Journal of Visualized Experiments
3D Printing – Evaluating Particle Emissions of a 3D Pen.
--Manuscript Draft--

Article Type:	Methods Article - JoVE Produced Video
Manuscript Number:	JoVE61829R1
Full Title:	3D Printing – Evaluating Particle Emissions of a 3D Pen.
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Additional Information:	
Question	**Response**
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TITLE:

3D Printing – Evaluating Particle Emissions of a 3D Printing Pen

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KEYWORDS:

3D printing, 3D printing pen, emission, emerging technologies, advanced materials, emitted nanoparticles, ultrafine particles, , inhalation, aerosols, indoor air quality, indoor pollutants

SUMMARY:

This protocol presents a method to analyze the emission of 3D printing pens. Particle concentration and particle size distribution of the released particle is measured. Released particles are further analyzed with transmission electron microscopy (TEM). Metal content in filaments is quantified by inductively coupled plasma mass spectrometry (ICP-MS).

ABSTRACT:

Three-dimensional (3D) printing as a type of additive manufacturing shows continuing increase in application and consumer popularity. The fused filament fabrication (FFF) is an inexpensive method used most frequently by consumers. Studies with 3D printers have shown that during the printing process particulate and volatile substances are released. Handheld 3D printing pens also use the FFF method but the consumer's proximity to the 3D pens gives reason to higher exposure compared to a 3D printer. At the same time, 3D printing pens are often marketed for children who could be more sensitive to the printing emission. The aim of this study was to implement a low cost method to analyze the emissions of 3D printing pens. Polylactide (PLA) and acrylonitrile butadiene styrene (ABS) filaments of different colors were tested. In addition, filaments containing metal and carbon nanotubes (CNTs) were analyzed. An 18.5 L chamber and

sampling close to the emission source was used to characterize emissions and concentrations near the breathing zone of the user.

Particle emissions and particle size distributions were measured and the potential release of metal particles and CNTs investigated. Particle number concentrations were found in a range of 10^5 - 10^6 particles/cm^3, which is comparable to previous reports from 3D printers. Transmission electron microscopy (TEM) analysis showed nanoparticles of the different thermoplastic materials as well as of metal particles and CNTs. High contents of metal were observed by inductively coupled plasma mass spectrometry (ICP-MS).

These results call for a cautious use of 3D pens due to potential risk to the consumers.

INTRODUCTION:

3D printing is a promising additive manufacturing method, which besides its industrial applications is also used in homes, schools and so-called maker spaces. 3D printers can now be purchased starting already from 200 €, thus making them attractive to consumers. These printers can be used to produce replacement parts, household items, gifts or other objects. Children can even make their own toys using 3D printers. Due to their easy handling and low price, printers based on fused filament fabrication (FFF)are the most widespread type in the hobby sector[1]. In this printing method a thermoplastic material, called filament, is melted, pushed through a nozzle and applied layer by layer using a movable print head until the three-dimensional object is finished. Digital computer-aided design (CAD) models needed for FFF printing are freely available online or can be designed in many different CAD drawing programs.

Initial studies have shown that during the printing process of the filament, ultrafine particles[2-8] and volatile substances[9-18] are released. Ultrafine particles can penetrate deeper into the respiratory system and might be harder to clear from the body[19]. In a study with employees regularly using 3D printers 59% have reported respiratory symptoms[20]. Most of the hobbyist's printers are not hermetically sealed and do not have exhaust fume extraction devices. Emissions are therefore released directly into the ambient air and could pose a risk to the user upon inhalation.

Previous studies have focused on emissions of the most commonly used filaments polylactide (PLA) and acrylonitrile butadiene styrene (ABS). Some studies have analyzed different filaments, such as nylon and high-impact polystyrene (HIPS)[4,10,13]. Furthermore, new filaments, which are provided with additives such as metal or wood, are constantly being launched to the market. Those filaments enable the consumer to print objects that look and feel like natural wood or metal. Other filaments allow to print conductive materials containing graphene or carbon nanotubes (CNTs)[21]. Metal nanoparticles[22] and CNTs show cytotoxic effects and caused DNA damage[23]. So far, only little research was conducted regarding filaments containing additives. Floyed et al.[13] analyzed PLA supplemented with bronze; Stabile et al.[3] investigated PLA blended with copper, wood, bamboo and a filament with carbon fiber. Both studies measured particle concentration and size distribution however the morphology and composition of the released particles was not further investigated. Especially high aspect ratio nanoparticles (HARN) such as

CNTs or asbestos fibers are known to cause hazardous health effects[24]. A recent study by Stefaniak et al.[25] analyzed filaments with CNTs and observed emission of respirable polymer particles containing visible CNTs.

3D pens use the same FFF method as 3D printers, but so far only one study examining 3D pens has been published[26]. The authors used PLA and ABS filaments, but none with additives were analyzed. Due to their handheld use, 3D pens are even easier to use than 3D printers. They are more intuitive, have a small size and do not require the use of CAD models. 3D pens can be used to draw or create objects, and moreover to repair 3D printed parts and other plastic items. Prices start from as low as 30 €, different shapes and colors are available to target lower age groups. But particularly, children are more vulnerable to particle emissions. Their lung defense mechanisms against particulate and gaseous pollution are not fully evolved and they are breathing a higher volume of air per body weight[27].

For a better understanding of the release and the health risks of 3D pen emissions, we investigated different filaments consisting of the standard materials PLA and ABS in different colors. Furthermore, filaments with copper, aluminum, steel and CNT additives and a filament with glow-in-the-dark effect were investigated. To gain comprehensive insights into the 3D pen printing process and the particulate emissions analysis was conducted by online aerosol measurement of particle number concentrations and size distributions, by transmission electron microscopy (TEM) examination for the morphology and materials identification and by inductively coupled plasma mass spectrometry (ICP-MS) for quantitative metal assessment of the filaments.

PROTOCOL:

1 Protocol requirements

1.1 Purchase a 3D printing pen capable of generating temperatures > 200 °C (**Figure 1**) to be able to print filaments with a higher print temperature (e.g., ABS or filaments with additives) to compare different filaments. Different 3D pens are available online.

1.2 Purchase filaments with a diameter of 1.75 mm, suitable for the 3D pen. A variety of standard PLA and ABS filaments as well as filaments with additives are available online on different websites.

1.3 For an easy setup, use a desiccator (18.5 L) as the emission chamber.

1.3.1. Make sure the chamber is clean. Choose a desiccator with an inlet on one side to be able to insert the 3D printing pen and an outlet on the top to insert the sampling tube.

1.3.2. Make sure that an air inlet at the connection to the 3D pen is established. Ambient air will used as background. The outlet tubing should be 10 cm away from the tip of the 3D printing pen to mimic the distance between the user's head and the emission source.

1.3.3. Use conductive tubing to minimize particle loss. The tubing length should be as short as possible and free of bends.

1.4 Use Condensation Particle Counter (CPC) and Scanning Mobility Particle Sizer (SMPS) or other particle tracking devices for the online measurement of particle concentration and particle size distribution (**Figure 2**).

1.5 Use a microwave and respective chemicals for digesting filament samples.

1.6 Use an ICP-MS or another multi-element analysis instrument to quantify the metal content in the samples.

1.7 Use an electron microscope to characterize the particle morphology.

2 Aerosol measurements of 3D Pen emissions

2.1 Preparation before the experiment

2.1.1 Switch on the respective online measurement instruments (SMPS, CPC). There is a button in the back of the machine. Warm up the instruments for around 10 min.

2.1.2 Preload the 3D pen with a chosen filament (start with PLA as the most used material) and let the pen cool down.

2.1.3 Attach a HEPA filter to the SMPS inlet and run a clean check measurement with the SMPS to ensure that the SMPS is not contaminated from previous measurements. Do not measure any particles if the SMPS is not clean.

2.1.4 Check the concentration inside the chamber with the CPC to ensure the chamber is clean ($< 10^3$ particles/m^3) and experiments are running under the same conditions. Connect the chamber outlet to the CPC inlet und start a measurement.

2.2 Experimental procedure

2.2.1 Insert the preloaded and cooled down 3D pen into the chamber.

2.2.2 Make sure the outlet tubing of the chamber is connected to the CPC.

2.2.3 Start the computer connected to the CPC. Open a new file with a name suitable to the measurements. Make sure the CPC flow setting is set to 0.3 L/min and sampling time is set to at least 90 minutes. Start the CPC measurement to measure the background concentration for 10 minutes.

NOTE: Flow settings of 0.3 L/min and the chamber volume of 18.5 L will result in an air exchange rate (ACH) of 1.0 h^{-1}.

2.2.4 After 10 min, switch on the 3D pen. Select the needed temperature for the chosen filament.

2.2.5 After the needed temperature is reached, start the printing process. Let the 3D pen print for 15 minutes.

NOTE: No object, but a continuous string will be printed and collected on the bottom.

