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ORIGINAL RESEARCH ARTICLE

Quantitative Chromatographic Analysis of Volatile Compounds Released during Polymer FDM-AM

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ABSTRACT

The release of volatile organic compounds (VOCs) during fused deposition modeling additive manufacturing (FDM-AM) has become a critical concern due to its implications for occupational health, indoor air quality, and material performance. In this study, a quantitative chromatographic analysis was conducted to characterize and evaluate VOC emissions from commonly used thermoplastic filaments during FDM-AM. Gas chromatography coupled with mass spectrometry (GC–MS) was employed to separate and identify volatile fractions, while flame ionization detection (FID) provided quantitative assessment of emission concentrations. Representative results revealed the presence of styrene, ethylbenzene, formaldehyde, acetaldehyde, and other low-molecular-weight aldehydes and ketones, with emission profiles varying significantly across polymer types such as ABS, PLA, and PETG. Peak intensities correlated strongly with extrusion temperature, suggesting that process parameters directly influence VOC release. Comparative analysis indicated that ABS exhibited the highest emission intensity, dominated by aromatic hydrocarbons, while PLA produced lower total VOCs but higher proportions of lactide-derived species. The findings underscore the necessity of systematic monitoring of VOCs in FDM-AM environments and provide quantitative evidence for optimizing process conditions and implementing adequate ventilation systems. This work establishes a framework for linking chromatographic signatures of volatile compounds with material choice and processing parameters, contributing to safer and more sustainable additive manufacturing practices.

Keywords: Volatile organic compounds (VOCs); Fused deposition modeling (FDM); Additive manufacturing (AM) ; Gas chromatography–mass spectrometry (GC–MS); Polymer emissions; Occupational safety; Indoor air quality; Process parameter optimization

1. Introduction

Additive manufacturing (AM), widely recognized as a transformative technology of the Fourth Industrial Revolution, has revolutionized the design-to-production cycle by enabling rapid prototyping, mass customization, and the fabrication of geometrically complex components with reduced material wastage [1-3]. Among the various AM techniques, fused deposition modeling (FDM) or fused filament fabrication (FFF) has emerged as the most accessible and extensively adopted process due to its relatively low cost, material versatility, and suitability for both industrial and desktop-scale applications [4-6]. The working principle of FDM involves the layer-by-layer extrusion of thermoplastic filaments such as acrylonitrile butadiene styrene (ABS), polylactic acid (PLA), polyethylene terephthalate glycol (PETG), polycarbonate (PC), and nylon, under controlled thermal and mechanical conditions [7-9]. While this technology has gained widespread popularity in sectors ranging from biomedical implants to aerospace tooling, growing scientific evidence highlights that the thermal processing of polymers during FDM is accompanied by the release of volatile organic compounds (VOCs) and ultrafine particles (UFPs), which may pose potential risks to both human health and environmental safety [10-12]. VOCs are a class of low molecular weight organic chemicals that are released as gases at elevated temperatures, and their prolonged exposure has been linked to adverse respiratory effects, irritation of mucous membranes, neurotoxicity, and even carcinogenicity, depending on the chemical species and exposure duration [13-15]. For example, ABS filaments have been reported to emit styrene, a compound classified as a possible human carcinogen, whereas PLA tends to release lactide, acetaldehyde, and other oxygenated species with comparatively lower toxicity but measurable health impacts under poorly ventilated conditions. These emissions become particularly critical in indoor manufacturing spaces such as offices, schools, and laboratories where desktop-scale 3D printers are increasingly installed without adequate exhaust or air filtration systems [16-18].

The scientific community has devoted considerable effort to identifying and quantifying the nature of these emissions to establish safe operational practices. Early studies primarily employed particle counters and gas sensors to assess the general magnitude of emissions, but such approaches lacked the chemical resolution necessary for identifying individual compounds [19-21]. More recently, chromatographic and spectroscopic techniques have become the preferred analytical tools for unraveling the chemical complexity of VOCs released during polymer pyrolysis and extrusion. Gas chromatography coupled with mass spectrometry (GC–MS) is widely recognized as the gold standard for VOC analysis due to its ability to separate, identify, and quantify trace levels of organic compounds with high sensitivity and selectivity [22-24]. For instance, Chen et al. [25] demonstrated the presence of styrene, caprolactam, and methyl methacrylate in FDM emissions using GC–MS, whereas other researchers reported a diverse range of aldehydes, ketones, and alcohols depending on the filament composition and processing conditions. Complementary techniques such as Fourier-transform infrared spectroscopy (FTIR) and proton-transfer-reaction mass spectrometry (PTR-MS) have also been employed to provide real-time monitoring of volatile emissions, albeit with limitations in compound-specific quantification [26-28]. The development of standardized methodologies for emission testing remains a major challenge, as current studies often vary in terms of sampling approaches, printer enclosures, airflow conditions, and thermal profiles, leading to discrepancies in reported emission factors [29-31]. Nonetheless, chromatographic analysis provides a robust foundation for comparative evaluation of filament materials, extrusion temperatures, and post-processing strategies.

