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Real-time monitoring of volatiles and particles emitted from thermoplastic filaments during 3D printing

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Abstract: The proliferation of consumer-grade three-dimensional (3D) printers using fused deposition, also known as fused filament fabrication, has given rise to concerns over the exposure of users to potentially harmful substances. Thermoplastic filaments made of different polymers are extruded through a heated printer nozzle and deposited layer by layer on a build platform to form the printed object. This process leads to the emission of both particles and gases, in particular volatile organic compounds (VOCs). While the emission of airborne particulate matter during 3D-printing has been relatively well researched [1], this is not the case with the monitoring of the associated emission of VOCs, and so we are far from understanding the emission profile of 3D-printers as a whole. The main reason for that is the difficulty with sampling the emitted volatiles with sufficient time resolution to investigate e.g. the effect of rapid heating of the nozzle, and so the available data mostly describes either the total emission of particular VOCs during printing, or the time-resolved emission of total VOCs, without the determination of particular compounds [2,3]. In order to bridge this gap, we have previously demonstrated that proton transfer reaction mass spectrometry (PTR-MS) can be used to monitor the emission of volatiles during 3D-printing in real-time, both qualitatively and quantitatively [4]. Here, we propose to combine this approach with the concurrent real-time measurement of the corresponding emission of particles to obtain a more detailed understanding of the profile of pollutants generated during 3D-printing and the factors which determine this process.

1. Materials and methods

1.1 3D printer.

A commercial, consumer-grade FDM 3D printer (Prusa i3 MK2S, Prusa Research a.s., Prague, Czech Republic) was used in the study. The printer was equipped with a 0.4 mm nozzle and housed in an enclosure with a total volume of 130 dm^3. The air within the enclosure was mixed using three 120 mm fans. Four different filaments were used for the printing, namely polyethylene terephthalate glycol (PETG), polylactic acid (PLA) Ecoline (standard) (Print-Me, Gorzów Wielkopolski, Poland), PLA Premium, and acrylonitrile butadiene styrene (ABS) (Nebula Filaments, Stare Bystre, Poland). All four filaments were of the “natural” type, i.e. without added pigments or colourants. The test print was a 10 mm cube with rounded corners, with 3 top, bottom and wall layers, and 30% infill. The size of the cube was adjusted to obtain a printing time of approx. 5 min. The print speed was set to 40 mm/s, travel speed to 100 mm/s, and layer thickness to 0.2 mm. The nozzle and build plate temperature was set to 235°C in the case of PETG and ABS, and 220°C in the case of PLA, while the build platform temperature was set to 60°C. The model was sliced using Cura v.3.2.1 (Ultimaker, Utrecht, Netherlands). The volatiles emitted during printing were sampled into the PTR-MS via a capillary enclosed in a transfer line heated to 70°C at 100 cm^3 min^{-1}. In order to condition the capillaries prior to each measurement they were flushed with tetrahydrofuran in the case of PLA and PETG, and with acetone in the case of ABS, and incubated at 90°C for at least an hour. The particulates were sampled into the CPC (condensation particle counter) at 600 cm^3 min^{-1} via a short segment of dedicated conductive tubing. A schematic representation of the experimental setup is shown in Fig.1. The prints with each filament type and the corresponding measurements were carried out in quadruplicate in an air-conditioned laboratory with the ambient temperature kept at 20°C. The enclosure was opened and purged with clean air after each measurement until a baseline concentration of VOCs and particulates was reached, and the printer nozzle and build platform reached the starting temperature. A background measurement during which the 3D printer was operated without a filament was carried out before each round of four prints and subtracted from the results of measurements for each filament.

1.2 Proton transfer reaction mass spectrometry.

The changes in the composition of the atmosphere within the enclosure during 3D-printing with various polymer filaments were monitored using the PTR TOF 1000 Ultra (IoniconGmbH, Innsbruck, Austria) PTR-MS coupled with a time-of-flight detector. The voltage in the drift chamber was set to 610 V which translated to the E/N value of 120 Td (E/N is the field strength of the PTR drift tube, 1 Td = 10^{-17} V cm^2 molecule^{-1}). The concentration of the monitored volatiles was determined based on the kinetics of the proton transfer reaction with the hydronium ion and the k reaction rate of 2×10^{-9} cm^3 s^{-1}, corrected for the isotopic abundances [5]. The mass spectra were recorded throughout each measurement in 1 s increments using IoniTOF v. 3.0.76 and processed using PTR-MS Viewer v. 3.3.9.1 (IoniconGmbH, Innsbruck, Austria). The principle of operation of proton transfer mass spectrometry is discussed in more detail by Ellis and Mayhew [6].

