an average time of extrusion. Despite the challenge, good reproducibility in peak areas of extracted VOCs were obtained provided that similar masses of filament were extruded. Relative standard deviations of triplicate measurements were in the acceptable range of 1.1% to 15.3% [37]. This challenge was not observed for the medium and fast speed settings, which enabled a fixed extrusion time to be used.

Fig. 2 shows a comparison of VOCs and their corresponding peak areas obtained for extractions using the DVB/Carbon WR/PDMS SPME fiber for Gizmodork filament while extruding at the three different speed settings. The detected VOCs at the three 3D pen speed settings are listed in Table S2. Extrusion rates (grams of filament per minute) at the fast, medium and slow speed settings were 0.74 g/min, 0.56 g/min and 0.07 g/min, respectively, with extrusion times of 6 minutes, 8 minutes, and 62 minutes. As observed in Fig. 2, the number of VOCs detected during extrusion of Gizmodork filament at the fast, medium and slow speed settings were 15, 16 and 20, respectively. Relatively less volatile compounds (VOCs with retention times later than 18.6 minutes) exhibited increased peak areas when the speed was set to slow, whereas relatively volatile compounds showed elevated peak areas at the medium speed setting. These data appear to indicate that slower speeds resulting in longer extrusion times not only produce greater amount of VOCs but also greater numbers of VOCs. Additionally, VOCs liberated in smaller amounts (especially those that were less volatile) may accumulate within the system, thereby permitting their detection by SPME-GC/MS.

3.2 Liberation of VOCs from 3D pen as a function of filament brands

To determine if different VOCs are liberated based on the filament brand, extrusion of four different ABS filaments from different suppliers (e.g., Mynt3D, Amazon Basics, Novamaker and Gizmodork) was carried out using an extrusion time of 6 minutes. The extrusion time was determined based on the time it took one spool of Mynt3D filament to be extruded from the 3D pen using the fast speed setting and nozzle temperature of 210 °C. Unlike FDM filaments used for 3D printers, filaments dedicated to the 3D pen are available as short spools since the

3D pen itself has smaller dimensions compared to 3D printers. The ABS filament provided by the Mynt3D pen manufacturer was 3 m in length, which enabled 6 minutes of filament extrusion. Refill packs of ABS Mynt3D filament were used for subsequent experiments. Amazon Basics, Novamaker, and Gizmodork filaments are often used with 3D printers that are compatible with filaments of 1.75 mm diameter. Since the 3D pen is compatible with any 3D printing filament possessing a diameter of 1.75 mm, the other three filaments were also used. Despite the fact that a greater amount and number of VOCs were liberated at the higher nozzle temperature (230 °C) and slow speed setting, the 3D pen was operated at a nozzle temperature of 210 °C and fast speed setting for this study as these are the manufacturer recommended conditions and are most likely to be employed by users. For each filament, the mass extruded from the 3D pen in 6 minutes was approximately 4.4 g. Extractions were carried out in triplicate using this extrusion time-course for each brand of filament using the SPME fiber and Arrow devices. A representative total ion chromatogram obtained by SPME- GC/MS using the DVB/Carbon WR/PDMS Arrow while extruding the four different brands of filament with the 3D pen is shown in Fig. 3. Table 2 displays all VOC peaks detected for the four brands of ABS filament using both the SPME fiber and Arrow devices upon extruding from the 3D pen under recommended temperature and speed settings. Peaks of VOCs are denoted in the table by their corresponding retention times.

A comparison of VOCs and their corresponding peak areas using the DVB/Carbon WR/PDMS SPME fiber for each filament is shown in Fig. 4a. When extractions were performed with the SPME fiber, a total of 23 VOCs were detected out of which 19, 15, 13 and 9 VOCs were detected for Mynt3D, Gizmodork, Novamaker and Amazon Basics filaments, respectively. As can be observed in Fig. 4a, only 7 VOCs were detected across all brands of filaments while other VOCs were detected and found to be unique to a particular filament brand. The obtained dataset was then subjected to hierarchical cluster analysis where a heatmap was generated, as shown in Fig. 4b, to visually perceive differences between the filaments. Filaments were compared based on the peak areas of corresponding VOCs denoted by their unique retention times. A dendrogram is a result of heatmap analysis and features three different clusters (see Fig. 4b) where the Mynt3D and Amazon Basics filaments reside as two different clusters and Gizmodork and Novamaker filaments reside as one cluster, indicating that Gizmodork and Novamaker filaments liberate similar types of VOCs while the VOCs emitted by Mynt 3D and Amazon Basics filaments differ not only from each other but also from the other two filaments. Colors for the heatmap cells convey information about the samples (filaments) wherein cells of a darker yellow color indicate the highest peak area for a specific VOC, while darker blue colors signify the absence of a particular VOC for a specific brand of filament [22,38]. Fig. S2a shows a comparison of probable VOCs and their corresponding peak areas when extractions were carried out with each filament using the DVB/Carbon WR/PDMS Arrow. A total of 26 VOCs were detected, out of which 20, 19, 14 and 9 VOCs were detected for the Mynt3D, Gizmodork, Novamaker and Amazon Basics filaments, respectively. A similar heatmap was generated, as shown in Fig. S2b, and similar clusters to those observed with the fiber were obtained.