2.2.6 After 15 minutes, stop the 3D pen, connect the outlet tubing to the SMPS and start the size distribution measurements every 3 minutes for the next 30 minutes.

2.2.7 After the experiment is finished remove the printed filament and clean the chamber.

2.2.8 Repeat every measurement three times.

3 Particle morphology using TEM

3.1 To ensure that the measured signals originate from emitted particles and not from vapor molecules use transmission electron microscopy (TEM) to analyze the aerosol.

3.2 TEM grid preparation

3.2.1 Use 400 mesh 3.5 mm copper grids.

3.2.2 Coat the grids with Collodion. Let the grids dry overnight and store them in a desiccation chamber until further use. Alternatively, use precoated grids (e.g., SF162-4 Formvar-Film on 400 mesh Cu-net).

3.2.3 On the day of the experiment, the grids should be hydrophilized with 2% Alcian Blue in 0.3% acetic acid solution.

3.2.4 Pipette 30 µL of the prepared Alcian blue solution on to a surface, for example a piece of parafilm. Let the grids float on the Alcian blue droplets for 5 to 10 minutes and dry them using a filter paper.

3.3 Place the prepared TEM grids inside the chamber during the printing process and leave in place afterwards for 5 hours to allow particle sedimentation.

NOTE: For easier handling of the grids, place the grids on a platform coated with parafilm.

3.4 Examine at least four different areas of each grid with TEM and use diffraction patterns from published resources to identify material composition.

4 Quantitation of metal content before and after printing using ICP-MS

4.1 Sample Preparation

4.1.1 Print filament on a plastic surface to avoid contamination with metal.

4.1.2 Weigh approximately 150 mg of bulk filament and printed filament. To avoid contamination with metal, use a ceramic knife to cut smaller pieces.

4.2 Microwave digestion

4.2.1 Transfer weighted filaments into microwave vessels.

4.2.2 Add 1.5 mL of water (e.g., MilliQ), 3.5 mL of nitric acid and 1 mL of hydrogen peroxide to each sample.

CAUTION: Add water first and then acid!

4.2.3 Place the vessels into the microwave and start the digestion. Heat up to 200 °C and hold for 20 minutes.

4.3 Determinate metal concentration with ICP-MS

4.3.1 Dilute all samples of filaments where a high metal concentration is known or suspected to avoid contamination of the ICP-MS.

4.3.2 Use a survey scan to determinate which metals are in the samples.

4.3.3 Quantify the metal content of the specific metals using the appropriate calibrations standards.

REPRESENTATIVE RESULTS:

Particle number concentration

The highest peak particle number concentration was measured for PLA-copper with 4.8 x 10^6 #/cm^3 and the lowest for PLA-black with 4.3 x 10^5 #/cm^3. In general, a higher emission for ABS > 10^6 #/cm^3 compared to PLA was observed. Nevertheless, some PLA filaments resulted in particle concentrations above 10^6 #/cm^3 (PLA-white and PLA-blue). The different particle concentrations might be related to the use of additives. Zhang et al.[28] have stated that particles might be formed by some additives as for example pigments, however not by the bulk material. Thus, the use of different pigments for different colors might influence the number of particles released.

In **Figure 3** examples of particle emission increase during the printing process are shown for PLA-black and ABS-black. The results are in agreement with previous 3D printer studies, showing particle concentrations of 10^5-10^6 #/cm³ and higher values for ABS compared to PLA[12,13]. Floyd et al.[13] measured peak concentration of 3.5 x 10^6 #/cm³ for ABS and 1.1 x 10^6 #/cm³ for PLA. It is important to mention, that ABS is generally printed at higher temperatures compared to PLA. To analyze the influence of the printing temperature on particle release, experiments using PLA-black were carried out at 210 °C (standard setting for ABS). Results were compared to the standard setting of 200 °C for PLA. With the higher temperature setting, particle concentration increased almost one order of magnitude. The average concentration during printing with PLA-black increased from 2.6 x 10^5 #/cm^3 at 200°C to 1.3 x 10^6 #/cm^3 at 210°C. Higher emissions caused by a higher printing temperature were already observed in earlier studies with 3D printers[3].

Particle size distribution in emissions of different filaments

Figure 4 shows particle size distributions for PLA at 200 and 210°C and for ABS at 210°C. Printing ABS resulted in a higher particle concentration and larger particles compared to PLA. The temperature increase during printing of PLA resulted in higher particle number concentrations but had no significant effect on the geometric mean diameter (GMD). This is in agreement with a previous study[28].

Figure 5 shows the GMD based on the number count for all measured filaments. There was a clear trend in difference observed between particles emitted during printing with ABS or PLA filaments. The ABS samples had the largest GMD ranging from 203.9 nm for *ABS-green* and up to 262.1 nm for *ABS-blue*. *ABS-green* is made by a different manufacturer than the other ABS filaments; this could be the reason of a slightly different particle size. PLA filaments emitted smaller particles with GMDs < 100 nm (63.8 nm for *PLA-clear* up to 88.3 nm *PLA-blue*). For the other filaments with additives, the GMD ranged from 73.1 nm for *PLA-steel* to 183.9 nm for *PLA-copper*. Reproducibility of measurements is evident from the low relative standard deviations (RSD) of particle size measurements. The range was mostly between 0.96 and 5.58%. Only in the case of PLA with steel (10.55%) and PLA with CNTs (18.52%) a higher range was observed. This could, however, be due to inhomogeneity in the filaments. Products with additives are a mixture of a thermoplastic (e.g., in this case PLA) and metal or other small particles. The particles might not be evenly distributed and could thereby cause a higher standard deviation. The geometric standard deviations ranged between 1.6 and 1.9, indicating a single modal distribution in the fine and ultrafine particle range, as observed in previous studies of 3D printers[13].

The results show a significant difference in particle emissions between PLA and ABS filaments; this was not yet clear from previous publications as often only one or two filaments had been analyzed[29]. Some authors described larger particles for ABS[5,12], some larger ones for PLA[2,9]. In further studies, no difference in size at all was observed[4,13]. Byrley et al.[29] reviewed 13 publications and described mean particle diameters ranging from 14.0 nm to 108.1 nm for PLA and from 10.5 nm to 88.5 nm for ABS. The difference in particle sizes could be due to measurements at different time points. Some measured at the highest concentration[12,13] and some reported the sizes for the whole printing process[5,9]. The only study of 3D pens available so far reports particles up to 60.4 nm for PLA and up to 173.8 nm for ABS[26], which is similar to the findings here.

The size distribution measurement represents a one moment snapshot only. In order to observe time variability regarding the size of the emitted aerosol the particle size distribution for Filament *PLA-black* was measured 10 times every 3 minutes after the printing was stopped (**Figure 6A**). The measurements show an increase in GMD (**Figure 6B**) and a decrease in particle concentration (**Figure 6C**) with each consecutive measurement run. The increase in particle size could be due to agglomeration, which would also explain the decrease in particle concentration. Interestingly, this occurrence of particle size increase and concentration decrease was not only observed after the printing has stopped, but also during printing processes. This shows that the measurement time is an important factor.

Quantitation of metal content before and after printing using ICP-MS

A comparison of the filaments containing metal additives before and after the printing process revealed no difference in regard to their metal content. This unchanged metal-polymer ratio indicates that the released particles are not solely polymer, as this would lead to a higher metal concentration in the printed material due to the polymer loss. Released metal nanoparticles could imply higher health risk for the user[22]. In general, the high amount of metal in advanced filaments should be noted. Metals may cause adverse health effects and especially the release of nanoscale particles requires safety precautions in daily life scenarios[30].

For the *PLA-copper* filament we measured a weight percentage of 70 for copper. For the steel filament we measured weight percentages of 30% Fe, 8% Cr and 6% Ni in the filament. Often the exact composition of the filaments is not declared, and possible risks are therefore not known to the user. Exposure to nickel may have adverse effects on human health and can cause skin allergies, lung fibrosis, cardiovascular and kidney diseases. The element is suspected human carcinogen[31].

Besides the metal filaments, *PLA clear* was analyzed before and after printing. Here, an increase of Cu, Zn, Fe, Cr and Ni was measured after the printing process. This could be due to other materials having been extracted through the 3D pen before and resulting in a memory effect. Measurements were repeated with a newly purchased 3D pen and here no significant increase could be observed (**Figure 7**).

Particle morphology using TEM

The TEM images confirmed the presence of particles and verified the difference in particle size between ABS and PLA, measured with the SMPS. TEM images showed particle sizes mostly around 50 nm for PLA (**Figure 8A**). ABS black showed almost consistently larger particles up to 100 nm (**Figure 8B**). The difference of particle sizes between PLA and ABS, as seen with the SMPS, could be confirmed. However, smaller sizes were measured by TEM. The smaller sizes could be due to the SMPS measuring particle agglomerates, as described previously, and TEM images showing non agglomerated particles.