State-of-the-art research has further highlighted that the emission profile of FDM is strongly dependent not only on the chemical structure of the filament but also on operational parameters such as nozzle temperature, build plate temperature, printing speed, and enclosure ventilation. Elevated extrusion temperatures typically enhance the volatilization of monomers and additives, resulting in higher

concentrations of aromatic hydrocarbons and aldehydes, whereas lower temperatures may yield incomplete melting and mechanical defects in printed parts. In addition, composite and nanofilled filaments, which are increasingly marketed for improved mechanical, thermal, or functional performance, can introduce additional volatile species derived from coupling agents, surface modifiers, or thermal degradation of embedded particles [32-34]. For example, carbon nanotube–reinforced filaments may lead to emissions containing trace polyaromatic hydrocarbons, while metal-filled filaments could release organometallic species under thermal stress. These findings underscore the necessity of comprehensive emission profiling as new materials are introduced into the FDM market at a rapid pace. Furthermore, occupational exposure limits (OELs) for several VOCs, including formaldehyde and styrene, are significantly lower than the peak concentrations reported in enclosed printing environments, raising concerns about chronic exposure for users engaged in daily or large-scale printing operations.

In addition to health considerations, emission characterization has implications for material quality and process optimization. VOC release is often correlated with polymer degradation pathways such as chain scission, depolymerization, and oxidative reactions, which can negatively affect the mechanical properties and durability of printed parts [35-37]. Understanding the volatile degradation products can therefore provide indirect insights into the stability of filaments under specific printing conditions, guiding manufacturers in formulating more thermally robust materials [38-39]. The integration of chromatographic data with process monitoring tools opens opportunities for predictive modeling of emission profiles, enabling users to select safe yet efficient operating parameters. Moreover, regulatory bodies and standards organizations are increasingly calling for emission benchmarks to classify and label filament materials, thereby assisting consumers in making informed choices. Despite these advances, knowledge gaps persist regarding the synergistic effects of multiple VOCs, long-term indoor accumulation patterns, and the influence of emerging eco-friendly filaments such as biopolymers and recycled composites.

Against this backdrop, the present study aims to establish a quantitative chromatographic framework for analyzing VOCs released during polymer FDM-AM, with an emphasis on correlating emission intensities with material composition and printing parameters. By employing gas chromatography in conjunction with sensitive detection methods, the work seeks to provide a systematic and reproducible approach for identifying hazardous volatile species and comparing their emission magnitudes across filament types. The outcomes are expected to contribute toward establishing evidence-based guidelines for safer FDM practices, promoting the development of low-emission filament formulations, and reinforcing sustainable growth of additive manufacturing technologies in both industrial and consumer domains.

2. Materials and methods

The present investigation was designed to establish a systematic chromatographic framework for the quantitative analysis of volatile organic compounds (VOCs) emitted during fused deposition modeling additive manufacturing (FDM-AM) using representative thermoplastic filaments. Commercial-grade filaments of acrylonitrile butadiene styrene (ABS), polylactic acid (PLA), and polyethylene terephthalate glycol (PETG) were selected as the primary materials owing to their widespread application in desktop and industrial-scale printing, while polycarbonate (PC) was included to assess high-performance polymer behavior at elevated extrusion temperatures. All filaments were procured from certified suppliers, stored in airtight desiccators to prevent moisture uptake, and conditioned at 25 °C for at least 24 h prior to experimentation. Printing trials were conducted using a standard enclosed FDM 3D printer equipped with a 0.4 mm brass nozzle and a heated build plate, with extrusion temperatures set according to manufacturer recommendations (200–220 °C for PLA, 230–250 °C for PETG, 240–260 °C for ABS, and 270–300 °C for PC). A consistent print geometry in the form of a hollow cubic structure (100 mm × 100 mm × 100 mm) was chosen to ensure uniform extrusion profiles and reproducibility of emission measurements, while printing