Using the SPME fiber and Arrow devices, the Amazon Basics filament was observed to liberate the fewest number of VOCs while the Mynt3D filament liberated the highest. Out of all detected VOCs, nine were identified by direct injection of their standards followed by matching of their retention times and corresponding mass spectra. The identified compounds were found to be toluene at a retention time of 6.8 min, ethylbenzene at 9.4 min, p-xylene at

9.6 min, styrene at 10.1 min, cumene at 10.9 min, benzaldehyde at 11.7 min, alpha-methyl styrene at 12.1 min, acetophenone at 13.7 min, and benzenemethanol, α-α-dimethyl at 14.0 min (see Fig. S3). Of the nine identified VOCs, four of them (styrene, ethylbenzene, cumene and benzaldehyde) were detected in all ABS filament brands. The International Agency for Research on Cancer (IARC) has classified ethylbenzene and cumene under Group 2B (possibly carcinogenic to humans) and styrene under Group 2A (probably carcinogenic to humans) [16,39]. As observed in Fig. 4a, 4b, S2a and S2b, the four commonly identified VOCs were liberated in greatest amounts by the Mynt3D filament (based on peak areas in Fig. 4a and S2a and by darker yellow cells in Fig. 4b and S2b) while the Amazon Basics filament liberated the smallest amount. Nine other VOCs were tentatively identified and are shown in Table 3. Table 3 lists all detected VOCs with their retention times, calculated RI values, reported RI values, and their names (for the identified VOCs). A total ion chromatogram obtained by injecting alkane standards ranging from C7 to C24 is shown in Fig. S4.

3.3 Comparison of SPME geometry based on detected VOCs

VOCs detected using the DVB/Carbon WR/ PDMS fiber and Arrow devices during extrusion with the 3D pen at a nozzle temperature of 210 °C under fast speed settings were compared based on their peak areas, as shown in Fig. 5. For most of the VOCs, the enhancement in peak area using the SPME Arrow was in the range of 1.4 to 4.1 times that of the SPME fiber. This is likely attributed to the greater phase volume, phase area and phase length of SPME Arrow compared to the fiber geometry [29]. Since the DVB/Carbon WR/PDMS coating is an adsorbent-type sorbent, SPME Arrow provides higher surface area for VOC adsorption. A total of 23 and 26 VOCs were detected when extracting with the SPME fiber and Arrow, respectively, as shown in Table 2. Three VOCs at retention times of 14.8 min, 18.6 min, and 20.2 min were detected only when using the Arrow geometry. The SPME Arrow is more effective in extraction of released VOCs as it can extract a greater amount of analyte compared to the fiber within the same extraction time [29,40] making it a more fitting choice for extractions, particularly those conducted over shorter durations of time.

3.4 Comparison of filament extrusion for 3D pen and 3D printer based on detected VOCs

In order to compare the 3D pen with an Ultimaker S3 desktop printer, the 3D pen was placed on the build plate of the 3D printer so that the pen would be enclosed within the same volume and the overall set-up would be similar for both processes. To enable a comparison, two experimental conditions were employed. Firstly, conditions of the 3D pen operated at the manufacturer's suggested nozzle temperature (210 °C) and speed setting (fast) were employed, while the 3D printer adhered to settings recommended by the Ultimaker Cura software (see Table S1). In the second condition, similar printing parameters for both the 3D pen and 3D printer were employed, as shown in Table S1. Gizmodork filament was used for extrusion/printing while the DVB/Carbon WR/PDMS Arrow was employed for the extraction of VOCs.

3.4.1 Comparison of 3D pen with 3D printer under recommended conditions

Fig. 6 shows a comparison of VOCs detected when extruding Gizmodork filament with the 3D pen as well as printing with the 3D printer under the recommended conditions. The mass of filament extruded, mass of objects printed, and time of extrusion/printing are provided in Table S1. Extrusion by 3D pen was carried out for 6 minutes while printing with the 3D printer was carried out for 90 minutes in order to obtain the same mass of object for both approaches. A total of 19 and 15 VOCs were detected while extruding from the 3D pen and while printing with the 3D printer, respectively, as shown in Table S3. As observed in Fig. 6, only 10 VOCs were common for both processes and included ethylbenzene, styrene, cumene, benzaldehyde, alpha-methylstyrene, acetophenone, benzenemethanol, α-α-dimethyl, longifolene, and other VOCs at retention times of 19.0 min and 19.4 min. While extrusion from the 3D pen was performed at very short time intervals (6 minutes) compared to the 90 min printing time with the 3D printer, higher peak areas were obtained for those commonly detected VOCs (except for benzaldehyde) during extrusion from the 3D pen. The peak areas for ethylbenzene and cumene (possible human carcinogen) were 5.9 times and 1.8 times higher, respectively, and for styrene (probable human carcinogen) was 2.7 times higher. Similarly for other commonly detected VOCs, the increase in peak area was in the range of 1.4 times to 25.6 times. Chromatographic peaks ranging from 6.8 min (RI=768) to 25.5 min (RI= 1774) were detected as VOCs originating from the 3D pen, while the 3D printer liberated VOCs ranging from 9.4 min (RI=867) min to 30.0 min (RI=2047). These data indicate that 3D pen extrusion for shorter periods of time results in the detection of very volatile VOCs while relatively less volatile compounds could also be detected upon liberation with the 3D printer. This could be due to the possibility that less volatile compounds may accumulate within the 3D printer over extended printing periods (due to its slower extrusion speed), enabling the Arrow to extract them at detectable levels. Thus, a greater number and amount of VOCs were found to be liberated while extruding from the 3D pen compared to the 3D printer under recommended conditions.