PLA-copper filament contained copper as well as PLA particles (**Figure 8C**). Copper was mostly in crystalline form with sizes around 150 nm. This fits the SMPS measurement of the copper filament, which resulted in mean GMD of 178 nm (**Figure 5**). **Figure 8D** possibly depicts a released CNT from the *PLA-CNT* filament. Furthermore, the release of small steel particles during the printing with *PLA-steel* filament was observed (**Figure 8E**). The aluminum filament was described as "PLA compound - with an incredibly high amount of silver aluminum-flakes added"[32]. **Figure 8F** shows possible an agglomeration of those flakes as the size is much bigger compared to the measured GMD of 124 nm using SMPS.

FIGURE AND TABLE LEGENDS:

Figure 1: Picture of 3D printing pens and schematic construction of a 3D printing pen. The 3D printing pen heats the filament to the chosen temperature and extrudes the melted thermoplastic.

Figure 2: Experimental setup for online aerosol measurement. The particle concentration is measured with a CPC and the particle size distribution with a SMPS.

Figure 3: CPC measurement of particle concentrations. The measurements show an increase after print start and higher concentrations for ABS compared to PLA.

Figure 4: Particle Size Distribution measured with SMPS with standard deviation (n=3). PLA printing results in smaller particle compare to ABS. Temperature increase results in higher concentration but shows no significant effect on the particle size.

Figure 5: Average geometric mean diameter with standard deviation (n=3) for all filaments analyzed. Printing with PLA resulted in smaller particles compare to ABS.

Figure 6: Particle size distribution measured just after print stop. (**A**) Particle size distribution measured every 3 minutes over a period of 30 minutes after a printing process with PLA black. (**B**) Increase of GMD. (**C**) Decrease in concentration.

Figure 7: Metal content in digested filaments measured with ICP-MS. Increase of metal content in PLA-clear filament after printing process.

Figure 8: TEM-Images of samples from printing process: (**A**) PLA-black filament resulting in PLA particles around 50 nm. (**B**) ABS-black filament resulting in ABS particles up to 100 nm. (**C**) PLA-copper filament resulting in Copper crystals (120-150 nm) in addition to PLA. (**D**) PLA-CNT filament resulting in CNT release. (**E**) PLA-steel filament resulting in released steel fragments. (**F**) PLA-Aluminum filament resulting in big aluminum particles. (**C**) – (**D**): Arrows indicating PLA and circles metal or CNT respectively.

DISCUSSION:

The protocol shows a fast, inexpensive and user-friendly method to analyze emissions of a 3D printing pen. Besides the comparison of PLA and ABS, filaments containing significant amounts of metals and CNTs can be investigated.

Critical steps are cleaning the chamber to avoid cross contamination and to ensure that the background concentration is low. We used a desiccator as an available chamber option, but other chambers might be used.

Particle concentrations and particle size distributions are measured online during and after the printing process. In this study, particle concentrations reaching values above 106 particles/cm^3 were recorded, which might be of concern. In particular, when particles smaller than 100 nm were found. The aerosol measurements allowed particle concentration measurements with the CPC in the size range 4 nm to 3 µm. The SMPS measurements only allowed particle size distribution measurements between 14.4 nm and 673.2 nm. Smaller or larger particles might be missed in those measurements.

The method confirms particle presence in 3D pen emissions by offline TEM analysis. In the study nanoparticles of the different thermoplastic materials as well as of metal particles and CNTs were detected.

For the TEM analysis, we relied on the sedimentation of the particles over time as other sampling methods did not work, but improvement or modification of the sampling might be useful. The concentration of the ambient air was very low and insignificant to the emissions concentrations, but the use of an inlet filters might be valuable. In the future, other chamber volumes will be used to compare the result to 3D printer emissions. The protocol focused on the release of particles, but open questions remain, as for example, with regard to the emission of volatile organic compounds (VOCs). For 3D printers it was already shown that in addition to particles, VOCs are being released[9-18,33]. It can be assumed that 3D pens may cause similar emissions.

3D printers can be started and then print without the user's presence. They are, however, handheld devices and are mostly operated manually. Therefore, the user remains closer to the device during the entire printing process resulting in a potentially higher exposure. This should especially be noted as 3D pens are often advertised for being usable by children. In general, particle emissions from FFF 3D processes are comparable to laser printers, in terms of particle number concentrations[34]. Accordingly, precautions should be taken to reduce the level of exposure. It seems reasonable to advice that 3D pens should be used at low printing temperatures and only in well ventilated environments. Filaments with metal or other additives should be used with care, as the release of potentially harmful metal nanoparticles or fibers is likely.

In the future, this protocol can be used to compare more filaments and different 3D printing pens to gain a better understanding of the emissions of these devices and the possible risk for consumers. Furthermore, this protocol can be used to analyze other aerosol generating cases (e.g., spray products).

ACKNOWLEDGMENTS:

Thanks to Sebastian Malke and Nadine Dreiack for laboratory support.

DISCLOSURES:

The authors have nothing to disclose.

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34 Uhde, E., He, C., Wensing, M. Characterization of ultra-fine particle emissions from a laser printer. *Proc. Int. Conf. Healthy Building.* **2**, 479-482 (2006).

Figure 1: Picture of 3D pens and schematic construction of a 3D pen.

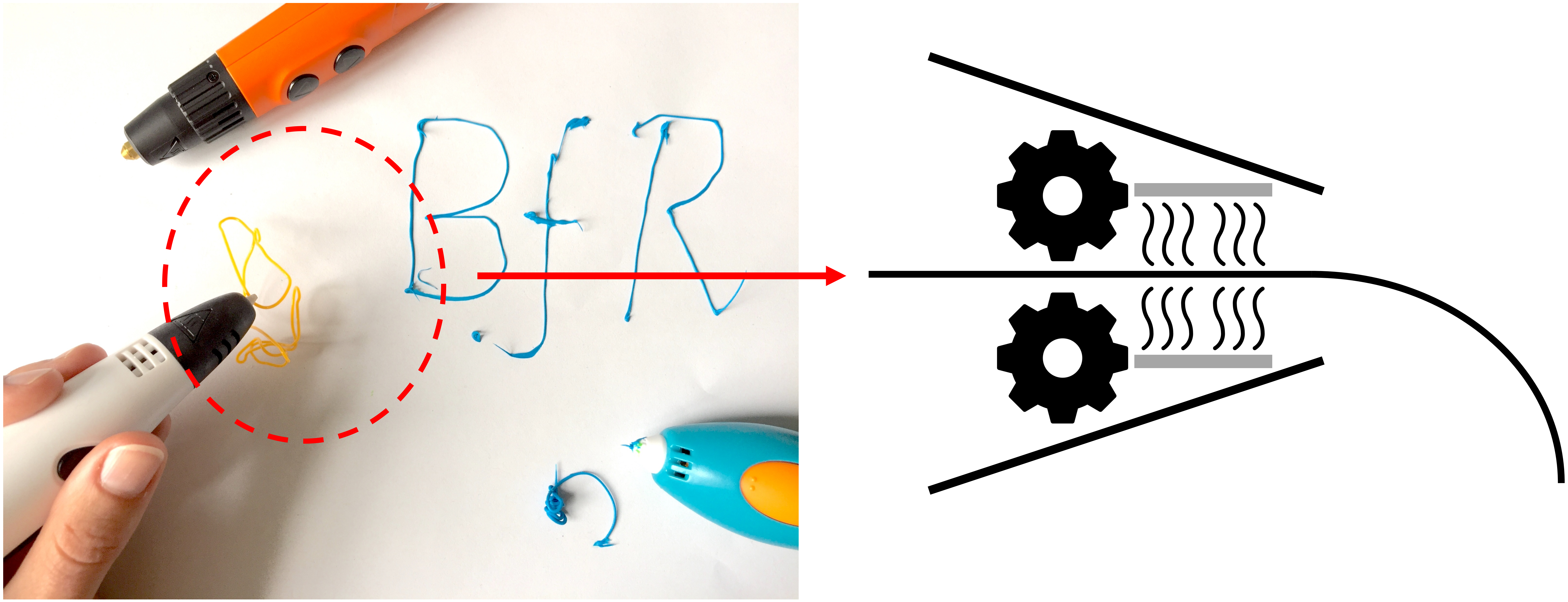


Figure 2: Experimental setup for online measurement of the particle concentration (CPC) and particle size distribution (SMPS)..