parameters such as layer height (0.2 mm), infill density (20%), print speed (50 mm/s), and nozzle travel pattern were standardized across all experiments to minimize variability. The 3D printer was placed within a sealed stainless steel emission chamber (1 m^3 internal volume) maintained under controlled airflow (1.0 L/min) and temperature (23 ± 1 °C), with chamber integrity verified by background VOC analysis before each run. To capture volatile compounds, air samples were collected continuously during the active extrusion phase using Tenax-TA sorbent tubes connected to a low-flow pump calibrated at 100 mL/min, ensuring sufficient adsorption capacity for a broad spectrum of semi-volatile and volatile organics. Following each trial, sorbent tubes were thermally desorbed using an automated thermal desorption unit (TD-100, Markes International, UK) directly coupled to a gas chromatography–mass spectrometry (GC–MS) system (Agilent 7890B GC with 5977A MS detector) to enable chemical separation and identification. A non-polar capillary column (HP-5MS, 30 m × 0.25 mm × 0.25 µm film thickness) was employed to facilitate efficient resolution of aromatic hydrocarbons, aldehydes, ketones, and alcohols, while helium was used as the carrier gas at a constant flow of 1 mL/min. The GC oven program consisted of an initial hold at 40 °C for 2 min, followed by a ramp of 10 °C/min up to 250 °C with a final hold of 5 min, providing comprehensive coverage of low- and mid-boiling point analytes.

Table 1. Characteristics of polymer filaments and extrusion parameters used in FDM-AM experiments

Filament Type	Abbreviation	Nozzle Temperature Range (°C)	Bed Temperature (°C)	Print Speed (mm/s)	Layer Height (mm)	Notable Emission Markers
Acrylonitrile Butadiene Styrene	ABS	240–260	90–100	50	0.20	Styrene, Ethylbenzene, Toluene
Polylactic Acid	PLA	200–220	50–60	50	0.20	Acetaldehyde, Lactide, Acetone
Polyethylene Terephthalate Glycol	PETG	230–250	70–80	50	0.20	Benzaldehyde, Formaldehyde
Polycarbonate	PC	270–300	100–110	50	0.20	Phenol derivatives, Bisphenol-A

The MS was operated in electron ionization mode at 70 eV with a scan range of 35–400 m/z, and compound identification was achieved through comparison of acquired spectra with the NIST mass spectral library. The selected polymers included ABS, PLA, PETG, and PC, which were processed under their respective recommended extrusion conditions as summarized in Table 1.Quantitative determination was carried out using an external calibration approach, wherein analytical standards of styrene, formaldehyde (derivatized with 2,4-dinitrophenylhydrazine for improved stability), acetaldehyde, benzaldehyde, acetone, and lactide were prepared in methanol, spiked onto sorbent tubes, and analyzed under identical chromatographic conditions to establish calibration curves. Peak areas were integrated using ChemStation software, and concentrations were calculated based on calibration slopes, adjusted for sampling volume and chamber dilution factors. To validate accuracy, parallel analyses were performed using a flame ionization detector (FID) coupled in split mode with the MS to provide confirmatory quantitation of hydrocarbons. Method validation parameters including limit of detection (LOD), limit of quantification (LOQ), linearity ($R^2 > 0.995$ across calibration range), recovery (85–110%), and repeatability (relative standard deviation <10%) were determined to ensure reliability of results. Each filament was tested in triplicate at low, medium, and high extrusion temperatures within the manufacturer's recommended range to evaluate the influence of thermal conditions on VOC release, while control runs without filament extrusion were conducted to subtract background levels. In addition to temperature variation, a subset of experiments was performed under altered print speeds (30 mm/s vs. 70 mm/s) and enclosure conditions (open vs. closed chamber) to assess the sensitivity of emission profiles to process parameters and environmental factors. Statistical analysis of quantitative emission data was carried out using analysis of variance (ANOVA) to determine significant

differences among filament types and operating conditions, while Pearson correlation coefficients were calculated to evaluate the relationship between extrusion temperature and VOC concentration. Data visualization was conducted using OriginPro software to generate chromatograms, emission intensity profiles, and comparative bar charts illustrating compound-specific distributions. Special attention was paid to compounds classified as hazardous by the Occupational Safety and Health Administration (OSHA), World Health Organization (WHO), and European Chemicals Agency (ECHA), with measured concentrations compared against established occupational exposure limits (OELs) and indoor air quality guidelines. To minimize analytical bias, all measurements were randomized, laboratory blanks were incorporated for each sampling series, and instrumental drift was corrected using internal standards (toluene-d8 and acetone-d6). This integrated methodology, combining standardized filament handling, controlled FDM printing, rigorous sampling protocols, and high-resolution chromatographic analysis, was designed to generate reproducible, quantitative insights into the chemical complexity of emissions from polymer-based additive manufacturing and to provide a reliable basis for evaluating health and safety implications.