1.3 Particle count.

The emission of particulates larger than 2 nm during 3D-printing was monitored using the Versatile Water-based Condensation Particle Counter model 3789 (TSI, Shoreview, Minnesota, USA) with critical orifice pressure of 56 kPa, and aerosol nozzle pressure of 3.9 kPa. The number concentration of particulates was averaged every second throughout the experiment and recorded using Aerosol Instrument Manager v. 2.3.0 (TSI, Shoreview, Minnesota, USA).

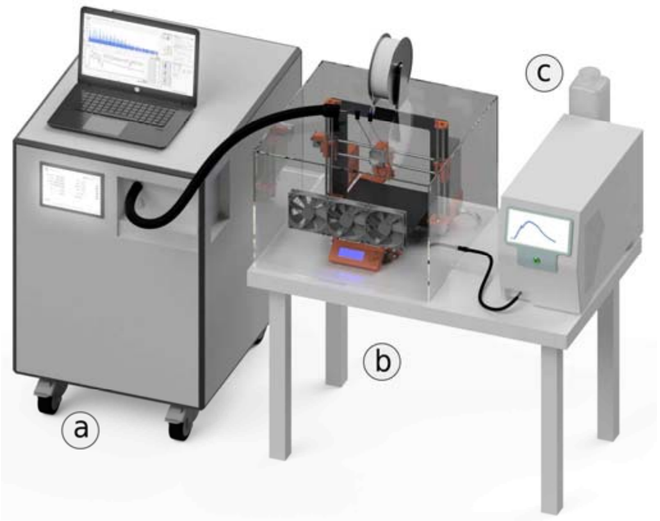

Figure 1. (previous page) The experimental setup consisting of a PTR-TOF-MS device with a heated transfer line (a), a chamber fitted with fans to facilitate air mixing within, enclosing an FDM 3D-printer (b), and a CPC (c).

2. Results and discussion

The main VOCs monitored in experiments with each of the four filaments were selected based on a 5 ppmv threshold. These were acetaldehyde (a product of secondary reactions of the most reactive VOCs, e.g. alkenes and dienes [7]) and the main products of thermal degradation of each polymer, i.e. lactide ($C_6H_8O_4H^+$, m/z=145 Th) and styrene ($C_8H_8H^+$, m/z=105 Th) in the case of PLA and ABS, respectively [8–10], and HC_2O^+ (m/z=42 Th), the product of dehydration of glyoxylic acid hydrate in the drift tube of PTR-MS, itself product of PETG degradation [11,12]. The changes in the relative concentration (after baseline correction) of the monitored VOCs and the corresponding concentration of particulates throughout printing are shown in Fig.2. It can be seen that the emission of main volatiles is not closely correlated with the overall emission of aerosol >2 nm. The concentration of VOCs increases steadily as the nozzle reaches the operating temperature and further during the printing until the printed object is completed due to the thermal degradation of the polymer matrices of the filaments. In the case of particulates, especially when printing using PETG and ABS, there is a sharp concentration increase as the nozzle temperature reaches the threshold value and a relatively large section of the filament within it is melted without the extruder motor yet activated, that is without the filament being continuously passed through the nozzle. When the printing starts and only a short segment of the filament is being melted in the nozzle at any given time the number concentration within the enclosure decreases, only to rise steadily throughout the printing as the particulates accumulate within it. This confirms the earlier reports that the heating process is the main contributor to the emission of particles, as opposed to the printing itself [13]. The higher and less uniform emission of particles when printing with “premium” PLA compared to printing with the less expensive product, and the corresponding lower emission rate of the main VOC, i.e. lactide (see Fig.2. and Tab.1.), is likely because the “premium” filament contains a larger proportion of additives such as plasticizers and flame retardants intended to improve the quality of the print [14].

Table 1. Average emission of particulates and selected volatiles during 3D-printing with four different polymer filaments per gram of filament used.

Filament	Acetaldehyde emission [cm^3 g^{-1}]	Main VOC* emission [cm^3 g^{-1}]	Particulates emission [10^{10} # g^{-1}]
PETG	60 ± 20	36 ± 11	19.8 ± 3.6
PLA Ecoline	32 ± 10	14.4 ± 5.6	5.2 ± 1.4
PLA Premium	24.3 ± 8.2	8.4 ± 3.7	13.1 ± 1.9
ABS	40 ± 14	59 ± 12	17.45 ± 0.60

* main VOCs: HC_2O^+, $C_4H_8O_4H^+$, and $C_8H_8H^+$ for PETG, PLA, and ABS, respectively.