3.4.2 Comparison of VOC liberation for 3D pen and 3D printer upon employing similar printing parameters

In order to perform a side-by-side comparison between the 3D pen and 3D printer, similar conditions were employed. The nozzle temperature, speed and mass of extruded filament were kept similar for the 3D pen and 3D printer, as shown in Table S1. A comparison of VOCs detected upon extruding Gizmodork filament with the 3D pen and printing with the 3D printer using the SPME Arrow is shown in Fig. S5. Using settings listed in Table S1, extrusion was performed for an average time of 65 minutes for the 3D pen while 69 minutes was employed for the 3D printer. Employing the DVB/Carbon WR/PDMS Arrow, a total of 29 and 17 VOCs were detected during extrusion from the 3D pen and 3D printer, respectively, as shown in Table S4. Out of these detected VOCs, 14 VOCs were commonly detected for both processes and included ethylbenzene, p-xylene, styrene, cumene, isocumene, benzaldehyde, alpha-methylstyrene, benzeneacetaldehyde, acetophenone, benzenemethanol, α-α-dimethyl, longifolene and other VOCs at retention times of 19.0 min, 19.4 min and 25.4 min. For all commonly detected VOCs, the obtained peak areas were higher when extractions were carried out while extruding from the 3D pen compared to the 3D printer. The peak areas for ethylbenzene, styrene, and cumene were found to be 8.2 times, 4.4 times and 5.4 times higher, respectively. In the case of other commonly detected VOCs, the peak areas were 1.7 times to 62.6 times higher.

The aforementioned comparisons demonstrated that the 3D pen liberates a greater number and amount of VOCs than the 3D printer when operated with similar printing parameters. The disparities between 3D pen and 3D printer in terms of number and amount of detected VOCs were found to be significantly more pronounced when comparing the 3D pen and printer under similar conditions (using similar printing parameters) than when they were compared under the recommended conditions. This disparity is likely attributed to the slower speed inherent in similar conditions, resulting in prolonged extrusion times for the 3D pen. Given that the VOCs generated by the 3D pen are likely to be in the breathing zone of users, caution should be exercised during its use. Ensuring adequate ventilation in the room or opting for filaments that produce fewer and less harmful VOCs is essential. Additionally, the use of high-quality masks can be considered as a preventive measure against inhaling the emitted fumes.

4. Conclusions

The DVB/Carbon WR/PDMS sorbent in both SPME fiber and Arrow geometries was used in this study to extract VOCs released during the extrusion of ABS filament from a 3D pen. The results indicated that SPME Arrow extracted a greater number and amount of VOCs compared to SPME fiber making it a more fitting choice for extractions conducted over shorter periods of time. When examining the 3D pen, four different brands of ABS filaments were investigated. The results revealed that Mynt 3D filament emitted the highest number and amount of VOCs, while Amazon Basics exhibited the lowest levels. Heatmap analysis allowed for the differentiation of the ABS filament brands based on the released VOCs, indicating that the amount as well as types of VOCs vary depending on the filament brands. Upon comparing the 3D pen to a desktop 3D printer, it was observed that the 3D pen released a greater number and amount of VOCs than the 3D printer using the recommended printing conditions as well as similar printing parameters. A total of 37 VOCs were detected in this study, with nine identified using standards and another nine being tentatively identified. Compounds with potential carcinogenicity, such as styrene, ethylbenzene, and cumene, were liberated by all filament brands. Precautions such as prioritizing well-ventilated spaces, considering high-quality masks, and opting for filaments that liberate small amounts of VOCs are advised to minimize inhaling liberated VOCs.

While the SPME approach shows potential as a sampling tool for qualitatively assessing released VOCs during filament printing/extrusion, challenges arise in the quantitative determination of these VOCs. Future efforts will focus on refining the system for better control and confinement as well as enabling accurate quantification for users exposed to VOCs. Furthermore, future investigations will involve testing additional filaments with the aim of identifying those that emit low levels of VOCs.

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Credit Authorization Statement

Bhawana Thapa: Methodology, Investigation, Visualization, Writing original draft, Literature review. **David Bell:** Conceptualization, Supervision, Investigation, Writing-review and editing. **Jared L. Anderson:** Conceptualization, Supervision, Writing-review and editing, Project administration, Funding acquisition.

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Table 1a. Mass of filament extruded and rate of extrusion for the Gizmodork filament from the 3D pen at nozzle temperatures of 210 °C and 230 °C using the fast speed setting of the 3D pen.