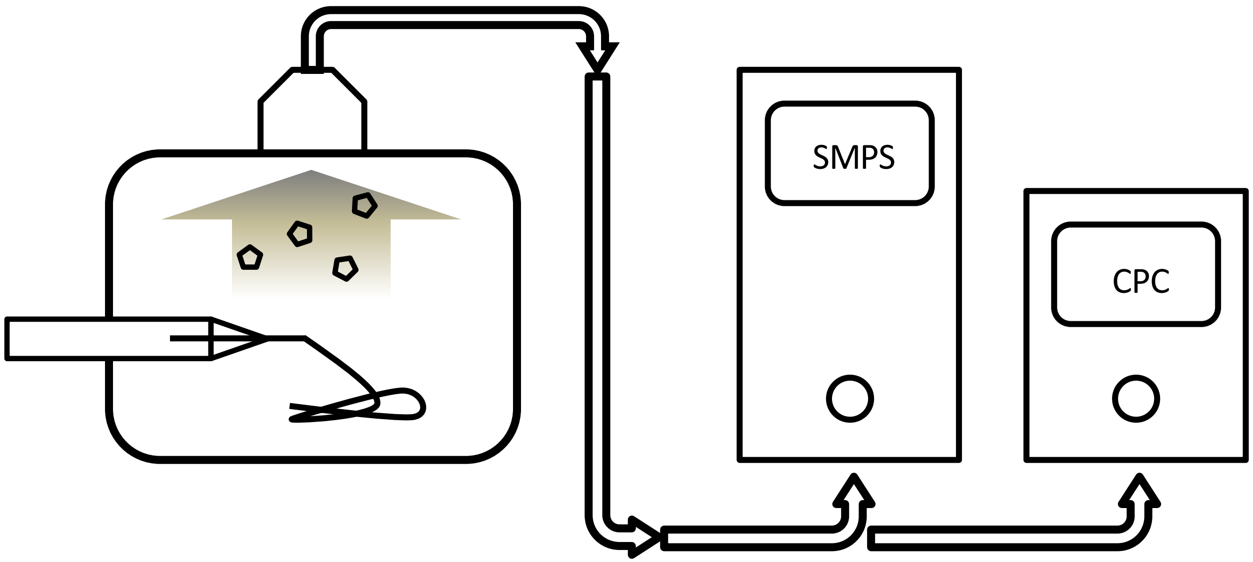


Figure 3: CPC measurement of particle concentrations show an increase after print start and higher concentrations for ABS compared to PLA.

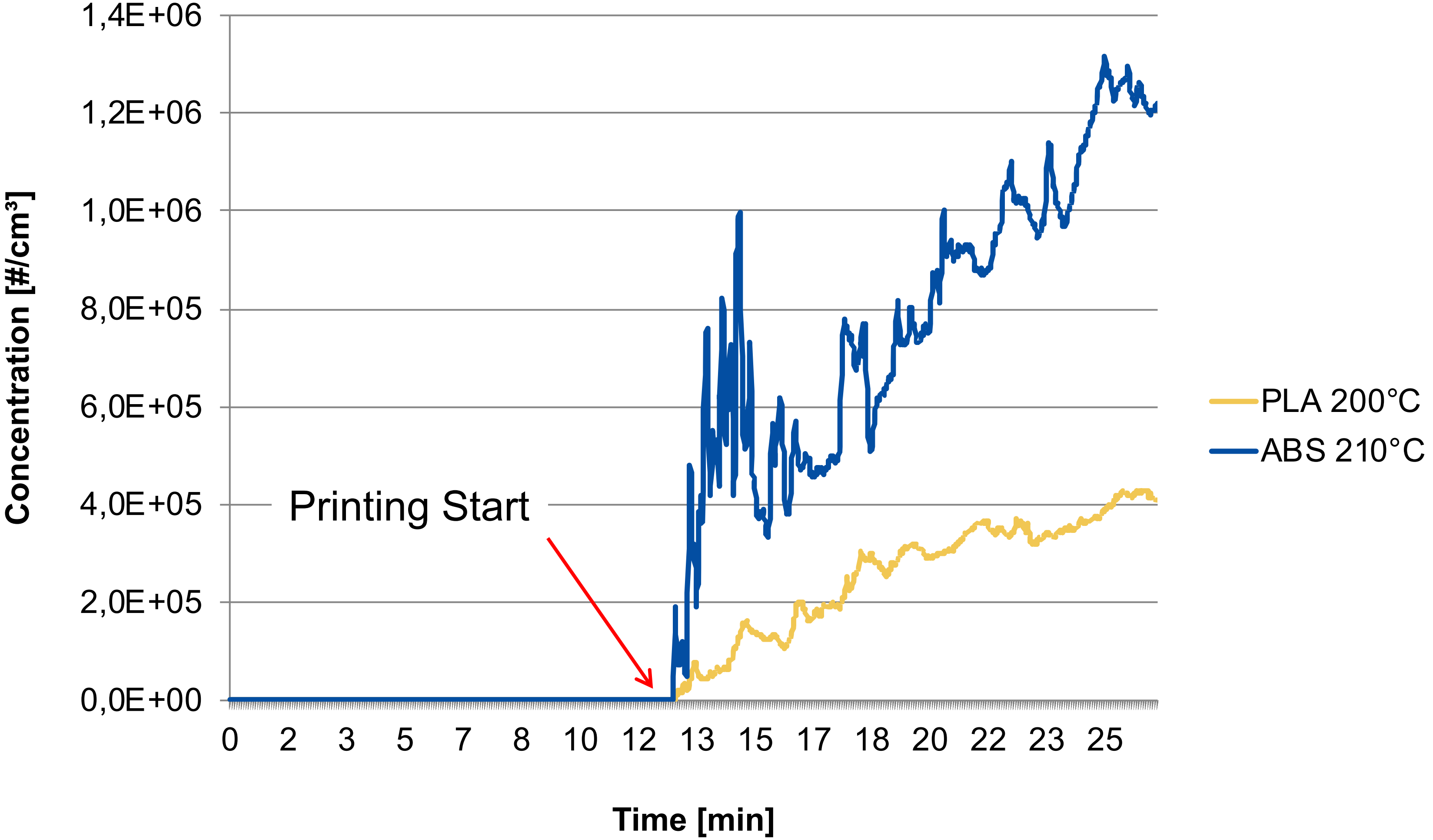


Figure 4: Particle Size Distribution measured with SMPS. PLA printing results in smaller particle compare to ABS. Temperature increase results in higher concentration but shows no significant effect on the

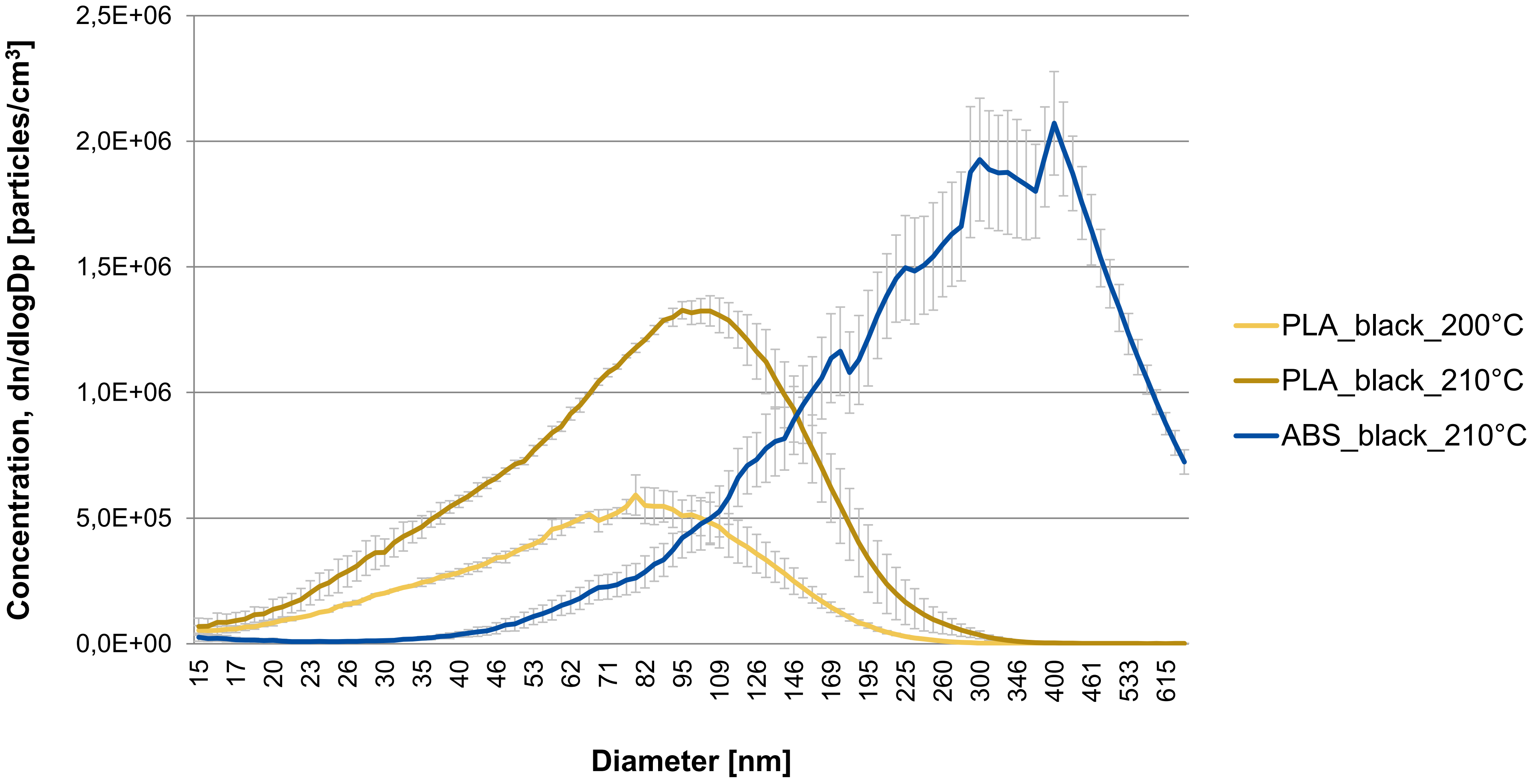


Figure 5: Average geometric mean diameter with standard deviation (n=3) for all filaments analyzed.