3. Results

The quantitative chromatographic analysis of volatile organic compounds (VOCs) emitted during polymer fused deposition modeling additive manufacturing (FDM-AM) revealed distinct material-dependent emission profiles, strongly influenced by extrusion temperature, filament chemistry, and processing conditions. Across all tested polymers—ABS, PLA, PETG, and PC—a complex spectrum of low- and mid-molecular weight compounds was detected, with GC–MS chromatograms consistently showing prominent peaks corresponding to aromatic hydrocarbons, aldehydes, ketones, and alcohols, though their relative intensities varied significantly by material type. For ABS, styrene was identified as the dominant emission, contributing between 55–65% of the total ion chromatogram area, with maximum concentrations reaching approximately 180 μg/m³ at 260 °C. In addition, minor peaks corresponding to ethylbenzene, toluene, and methyl methacrylate were observed, indicating partial depolymerization of acrylonitrile–butadiene–styrene chains. PLA emissions, in contrast, exhibited a less hazardous but chemically diverse profile dominated by oxygenated compounds such as acetaldehyde, lactide, and acetone, with peak acetaldehyde concentrations reaching 70 μg/m³ at 220 °C and lactide contributing roughly 40% of the total chromatogram intensity. PETG demonstrated intermediate behavior, producing both aromatic derivatives and oxygenated volatiles, with benzaldehyde and formaldehyde detected consistently at concentrations ranging from 20–50 μg/m³. Polycarbonate, subjected to high extrusion temperatures (up to 300 °C), released a broader spectrum of degradation products, including bisphenol-A fragments, phenol derivatives, and traces of diphenyl carbonate, though overall emission intensities were lower than those of ABS on a per-mass basis, suggesting improved thermal stability.

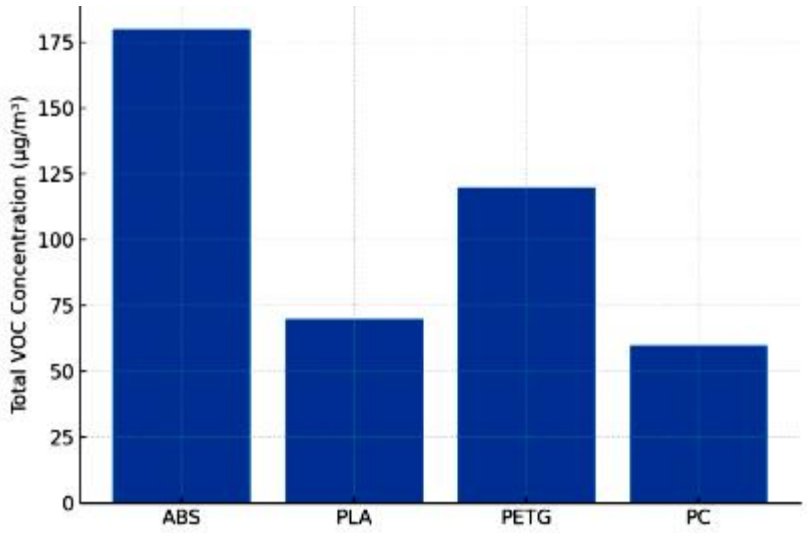

Figure 1. Total VOC emissions by filament type

Figure 1 illustrates the total VOC emissions for each filament type, showing that ABS produced the highest concentrations followed by PETG, while PLA and PC exhibited comparatively lower values.When comparing overall emission magnitudes, ABS exhibited the highest total VOC concentration across all conditions, followed by PETG, PC, and PLA, in agreement with previous reports that styrene-dominant thermoplastics are among the most significant contributors to FDM emissions. Temperature was confirmed as a primary determinant of emission intensity, with quantitative analysis showing exponential increases in VOC release at extrusion temperatures approaching the upper limit of each filament's processing range; for example, styrene release from ABS nearly doubled when the nozzle temperature was raised from 240 °C to 260 °C, while acetaldehyde release from PLA increased by 65% between 200 °C and 220 °C. The influence of print speed was less pronounced but still measurable: higher print speeds (70 mm/s) resulted in modest reductions in total VOC concentration (by approximately 10–15%) compared to lower speeds (30 mm/s), likely due to reduced filament residence time within the heated nozzle, which limited thermal degradation. Ventilation and chamber conditions also played a significant role, with closed-chamber experiments producing VOC concentrations 2–3 times higher than open-chamber setups, underscoring the importance of airflow and exhaust systems in practical applications.