Nozzle temperature (°C)	Mass extruded (g)	Rate of extrusion (g/min)
210 °C	4.4742	0.75
230 °C	4.5704	0.76

[a] = average of three extrusions

Table 1b. Mass of filament extruded and rate of extrusion of Gizmodork filament from the 3D pen using fast, medium and slow speed settings using with a nozzle temperature of 210 °C.

Speed setting	Mass extruded (g)	Extrusion time (min)	Rate of extrusion (g/min)
Fast	4.4742	6	0.75
Medium	4.5572	8	0.56
Slow	4.5177	62	0.07

[a] = average of three extrusion

Table 2. Probable VOC peaks detected for the Mynt3D (M), Gizmodork (G), Novamaker (N) and Amazon Basics (AB) filaments upon extraction with the DVB/Carbon WR/PDMS SPME fiber and Arrow using a 6 minute extrusion from the 3D pen. Peaks are denoted by their retention times and, when applicable, their corresponding names for identified compounds. The detected peaks are marked with the symbol "X".

Peaks	RT (min)	Identified compounds	SPME Arrow				SPME fiber			
			M	G	N	AB	M	G	N	AB
1	6.8	Toluene		X	X			X	X	
2	8.7	Cyclohexene, 4-vinyl-		X				X		
3	9.4	Ethylbenzene	X	X	X	X	X	X	X	X
4	9.6	P-xylene	X	X			X			
5	10.1	Styrene	X	X	X	X	X	X	X	X
6	10.9	Cumene	X	X	X	X	X	X	X	X
7	11.5	Isocumene	X		X	X	X		X	X
8	11.7	Benzaldehyde	X	X	X	X	X	X	X	X
9	12.1	Alpha-methylstyrene	X	X	X		X	X		
10	12.7	Benzene, (1-methylpropyl)	X				X			
11	12.8	4-Cyanocyclohexene	X				X			
12	13.0		X				X			
13	13.3	Benzeneacetaldehyde		X					X	
14	13.7	Acetophenone	X	X	X		X	X	X	
15	14.0	Benzenemethanol, α-α-dimethyl	X	X	X		X	X	X	
16	14.8					X				
17	15.3					X				X
18	17.9	4-Phenylcyclohexene	X				X			
19	18.6	Longicyclene	X	X						
20	19.0		X	X			X	X		
21	19.1	Longifolene	X	X	X		X	X		
22	19.4		X	X	X	X	X	X	X	X
23	19.9		X	X	X	X	X	X	X	X
24	20.2			X						
25	24.2	Trans-1, 2-Diphenylcyclobutane	X	X	X		X	X	X	
26	25.5		X	X	X		X	X	X	X

Table 3. Detected VOCs with their retention times (RT), calculated retention indices (RI), match factors and reported RI values (in case of tentatively identified compounds) and names of the identified compounds.

No.	RT (min)	Compound	Match factor	RI calculated ($RI_{calc.}$)	RI reported ($RI_{rep.}$)	$RI_{calc.} - RI_{rep.}$
1	**6.8**	**Toluene***	**940**	**768**	**762**	**6**
2	**8.7**	**Cyclohexene, 4-vinyl-**	**896 (RM)**	**840**	**838**	**1**
3	**9.4**	**Ethylbenzene***	**962**	**867**	**858**	**9**
4	**9.6**	**P-xylene***	**893**	**875**	**870**	**5**
5	**10.1**	**Styrene***	**978**	**894**	**898**	**4**
6	**10.9**	**Cumene***	**874**	**931**	**929**	**2**
7	**11.5**	**Isocumene**	**852**	**959**	**950**	**9**
8	**11.7**	**Benzaldehyde***	**914**	**969**	**962**	**7**
9	**12.1**	**Alpha-methylstyrene***	**921**	**988**	**988**	**0**
10	**12.7**	**Benzene, (1-methylpropyl)**	**805**	**1019**	**1006**	**12**
11	**12.8**	**4-Cyanocyclohexene**	**843**	**1024**	**1008**	**16**
12	**13.0**			**1035**		
13	**13.3**	**Benzeneacetaldehyde**	**935**	**1052**	**1046**	**6**
14	**13.7**	**Acetophenone***	**899**	**1074**	**1086**	**12**
15	**14.0**	**Benzenemethanol, α-α-dimethyl***	**927**	**1090**	**1080**	**10**
16	**14.8**			**1139**		
17	**15.3**			**1170**		
18	**15.9**			**1208**		
19	**17.6**			**1325**		
20	**17.9**	**4-Phenylcyclohexene**	**858**	**1346**	**1345**	**1**
21	**18.1**			**1361**		
22	**18.2**			**1368**		
23	**18.6**	**Longicyclene**	**885**	**1349**	**1374**	**25**
24	**18.8**	**Isolongifolene**	**879**	**1412**	**1391.1**	**21**
25	**19.0**			**1427**		
26	**19.1**	**Longifolene**	**901**	**1434**	**1413**	**21**
27	**19.4**			**1456**		
28	**19.9**			**1442**		
29	**20.2**			**1513**		
30	**20.9**	**α R-Himachalene**	**826**	**1555**	**1542**	**14**
31	**21.7**			**1603**		
32	**24.2**	**Trans-1, 2-Diphenylcyclobutane**	**868**	**1718**	**1720**	**2**
33	**25.5**			**1774**		
34	**25.9**			**1791**		
35	**28.2**			**1920**		

36	**29.6**			**2016**		
37	**30.0**			**2047**		

*Compounds identified by directly injecting standards.