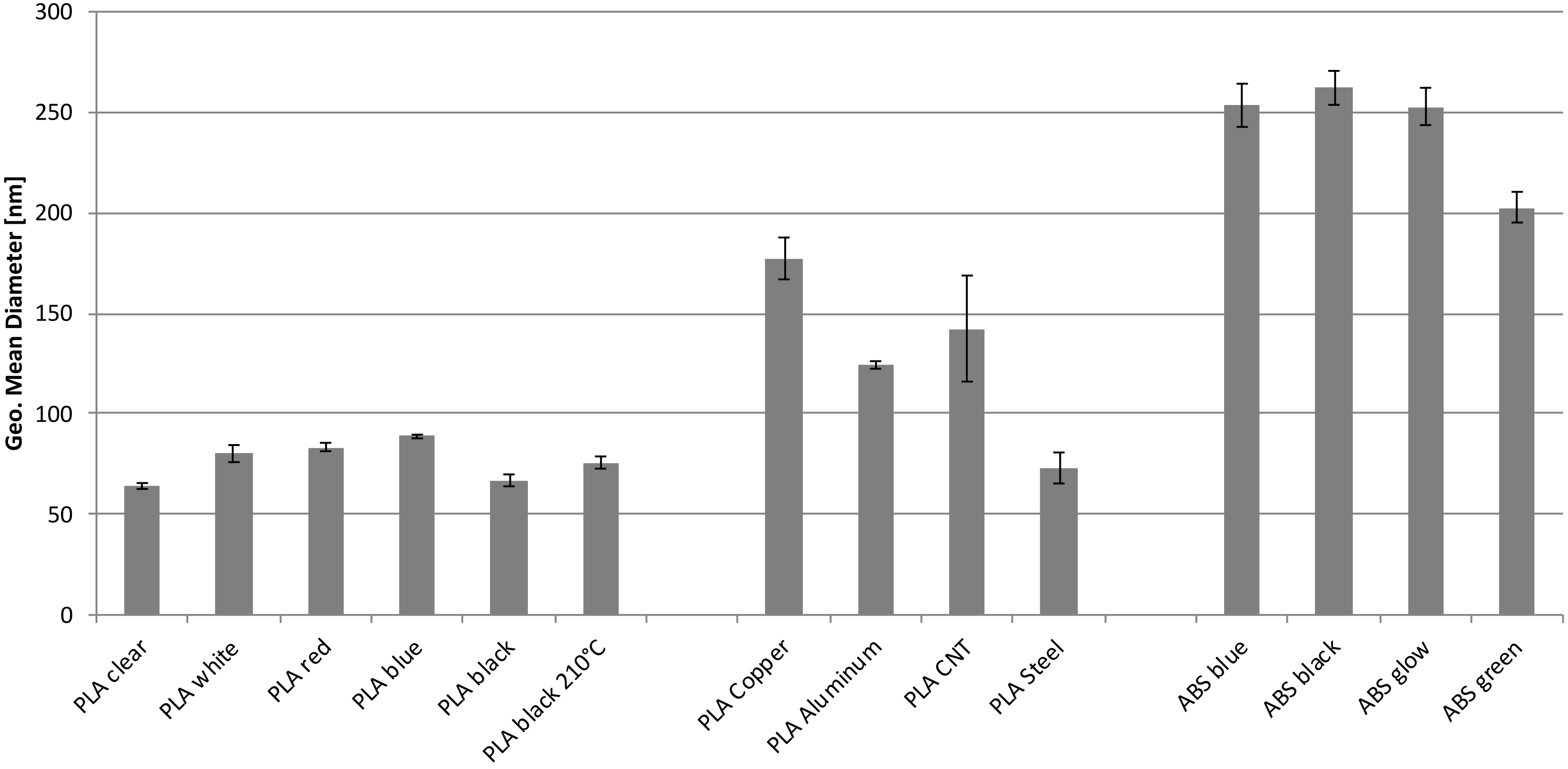


Figure 6: (A) Particle size distribution measured every 3 minutes over a period of 30 minutes after a printing process with PLA black. (B) Increase of GDM. (C) Decrease in concentration.

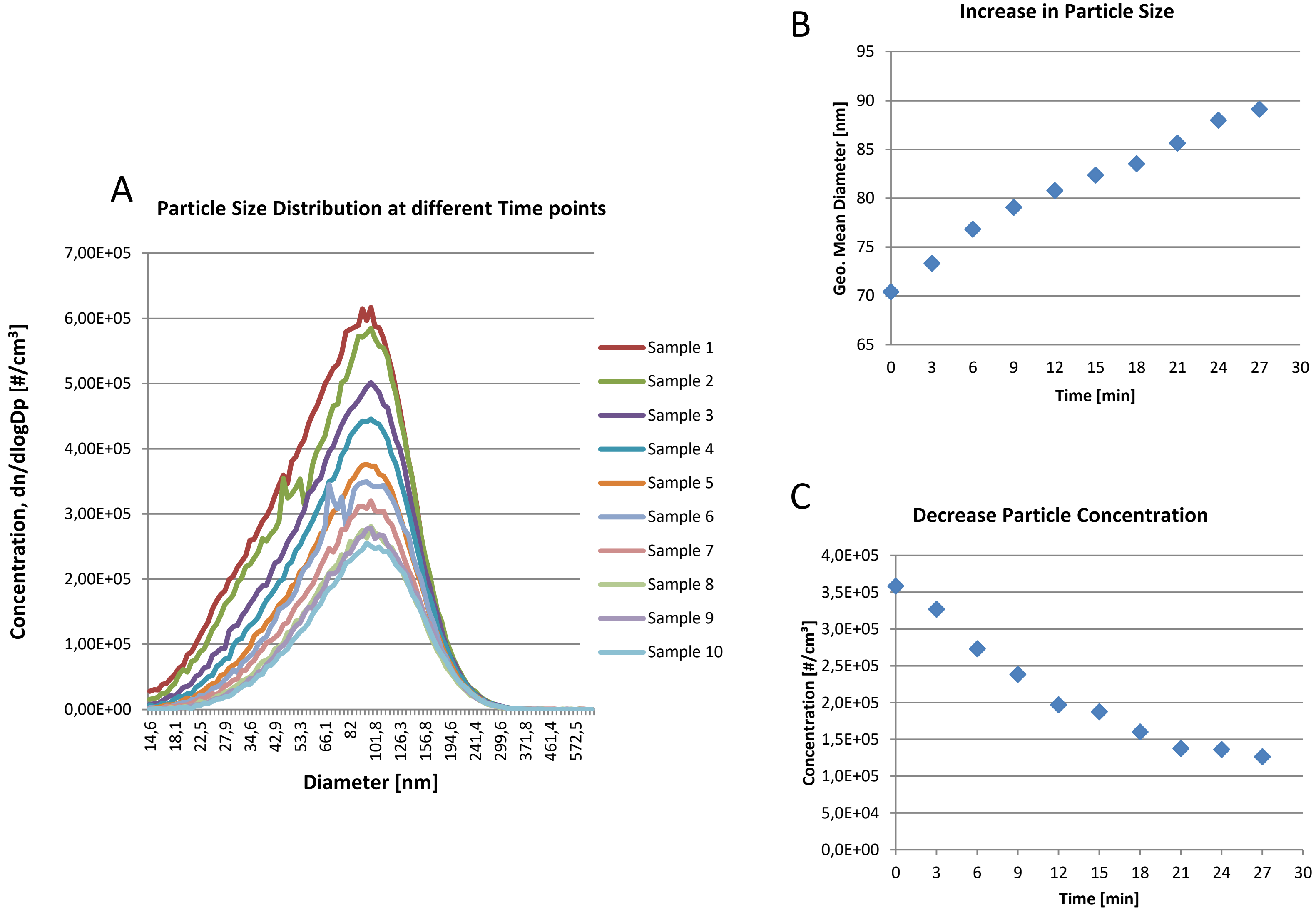


Figure 7: Increase of metal content in PLA-clear filament after printing process.