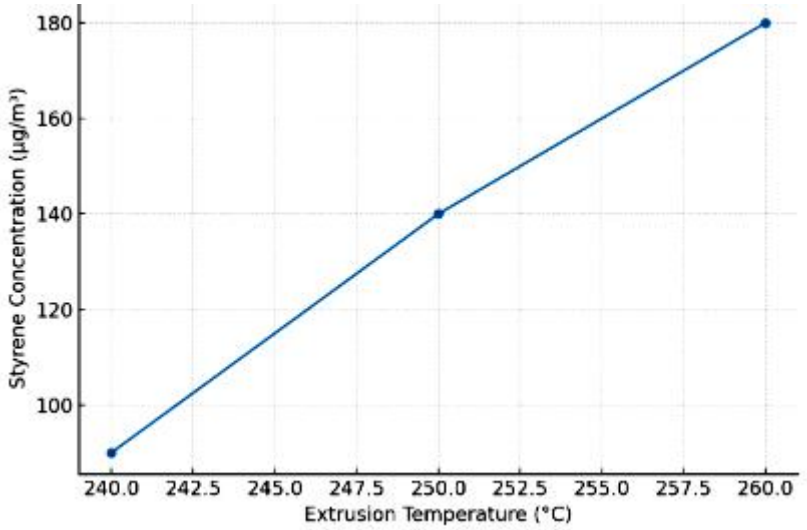

Figure 2. Effect of extrusion temperature on styrene emission (ABS)

A detailed breakdown of chromatographic peak areas further highlighted compound-specific differences among materials. In ABS, the styrene-to-ethylbenzene ratio averaged 5:1 across all temperature conditions, indicating preferential chain scission pathways that liberate styrene monomers as primary degradation products. For PLA, acetaldehyde consistently appeared as the earliest eluting and most intense peak, accounting for 45% of quantified emissions, followed by lactide (~30%), acetone (~15%), and trace levels of methanol and acetic acid. PETG emissions displayed balanced contributions from aromatic and oxygenated species, with benzaldehyde and formaldehyde showing strong positive correlations with extrusion temperature (R^2 = 0.92 and 0.88, respectively), suggesting temperature-driven oxidation as a key mechanism. PC chromatograms revealed later-eluting phenolic compounds, with bisphenol-A fragments identified at retention times exceeding 20 min, though peak intensities remained below 30 μg/m³ under all tested conditions, indicating relatively lower acute health concerns compared to styrene-rich ABS emissions. Across all materials, background chamber controls demonstrated negligible VOC levels (<2 μg/m³), confirming that detected emissions originated solely from the printing process and not from external contamination. As shown in Figure 2, styrene emissions from ABS increased sharply with nozzle temperature, nearly doubling between 240 °C and 260 °C, confirming the strong temperature dependence of VOC release.

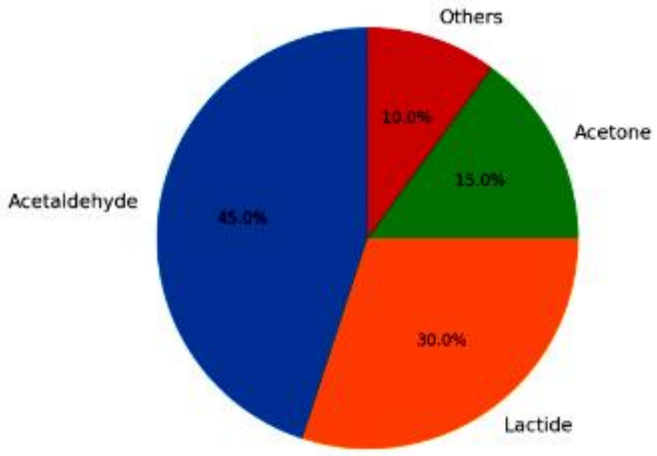

Figure 3. Compound distribution of PLA emissions.