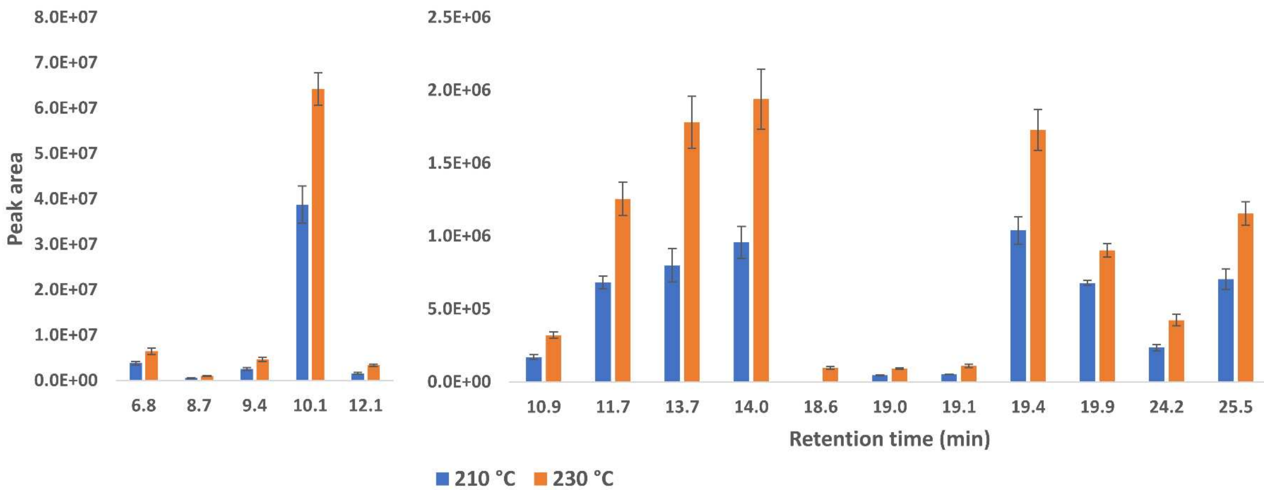
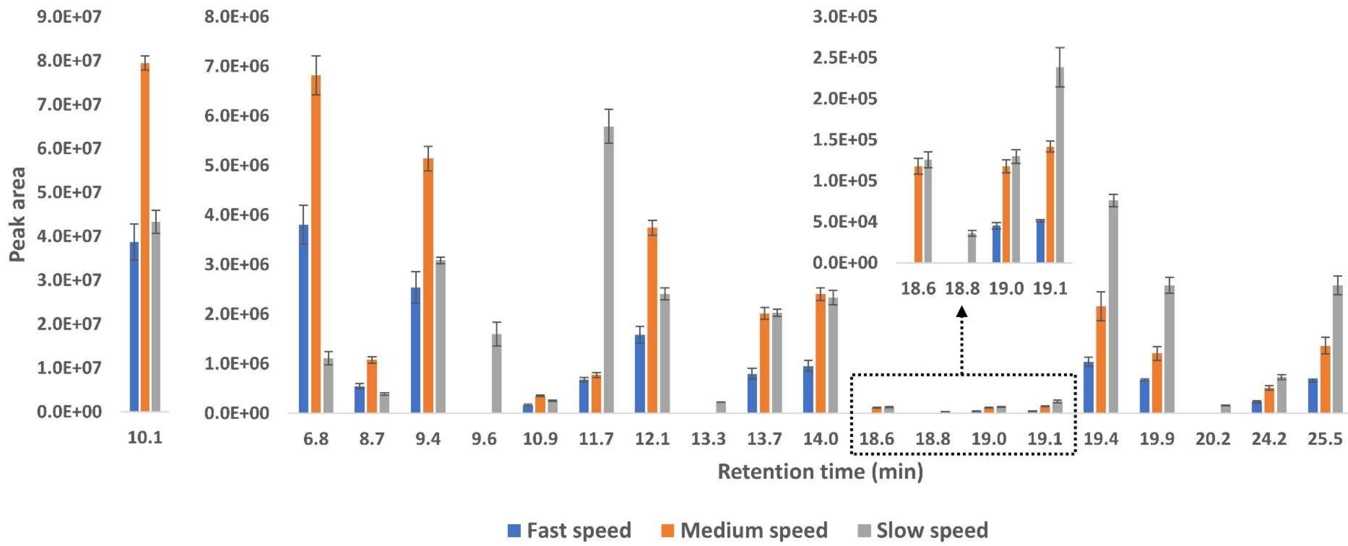


Fig. 1. Peak areas of detected VOCs upon extrusion of Gizmodork filament from the 3D pen at nozzle temperatures of 210 °C and 230 °C using the fastest speed setting. Extractions were carried out in triplicate for each fiber using the DVB/Carbon WR/PDMS fiber.



