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Measuring and controlling emissions from polymer filament desktop 3D printers

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Affordable desktop 3D printers are being widely used in businesses, schools and colleges. Some of these printers use filaments to deposit polymer through a heated nozzle to build three dimensional objects. This type of desktop printer is generally unenclosed and some published studies have raised concerns that they may release potentially harmful fumes and particles. The scientific evidence base on exposures and potential health endpoints is being developed internationally.

This report describes initial research in a laboratory setting to a) measure emissions of particulates and volatile organic compounds from desktop 3D printers and b) investigate the effectiveness of control measures to reduce these printer emissions. Two common filament materials were investigated: polylactic acid (PLA) which is generally used in schools, and acrylonitrile butadiene styrene (ABS).

The research found that the heated filaments emitted large numbers of very small particles and volatile organic chemicals which could be breathed in. However, more research is required to establish if under real use conditions these printers release sufficient concentration of emissions to cause harm. The research identified that exposures are significantly reduced by: (1) setting a lower printer nozzle temperature; (2) using a filament with a lower emission rate; (3) placing the printer in a clear enclosing hood fitted with an extraction fan and particulate filter and (4) maintaining a hood 'clearance time' of about 20 minutes.

These findings have informed the development of a new good practice guide for schools published by CLEAPSS in 2019. This guide provides advice about precautionary measures for safe use of desktop 3D printers and measures to minimise health risks for students and school employees.

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Measuring and controlling emissions from polymer filament desktop 3D printers

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KEY MESSAGES

- Recent published evidence has raised concerns about potential risks to health for those using affordable polymer filament desktop 3D printers.
- HSE formed a working group including experienced individuals from the education sector, a 3D printer manufacturer, standards bodies, healthcare advisors, and HSE scientific and regulatory staff to discuss health and safety concerns about using desktop 3D printers in schools. The working group identified the need for evidence based advice to schools on the safe use of desktop 3D printers.
- HSE undertook laboratory tests to assess whether polymer filament desktop 3D printers released hazardous particles and vapours which a person nearby could breathe in; they also investigated control measures to reduce these emissions.
- These printers emitted many particles of a size range that can potentially enter the airways and lungs. Some plastic filament materials, when heated, were found to release vapours known to be hazardous to health.
- Emissions could be controlled by the following means:
  - using polymer filaments from reputable suppliers;
  - choosing filament materials with a lower emission rate;
  - setting a lower operating temperature for the nozzle of the printer through which the polymer filament passes;
  - placing the printer inside an enclosing hood fitted with a suitable air filtration system;
  - waiting sufficient time for printer emissions to clear (i.e. the clearance time) before opening the enclosing hood.
- A securely locked enclosing hood also reduces the risk of incidents and injuries e.g. trapping fingers in moving parts or sustaining burns from hot areas of the printer.
- Based on the results of this research, working group members identified safe working practices for schools using polymer filament desktop 3D printers. This information contributed to the development by CLEAPSS (Consortium of Local Education Authorities for the Provision of Science Services) of a good practice guide.

EXECUTIVE SUMMARY

Background

HSE formed an advisory panel including experienced individuals from the education sector, a 3D printer manufacturer, standards bodies, healthcare advisors, and HSE scientific and regulatory staff to discuss health and safety concerns about using polymer filament desktop 3D printers in schools. When the working group was formed (8th September 2015), there was limited published research characterising emissions from Fused Filament Fabrication (FFF) / Fused Deposition Modelling™ (FDM) desktop 3D printers. The few published studies examining risks to health from desktop 3D printers supported concerns about the health implications of breathing in these emissions if exposures are not effectively controlled. The working group recognised the need for an evidence based good practice guide for schools on safe use of these desktop 3D printers; including recommendations on how to reduce printer emissions to minimise risks to health.

Aim and Objectives

This project aimed to investigate particulate and volatile emissions from FFF/FDM™ desktop printers by:

1. Applying a standardised pyrolysis test to identify filament constituents.
2. Characterising the particulate and volatile emissions resulting from the FFF/FDM™ process used by small desktop 3D printers with consideration of the range of filament material available.
3. Investigating the effectiveness of potential exposure controls.

Methodology

Research was carried out in a laboratory setting. Three desktop 3D FFF/FDM™ printers were tested inside a bespoke test chamber based on the design described in British Standard BS EN 1093. These printers were used make a standard test object with a range of filament materials including Polylactic Acid (PLA) and Acrylonitrile Butadiene Styrene (ABS). Real-time aerosol monitoring instruments were used to characterise particulate emissions for: a combination of printers and filament materials; a range of printer nozzle temperatures; and with and without an enclosing hood in place. Further tests were carried out to measure the build-up of particles inside an enclosing hood and its clearance time, i.e. the time taken for the particles to be filtered and the concentration inside the enclosure to return to background levels.

One printer was placed inside a sealed box and sorbent tubes were used to sample the Volatile Organic Compound (VOC) species inside the box at different 3D printer nozzle temperatures.

A standardised pyrolysis test was used to investigate the VOC species released when a wide range of filament materials were heated to temperatures comparable to that of the 3D printer nozzle.

Transmission Electron Microscopy (TEM) and Energy Dispersive X-ray (EDX) analysis were used to identify particulate emissions, particularly those from filament containing embedded metal.

Results

When printing with ABS filament, particle emission rates varied from 1.12×10^{11} to 8.03×10^{11} particles.min^{-1} in the nozzle temperature range 245°C to 260°C. The average particle size

did not increase above 10 nm, which was the lowest size detectable by any of the particle measurement instruments used.

When printing with PLA filament, particle emission rates varied from 3.26×10^{9} to 8.23×10^{10} particles.min^{-1} and average particle sizes varied from 69 nm to 24 nm as the nozzle temperature ranged from 220°C to 240°C (measurements made with Testo DISCmini).

Placing the desktop 3D printer inside an enclosing hood with filtered ventilation reduced particle emission rates by 97% when exhausting the air from inside the hood and by 99% when the air was recirculated inside the hood. Particulate and VOC emissions accumulated inside the enclosing hood during printing and took around 20 minutes to clear to background concentrations.

Pyrolysis tests indicated that both the duration of heating, and the temperature of the filament material, affected the products released. Some filament materials released hazardous chemicals such as styrene and isocyanates.

TEM EDX analysis identified very small metal particles in the emissions from heated filament containing embedded metals.

Conclusions

Particle emissions:

- Emitted particles were in the size range to potentially enter the airways and lungs and the emission rates when printing with ABS were higher than for PLA.
- Particle emission rates varied for different filament material on the same printer.
- Particle emission rates and size distributions for the same filament materials varied for different printers.
- Particle emission rates increased and the average particle size decreased as the 3D printer nozzle temperature increased.

Volatile emissions:

- The information provided by some suppliers of filament material was found to be unreliable and uninformative with respect to the release of hazardous volatile constituents.
- Pyrolysis testing was a repeatable method to test a wide range of filament materials for VOC emissions.
- Pyrolysis tests indicated that the temperature and duration of heating the filament affected the emissions released from each filament material.
- Hazardous chemicals such as styrene and methylene diphenyl di-isocyanate (MDI) were released from some types of polymer filament materials. It is not yet clear whether in real use, concentrations of these chemicals are sufficient to cause harm if inhaled.

Effectiveness of enclosing hood for controlling exposure:

- When a filtered enclosing hood was placed over the 3D printer this reduced particle emissions released to the room by 97% when exhausting air from the hood and by 99% in the recirculating air mode.
- Particulate and VOC emissions accumulated inside the test enclosure during printing and took approximately 20 minutes to clear, therefore removing the enclosing hood before this time could result in exposure to these emissions.

CONTENTS

1 INTRODUCTION

1.1 BACKGROUND

Desktop 3D printer technology and its applications: With an increasing number of industries and businesses considering using three-dimensional (3D) printing technologies, and many already doing so (Floyd *et al*, 2017), it is important that any potential exposure risks produced by these processes in the workplace are identified and if necessary controlled. One large market for 3D printers is the education sector, with many educational establishments purchasing the machines for use in classrooms by staff and students including young children. As these printers are designed to be positioned on a desktop and can take hours to complete the printing of even a simple model, it is possible that an employee or student could be sat within close proximity for several hours.

Professional users such as designers and architects have begun to adopt the technology for concept visualisation, and the manufacturing industry are utilising the technology for rapid prototyping. Community spaces where members of the public and industry creatives can meet to work together with access to 3D printers are becoming more common in the United Kingdom (UK) including in public spaces such as cafés and libraries.

This report mostly concerns the use of Fused Filament Fabrication (FFF) desktop 3D printers. These may also be referred to as Fused Deposition Modelling™ (FDM) desktop 3D printers. From this point onwards, the term FFF will be used to describe the process.

Emissions from desktop 3D printers: Evidence from published research investigating both particulate and volatile emissions from FFF desktop 3D printers demonstrated that this process may pose an inhalation risk (Mendes *et al*, 2017; Stefaniak *et al*, 2017; Azimi *et al*, 2016; Yi *et al*, 2016 and Stephens *et al*, 2013); these are discussed further in Section 4. Only Floyd investigated particle morphology. Stefaniak *et al* repeated measurements with and without a 'manufacturer-provided cover', but none of the published studies reviewed as part of this research included a detailed evaluation of potential exposure control methods.

Findings from these published studies suggest that ultrafine (<100 nm diameter) particles are likely to be emitted from the 3D printer as the filament is extruded through the nozzle. There is evidence that inhaled ultrafine particles in polluted air initiate inflammatory responses in the airways and lungs. Epidemiological studies into human exposure to ambient air pollution have suggested that in addition to effects in the lungs, people inhaling air that contains high levels of ultrafine particles are more likely to suffer from lung and cardiovascular disease (Bourdrel *et al,* 2017). However, the factors that determine the severity of this response are not fully understood and the longer term health consequences for repeated exposure are in many cases unknown (http://www.hse.gov.uk/nanotechnology/understanding-hazards-nanomaterials.htm).

In addition to the differences in the design of the desktop printers, an extensive range of filament material is available from a wide range of suppliers. These vary in mechanical and aesthetic properties making them useful for different applications. With the increasing use of commercial names, such as 'NinjaFlex®' and 'BendLay', it may be difficult to immediately identify the constituents of the filament material. It is likely that the same printing process will create different risks depending on the filament material used, which is important to note as new filament materials are continuously being manufactured and these may all emit particles and VOC at different rates.

Printer emissions and risks to health: It was not an objective of this HSE research to determine the long-term health effects from inhaling emissions from 3D printers. A search of published research located some studies reporting hazardous emissions, as well as ill-health or symptoms in those exposed. These studies included a case study, an inhalation volunteer challenge study, a small cross-sectional survey of symptoms, and other studies that considered the hazardous properties of these emissions.

House *et al* (2017) reported a case study of a twenty-eight year-old self-employed businessman who had first developed asthma at the age of eight. This condition only recurred in later life when he started to use an FFF 3D printer with Acrylonitrile Butadiene Styrene (ABS) filament in a small work area (~85 m^3). He experienced recurrent chest tightness, shortness of breath, and coughing. When given a methacholine inhalation challenge at 4.0 $mg.ml^{-1}$ this resulted in a 20% fall (PC20) in forced expiratory volume in one second (FEV1) consistent with mild asthma. After three months his workplace reduced the number of printers and introduced Polylactic Acid (PLA) filament, as well as HEPA filtration with organic cartridges to remove organic pollutants from the air. After this intervention his symptoms gradually improved and after a second methacholine challenge his FEV1 was normal and the PC20 value was > 16 $mg.ml^{-1}$. However, he continued to occasionally use his salbutamol inhaler.

A small volunteer challenge study (26 volunteers) analysed the effects of one-hour inhalation of fumes from a printer either using PLA or ABS filament, and monitored the expression of nasal inflammatory markers (cytokines, prostaglandins and exhaled nitric oxide) and self-reported symptoms. This acute exposure did not significantly alter the expression of cytokines and other inflammatory markers except for exhaled nitric oxide which was raised after inhalation of the ABS fumes. The ABS fumes were also reported to cause a greater odour nuisance response from the volunteers (Gumperlein *et al,* 2018).

A small cross section survey was undertaken by Chan *et al* (2018) who asked employees in 17 companies using FFF 3D printers to self-report health symptoms. Of the 46 surveyed, 27 (59%) reported work related respiratory symptoms at least once per week for the previous year. Those working more than 40 hours a week with these 3D printers were significantly more likely to have been diagnosed with asthma or allergic rhinitis.

Zontek *et al* (2017) examined particulate and chemical emissions from desktop 3D polymer printers in a ventilated laboratory, a poorly ventilated laboratory, and a ventilated 'domestic sized' room. During printing >99% of the particle emissions were ultrafine. Chemical analysis demonstrated isocyanic acid and n-decane, and microscopic and elemental analysis showed the presence of aggregated combustion particles with metal resides. The authors concluded that the risks to health from 'off-gassing' of vapour constituents from the printing were low. However, the concentrations of ultrafine particles were more concerning given the growing evidence that ultrafine pollutant particles cause inflammation in the airways and cardiovascular system (Bourdrel *et al*, 2017).