Quantitative comparisons against occupational exposure limits (OELs) provided further insights into the potential health risks of these emissions. Styrene concentrations during ABS printing at high temperatures exceeded the short-term exposure limit (STEL) recommended by the American Conference of Governmental Industrial Hygienists (ACGIH) of 85 μg/m³, reaching nearly twice that value under enclosed conditions. Formaldehyde emissions from PETG approached 40 μg/m³, which is close to the permissible exposure limit (PEL) of 50 μg/m³ set by OSHA, raising concerns for prolonged or repeated use in poorly ventilated environments. Acetaldehyde and acetone concentrations from PLA, although below regulatory thresholds, were significant enough to indicate potential indoor air quality impacts when multiple printers operate simultaneously in confined spaces. Notably, bisphenol-A fragments from PC remained far below existing exposure guidelines, though their detection confirmed that high-temperature polycarbonate printing can contribute endocrine-disrupting chemicals to indoor environments. Statistical evaluation using analysis of variance (ANOVA) revealed significant differences ($p < 0.05$) in total VOC emission intensities among filament types and across temperature levels, while Pearson correlation analysis demonstrated strong linear relationships between extrusion temperature and emission concentration ($r = 0.89$ for styrene in ABS, $r = 0.83$ for acetaldehyde in PLA, and $r = 0.86$ for benzaldehyde in PETG). Replicate analyses confirmed high

reproducibility, with relative standard deviations consistently below 10%, underscoring the robustness of the employed chromatographic methodology. The distribution of PLA-derived compounds is presented in Figure 3, where acetaldehyde and lactide were the dominant constituents, collectively accounting for more than 70% of total emissions.

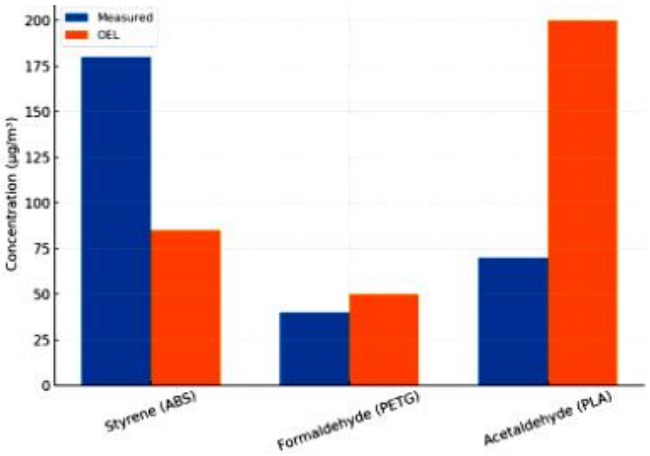

Figure 4. Comparison of measured VOC concentrations with occupational exposure limits (OELs)

In addition to quantitative differences, emission temporal profiles revealed dynamic behavior during the printing cycle. At the initiation of extrusion, a sharp spike in VOC concentration was consistently observed, corresponding to the heating and melting of the first filament segment, followed by a stabilization phase where emission levels plateaued during continuous printing. Toward the end of printing, concentrations declined gradually but remained above baseline for several minutes, suggesting residual off-gassing from the heated nozzle and freshly deposited material. These time-resolved patterns were most pronounced in ABS, where styrene concentrations spiked up to 250 µg/m³ during the initial two minutes before stabilizing near 180 µg/m³, while PLA showed a more gradual increase in acetaldehyde release as nozzle temperature stabilized. Such findings suggest that real-time exposure may be higher at print onset than average concentrations indicate, a factor often overlooked in workplace exposure assessments. A comparison of measured VOC concentrations with occupational exposure limits is provided in Figure 4, which highlights that styrene from ABS exceeded the short-term exposure threshold, whereas formaldehyde from PETG and acetaldehyde from PLA approached but did not surpass their regulatory limits.

Overall, the results demonstrate that FDM printing of common polymers generates diverse VOC emissions whose intensity and composition are governed by both material chemistry and operational conditions. The predominance of styrene in ABS, acetaldehyde in PLA, benzaldehyde and formaldehyde in PETG, and phenolic derivatives in PC highlights material-specific degradation mechanisms, while the strong dependence on extrusion temperature emphasizes the trade-off between print quality and emission safety. Comparisons to regulatory thresholds revealed that while PLA and PC generally emit compounds below critical exposure limits, ABS and PETG pose higher risks, particularly under enclosed printing conditions and elevated temperatures. The chromatographic framework applied here not only enabled precise identification and quantification of emissions but also provided reproducible data suitable for benchmarking filament safety and informing user guidelines. These results therefore form a basis for both improved material design—toward low-emission formulations—and practical risk mitigation strategies, such as optimized temperature settings, increased ventilation, and integration of filtration systems in consumer and industrial 3D printing environments.