Since the particles generated during 3D printing are a mixture of solids and liquids, the latter possibly formed by semi-volatile organic compounds (SVOCs) [15], and also of volatiles, it is necessary to use a variety of analytical techniques to comprehensively assess the potential exposure associated with 3D-printing. While the differences in overall emissions of both particulates and volatiles between different filament materials are significant and correlated, the same cannot be said about the relationship between the emission of particular VOCs and the corresponding total emission of particles. In order to investigate the dynamic changes in the emission rates during 3D-printing in more detail, it might be necessary to include another dimension in the analysis, i.e. the size of the measured particles, e.g. by combining CPC with an electrostatic classifier. This could reveal the relationship between the temporally-resolved composition of the aerosol within the printer enclosure with the corresponding concentration of VOCs determined in real-time using the PTR-MS. The proposed approach is a step towards obtaining a comprehensive emission profile of 3D-printers which could help to better understand the risk of exposure associated with using this technology and the relationship between the composition of the thermoplastic filaments and the emission of both volatiles and particulates.

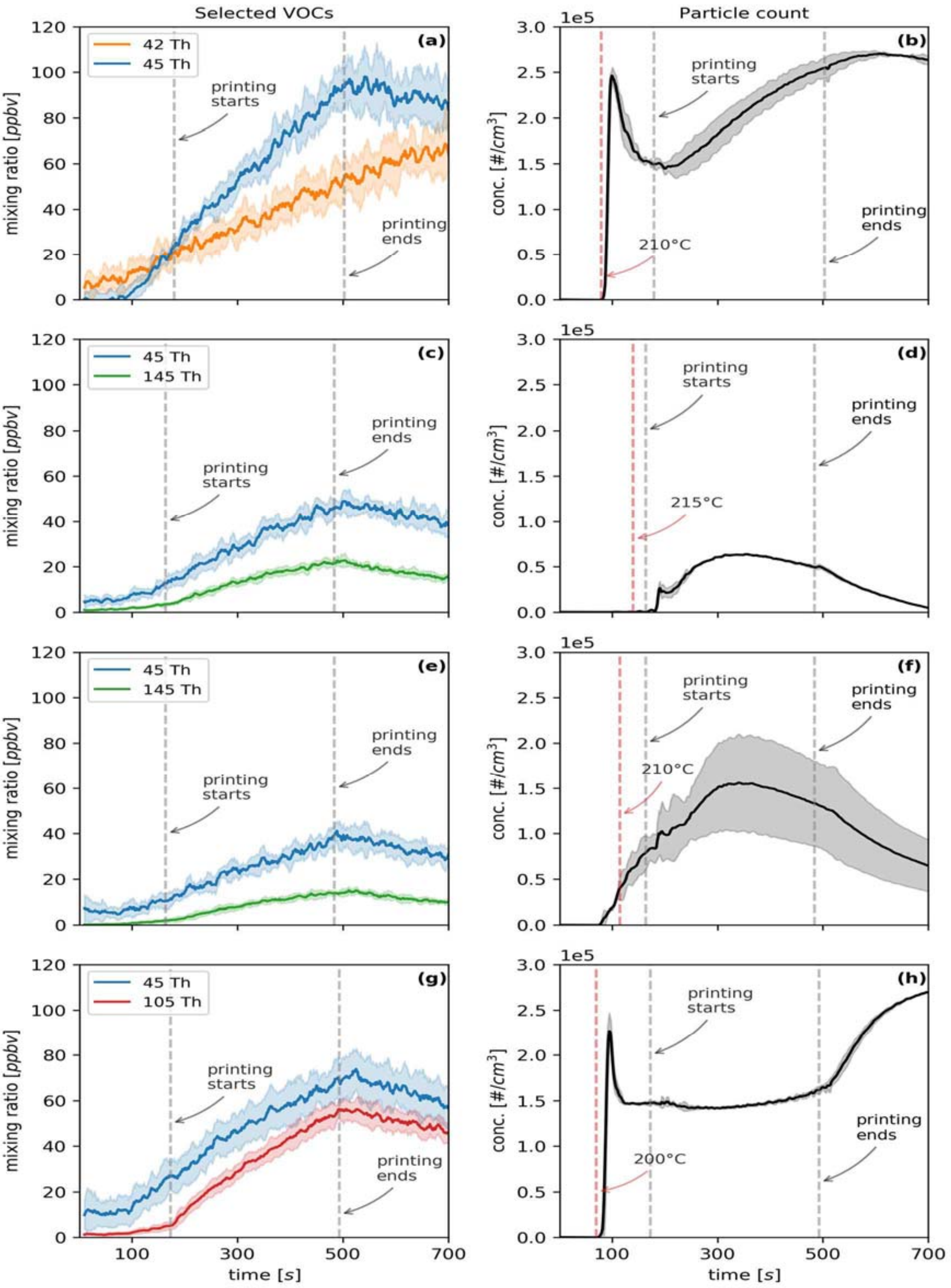

Figure 2. (previous page) Changes of the relative concentration (mixing ratio) ± SD of selected VOCs (protonated pseudo-molecular ion, MH^+) of PET-G (a), PLA Ecoline (c), PLA Premium (e), and ABS, and the corresponding changes of the concentration of particulates (b, d, f, h, respectively) within an enclosure during FDM 3D-printing.

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