Mendes *et al* (2017) measured the concentration of emitted nanoparticles from 3D printing with ABS and PLA filaments in a room. The authors concluded that considerable concentrations were possible during long exposure periods when printing with ABS, but that this was much less likely for PLA. Only very low concentrations of VOCs were released and were not considered likely to cause adverse health risks. However, the concentrations were produced by one printer and caution was advised when using multiple printers in enclosed rooms.

Developing good health and safety practices: Some organisations have started to produce their own guidance to specifically address the safe use of 3D printers, for example the fact sheet produced by Carnegie Mellon University (http://www.cmu.edu/ehs/fact-sheets/3D-Printing-Safety.pdf). However, much of this guidance tends to focus on large industrial printers using metal source material or broadly spans many different 3D printing technologies, and often lacks supporting evidence. Existing health and safety information relating to more traditional practices could also be applied to 3D printing, such as the information sheet PPIS13 'Controlling fume during plastics processing' produced by HSE (HSE, 2013), which provides guidance on how to minimise and control plastics fume during processes including extrusion.

HSE formed a working group including experienced individuals from the education sector and 3D printer manufacturing to share knowledge and experience. The members are:

- Manufacturing Technology Centre;
- KORA 3D (Secure Micro Solutions Ltd);
- CLEAPSS (Consortium of Local Education Authorities for the Provision of Science Services);
- Peritus Health Management;
- British Standards Institute; and
- Health and Safety Executive regulatory specialists and scientists.

The working group highlighted the need for practical and simple good practice guidance for schools on the safe use of these machines and materials. It identified that in order to develop this advice there is a need for scientific evidence, including emissions of particulates and vapours and effective ways to control exposure to people.

CLEAPSS is an advisory service supporting science and technology teaching for a consortium of local authorities and their schools. The Department for Education funded a pilot in 2012/13 to explore how 3D printing could be applied to the Science Engineering Technology and Mathematics (STEM) curriculum (DfE, 2013), since then the CLEAPSS helpline have received many requests for a model risk assessment for the use of 3D printers. The leading concerns raised on these forums, related to the use of 3D printing equipment were the heat of the extrusion area, the possibility of entrapment in moving parts, and concerns about the hazardous nature of fumes released from the equipment. CLEAPSS has highlighted that the lack of evidence on the health and safety risks associated with using 3D printers has limited the advice they can provide to schools.

1.2 AIM AND OBJECTIVES

The aim of this project was to investigate particulate and VOC emissions from desktop FFF 3D printers.

To achieve this aim, the following objectives were set:

1. Apply a standardised pyrolysis test to identify filament constituents.
2. Characterise the particulate and volatile emissions resulting from FFF processes used by small desktop 3D printers with consideration of a range of filament materials.
3. Investigate the effectiveness of exposure controls.

1.3 FUSED FILAMENT FABRICATION DESKTOP 3D PRINTERS

1.3.1 Fused Filament Fabrication (FFF)

FFF desktop 3D printers are increasingly commonplace and using a computer aided design (CAD) file which determines the motion of an extruder nozzle and print bed objects can be printed using a three-axis motion system. As the extruder nozzle moves it extrudes polymer material, drawn from a spool of filament feedstock, typically 1.75 to 3.00 mm in diameter. A drive gear engages the filament and forces it through a thermistor-regulated heating block and the nozzle, which produces a strand of molten plastic that deposits on the print bed and subsequently cools. This deposition builds up layers one atop the next, as the relative distance between the extruder nozzle and print bed is adjusted in a fixed increment to produce a 3D printed object (Steuben *et al*, 2015). A labelled diagram of an FFF desktop 3D printer is shown in Figure 1.

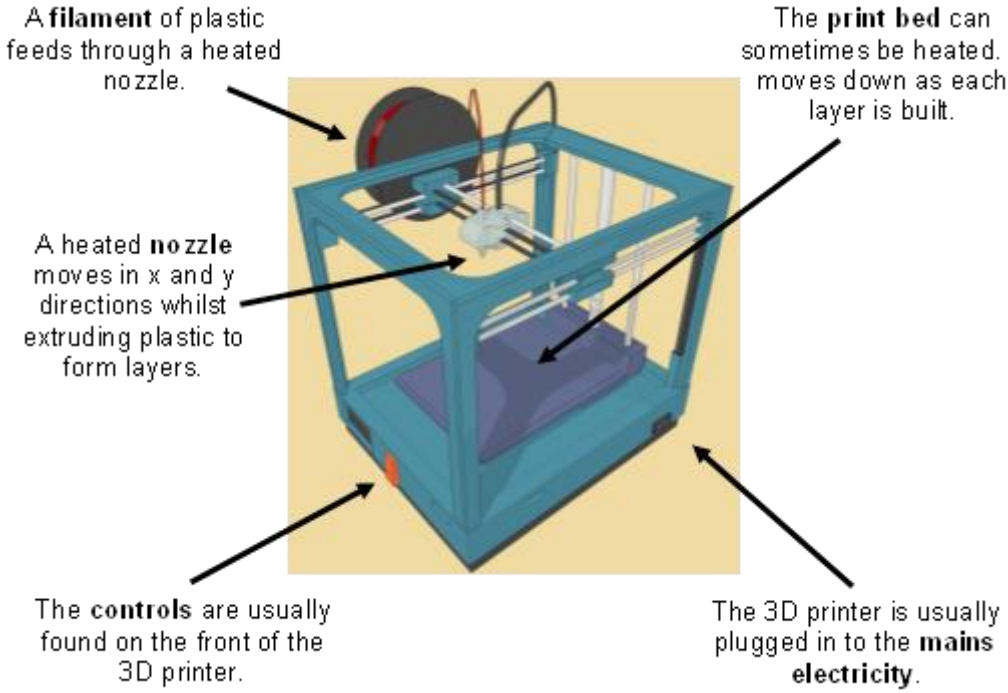

Figure 1 Key features of an FFF desktop 3D printer

1.3.2 Desktop FFF 3D printers

The 3D printers selected for the experimental work were chosen due to their medium-range cost and open-frame design. Each printer was easily available to purchase online and each manufacturer actively promoted their machine for use in the education sector. The maximum build size of the printers selected was slightly larger than that of lower cost desktop printers, making them more suitable for business or education applications but less so for hobbyists.

The make, model and filament diameter of the FFF 3D printers tested were:

- Ultimaker 2, with 3.00 mm diameter filament
- KORA MIDI, with 1.75 mm diameter filament
- Makerbot Replicator 2, with 1.75 mm diameter filament

1.4 PRINTER FILAMENT

The two most common filament materials used in commercially available desktop 3D FFF printers are:

- PLA, which is a biodegradable plastic that prints at temperatures around 220^{o}C; and
- ABS, which is non-biodegradable and prints at higher temperatures of approximately 250^{o}C (Ragan, 2013).

However, many different types of filaments are available for use in these printers, varying in terms of mechanical properties, visual appearance, and physical properties, all of which determine the filament an operator will choose.

The initial plan was to test three to four different filament materials on each of the three printers. Four filament materials; PLA, ABS, High Impact Polystyrene (HIPS) and NinjaFlex® (thermoplastic polyurethane); were chosen for comparison in the test chamber experiments. However, it was not possible to collect comparable data across all printer-filament combination as some of these filaments were incompatible with the selected printers. A wider range of filament materials, including a range of colours and other properties, were included in the pyrolysis testing.

- Only the Ultimaker 2 was successful in printing with 'clearwater' NinjaFlex® filament;
- the Makerbot Replicator 2 could not print with ABS as it requires a heated print bed which the Makerbot Replicator 2 does not have;
- and the KORA MIDI was alone in producing repeatable prints with white HIPS.

2 METHODS

2.1 TEST PIECE

To standardise the tests, CAD software was used to design a cube shaped test piece with a lattice internal structure as shown in Figure 2.

These 'print files' contained the dimensions of the object to be printed and the nozzle and print bed temperatures for each filament when used in each printer. Parameters such as nozzle temperature for each printer-filament combination were chosen to produce the best quality of printed object as advised by an experienced user of 3D printing equipment. Print files lasting approximately one to eight hours duration were used to produce different sized cubes. The cube shape of the printed object was considered appropriate as Azimi *et al* (2016) found that the size and shape of the test piece did not meaningfully alter the magnitude of ultrafine particle (UFP) emission rates.

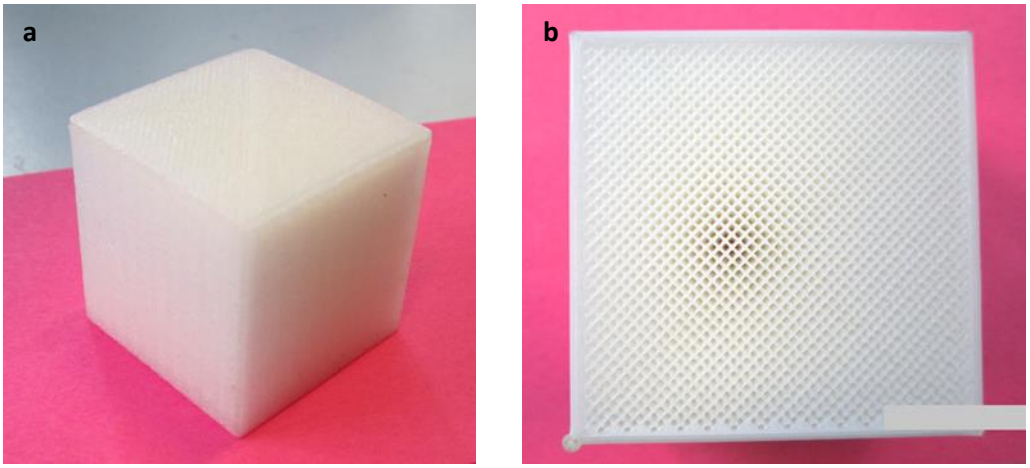

Figure 2 a) Test print cube b) Internal structure of the test print

2.2 TEST CHAMBER

2.2.1 Design

A bespoke wooden test chamber was designed and built, based on BS EN 1093 (Figure 3), in which the FFF 3D printers were tested.

The volume flow rate of air through the test chamber was 268 $m^3.h^{-1}$ with resulting mean air velocities of 0.05 $m.s^{-1}$ and 1.0 $m.s^{-1}$ through the main chamber and the steel connecting duct respectively. This was achieved by connecting a fan to the end of the duct to pull air through the enclosure, as shown in Figure 3.

The airflow rate was monitored downstream of the measurement section, using a 100 mm diameter duct Wilson Flowgrid (Airflow Instruments, TSI Inc.) and a digital micromanometer MP6KS (Air Neotronics Ltd.). The differential pressure across the flowgrid maintained a constant pressure of 98 Pa ±1 throughout the experiment indicating excellent airflow stability.

One wall of the test chamber consisted of two 1220 mm x 610 mm high efficiency filters (99.997% (BS 3928)). The laboratory air was filtered through this wall as it entered the test chamber resulting

in particle background levels as close to zero as possible. Seals around the filters were also taped to reduce the chance of air bypassing the filters.

The test chamber had a hinged access door containing glove ports to allow operation of the printers without the need to open the chamber and a glass window to monitor the printer throughout each test. Each printer was positioned inside the test chamber on an elevated wooden platform to raise the printer nozzle to a central position within the chamber, as the nozzle was considered likely to be the main particulate and VOC emissions source.

A mixing fan was suspended inside the conical section of the test chamber, level with the duct and directing its airflow back in to the test chamber to create turbulence to aid mixing and unbiased sampling. Background particle concentrations were measured with and without the mixing fan switched on to confirm that the fan did not contribute to the measurements and that no correction was required.

Measurements of the emissions from the printers were taken at a cross section of the connecting steel duct; 2.6 m downstream from the test chamber (Section 2.3.2); in accordance with BS EN 1093.