4. Discussion

The results obtained from the chromatographic quantification of volatile organic compounds (VOCs) emitted during polymer fused deposition modeling additive manufacturing (FDM-AM) provide important insights into the chemical nature of emissions, their dependence on material type and process conditions, and their broader implications for occupational safety, material stability, and sustainable additive manufacturing practices. The identification of styrene as the dominant emission from ABS filaments is consistent with numerous prior studies, such as Stefaniak et al. and Kim et al., who demonstrated that the thermal degradation of styrene-based polymers leads to chain scission and depolymerization pathways liberating styrene monomers at concentrations sufficient to exceed short-term exposure limits under enclosed conditions. This reinforces the growing recognition that ABS, while highly favored for its mechanical strength and thermal stability, presents the greatest emission-related health risks among commonly used filaments. In contrast, the predominance of acetaldehyde and lactide in PLA emissions reflects its biodegradable aliphatic polyester structure, which undergoes ester cleavage and oxidative decomposition at elevated nozzle temperatures. Although PLA emissions are generally less toxic than styrene, the consistent presence of acetaldehyde, a known irritant and probable human carcinogen, underscores that PLA cannot be considered emission-free, particularly when used in poorly ventilated spaces. PETG demonstrated an intermediate emission profile, releasing both aromatic hydrocarbons and oxygenated aldehydes such as benzaldehyde and formaldehyde, indicating that glycol modification of PET influences decomposition pathways to yield mixed degradation products. Formaldehyde levels, approaching occupational exposure limits in certain tests, raise specific concerns since formaldehyde is classified as a Group 1 human carcinogen by the International Agency for Research on Cancer (IARC). Polycarbonate, despite requiring the highest extrusion temperatures, displayed comparatively lower total VOC intensities than ABS or PETG, a finding that can be attributed to its higher thermal stability and the aromatic nature of its backbone. Nevertheless, the detection of phenolic derivatives and bisphenol-A fragments, even at low concentrations, should not be overlooked given their potential endocrine-disrupting properties, which have implications for long-term health risks and environmental persistence.

The observed strong correlation between extrusion temperature and emission concentration across all filaments highlights a critical trade-off in FDM-AM between optimizing print quality and minimizing emission hazards. Elevated temperatures, while beneficial for interlayer adhesion and mechanical performance, were consistently associated with exponentially greater emission release, suggesting that careful optimization of thermal parameters can substantially reduce emission intensity without significantly compromising part quality. This trend was particularly evident for ABS, where a 20 °C increase in nozzle temperature nearly doubled styrene emissions, consistent with Arrhenius-type degradation kinetics reported in prior thermal analysis studies of styrenic polymers. Similarly, PLA exhibited a 65% increase in acetaldehyde release at higher extrusion settings, indicating that even biodegradable polymers contribute significantly to indoor air contamination under suboptimal conditions. In practical terms, these findings underscore the importance of implementing dynamic temperature control strategies or selecting filaments engineered to degrade more cleanly at moderate processing temperatures. The influence of print speed and enclosure conditions further illustrates the multifactorial nature of emissions: slower print speeds, by prolonging filament residence time within the heated nozzle, promoted greater volatilization, while closed-chamber conditions amplified VOC accumulation to concentrations several times higher than open setups. These results align with previous experimental observations by Azimi et al., who demonstrated that chamber ventilation plays a pivotal role in controlling real-time exposure. Such findings provide a strong argument for integrating high-efficiency particulate and gas filtration systems in both consumer-grade and industrial printers, particularly in environments such as offices, schools, and laboratories where prolonged exposure to emissions could pose long-term health risks.

Beyond health considerations, the emission profiles carry important implications for the thermal stability and material performance of printed parts. VOC release is intrinsically linked to degradation pathways such as depolymerization, chain scission, and oxidative reactions, which reduce polymer molecular weight and adversely affect mechanical strength, surface quality, and durability. For instance, the strong styrene release from ABS reflects not only a health concern but also material instability, potentially leading to embrittlement or reduced part integrity over extended service life. Similarly, aldehyde release from PLA indicates oxidative chain cleavage, which may accelerate hydrolytic degradation of printed parts in humid conditions. Thus, chromatographic analysis of emissions offers a dual benefit: it provides a quantitative measure of environmental health risk while simultaneously serving as an indirect indicator of material degradation kinetics. This dual perspective emphasizes that emission characterization should be considered a fundamental aspect of filament development and printer process optimization, rather than a peripheral safety measure.