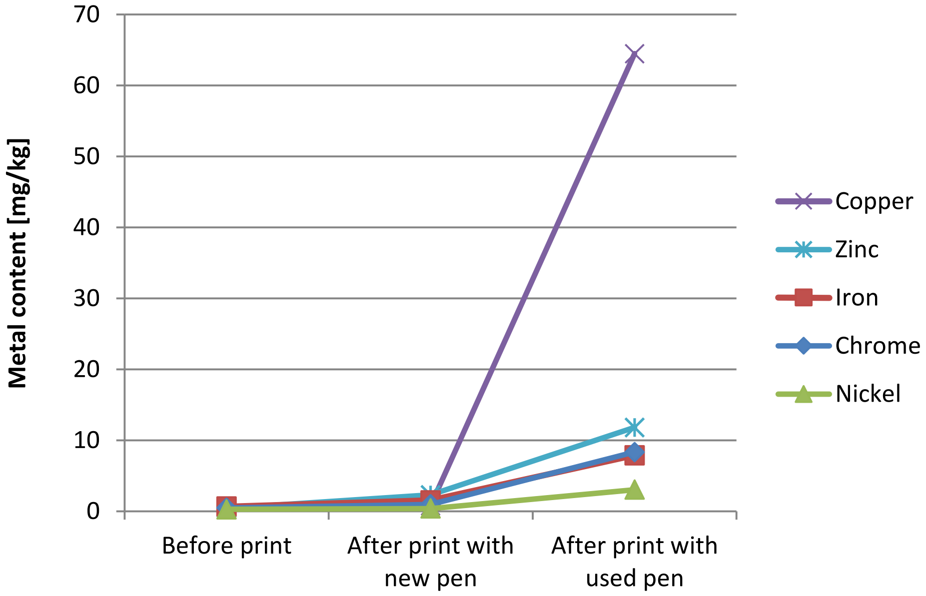
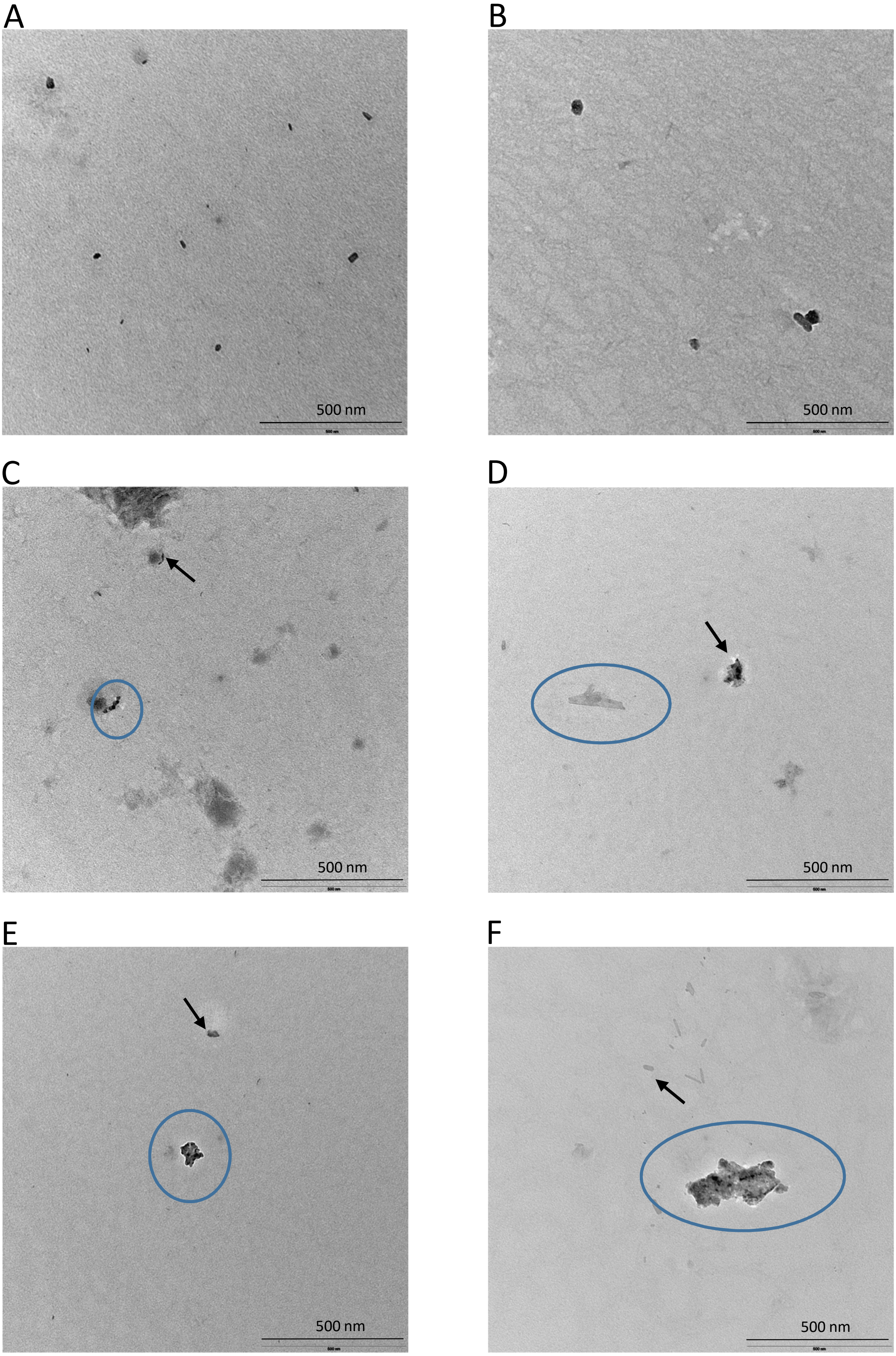


Figure 8: TEM-Images of samples from printing process: (A) PLA-black filament resulting in PLA particles around 50 nm. (B)



Name of Material/Equipment	Company	Catalog Number
3D printing pen	lovebay	
ABS black	Filamentworld	ABS175XBLK
ABS blue	Filamentworld	ABS175XSB
ABS glow in the dark	Formfutura	ABS175XGID
Alcian Blue	Sigma Aldrich, Germany	
Collodion	Electron Microscopy Services GmbH, Germany	
CPC	TSI Inc.	Model 3775
Hydrogen peroxide	Merck KGaA	
Imaging camera	Olympus, Germany	Veleta G2 camera
iTEM software	Olympus, Germany	
MilliQ water	Merck KGaA	
Nitric acid		
PLA black	Filamentworld	PLA175XBLK
PLA blue	Filamentworld	PLA175XSBL
PLA clear	Filamentworld	PLA175XCLR
PLA red	Filamentworld	PLA175XRED
PLA white	Filamentworld	PLA175XWHT
PLA wiht Aluminium	Formfutura	GPLA175XTSI
PLA wiht CNTs	3DXTech	3DX175XPLAESD
PLA with Copper	Formfutura	MFL175XCOP
PLA with Steel	Proto-Pasta	PP175X500SST
SMPS	TSI Inc.	Model 3938
TEM	Jeol GmbH, Germany	Jeol 1400 Plus

TEM grids alternative (plastic coated): Formvar-Film auf 400 mesh Cu-Netzchen	Plano GmbH, Germany	SF162-4
TEM grids: 400 mesh 3.5 mm copper grids	Plano GmbH, Germany	

Comments/Description
bought on: www.amazon.de
bought on: www.filamentworld.de
bought on: www.filamentworld.de
bought on: www.filamentworld.de
other particle tracking measurement devices can be used
30%, suprapur
Milli-Q® System
69%, In-house cleaned by distillation
bought on: www.filamentworld.de
bought on: www.filamentworld.de
bought on: www.filamentworld.de
bought on: www.filamentworld.de
bought on: www.filamentworld.de
bought on: www.filamentworld.de
bought on: www.filamentworld.de
bought on: www.filamentworld.de
bought on: www.filamentworld.de
other particle tracking measurement devices can be used

Manuscript ID: JoVE61829

Title: 3D Printing – Evaluating Particle Emissions of a 3D Pen

Dear Editor,

We would like to thank the editorial office and reviewers for their helpful comments on our original submission. We have revised our paper according to these comments. In response to reviewers query and suggestions, we adjusted the manuscript. For the editors and reviewer comments, please refer to the specific changes described in the following text. We have incorporated changes into the main manuscript and we have marked our response as answer highlighted in green. We hope the editorial office find the revised version appropriated and worth publishing in JoVe Methods. We look forward to hearing from you regarding our submission. We would be glad to respond to any further questions and comments that you might have.