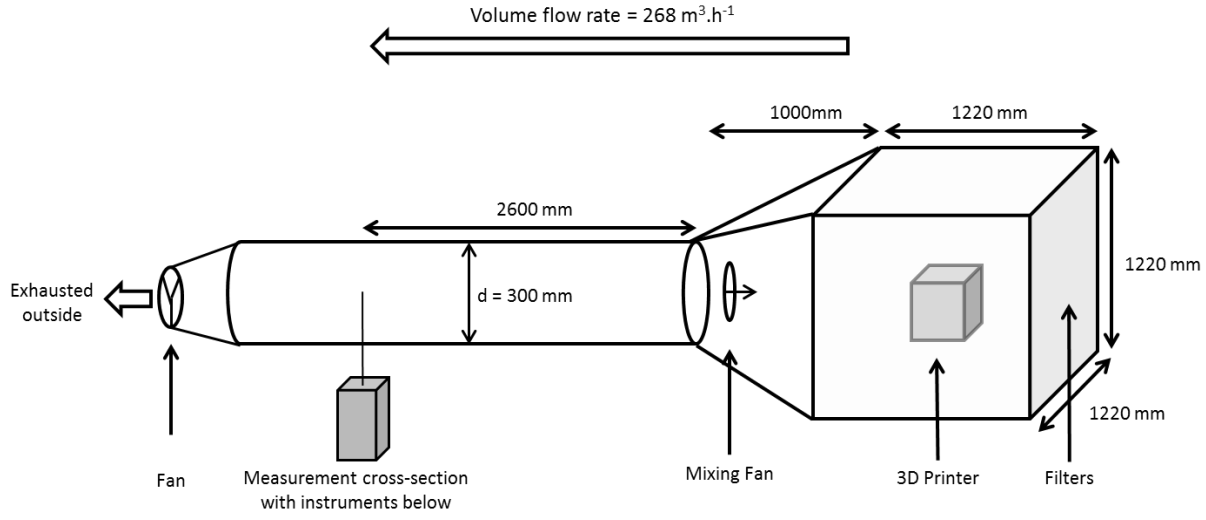

Figure 3 Design and dimensions of the test chamber (not to scale)

2.2.2 Commissioning

Aerosol measurements made through different sampling probe positions at the measurement cross section were uniform; simultaneous particle count measurements were made using two pTrak 8525 ultrafine particle counters (TSI Inc.). One instrument was used as a reference; sampling from a fixed position at the centre of the duct. The second instrument sampled for ninety seconds every two centimetres across the duct, completing both a vertical and horizontal traverse. Other conditions such as the volume flow rate and the mixing fan were set as described in Section 2.2.1. Traverse measurements indicated a variation in particle count measurements of <5% across the both diameters of the duct.

2.3 PARTICLE EMISSIONS

2.3.1 Real-time aerosol instruments

The real-time aerosol instruments used to characterise 3D printer particulate emissions are listed with operating parameters in Table 1. The flow rate of each instrument was checked with a TSI flowmeter 4100 series at the start of each day of testing.

Table 1 Real-time aerosol instruments used to characterise the 3D printer particulate emissions

Instrument	Measurement metric	Particle size range / µm	Particle concentration range	Flow rate / l.min^{-1}
TSI pTrak 8525 ultrafine particle counter	Particle number concentration	0.02 - 1.0	0 to 5 × 10^5 particles.cm^{-3}	0.70
GRIMM SMPS Condensation Particle Counter model 5403 with electrostatic classifier "Vienna"- L-DMA	Particle size distribution	0.01 – 1.1	0 to 14,000 particles.cm^{-3} (single particle counting with coincidence correction), to 10^7 particles.cm^{-3} with photometric mode	0.30
Testo DISCmini diffusion size classifier	- Particle number concentration - Average particle size	Mean Particle size: 0.01 to 0.3 Particles counted: 0.01 to 0.7	Dependant on particle size and averaging time: 20 nm: 2 x 10^3 to 1 x 10^6 particles.cm^{-3} 100 nm: 5 x 10^2 to 5 x 10^5 particles.cm^{-3}	1.00
Thermo-scientific personal DataRAM pDR-1500 aerosol monitor	Particle mass concentration	0.1 - 10	0.001 to 400 mg.m^{-3}	3.50
Beckman Coulter MET ONE HHPC 6+ Optical particle sizer	Particle number concentration in 6 size channels	0.3 – 10 (6 channels)	0 to 141 particles.cm^{-3}	2.83
DEKATI ELPI®+	Particle size distribution	0.006 - 10	1.7 x 10^5 (10 µm) to 7.9 x 10^7 (0.006 µm)	10.0

2.3.2 Sampling location of real-time aerosol instruments

The real-time aerosol instruments were located outside of the enclosure and probes were fed into the duct at the positions shown in Figure 4. The inlet of each probe was directed into the duct airflow and its diameter was determined by the flow rate of each instrument stated in Table 1, to achieve isokinetic sampling (air velocity into probe = air velocity through duct). The unused probe was replaced with a larger diameter probe part way through the testing schedule as the GRIMM SMPS was replaced by the DEKATI ELPI®+ and the existing probe was not of suitable diameter for the higher flow rate of the instrument.

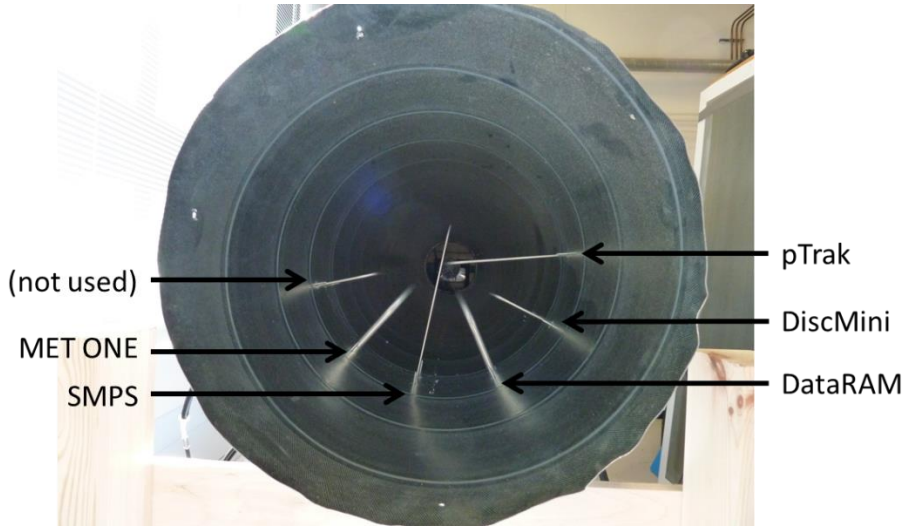

Figure 4 Cross-sectional view of the duct showing the position of the sampling probes facing into the airflow: labelled with corresponding real-time instruments attached

2.3.3 Characterising particle emissions with the Transmission Electron Microscope

The Ultimaker 2 3D printer was positioned inside the test chamber and printed a one-hour test print with white ABS filament. A sample of particles emitted by the printer during the printing process was collected as air was drawn at 1.5 $l.min^{-1}$ using Gilain GilAir-5 pumps, through two 25 mm diameter 0.2 µm pore size polycarbonate filters positioned with the printer in the main section of the test chamber (Figure 5). Three Transmission Electron Microscope (TEM) grids with holey carbon film were affixed to each filter and particles were collected on the carbon film for observation by TEM. Particles on the film were also analysed by Energy Dispersive X-ray (EDX) spectroscopy, and micrographs and EDX spectra were taken to further characterise examples of each particle type.

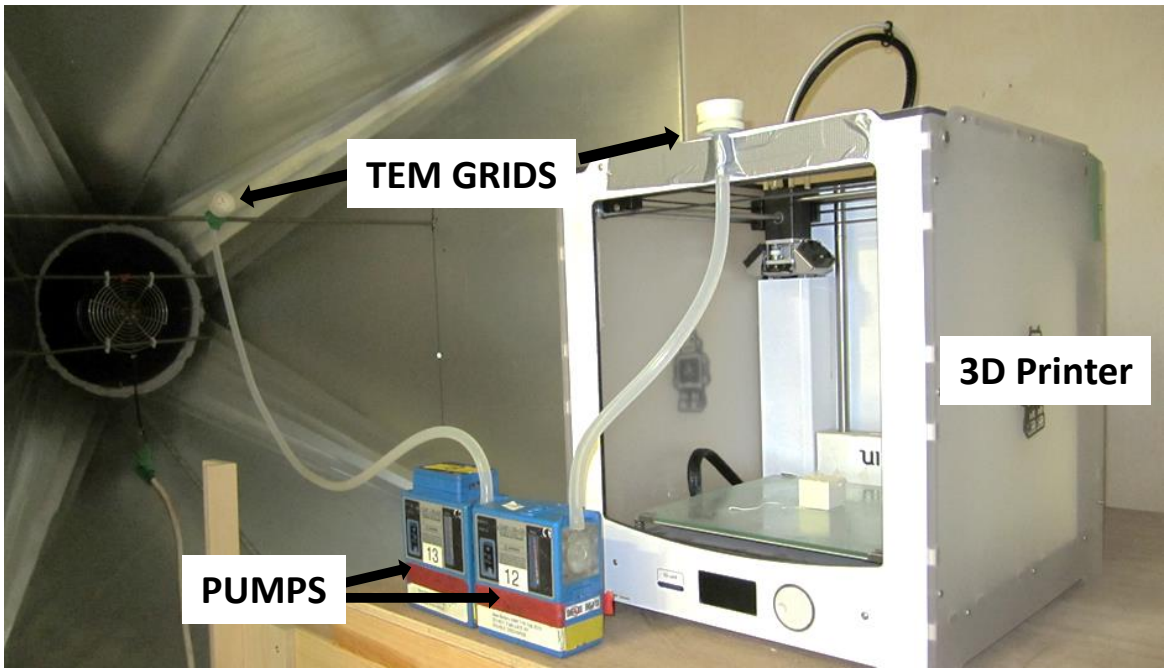

Figure 5 Position of the TEM grids and pumps inside the test chamber

2.3.4 Filament containing embedded metals

The emissions from three samples of filament containing embedded metal particles were sampled to determine whether metals were released during heating of the filament in the laboratory to temperatures comparable to those of a 3D printer nozzle. The printer nozzle itself was not used due to the increased difficulty in printing with this type of filament material. The three filament materials tested were:

- Copper FLEX (Reprapper Tech Ltd.)
- BrassFill (colorFabb BV)
- BronzeFill (colorFabb BV)

In turn, portions of filament material were heated in a 3 mm inner diameter quartz tube placed in a SGE Pyrojector furnace (SGE International Pty. Ltd.) The furnace temperature was set to 350°C, however the airflow through the tube resulted in an actual temperature of approximately 290°C measured using a Digitron™ thermocouple. A flow rate of 750 $ml.min^{-1}$ and a sampling time of two minutes produced a sample volume of 1.5 litres.

As before, particulate emissions were sampled onto three TEM grids with holey carbon film affixed to a 25 mm diameter 0.2 µm pore size polycarbonate filter. The particles caught on the carbon film were observed by TEM and analysed by EDX spectroscopy. Micrographs and EDX spectra were taken for examples of each particle type found.

2.4 VOLATILE ORGANIC COMPOUNDS

2.4.1 Sampling tubes

Specialist sampling tubes (inert steel tubes packed with Tenax TA) were used to collect any VOCs generated by the printing process. Prior to use, the tubes were conditioned at 300°C for 60 minutes. During testing, air was drawn into the sampler by a Gilian GilAir 5 pump at a flow rate of approximately 0.1 $l.min^{-1}$ allowing airborne vapours to be absorbed onto the sorbent inside the tube.

The tube was then heated in a stream of inert carrier gas, transferring a proportion of the sorbed analytes to a capillary gas chromatograph (GC) where they were separated and detected. Initial analysis of the collected sample was undertaken using a TurboMatrix™ TD650 and Clarus® GC with flame ionisation detection (TD/GC/FID) system and TotalChrom™ control software (PerkinElmer Inc.). This had the capability to split the sample flow path to allow recollection of part of the desorbed sample back on to the original sample tube to allow the possibility of further analysis. Further analysis of the recollected sample was undertaken using a TurboMatrix™ TD350 thermal desorption and a Clarus® GC with mass selective detection (TD/GC/MS) system and Turbomass™ control software.

Tests were also performed without the printing process to establish background VOC quantities.

2.4.2 Sampling inside the test chamber

A sorbent tube (Section 2.4.1) was inserted into the duct of the test chamber through a hole at the measurement cross-section during each test print.

When printing with PLA, specialised sampling tubes containing silica gel impregnated with 2,4-Dinitrophenylhydrazine (DNPH) a derivatising agent were also included adjacent to the other sorbent tube at the measurement cross-section shown in Figure 3. These specialised tubes actively sampled to collect aldehyde compounds at an approximate rate of 0.2 $l.min^{-1}$.

Upon analysis of these sampling tubes, it was determined that the dilution of emissions with the filtered inlet air inside the test chamber was too great to collect adequate sample quantities for analysis. This was due to the high-volume flow rate required for optimum use of the particle characterising instruments. It was determined that this was not an effective method for measuring VOC emission rates released during 3D printing.

2.4.3 Alternative method - sampling inside an enclosed box

The printer was positioned inside an unventilated Perspex box atop the bench (Figure 6a). To avoid overloading the sorbent sampling tubes, a small trolley coin (Figure 7) was printed rather than a cube, taking just seven minutes to complete. Gilian GilAir-5 pumps were connected to four sorbent tubes (Section 2.4.1) and actively sampled at 0.1 $l.min^{-1}$ during the time the printer heated in preparation for the print and for the duration of the printing, totalling twelve minutes. The tubes were positioned at different points within the enclosure (Figure 6b). The test was then repeated at printer nozzle temperatures in five-degree intervals from 220 to 235^{o}C.