641 **Fig. 2.** Bar graph showing a peak area comparison of detected VOCs upon extrusion of Gizmodork filament from the 3D pen at fast, medium and slow speeds at a nozzle temperature of 210 °C. Extractions were performed in triplicate for each fiber using DVB/ Carbon WR/PDMS fiber.

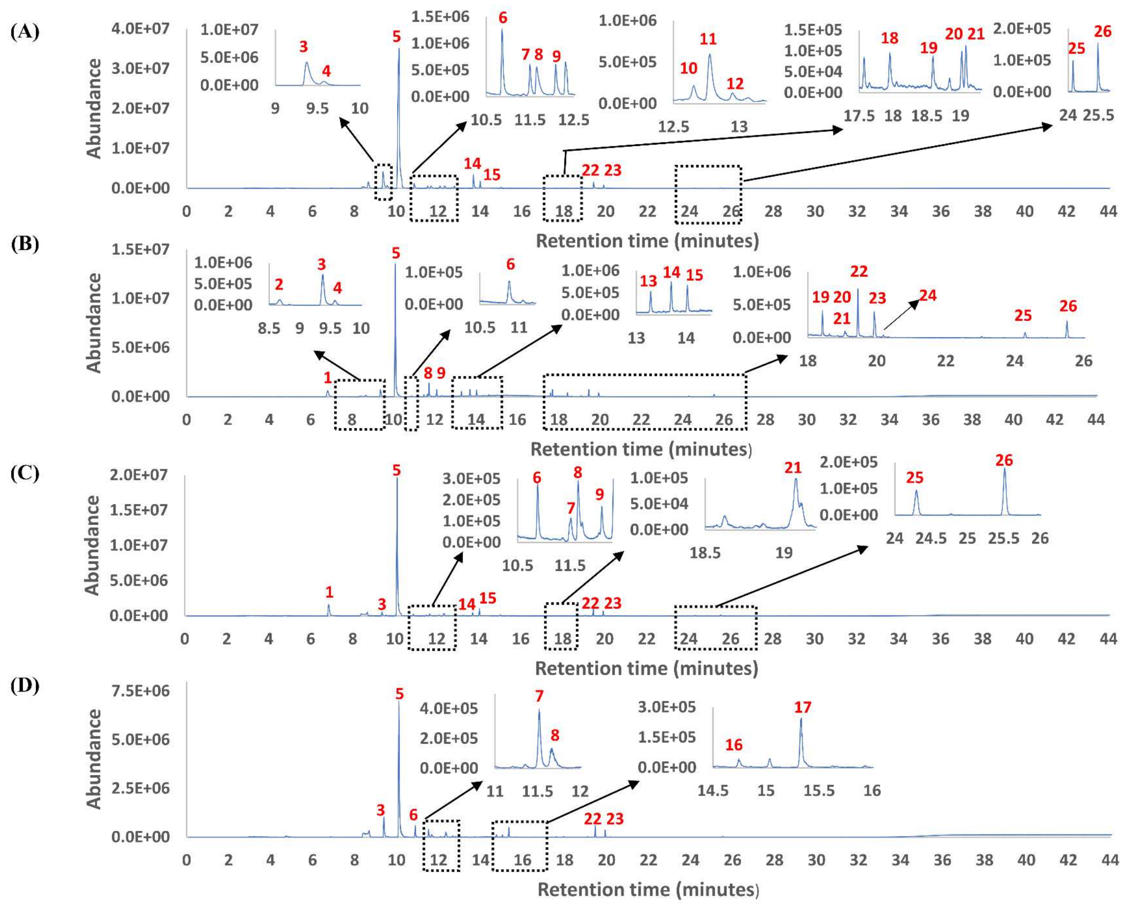


Fig. 3. Total ion chromatograms obtained by SPME- GC/MS using the DVB/Carbon WR/PDMS Arrow while extruding the (A) Mynt3D, (B) Gizmodork, (C) Novamaker and, (D) Amazon Basics ABS filaments from 3D pen. The detected VOCs are denoted by their corresponding peak number, as shown in Table 2. Extrusions were carried out at nozzle temperature of 210 °C using the fastest speed setting of the 3D pen. Note: Y-axes are not set to the same scale for better visualization of peaks in all chromatograms.