Response to Editorial comments

Changes to be made by the Author(s):
1. Please take this opportunity to thoroughly proofread the manuscript to ensure that there are no spelling or grammar issues. The JoVE editor will not copy-edit your manuscript and any errors in the submitted revision may be present in the published version.
2. Please format the manuscript as: paragraph Indentation: 0 for both left and right and special: none, Line spacings: single. Please include a single line space between each step, substep and note in the protocol section. Please use Calibri 12 points
3. Please provide an email address for each author.
Corrected.

4. Please define all abbreviations during the first-time use.
Corrected.

5. Please ensure there are 6-12 keywords or phrases.
Corrected.

6. JoVE cannot publish manuscripts containing commercial language. Please remove all commercial language from your manuscript and use generic terms instead. All commercial products should be sufficiently referenced in the Table of Materials and Reagents.
For example: Amazon, https://www.filamentworld.de/), etc.
Corrected.

7. Please ensure that all text in the protocol section is written in the imperative tense as if telling someone how to do the technique (e.g., “Do this,” “Ensure that,” etc.). The actions should be described in the imperative tense in complete sentences wherever possible. Avoid usage of phrases such as “could be,” “should be,” and “would be” throughout the Protocol. Any text that cannot be written in the imperative tense may be added as a “Note.” However, notes should be concise and used sparingly.

8. Please add more details to your protocol steps. Please ensure you answer the “how”

question, i.e., how is the step performed? For this please include button clicks in the software, command lines, mechanical actions etc.
9. 2.1.1 How is this done? Do you perform any button clicks, or knob turns?
10. 2.1.2. What is the chosen filament in your case? Volume used?
11. 2.1.3, 2.1.4, 2.2.3: How is this done?
12. 3.2: Please include how each step is performed.
13. There is a 10-page limit for the Protocol, but there is a 2.75-page limit for filmable content. Please highlight 2.75 pages or less of the Protocol (including headings and spacing) that identifies the essential steps of the protocol for the video, i.e., the steps that should be visualized to tell the most cohesive story of the Protocol.
Answers: Details have been added to the revised manuscript. Please refer to the protocol section.

14. Please ensure that all the figures are referenced in order.
Corrected.

15. Please check line 242. There seem to be some error here.
Corrected.

16. Each Figure Legend should include a title and a short description of the data presented in the Figure and relevant symbols.
17. Please obtain explicit copyright permission to reuse any figures from a previous publication. Explicit permission can be expressed in the form of a letter from the editor or a link to the editorial policy that allows re-prints. Please upload this information as a .doc or .docx file to your Editorial Manager account. The Figure must be cited appropriately in the Figure Legend, i.e. "This figure has been modified from [citation]."
Corrected.

18. As we are a methods journal, please ensure that the Discussion explicitly cover the following in detail in 3-6 paragraphs with citations:
a) Critical steps within the protocol
b) Any modifications and troubleshooting of the technique
c) Any limitations of the technique
d) The significance with respect to existing methods
e) Any future applications of the technique
The Discussion was adjusted.

19. Please sort the materials table in alphabetical order.
Done.

Response to Reviewers Comments

Reviewers' comments:
Reviewer #1:
Manuscript Summary:
The article discusses the measurements of particulate levels from handheld 3D printing pens, adopting aerosol measurements, TEM and ICP-MS. This is an interesting topic that is of public health and safety concerns. Paper is relatively well written with comments as follow

Major Concerns:
1. There had been several work on emissions from 3D printing from different research groups which the authors cited. The authors should review these papers and justify its novelty, which probably is in the metal and CNT additives parts which is less studied in 3D printing emissions. In addition, i think the entire protocol is not specific to 3D printing pens alone. Can also be for desktop 3D printers as it is afterall study of filament thermal decomposition, which the title is probably more valid in the lines of Evaluating particle emissions from 3D printing of polymer filaments with additives

Studies with 3D printers exist, but only one with 3D Pen and they did not use filaments with metal or other additives. We focused on the use of 3D printing pens as they have not been studied in detail. Furthermore 3D printing pens are handheld devices and the user remains closer to the device during the entire printing process resulting in a potentially higher exposure. This should especially be noted as 3D pens are often advertised for being usable by children. Therefore it makes user more prone to vital organs (e.g. eyes) exposure and inhalation of emissions from 3D pens, which we strongly believe is a hot topic as emerging technology in regulatory research.

2. In the protocol for Aerosol Measurement, the suggested size of the chamber and also ACH, if any, should be mentioned and whether well-mixed conditions are attempted to be achieved. Furthermore, protocol should also mention the object of printing as this will affect printing emission levels if comparisons were to be made between filament materials and brands. Were the experiments to be repeated and is there consistency in results for repeated measurements?

- ACH (1.0 h^{-1}) and chamber size (18.5l) was added to the protocol
- We did not print any object, but a continuous string was printed and collected on the bottom.
- Experiments were repeated 3 times. Please see Figure 5. The information was also added to Figure 4.

3. As chamber and room size varies which affect concentration levels, it will be useful to calculate the emission rate (#/min), which gives another indication of comparisons with studies on filament emissions. See Ding et al. The characteristics and formation mechanisms of emissions from thermal decomposition of 3D printer polymer filaments, 2019.

Answer: It was decided to focus on the particle concentration since different calculations can and have been used in previous literature. For example, Byrley et al. 2019 mentioned 5 different used equations, making it more difficult to compare. Therefore we focused on the particle concentration.

See: Byrley, P., George, B. J., Boyes, W. K. & Rogers, K. Particle emissions from fused deposition modeling 3D printers: Evaluation and meta-analysis. *Science of The Total Environment.* **655** 395-407, (2019).

4. Another aspect for protocol is also the treatment of the filaments before printing. Are they used immediately after removing from packaging? Humidity and moisture levels affect the amount of emissions.

Answer: We thank reviewers raising this important point. We tested filaments fresh from the packaging and after being exposed to humid air as we also expected some influence. But so far we did not see a difference in emission.

Minor Concerns:
1. What is the reason for using CPC during printing and then SMPS after printing? Why not the same instrument throughout?
Reply: During printing no stable aerosol state was achieved. Due to the SMPS working principle of repeated runs measuring all size bins consecutively, a stable aerosol state is normally required. Therefor we decided to start the SMPS measurement only when 3D printing had stopped since then no further emission would introduced into the chamber. Although a decrease in aerosol concentration and possible change in particle size distribution will occur over time after printing, this seemed to be the better compromise. Additionally due to the used SMPS parameters on complete run (14.4 nm to 673.2 nm) took about 3 minutes. With the CPC we were able to measure the concentration every second and in a bigger particle size range (4nm – 3µm).

2. 2.1.4 - ensure not insure
Corrected.Thanks!

3. Error ref missing in line 242
Corrected.Thanks!

4. Figure 6 You used GDM. Should be GMD
Corrected.Thanks!

Reviewer #2:
Manuscript Summary:
In this manuscript, the authors present a protocol to measure the emissions from pen devices that are used by children to make 3-dimensional objects. The pens utilize similar technology to desktop-scale 3-dimensional printers. Two types of thermoplastics, PLA and ABS, were tested. These types represent the most common filaments and are representative of what consumers would often use. The overall protocol followed logical steps, though it did not acknowledge several critical factors related to chamber qualification, air sampling, and analysis. Herein comments are provided from my review.

Major Concerns:
Line 109: Understandably, this section is brief as it is a high-level overview of the protocol; however, many critical requirements are glossed over in this section. UL has published test method 2904 for evaluation of 3D printer emissions using a test chamber that would cover pen devices. Additionally, there are numerous standard test methods for assessing emissions from products published by ISO and ASTM International. All of these standards have in common requirements for chamber qualification, which include: 1) leak test using a tracer gas, 2) air exchange rate using a tracer gas, 3) mixing efficiency using a tracer gas, and 4) wall loss test for representative organic compounds. At a minimum, the protocol should make clear that emissions testing is not as simple as "Prepare a chamber", but rather it is a highly complex and detailed process to perform correctly.

ANSI/CAN/UL 2904: Standard Method for Testing and Assessing Particle and Chemical Emissions from 3D Printers
ASTM D5116: Standard Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/Products
ASTM D6670: Standard Practice for Full-Scale Chamber Determination of Volatile Organic

Emissions from Indoor Materials/Products
ISO 16000-9: Indoor air — Part 9: Determination of the emission of volatile organic compounds from building products and furnishing — Emission test chamber method
ISO/IEC 28360: Information technology — Office equipment — Determination of chemical emission rates from electronic equipment
Yes, for comparability a standard chamber would be useful, but our method was a low cost method, which could be implemented easily to get some first ideas about the emissions of 3D printing pens and the influencing parameters. We added some important points regarding the used method e.g. chamber size (18.5l).