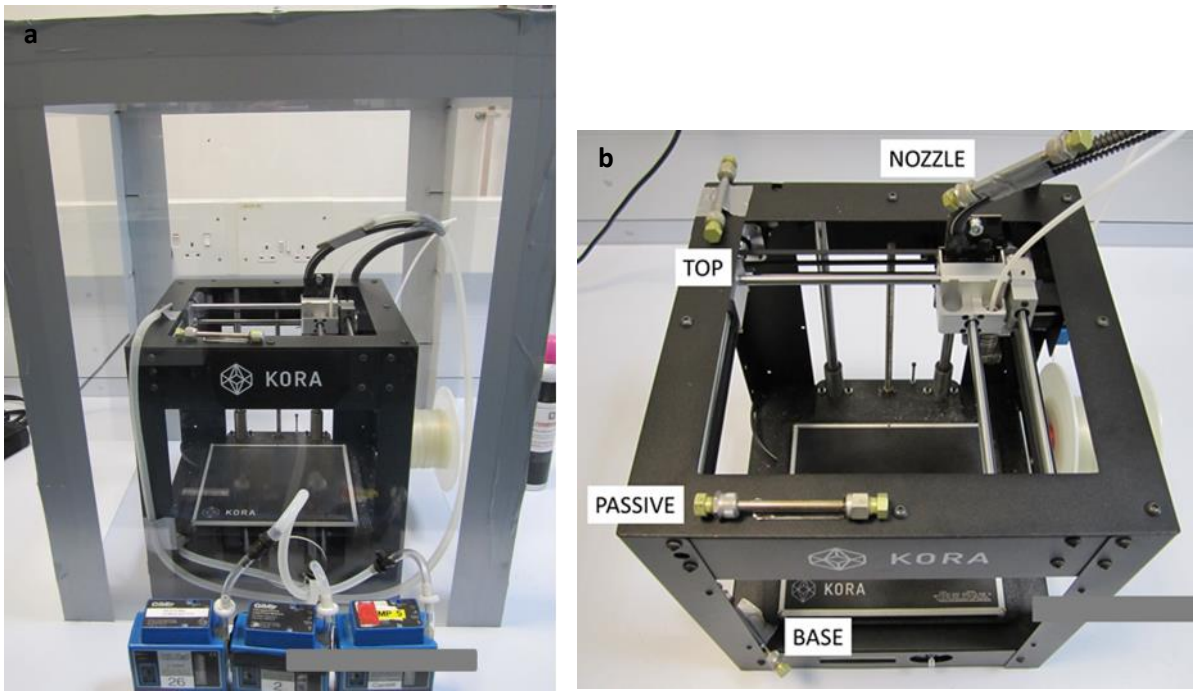

Figure 6 a) KORA MIDI 3D printer inside the enclosed Perspex box with pumps positioned outside attached to thermal desorption tubes b) Positions and labels of thermal desorption tubes for sampling VOCs inside the enclosed Perspex box

Figure 7 Trolley coin test print

2.4.4 Pyrolysis testing

Eleven filaments were tested using a pyrolysis test:

- PLA ‘natural’ (Reprapper Tech Ltd.)
- ABS ‘natural’ (Reprapper Tech Ltd.)
- ABS ‘fluorescent yellow’ (Reprapper Tech Ltd.)
- HIPS ‘white’ (Reprapper Tech Ltd.)
- Nylon 6 ‘white’ (Reprapper Tech Ltd.)
- Nylon ‘645’ (taulman3D, LLC)
- Nylon ‘618’ (taulman3D, LLC)
- NinjaFlex® ‘clearwater’ (NinjaTek™)
- bronzeFill (colorFabb BV)
- brassFill (colorFabb BV)
- Copper FLEX (Reprapper Tech Ltd.)

The pyrolysis method was conducted by rapidly heating a small sample of filament material, typically 50 - 500 µg in a flow of helium carrier gas. The evolved components were transferred, via a heated valve and transfer line, to a GC equipped with a mass spectrometer (MS) detector, which allowed the evolved components to be identified and quantified. A schematic diagram of the test set up is shown in Figure 8.

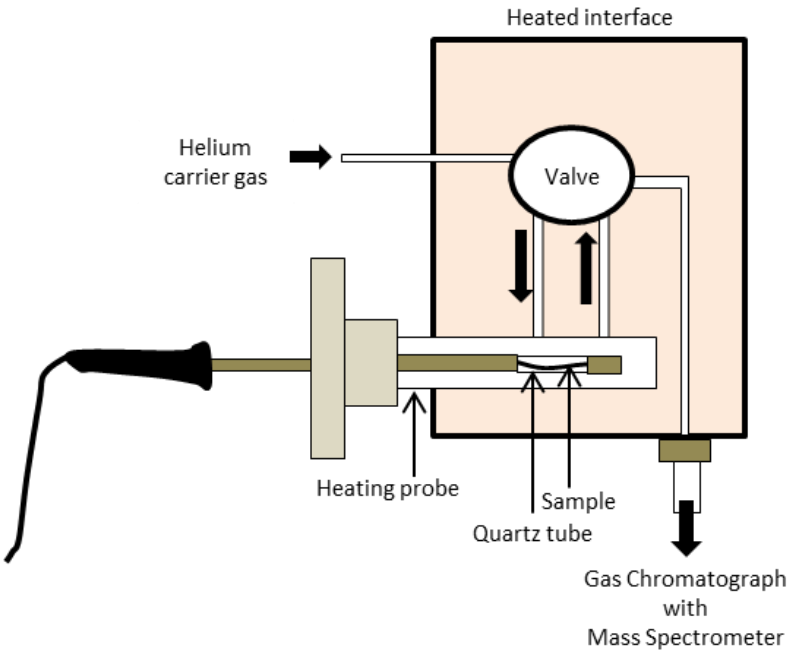

Figure 8 Schematic diagram of the pyrolysis testing equipment

Each sample was loaded into a quartz tube, which was placed inside a heating probe. The probe was then placed inside a heated interface within the pyrolyser for testing. Initial tests (method 1) were carried out using standard system settings:

- The interface was initially maintained at approximately 40°C. When the test started, it rapidly heated to 250°C or 300°C in approximately 20 seconds.
- The sample was then pyrolysed to the desired temperature of either 250°C or 300°C for 10 seconds. These two temperatures were initially chosen as the user manual indicated that the temperature inside the sample tube was typically around 100°C less than the chosen pyrolysis temperature, i.e. around 150°C and 200°C.
- The components generated passed to the GC-MS system via a heated valve and transfer line which remained at a constant 280°C. The interface remained at 250°C for 2 minutes before returning to 40°C.
- Each sample was weighed before and after the pyrolysis test to determine the percentage weight loss.

Initially, unexpectedly high levels of weight loss were observed for some of the filament samples, therefore the method was modified. The modified method (method 2) pyrolysed the sample to temperatures of 150°C, 200°C, 250°C or 300°C for 10 seconds. The generated components were passed to the GC-MS system via the heated valve and transfer line, which remained at a constant 280°C. For this modified method, the interface remained at 250°C for 20 seconds before returning to 40°C. The samples were again weighed before and after the pyrolysis test to determine the percentage weight loss.

2.5 EXPOSURE CONTROL

2.5.1 Description of the enclosing hood

The exposure control method evaluated was an enclosing hood consisting of a Perspex box, of outer dimensions 550 x 500 x 700 mm (length x width x height) and volume 0.1925 m^3, placed over the 3D printer. A circular access point (40 mm diameter) in the front panel allowed the 3D printer controls to be used without the need to lift the hood. A hole in the roof of the enclosing hood allowed a panel to be fitted, which housed a fan and a H13 High Efficiency Particulate Air (HEPA) filter with active carbon coating on the internal filter face.

The fan could be orientated to allow the enclosing hood to function in two modes: exhausting and recirculating. In exhausting mode, the hood was raised by 5 mm from the surface on which it rested by slotting four Perspex feet at the corners. This allowed air from the room to enter the hood at its base, which was then filtered as the fan exhausted it back in to the room. In recirculating mode, the feet were removed to close the gap at the base of the hood and the filter panel was adjusted so that the fan recirculated the air within the enclosing hood.

The airflow rate of the enclosing hood's fan was determined using a 'balanced pressure technique' similar to that used by Bancroft *et al* (1980), and was found to equal 37 $l.min^{-1}$.

2.5.2 Testing the enclosing hood in the test chamber

The printer was placed inside the enclosing hood and both were positioned inside the test chamber. A smoke tube was used to visualise airflows around the base of the hood and to determine that the airflow into the enclosing hood was sufficient to overcome any movement caused by airflow through the test chamber.

Four test prints were completed using ABS filament; two tests in exhausting mode and two in recirculating mode. The results of these tests were compared with those from the same test carried out without the enclosing hood. During these tests, the print bed was set to 78°C and the nozzle temperature was set to 250°C.

2.5.3 Testing the enclosing hood on an open bench

The printer was placed inside the enclosing hood on an open bench in the laboratory and printed a one-hour test print using PLA filament. Two TSI pTrak instruments were used to compare the particle concentration inside the hood with the particle concentration outside the hood. Both instruments were positioned outside the enclosing hood and one was attached to tubing that passed to a position below the filter inside the enclosing hood. Both instruments sampled for thirty seconds every ten minutes. The temperature inside the enclosing hood was also monitored throughout the test. Logging was not continuous to avoid influencing the particle concentration that may result as air is removed from the enclosing hood by the pump of the TSI pTrak instrument.

The pTrak instrument was used for these tests as the average particle size was within its detectable size range and two instruments were available.

The experimental setup is shown in Figure 9. Four tests were completed; two in exhausting mode and two in recirculating mode.

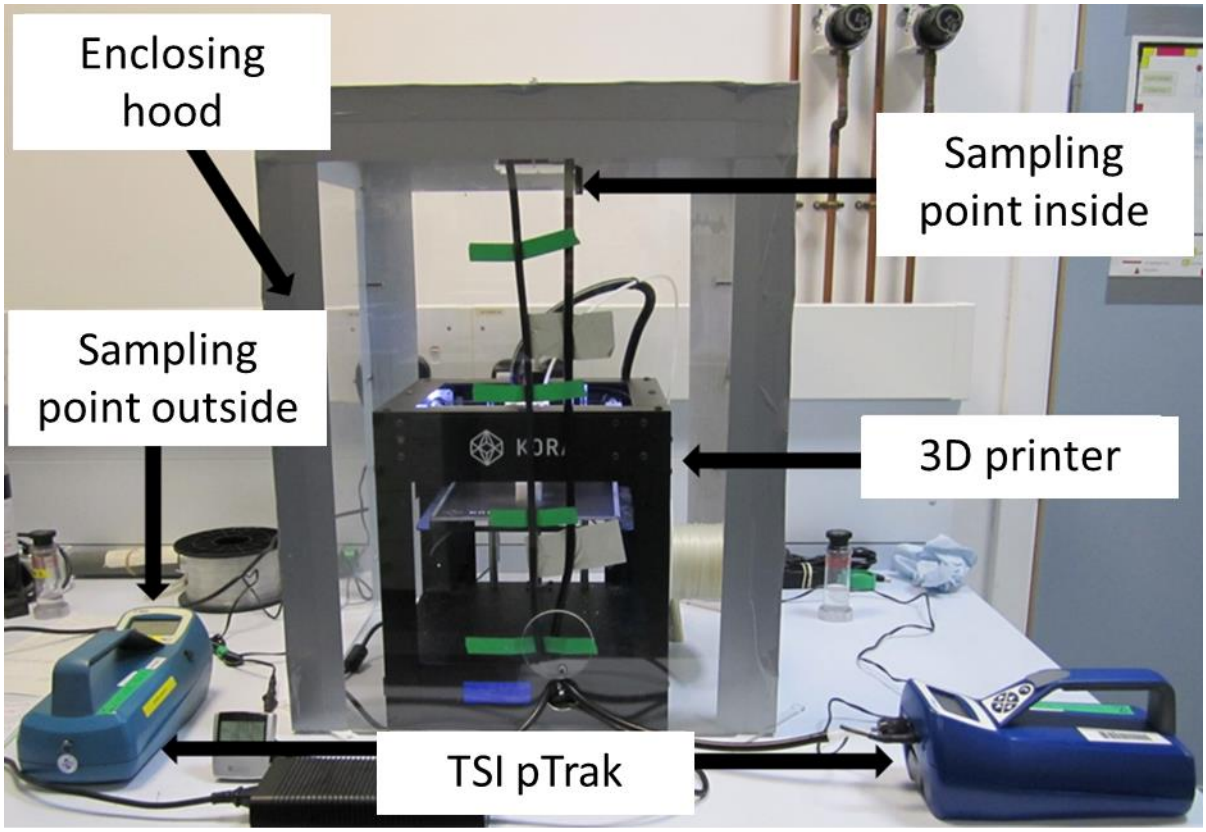

Figure 9 Experimental set up for measuring the particle concentration inside and outside the enclosing hood during a 3D print using TSI pTrak instruments

3 RESULTS

3.1 PARTICLE EMISSIONS

3.1.1 Printing with the same filament on different printers

The KORA MIDI printer was positioned inside the test chamber and set to print with 1.75 mm diameter PLA filament with a nozzle temperature of 220°C and a print bed temperature of 50°C. The filament was then transferred to the Makerbot Replicator 2 which printed a slightly longer test at 230°C nozzle temperature. The Makerbot Replicator 2 did not have a heated print bed so this remained at the ambient temperature inside the test chamber. These tests were repeated to produce three data sets for each printer. The average particle concentration, measured with the TSI pTrak, for both FFF 3D printers using PLA filament is presented in Figure 10. This filament could not be used in the Ultimaker 2 as it requires 3 mm filament.