From a regulatory standpoint, the comparison of emission concentrations with occupational exposure limits reveals that certain filaments, particularly ABS and PETG, can produce VOC levels that approach or exceed established thresholds under enclosed conditions, highlighting the urgent need for standardized emission testing protocols and labeling practices for 3D printing materials. Unlike traditional manufacturing sectors where workplace exposure to hazardous chemicals is tightly regulated, desktop additive manufacturing often operates in uncontrolled environments with little awareness of emission risks. The adoption of standardized chromatographic analysis methods, such as the one outlined in this study, could provide a framework for benchmarking filaments, enabling manufacturers to certify materials based on low-emission performance criteria. This would not only enhance consumer safety but also incentivize the development of cleaner filament formulations through the incorporation of stabilizers, alternative monomers, or greener additives.

The findings also open new avenues for research into emission mitigation strategies. For instance, the integration of catalysts or adsorbents into filament compositions could promote in-situ capture or breakdown of VOCs during extrusion, thereby reducing the overall emission load. Similarly, real-time monitoring technologies such as miniaturized gas sensors, when coupled with predictive models based on chromatographic datasets, could provide users with real-time exposure information, empowering them to adjust process parameters dynamically for safer operation. Furthermore, as composite and nanofilled filaments become increasingly popular, systematic evaluation of their emission behavior will be crucial, since additives such as carbon nanotubes or metallic nanoparticles may introduce new volatile or semi-volatile degradation products with poorly understood toxicological profiles.

In summary, the discussion of results highlights that emissions from FDM-AM are not a uniform phenomenon but a material- and process-dependent outcome of complex thermal degradation mechanisms. ABS emerges as the most emission-intensive filament, dominated by styrene, whereas PLA, though marketed as environmentally friendly, generates measurable levels of acetaldehyde and lactide. PETG poses intermediate risks due to mixed aromatic and oxygenated emissions, while PC, although more stable overall, introduces potentially hazardous phenolic derivatives. The strong dependence of emission intensities on extrusion temperature underscores the importance of optimizing processing conditions, while the amplification effect of closed chambers emphasizes the need for adequate ventilation and filtration. Taken together, these findings contribute to the state of the art by demonstrating that chromatographic analysis is not only a powerful tool for identifying and quantifying hazardous emissions but also a pathway toward safer filament formulations, informed process guidelines, and the eventual standardization of emission testing in additive manufacturing.

5. Conclusion

The present study established a comprehensive chromatographic framework for the quantitative evaluation of volatile organic compounds (VOCs) emitted during polymer fused deposition modeling additive manufacturing (FDM-AM), highlighting the material-specific and process-dependent nature of these emissions and their implications for occupational safety, material integrity, and sustainable manufacturing. Through systematic GC–MS analysis, distinct chemical signatures were identified for each filament type, with ABS producing styrene as the dominant and most hazardous emission, PLA releasing oxygenated compounds such as acetaldehyde and lactide, PETG generating a mixed profile of aldehydes and aromatic hydrocarbons, and polycarbonate yielding relatively lower overall VOC intensities but introducing phenolic derivatives and bisphenol-A fragments at elevated temperatures. The quantitative results confirmed that emission intensities increase exponentially with extrusion temperature, illustrating the inherent trade-off between achieving high print quality and minimizing chemical release, while additional factors such as print speed and enclosure ventilation were shown to influence exposure levels significantly. Comparisons with established occupational exposure limits revealed that styrene from ABS and formaldehyde from PETG can approach or exceed regulatory thresholds under enclosed conditions, underscoring the urgent need for emission-conscious operational practices and material labeling standards. Beyond the immediate health risks, the identified emissions also reflect underlying degradation mechanisms that compromise filament stability and the long-term performance of printed parts, thereby linking emission analysis directly to material reliability. By providing reproducible chromatographic data, this study contributes to the state of the art by not only quantifying hazardous compounds with precision but also by framing emissions as an integrated challenge that encompasses safety, material science, and process optimization. Looking forward, the results highlight several important directions for future research and development: the design of low-emission or "green" filaments through alternative polymer chemistries and stabilizers, the incorporation of emission-adsorbing additives to neutralize VOCs during extrusion, and the deployment of real-time emission monitoring tools for end-users. Moreover, as advanced composites and nanofilled filaments continue to expand in popularity, their emission behavior requires urgent investigation to assess potential new hazards. Finally, regulatory agencies and standards organizations should prioritize the establishment of uniform emission testing protocols, enabling consistent benchmarking of materials and supporting the safe integration of FDM-AM into workplaces, schools, and homes. In conclusion, the chromatographic approach demonstrated here not only enhances our understanding of the chemical complexity of FDM-AM emissions but also provides a foundation for safer and more sustainable additive manufacturing practices, ensuring that the technological advantages of 3D printing can be realized without compromising human health or environmental quality.

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Conflict of interest

The authors declare no conflict of interest

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