Lines 109-113: As with the chamber qualification, monitoring of emissions is also highly complex and goes beyond using conductive tubing and turning on a CPC or SMPS. Additional information includes using as short a length of conductive tubing as possible that is free of bends or elbows; potential for line losses, especially for smaller particles; limitations of CPCs in terms of lower size cut-off being relatively large (usually 10 to 20 nm, depending on the manufacturer) that can result in significant underestimation of particle concentrations; size range of SMPS can be modulated by changing instrument settings and even the lower-size cutoff of a mobility particle sizer may still significantly underestimate particle counts (see Poikkimaki. Environ Sci Technol. 53:13618-13628 (2019)).
We added the information about tubing to the protocol. Yes, CPC and SMPS have their size and we added this limitation to the discussions part.

Lines 124-153: Please add in when to start samples for particle collection for off-line metals and TEM analyses. A rationale is needed for why the particle size distribution measurements are not initiated until after the print job is completed? Why not monitor during printing? Presented results show that particle size changed over time.
Reply: The TEM Grids were placed inside the chamber just before print start and left there until 5 hours after print stop. (This is described in the protocol)

During printing no stable aerosol state was achieved. Due to the SMPS working principle of repeated runs measuring all size bins consecutively, a stable aerosol state is normally required. Therefor we decided to start the SMPS measurement only when 3D printing had stopped since then no further emission would introduced into the chamber. Although a decrease in aerosol concentration and possible change in particle size distribution will occur over time after printing, this seemed to be the better compromise. Additionally due to the used SMPS parameters on complete run (14.4 nm to 673.2 nm) took about 3 minutes. With the CPC we were able to measure the concentration every second and in a bigger particle size range (4nm – 3µm).

Line 157: Nanoparticles will remain airborne for many hours so it is unclear how well settling plate samples with TEM grids will collect particles? Please include data to support the feasibility of settling plates rather than active sampling using a thermophoretic or electrostatic precipitator or even a grid on a filter housed in a sampling cassette?
Reply: We tried to use a TEM sampler to actively collect particles, unfortunately in this case the collected amount of particles on the TEM Grid was too high and measurement were not possible.

Line 184: ICP analysis is more complex than presented herein. I have discussed metals analysis with many researchers and the digestion step is critically important to maximize the accuracy of measurements. Even then, not all elements are recovered equally and some

may be overestimated while others are underestimated. The authors should include robustness data on the ICP measurement procedure.
It is correct that especially sample preparation for ICP-MS is critical when dealing with complex matrix or samples. At the moment there is no reference for metal-containing filaments available but would be needed for a validation of the digestion method. Therefor a digestion was done following the SOP developed in the RIVM NANoREG project. Although this protocol was developed for organic matrices it should ensure the complete digestion of the nanoparticles and no solid fraction was found. To check the usability of this approach for the filaments the metal content values provided by the manufacture in the datasheets were used as reference in comparison to the unprinted filaments and agreed well with our measurements.

Line 212: Expression of results in concentration units severely limits inter-study comparison of data that will be collected using this protocol. Concentration will depend on several chamber-related factors, including size, air exchange rate, wall losses and so on. At a minimum, all results should be presented as emission rates (# particles per minute) though ideally, they would be presented as yield values (# particles per gram of filament extruded). See UL 2904 and more recent literature on 3-D printer emissions for models to calculate emission rate and yield values.

Answer: It was decided to focus on the particle concentration since different calculations can and have been used in previous literature. For example, Byrley et al. 2019 mentioned 5 different used equations, making it more difficult to compare. Therefore we focused on the particle concentration

See: Byrley, P., George, B. J., Boyes, W. K. & Rogers, K. Particle emissions from fused deposition modeling 3D printers: Evaluation and meta-analysis. Science of The Total Environment. 655 395-407, (2019).

Minor Concerns:
Line 31 (and throughout the manuscript): Fused deposition modeling is the name trademarked by Stratasys Inc and generally refers to industrial-scale prototyping machines. When Stratasys' patent expired, new companies began to offer desktop-scale machines that utilize similar technology but referred to it as fused filament fabrication (FFF) to avoid intellectual property issues with Stratasys. FFF is the technology used in 3-D printers and pens and suggest using this term rather than FDM™.
We changed FDM to use filament fabrication (FFF). Thanks!

Reviewer #3:
Manuscript Summary:
The study on particle concentration is well described. The TEM and morphology also discussed in good manner.

Major Concerns:
1. The sampling during chamber experiment is not well described. It is suggest to further elaborate on chamber size, how the air flow coming to the chamber, sensor location and others,
Details were added.
2. Highlight on the exposure guidelines and particle exposure limit to the consumers are missing.
3D processes are comparable to laser printers, in terms of particle number concentrations and accordingly precautions should be taken to reduce the level of exposure. This is stated

in the manuscripst

Minor Concerns:
The abstract can be rewrite and contribute to the result from experimental study.
Abstract was rewritten.

Reviewer #4:
Manuscript Summary:
This paper presents a test protocol for measuring particle emissions from 3D printing pens and presents results from testing several filaments with a 3D printer pen. The method involves measuring particle number concentrations and size distributions during operation as well as transmission electron microscopy (TEM) to examine particle morphology and compositional analysis of metal in metal-containing filaments by inductively coupled plasma mass spec (ICP-MS). The authors report particle number concentrations in the tested space to be ~10^5 to ~10^6 #/cm3, and they report aspects of their compositional analysis as well.

Overall, the work is useful, but less so in terms of the novelty of the methods/protocols and more so because of the results. I have several suggestions for improvement below.

Major Concerns:
- details on some of the chamber and test protocol aspects are lacking
Details were added to the protocol.

- emission rates aren't calculated so comparisons to other studies is not necessarily appropriate
Answer: It was decided to focus on the particle concentration since different calculations can and have been used in previous literature. For example, Byrley et al. 2019 mentioned 5 different used equations, making it more difficult to compare. Therefore we focused on the particle concentration

See: Byrley, P., George, B. J., Boyes, W. K. & Rogers, K. Particle emissions from fused deposition modeling 3D printers: Evaluation and meta-analysis. Science of The Total Environment. 655 395-407, (2019).

Minor Concerns:
Line by line comments:
Abstract (lines 30-43): I think the abstract would be stronger if the intro was shortened and additional results were shown, including the TEM and ICP-MS results. Also, details of the test environment should be included in the abstract too because reporting concentrations alone (instead of emission rates) is such a function of the space in which they operate that these details should be included up front, at least to some degree.
Abstract was adjusted.

I also have a broader nomenclature suggestion: in the abstract and elsewhere the term "3D pens" is used to describe what is really, in a more detailed sense, "3D printing pens." I know both terms are used throughout, but in my opinion the abbreviated "3D pens" is over-used because really the key word is "printing" - isn't every pen 3-dimensional? It's just not the most helpful shorthand in my opinion.
“3D pen” was replaced with “3D printing pen”. Thank you for that note.

Protocols (I find this section somewhat odd, but I assume it's a requirement for the journal).

For example:
Line 101: I don't understand why the experimental protocol has to hinge on PLA or ABS filaments alone; that seems too narrow for a test methods (also no reason to mention Amazon in the "available online" comment).
Reply: The protocol is not only limited to PLA and ABS but can be extended to other filaments. 3D printing pens are limited in the temperature range. Some pens only allow for temperatures below 200°C which is not suitable for ABS. Therefore we decided to use a pen with the highest possible printing temperature to be able to use ABS in addition to PLA.

Commercial name were deleted from the text.

Line 109: no details on chamber size or material or what constitutes "fresh air"
Details were added

Line 115: I did not understand the protocol about using a microwave to digest samples; I guess that's for offline chemical/elemental analysis?
Reply: Yes, it is for offline analysis of metal contents.

Also, I did not see any discussion of how far the sampling line inlet was from the 3D printer pen. Is the goal to characterize emissions and concentrations near the breathing zone of the user? (it seems to me that it should given the very different nature of using a 3D printer pen compared to desktop 3D printer).

Reply: Yes, the goal was to better understand the risk of 3D printing pens, which are used in close distance to the breathing zone of the user compare to 3D printers. The sampling inlet was 10 cm away from the printing outlet to mimic the distance between the users head and the 3D printing pen. The 10 cm was used after observing some people during the use of a 3D printing pen. This aspect is added to the text.

Results:
Lines 215-233: I didn't see the chamber volume reported, but that would be useful for understanding these concentrations, and would allow for comparison to the literature as they demonstrate currently. Without reporting chamber volumes from this study and others, we can't directly compare these concentrations. Moreover, the authors should follow other literature on 3D printer particle emissions and use the data to back calculate emission rates, which are more directly comparable across filaments and printer types.

Reply: The chamber volume of 18.5L is added to the text.