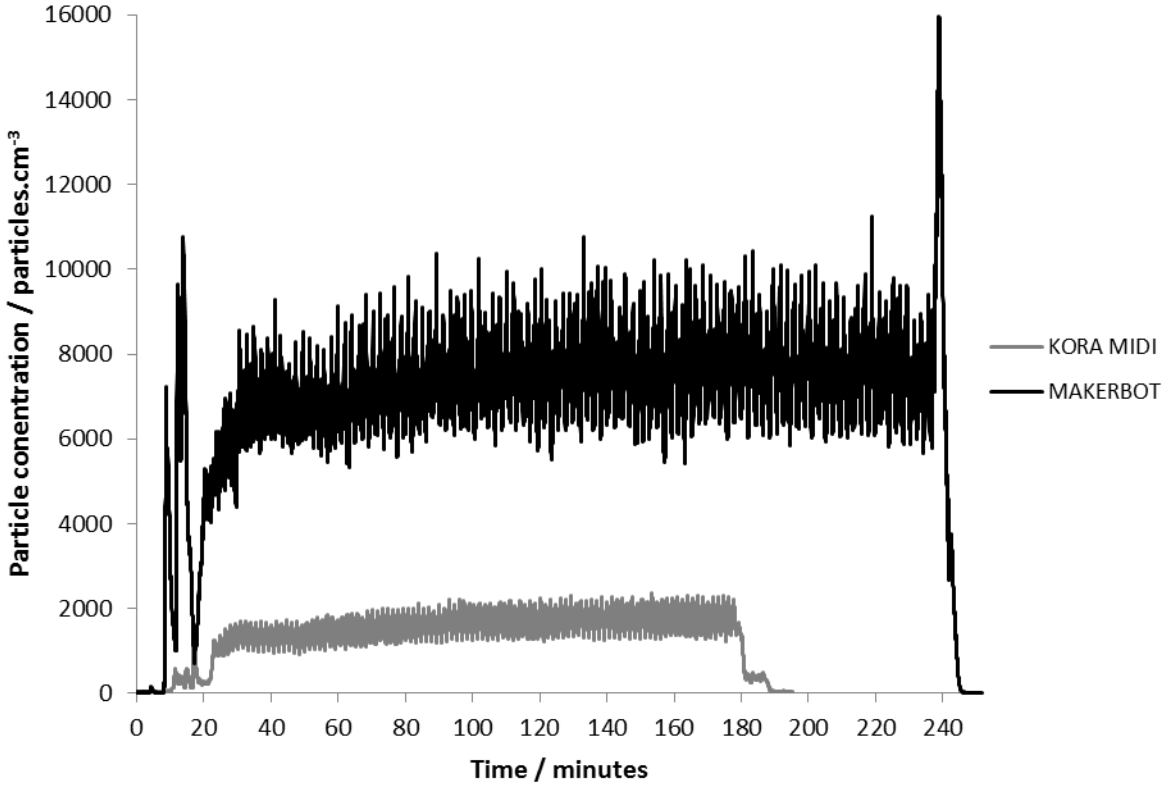

Figure 10 Average particle concentration measured with the TSI pTrak during a print using the same PLA filament spool on the KORA MIDI (nozzle = 220°C and print bed = 50°C) and the Makerbot Replicator 2 (nozzle = 230°C and print bed = ambient temperature)

The particle size distribution was measured throughout the tests using the GRIMM SMPS instrument. These results are presented in Figure 11 and Figure 12 respectively.

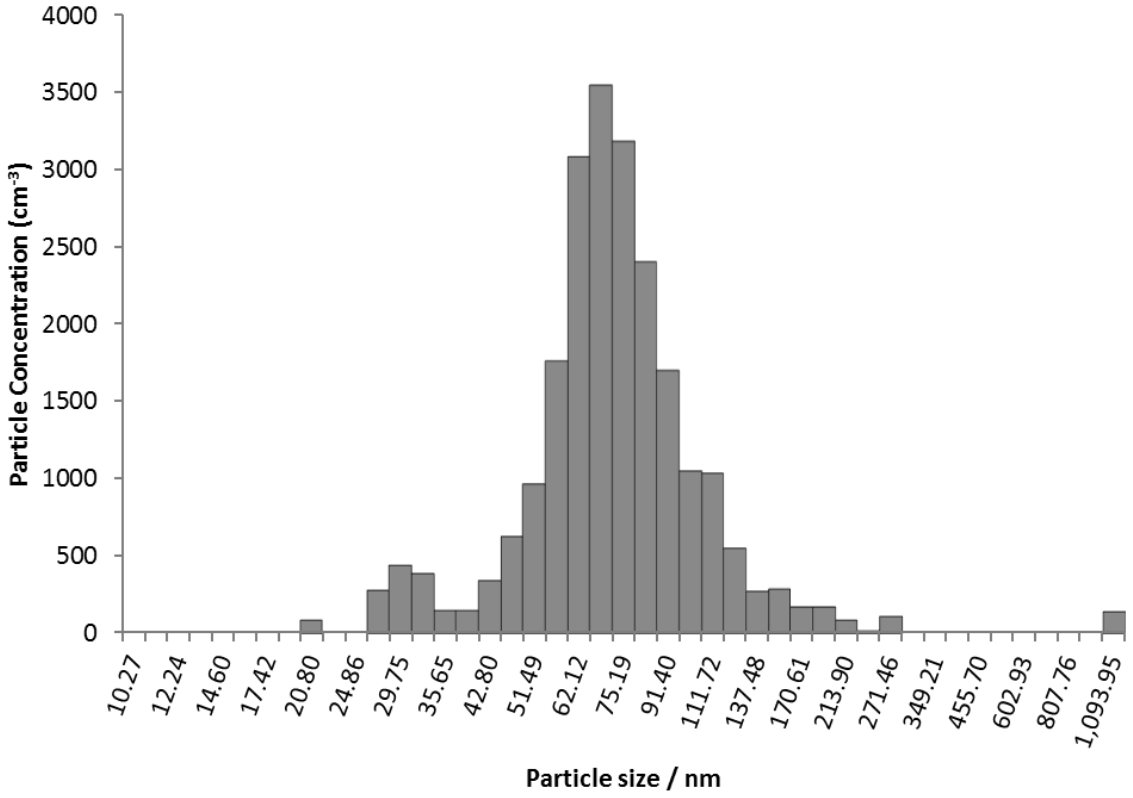

Figure 11 Particle size distribution measured with the GRIMM SMPS during a print with PLA filament on the KORA MIDI (nozzle = 220°C and print bed = 50°C)

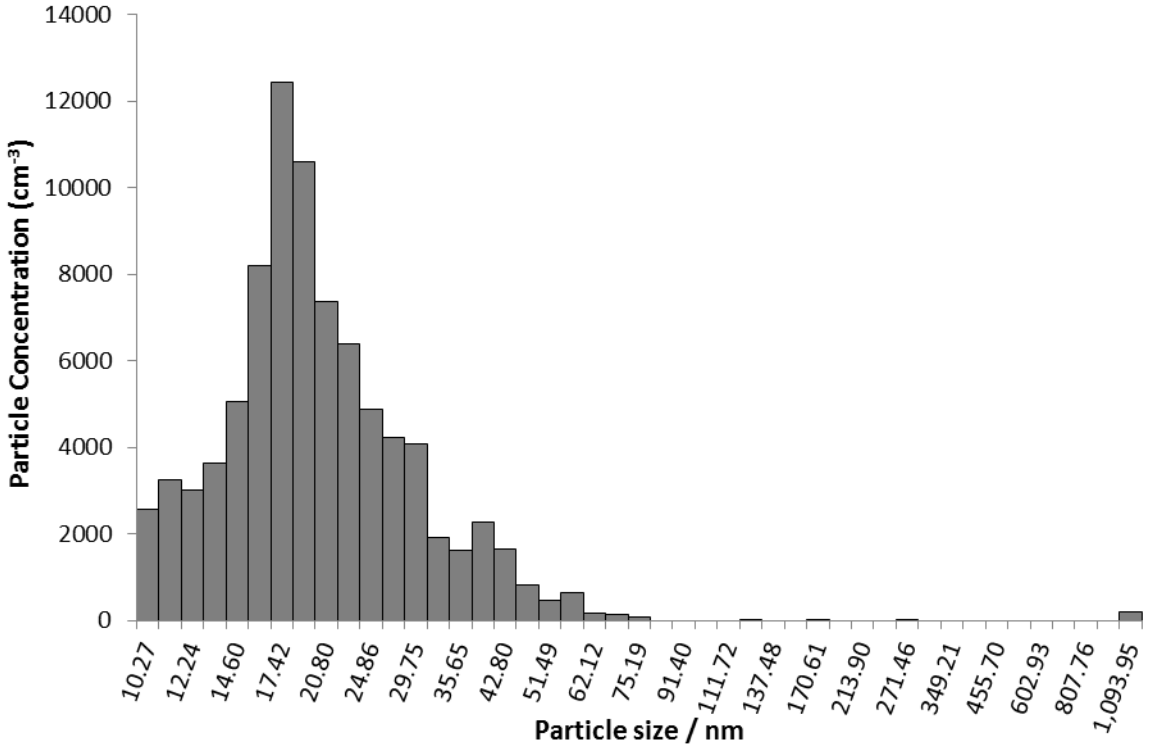

Figure 12 Particle size distribution measured with the GRIMM SMPS during a print with PLA filament on the Makerbot Replicator 2 (nozzle = 230°C and print bed = ambient temperature)

3.1.2 Printing with different filament materials on the same printer

The Ultimaker 2 printer was positioned inside the test chamber and set to print three repeat tests with ABS filament at a nozzle temperature of 260°C and a print bed temperature of 80°C. Three test prints were then conducted with NinjaFlex filament at 240°C nozzle temperature and at a print bed temperature of 75°C. The average particle concentration, measured with the Testo DISCmini, for both filament materials is presented in Figure 13. This instrument was used in this case due to its lower detectable size limit (Table 1) and the lower average particle size of the ABS filament. Good agreement between the pTrak and DISCmini data was observed at larger particle sizes but less so in the smaller particle size range (Appendix A). Reasons for this are discussed further in Section 4.1.

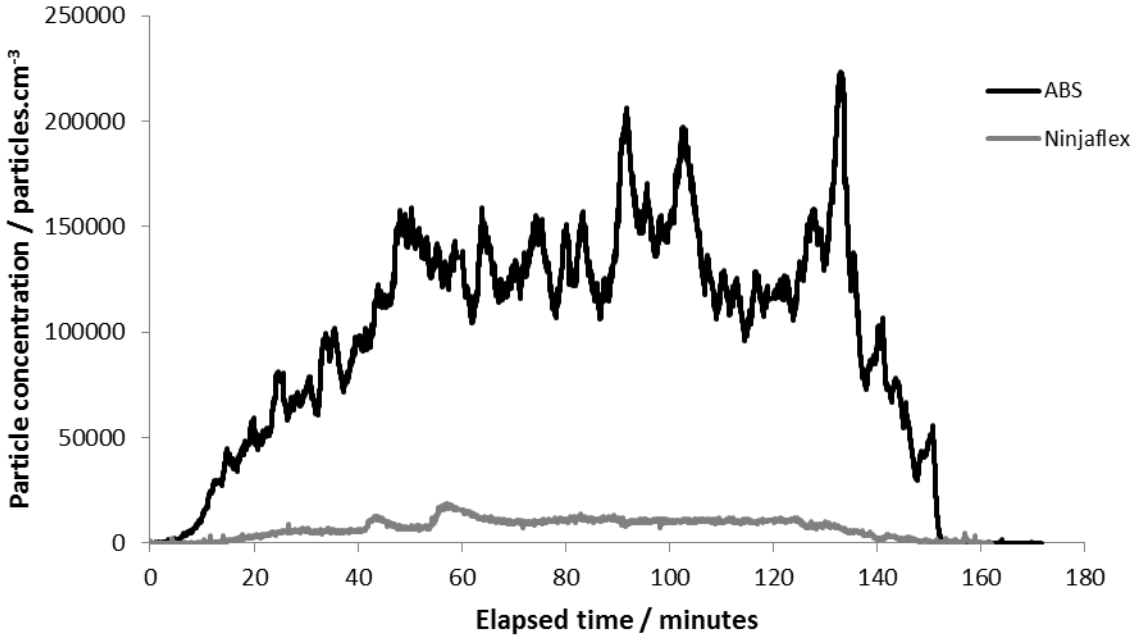

Figure 13 Average particle concentration measured with the Testo DISCmini when printing with 3 mm diameter ABS (nozzle = 260°C and print bed = 80°C) and NinjaFlex® (nozzle = 240°C and print bed = 75°C) filament on the Ultimaker 2

3.1.3 Effect of nozzle temperature on emission rate

To reduce the number of variables i.e. the printer, filament, nozzle temperature, bed temperature etc. the KORA MIDI and ABS; were chosen for additional tests to investigate the relationship between the printer nozzle temperature and the emissions characteristics.