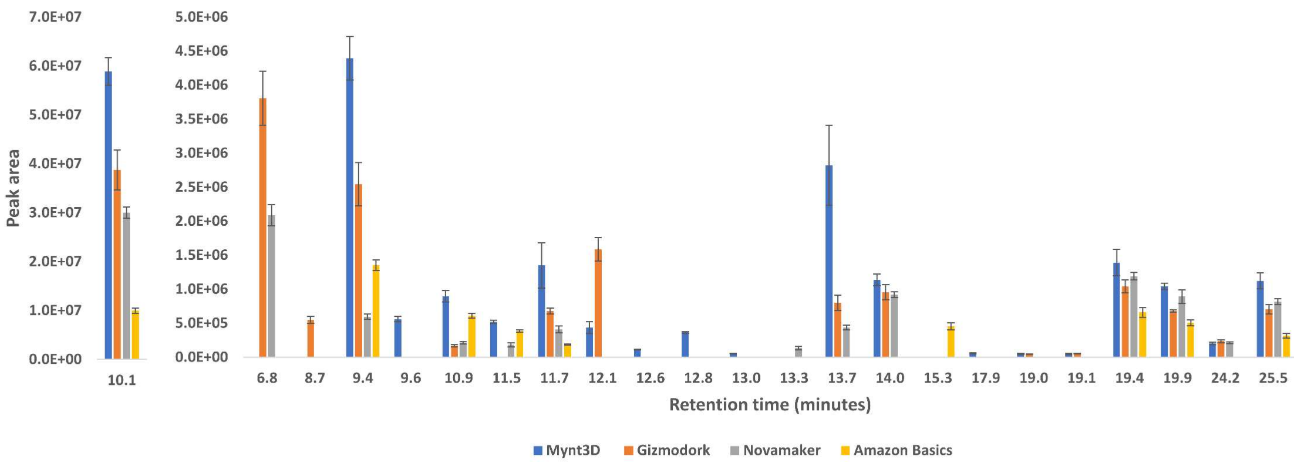


Fig. 4a. Bar graph comparing peak areas of VOCs detected upon extraction using DVB/Carbon WR/PDMS fiber while extruding the Mynt3D, Gizmodork, Novamaker and Amazon Basics ABS filaments.

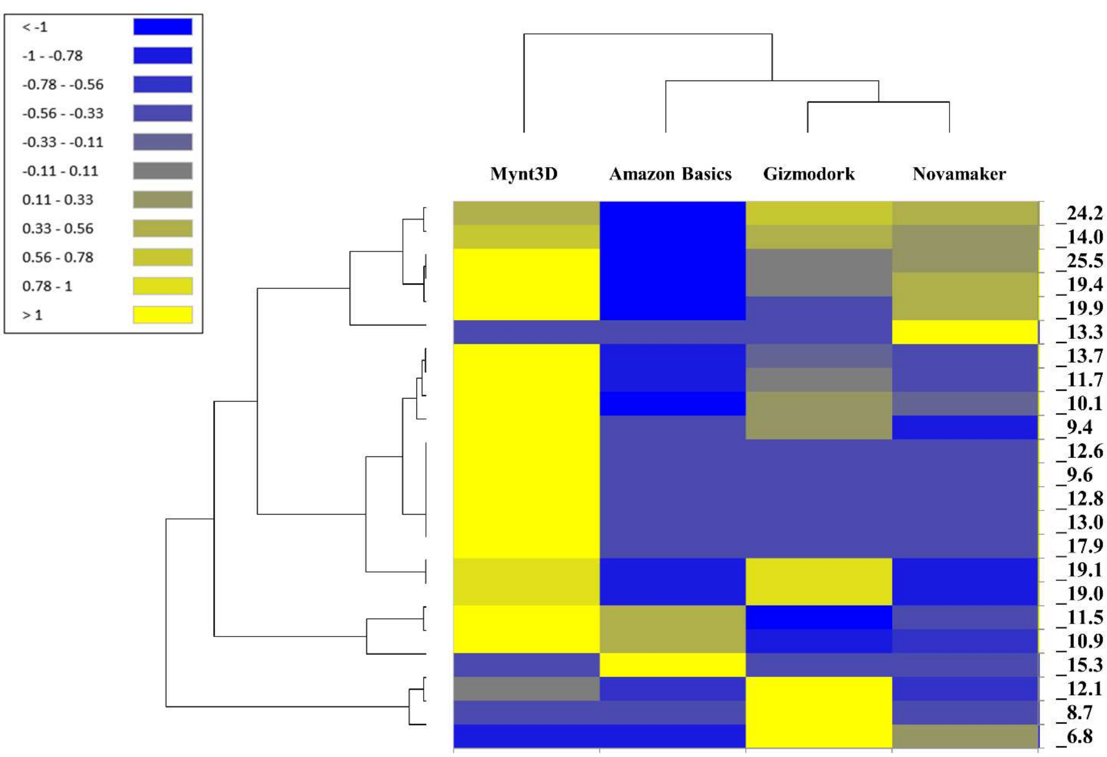


Fig. 4b. Heatmap showing a comparison of the four different brands of ABS filaments upon extraction of VOCs using the DVB/Carbon WR/PDMS fiber.