The KORA MIDI printer was positioned inside the test chamber and set to print with ABS filament with the print bed temperature set to 78°C. The printer completed four one-hour prints with the nozzle temperature increasing by 5°C for each test: 245°C, 250°C, 255°C and 260°C. Each test was then repeated a number of weeks later. Emission rates were calculated using the data logged during the time that the filament was extruded and are presented in Figure 14. It was not possible to test at higher temperatures than 260°C as the nozzle temperature for the KORA MIDI printer was restricted.

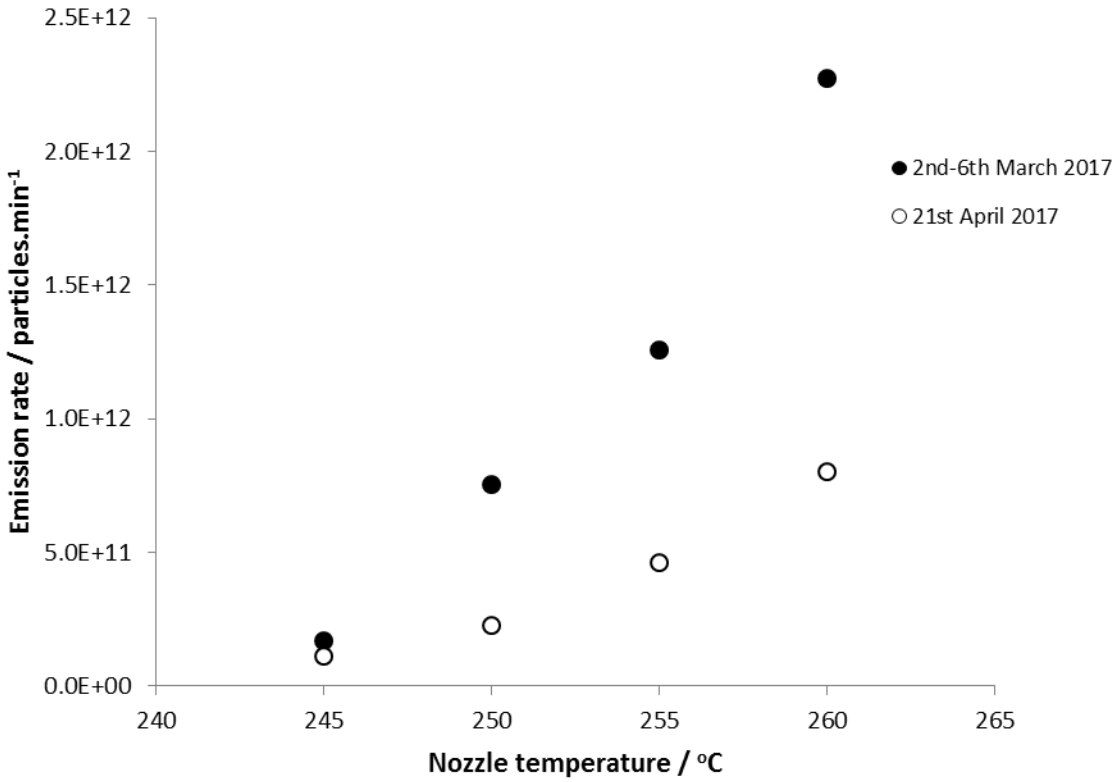

Figure 14 The effect of nozzle temperature on the emission rate using ABS filament with the KORA MIDI (print bed = 78°C); measured using the DISCmini. Data from two repeat tests are plotted for each temperature

The KORA MIDI printer was then set to print with PLA filament with the print bed temperature set to 50°C. The printer completed five one-hour prints with the nozzle temperature increasing by 5°C for each test; 220, 225, 230, 235 and 240°C. Each test was then repeated. Emission rates for each test were calculated using the average of the data logged during the time that the filament was extruded; these are presented in Figure 15.

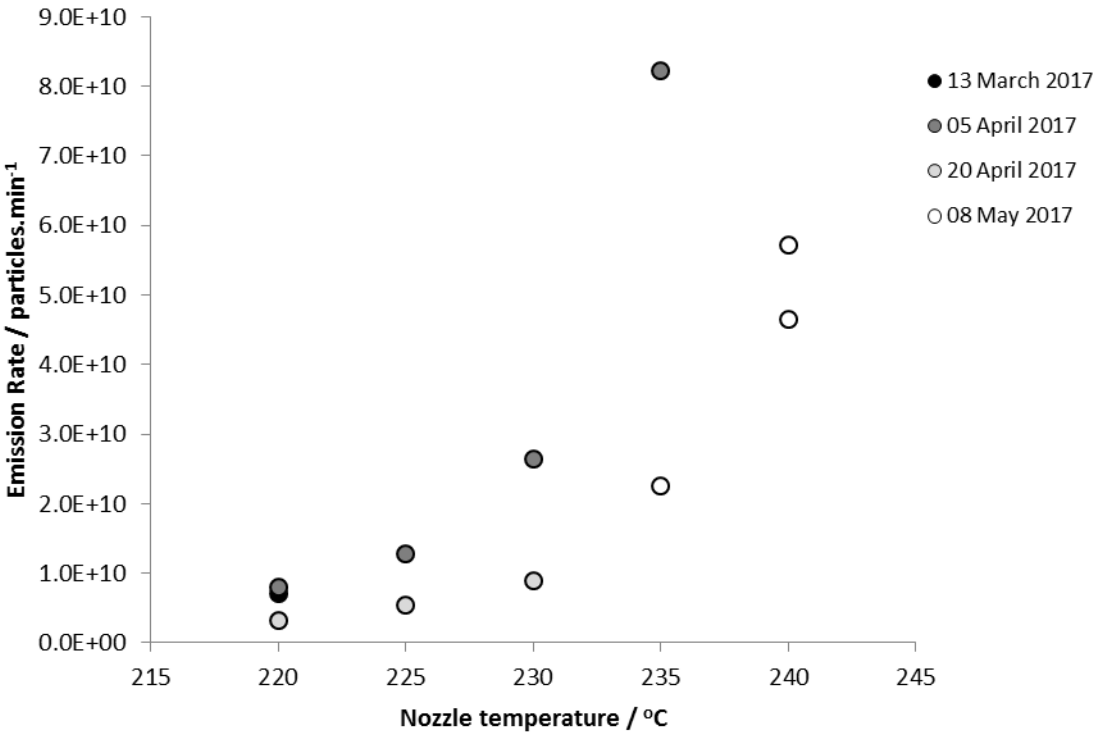

Figure 15 The effect of nozzle temperature on the emission rate using PLA filament with the KORA MIDI; measured using the DISCmini. Two emission rates are plotted for each temperature from repeat tests (three for 220°C)

3.1.4 Effect of nozzle temperature on particle size

Further to investigating the relationship between nozzle temperature and emission rate, the DISCmini was also used to measure the average particle size during the tests described in Section 3.1.3. When the KORA MIDI printed with ABS filament, the average particle size measured as the filament was being extruded did not rise above 10 nm (Table 2), which is the lower particle size limit for the DISCmini instrument. The average particle sizes measured for all tests with PLA were above the lower particle size limit of the instrument. The results are presented in Figure 16.

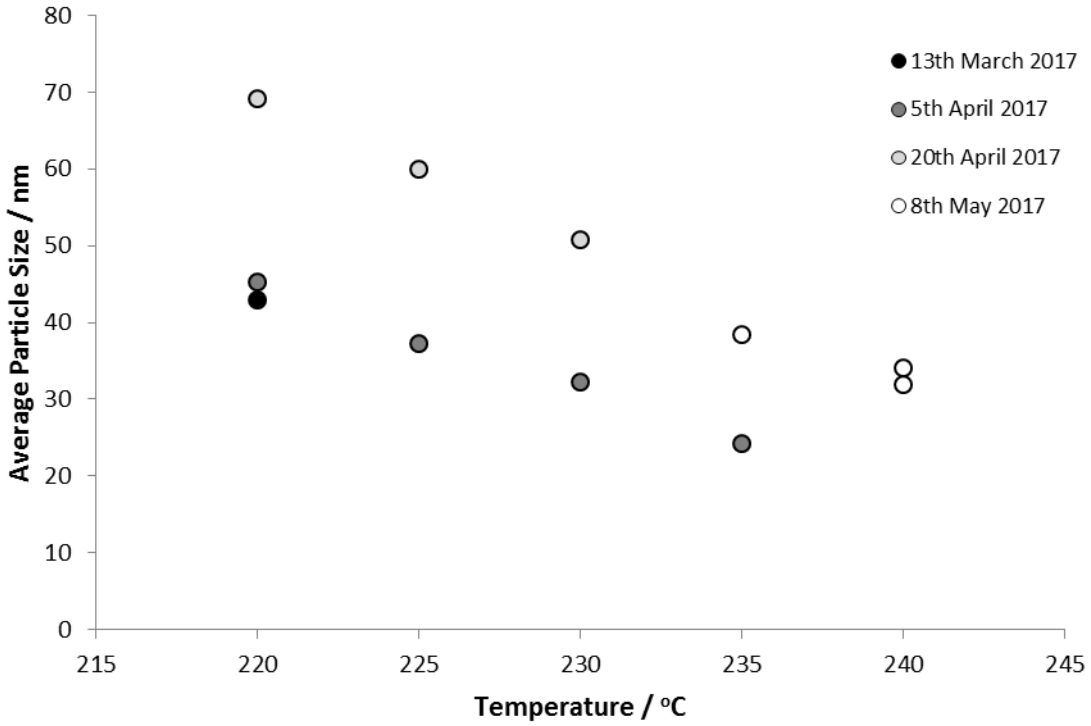

Figure 16 The effect of nozzle temperature on the average particle size using PLA filament with the KORA MIDI; measured using the DISCmini. Emission rates from two repeat tests are plotted for each temperature (three for 220°C)

3.1.5 Data summary of the effects of increasing the nozzle temperature

The emission rate and average particle size measured at increasing nozzle temperatures for ABS and PLA are presented in Tables 2 and 3 respectively.

Table 2 Emission rate and average particle size for KORA MIDI and ABS filament with increasing nozzle temperatures

Temperature / °C	Emission Rate / particles.min^{-1}		Average Particle Size / nm	
	Test 1	Test2	Test 1	Test 2
245	1.70 x 10^{11}	1.12 x 10^{11}	10	10
250	7.52 x 10^{11}	2.27 x 10^{11}	10	10
255	1.26 x 10^{12}	4.61 x 10^{11}	10	10
260	2.27 x 10^{12}	8.03 x 10^{11}	10	10

Table 3 Emission rate and average particle size for KORA MIDI and PLA filament with increasing nozzle temperatures

Temperature / °C	Emission Rate / particles.min^{-1}			Average Particle Size / nm	
	Test 1	Test2	Test 3	Test 1	Test 2
220	8.08×10^{9}	3.26×10^{9}	7.04×10^{9}	45	69
225	1.28×10^{10}	5.49×10^{9}	N/A	37	60
230	2.65×10^{10}	8.85×10^{9}	N/A	32	51
235	8.23×10^{10}	2.26×10^{10}	N/A	24	38
240	5.72×10^{10}	4.64×10^{10}	N/A	32	34

3.1.6 Characterising particle emissions with the TEM

Emissions from the printer were sampled in the test chamber to characterise the polymer particles emitted. However, despite high particle concentrations measured downstream, no polymer particles were observed by TEM on the grids. Possible reasons for this are discussed in Section 4. Some metal particles were observed and images and EDX spectra of examples of these particles can be found in Appendix B.1. This analysis was qualitative only, providing information on the particle types present, but not on the concentration.

3.1.7 Filament materials containing embedded metal

Particulate emissions were sampled onto three TEM grids as samples of Copper FLEX, brassFill and bronzeFill filament materials were heated (Section 2.3.4). The particles caught on the carbon film were observed by TEM and analysed by EDX spectroscopy. Micrographs and EDX spectra were taken for examples of each particle type found.

Copper FLEX

One particle type composing primarily of copper was found. These were generally in the range of 2 - 10 µm in diameter. Other particles composed primarily of iron and a few composed primarily of calcium were also observed; these were generally smaller at approximately 50 - 500 nm.

Images and EDX spectra of the copper particles are included in Appendix B.2. The iron and calcium particles were very similar to those found in the other samples. An example of each of these particle types is shown in the results for the bronzeFill sample (Appendix B.4).

brassFill

One particle type, composing predominantly of copper and zinc, was found. These particles were generally between 0.2 and 2 µm in diameter. Other particles composed primarily of iron and a few composed primarily of calcium were also observed. These particles were generally smaller at approximately 50-500 nm.

Images and EDX spectra of examples of the copper particles are included in Appendix B.3. The iron and calcium particles were very similar to those found in the other samples. An example of each of these particle types is shown in the results for the bronzeFill sample (Appendix B.4).

bronzeFill

One particle type composing predominantly of copper and tin; some also containing chromium; were found. These particles varied in size from approximately 0.2 µm to 5 µm in diameter. Other particles composed primarily of iron and a few composed primarily of calcium were also observed. These particles were generally smaller with diameters between approximately 50 and 500 nm.

Images and EDX spectra of examples of all the particle types observed are included in Appendix B.4.

3.2 VOLATILE ORGANIC COMPOUNDS

3.2.1 Sampling inside an enclosed box over a range of nozzle temperatures

The recovered VOC species from the sampling tube positioned close to the nozzle of the KORA MIDI printer (Figure 6b), whilst printing with PLA, inside an enclosed box are presented in Figure 17. The concentration of each VOC detected in the sample tube can be compared to a corresponding concentration in the 'blank' sample; taken from the box when printing was not taking place. These results are also presented in Figure 17.

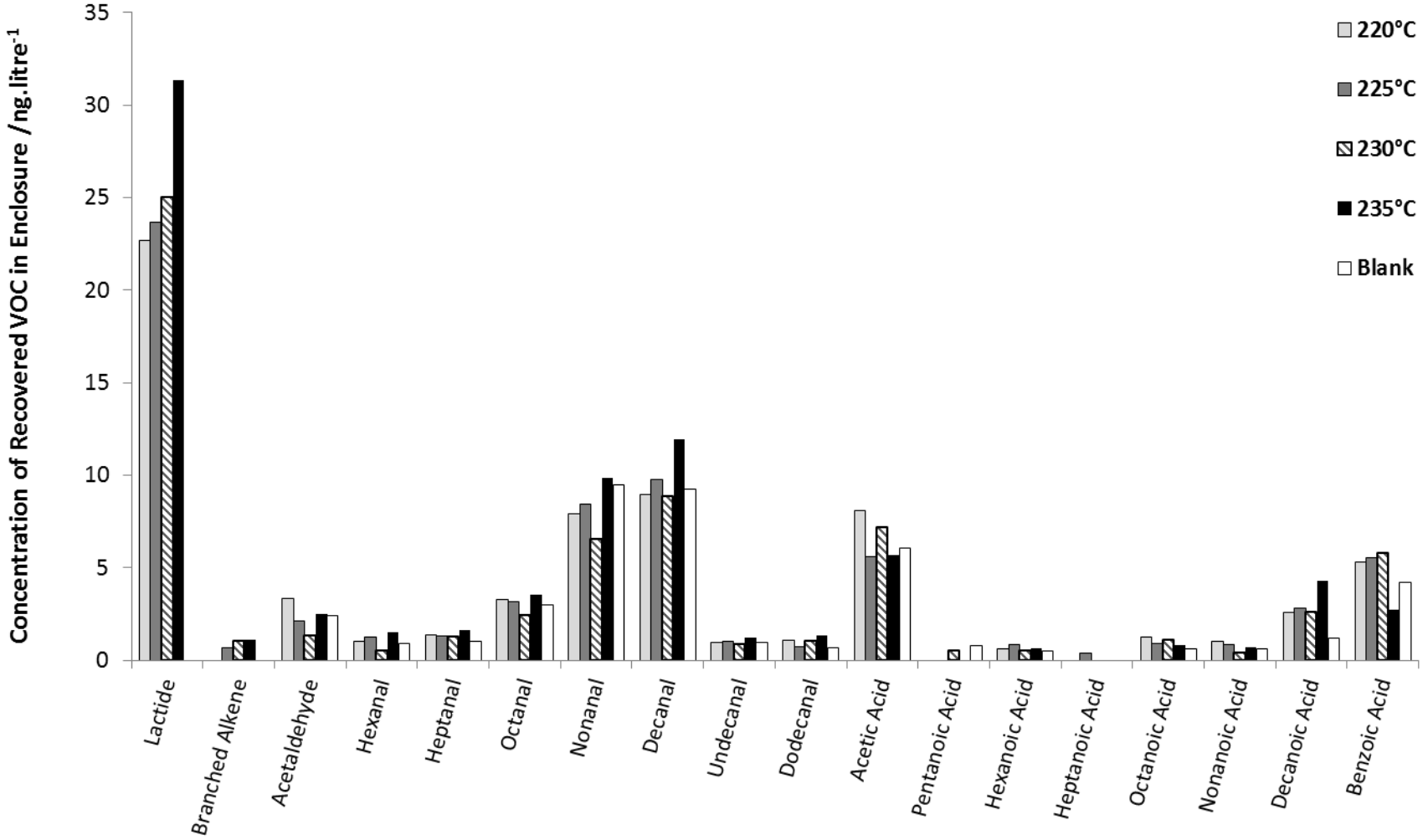

Figure 17 Recovered VOC species from a sampling tube at the nozzle of the KORA MIDI whilst printing with PLA inside an enclosed box across a range of nozzle temperatures 200°C – 235°C.

3.2.2 Pyrolysis testing

The percentage of the emissions made up by each component using the two test methods described in Section 2.4.4 are shown in Tables 4-6 for PLA 'natural', ABS 'natural' and NinjaFlex® 'clearwater' filaments. The complete set of results for pyrolysis testing of all 12 filament materials can be found in Appendix C.

Table 4 Percentage of the emissions made up by each compound produced using pyrolysis methods 1 and 2 with PLA 'natural'

Filament Material: PLA 'natural'		
COMPOUNDS	PROPORTION - Method 1	PROPORTION - Method 2
Lactide (Isomer 1)	2.6%	15.5%
Lactide (Isomer 2)	33.8%	68.0%
Aliphatic Hydrocarbon Oil	63.6%	2.7%
Other (mainly lactide oligomers)	0.0%	13.8%
TOTAL	100%	100%

Table 5 Percentage of the emissions made up by each compound produced using pyrolysis methods 1 and 2 with ABS 'natural'

Filament Material: ABS 'natural'		
COMPOUNDS	PROPORTION - Method 1	PROPORTION - Method 2
Butadiene Dimer	0.2%	0.5%
Ethylbenzene + Xylene	0.6%	0.0%
Styrene	8.4%	1.2%
Styrene Oligomers	2.4%	0.0%
Styrene-Nitrile Oligomers	49.7%	47.8%
Styrene-Nitrile Oligomers	11.8%	16.6%
Aromatic Compounds	18.5%	17.8%
Aromatic Compounds	2.6%	3.8%
Other (mainly aromatic)	5.9%	12.4%
TOTAL	100%	100%

Table 6 Percentage of the emissions made up by each compound produced using pyrolysis methods 1 and 2 with NinjaFlex® 'clearwater'

Filament Material: NinjaFlex® 'clearwater'		
COMPOUNDS	PROPORTION - Method 1	PROPORTION - Method 2
Tetrahydrofuran	3.2%	0.9%
Butanediol	3.8%	7.9%
Diisopropenylbenzene	0.8%	0.5%
Other Aromatic Isocyanates	4.2%	0.8%
C12 Cyclic Diester	6.2%	0.2%
Aliphatics (cyclic/unsaturated)	23.4%	1.4%
MDI (mainly 4,4-)	58.4%	88.4%
TOTAL	100%	100%

3.3 EXPOSURE CONTROL

3.3.1 Measuring emissions inside the test chamber with and without the enclosing hood in place

The enclosing hood was used in both modes (exhausting and recirculating). Measurements made with and without the enclosing hood in place, in both operating modes, were compared. Emission rates were calculated from the data collected at the measurements cross-section with the DISCmini during the time that the printer was extruding. The results are presented in Table 7.

Table 7 Emission rates of KORA MIDI printer and ABS filament (nozzle = 250°C and print bed = 78°C); no control, exhausting mode, and recirculating mode; measured with the DISCmini. All values presented are averaged over two repeat tests

Control	Emission Rate / particles.min^{-1}	Reduction in emission rate compared with no control / %
No control	4.90 x 10^{11}	N/A
Exhausting	1.48 x 10^{10}	97.0
Recirculating	2.73 x 10^{9}	99.4

3.3.2 Measuring particle concentrations inside the enclosing hood and determining the particle clearance time

The concentration of particles inside and outside the enclosing hood when printing with PLA filament are presented in Figures 18 and 19 for the exhausting and recirculating modes respectively.

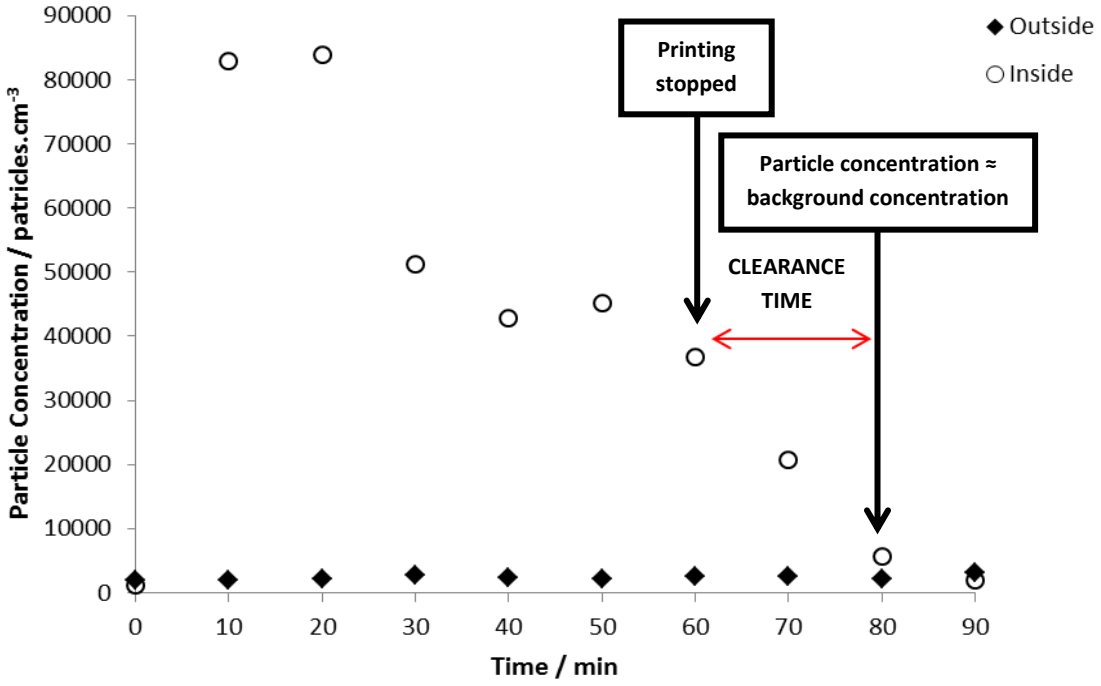

Figure 18 Particle concentration measured with two pTrak instruments inside and outside the enclosing hood as the KORA MIDI printed with PLA filament (nozzle = 220°C and print bed = 50°C). The enclosing hood was set to exhausting mode.

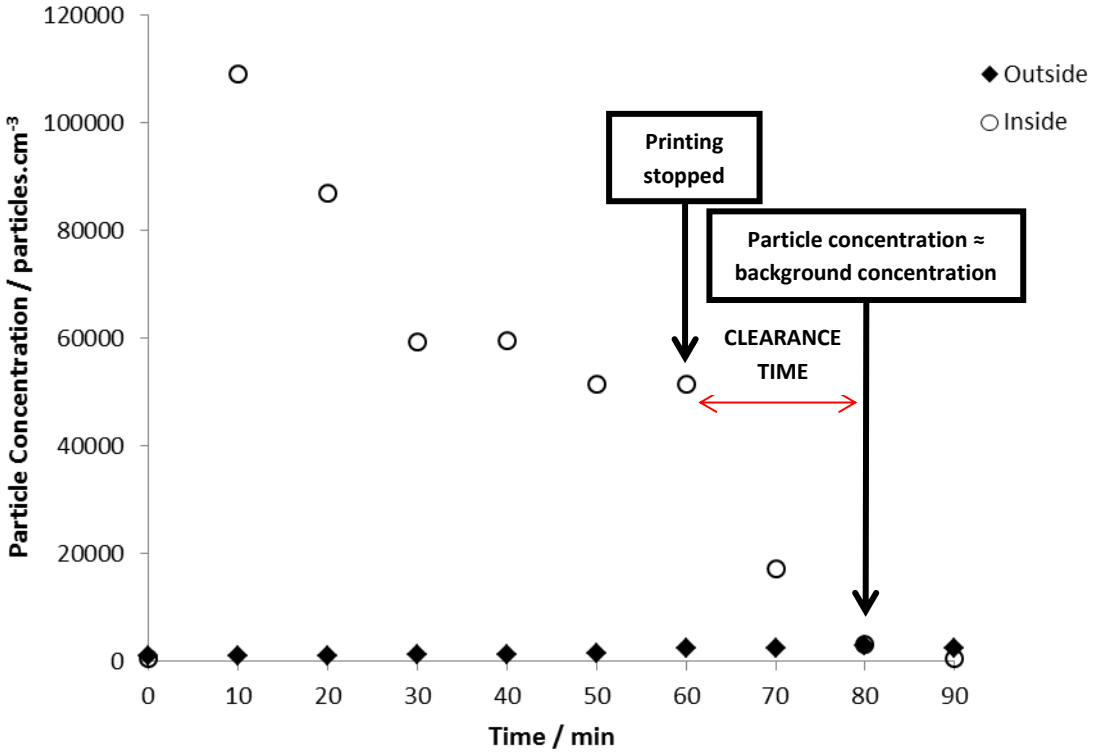

Figure 19 Particle concentration measured with two pTrak instruments inside and outside the enclosing hood as the KORA MIDI printed with PLA filament (nozzle = 220°C and print bed = 50°C). The enclosing hood was set to recirculating mode.