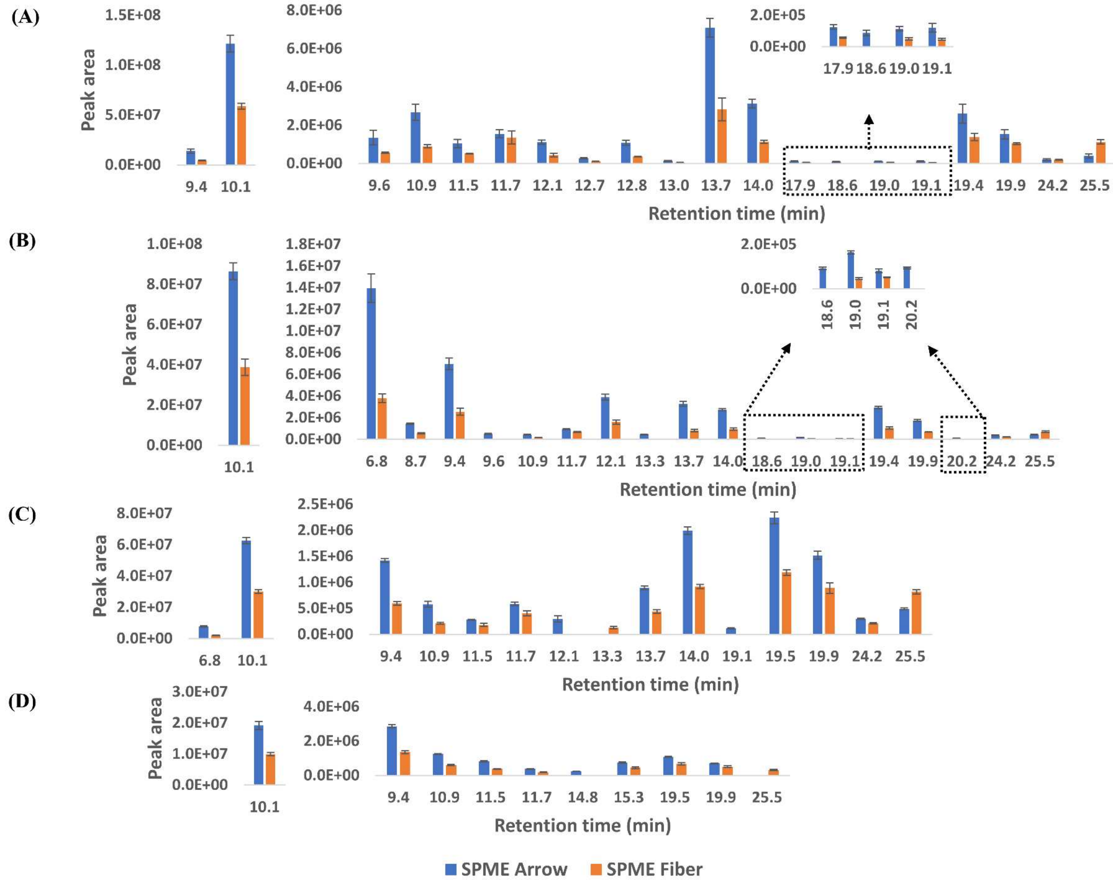


Fig. 5. Comparison of traditional SPME fiber with SPME Arrow based on the peak areas of detected VOCs upon extruding (A) Mynt3D, (B) Gizmodork, (C) Novamaker and (D) Amazon Basics ABS filaments from the 3D pen.

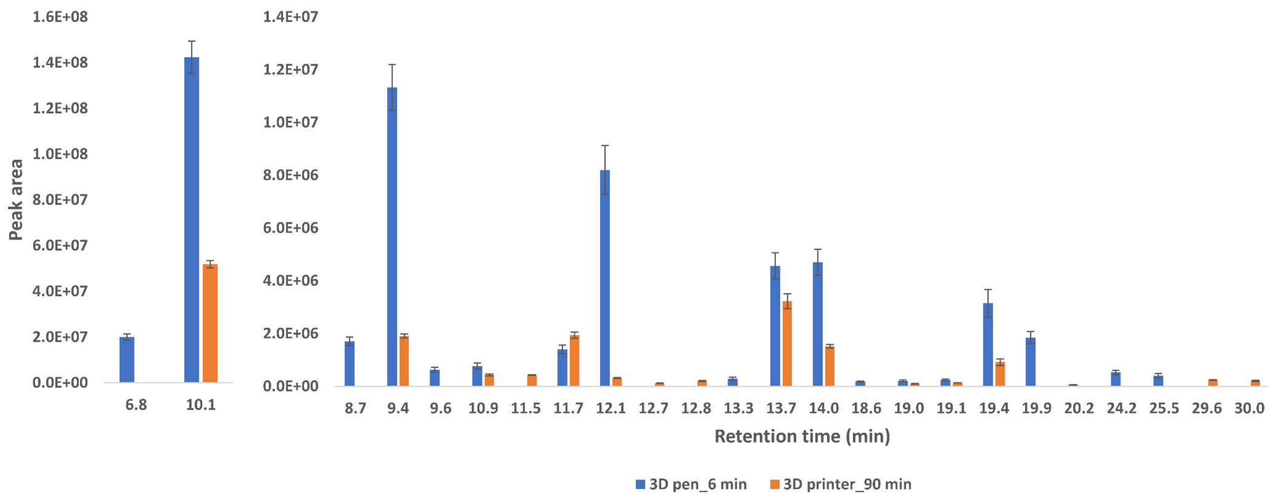


Fig. 6. Comparison of VOCs detected upon extruding Gizmodork filament with 3D pen and 3D printer under recommended conditions. Extractions were carried out in triplicate with the DVB/Carbon WR/PDMS Arrow.