4 DISCUSSION

4.1 EMISSION RATES

The test method used to measure the particulate emissions from the FFF 3D printers for this project was based on BS EN 1093. This method differs from that used in a number of other published studies e.g. Floyd *et al* (2017), Azimi *et al (*2016), Kim *et al (*2015). The measurement method used here was considered preferential to that used by others as it reduced the possibility of sampling bias through mixing of the aerosol. The time for the aerosol to travel from the printer to the measurement cross-section of the test chamber was calculated to be approximately 17 seconds and therefore considered negligible in comparison to the length of each test of one to two hours.

The range of real-time instruments used enabled characterisation of the size and concentration of particulate emissions. Data from the DataRAM and MetOne instruments are not reported here as the measurements did not rise significantly above the background level for the duration of all tests. This is principally because the maximum size of particles emitted from the printer was below the detectable size range of these instruments (Table 1).

The initial plan was to test a range of three to four different filament materials (Section 1.4) on three different printers (Section 1.3.2). However, it became apparent that this would not be possible as some printers were not compatible with printing certain filament materials. Only the Ultimaker 2 was successful in printing with 'clearwater' NinjaFlex® filament and the KORA MIDI was alone in producing repeatable prints with white HIPS. Therefore, it was not possible to collect comparable data across all printer-filament combinations.

The KORA MIDI and the Makerbot Replicator 2 both printed with 'natural' PLA filament. The spool of filament was transferred from one printer to the next for comparison. When a 3.00 mm diameter PLA filament was used with the Ultimaker 2, it failed to feed filament to the nozzle. The results of these tests (Figure 10) showed a significant difference in the concentration measured with the pTrak when the same PLA filament was used in different printers. The KORA MIDI produced an average particle concentration of approximately 1500 particles.cm^{-3} compared to 7500 particles.cm^{-3} produced with the Makerbot 2. Although the filament material was the same in both cases, the selected printer temperatures were different. The nozzle temperatures were 220°C and 230°C and the print bed temperatures were 50°C and 'ambient' on the KORA MIDI and the Makerbot Replicator 2 respectively. These differences are likely to be the main reason for the difference in particle concentrations observed.

The particle size distributions of the emissions were also different (Figure 11 and Figure 12). The Makerbot Replicator 2 distribution represented a much smaller particle size. Despite the print bed being approximately 30°C cooler than that of the KORA MIDI, the nozzle of this printer was ten degrees hotter and this was considered the reason for this result. From this it was concluded that the printer's nozzle temperature was more significant in affecting the emissions than the temperature of the print bed.

The KORA MIDI and the Ultimaker 2 both printed with transparent ABS filament. The same spool of filament could not be used in both printers since the KORA MIDI uses a 1.75 mm diameter filament and the Ultimaker 2 a 3.00 mm diameter filament. Both ABS spools were purchased from one manufacturer. The Makerbot Replicator 2 was not compatible with ABS printing as it did not have a

heated print bed. The particle concentration measured when the Ultimaker 2 printed with ABS (Figure 13) was less stable across the print duration than that observed when printing on the KORA MIDI, which showed a similar pattern to that for PLA printing (Figure 10). The reason for this was unknown but could be due to the larger diameter filament used in the Ultimaker 2.

It was determined upon review of the initial results for the different printer-filament combinations that the number of variables i.e. the printer, filament, nozzle temperature, bed temperature etc. in each test should be reduced. Therefore, one printer and one filament; the KORA MIDI and ABS; were chosen for additional tests to investigate the relationship between the printer nozzle temperature and the emissions characteristics.

At a bed temperature of 78°C, the KORA MIDI's nozzle temperature was increased in five degree increments between 245 – 260^{o}C for each test. In this temperature range, the particle emission rate increased as the nozzle temperature increased (Figure 14). This compared with results obtained by Mendes *et al* (2017), who found that when increasing the nozzle temperature from 238^{o}C to 250^{o}C for ABS printing, the particle emission rate increased, on average, ten times.

The DISCmini was also used by HSE to measure the average particle size however, no relationship between the particle size and the nozzle temperature could be determined from these tests as the value did not exceed 10 nm, which was the lower size limit of the instrument. Mendes *et al* (2017) were the first to present particle size measurements smaller than 10 nm, and measured particles in the size range 1 – 3 nm in great abundance in all the print cycles. They reported mean particle sizes of 7.6 - 10.5 nm for PLA and ABS, which was smaller than other recent studies (Stephens *et al,* 2013 and Kim *et al,* 2015). This agreed more closely with the average size of ABS emissions measured by HSE but was smaller than the average particle size of PLA emissions.

To investigate the relationship between the average particle size of the emissions and the nozzle temperature of the KORA MIDI, further tests were carried out using PLA filament at a constant print bed temperature of 50°C. The nozzle temperature was increased in 5°C increments through the range 220 – 240^{o}C. As the nozzle temperature increased through this range, the average particle size decreased (Figure 16).

Despite good repeatability of tests when performed within a short timeframe (days); there were distinct differences in the absolute emission rate values (Figures 14 and 15) and the average particle size (Figure 16) when the period of time between tests was longer (weeks/months). However, when considering the data taken within each shorter time frame as separate sets, i.e. 2nd - 6th March set one and 21st April set two (Figure 14), both show a similar trend between the nozzle temperature and emission rate. Azimi *et al (*2016) also found that data from two sets of duplicate tests demonstrated some inherent variability in UFP emissions.

The emission rates measured in this research are comparable to those reported by other researchers, such as Stephens *et al (*2013). They estimated that total UFP emission rates varied from 2.0 x 10^{10} to 1.9 x 10^{11} particles.min^{-1} and depended on the filament material. The results of this work showed that emission rates exceeding this range were possible when printing at higher printer nozzle temperatures (Table 2).

A comparison was made between the calculated emission rates from this study and those reported by He *et al* (2007) for traditional printers currently found in the office environment. He *et al* found that of 62 traditional printers in an office building, 60% did not emit sub-micrometre particles.

Emission rates for those printers that did emit sub-micrometre particles were estimated to be in the range of $4.0 \times 10^{7} – 1.6 \times 10^{11}$ particles.min^{-1}. All of the 3D FFF printers in this research emitted sub-micrometre particles across all of the filament material tested. The highest emission rate measured by He *et al* was comparable to the lowest emission rate measured for the KORA MIDI printer printing with ABS filament (Table 2). Emission rates measured for the KORA MIDI printing with PLA filament were lower than those for ABS and below the highest emission rates measured by He *et al*. However, the lowest emission rate for PLA filament was two orders of magnitude greater than the lowest measured for office printers (Table 3).

Data presented in Appendix A shows that there was good agreement in the particle concentration measured with the pTrak and the DISCmini when printing with PLA. However, differences between the data from these instruments were observed when printing with ABS, with the concentration reading higher with the DISCmini. This would be expected due to its lower detectable size limit and the smaller average particle size produced by ABS filament. The DISCmini is also known to overestimate particle concentrations at particle sizes <20 nm (Todea, 2017).

When analysing the TEM grid samples from inside the test chamber whilst printing with ABS using the Ultimaker 2 printer, polymer particles were not observed. The direct sampling method used (Section 2.3.3), meant that there was no phase of sample preparation during which these particles could have dissolved or interacted with a reagent. One possible reason for not observing polymer particles could be due to the significantly reduced contrast in TEM images of this type of particle. Another reason could be the small size of these particles relative to the pore size of the grid, resulting in the majority of these particles bypassing the grid. Mendes *et al* (2017) also found that their TEM sample analysis showed very little number or none detectable particles and did not allow further conclusions. These tests could be repeated with a filament such as PLA that generates larger average particle size. Some metal particles were observed and images and EDX spectra of examples of these particles can be found in Appendix B.1.

The TEM and EDX analysis of emissions from filament containing embedded metals found that metal particles were generated during heating to temperatures comparable with those of a 3D printer nozzle. This test was a simulated experiment conducted inside a small heated chamber in the laboratory (Section 2.3.4). Comparable samples were not collected during 3D printing with these materials as this was beyond the scope of the test plan. This area may be of interest for future work.

The EDX spectra will always present a peak for the metal of which the TEM grid is composed. For the analyses in this research, the grids were made of copper, which is why, for example, the EDX of the iron particle also contains a copper peak. The copper peak observed in the EDX spectra of the copper-zinc particles was much stronger than would be expected for a background peak, confirming that copper was present in the sample.

4.2 PYROLYSIS TESTING

An advantage of applying the pyrolysis test was that it allowed the VOC emissions from a wide range of filaments to be analysed in a short space of time compared to completing a 3D print with each material. It was a reproducible method, which replicated temperatures comparable to those of the 3D printer nozzle.

The pyrolysis results indicate that for some filament material, it is not only temperature but heating time which is critical; the polyurethane-based Ninjaflex® in particular generated significantly more material using method 1 than with method 2 (as described in Section 2.4.4), which had total heating times of 2 minutes and 30 seconds respectively. However, other materials, such as ABS and HIPS appeared to give fairly similar results from the two methods. The chemical components evolved were largely similar using both methods. It was also noted that the different nylon products, whilst fairly similar in composition showed significantly different weight losses.

The constituents produced from the different filament materials were mostly as expected e.g. PLA produced lactide and ABS produced styrene. However, some of the filament did produce unexpected emissions. When heated, the Ninjaflex® filament released Methylene Diphenyl di-Isocyanate (MDI). Over 88% of the total emissions were MDI when using method 2 of the pyrolysis testing. Inhalation of isocyanates can irritate the eyes, nose and throat and cause occupational asthma in some individuals.

4.3 EXPOSURE CONTROL

Emissions from FFF 3D printers are likely to be released into the general environment because many of desktop printers have no form of control or particle capture. Many manufacturers have started to produce structures that enclose the printing process. However, manufacturers generally provide these enclosures to improve the quality of the print by controlling the atmosphere rather than to reduce emissions. The level of filtration of the air leaving the enclosures, if any, is difficult to establish as information provided by manufacturers is minimal. Azimi *et al* (2016) tested some models of desktop 3D printer designed with an integral enclosure. The enclosures were not airtight or filtered and they only moderately reduced the UFP median emission rates by approximately ~35%; this was determined with limited data so is more of an indicative result.

However, there is a risk that if a printer is enclosed without a suitable filtration system, the operator and bystanders could be exposed to high concentrations of particulates and VOCs when opening the enclosure.

The exposure control method evaluated for this research was a Perspex enclosing hood, which could be placed over the top of the printer. Any particulate emissions were filtered from the air inside the hood in one of two ways:

- ‘Exhausting mode’ - Air was passed through a filter as it was exhausted from the hood and surrounding ‘clean’ air was drawn in at the base;
- ‘Recirculating mode’ - Air was continually passed through a filter as it recirculated inside the hood and no new air was introduced.

To investigate the effects of the enclosing hood, the KORA MIDI printed ABS filament inside the test chamber: with no exposure control in place, in exhausting mode, and in recirculating mode (Table 7). Particulate emission rates were reduced by 97% and 99% for the exhausting and recirculating modes respectively with the enclosing hood in place compared to measurements made with no exposure control.

The time taken for the hood to clear of particles once the emissions were no longer being produced, i.e. the ‘clearance time’, is seen in Figures 18 and 19 to be approximately 20 minutes. A qualitative assessment using smoke corroborated this value. It is important that the user is aware of this

clearance time so that they know how long to wait before accessing the enclosure. This clearance time could be reduced by increasing the airflow rate and/or reducing the volume of the enclosure. The particle concentration measured inside the hood, when set to recirculating mode, was also seen to reach a lower value approaching zero compared with the laboratory air background measured outside the hood (Figure 19). This was expected as no new air from the laboratory was being introduced to the hood. The clearance time may vary depending on the volume flow rate, the volume of the enclosure and the efficiency of the filtration system if recirculating the air inside the enclosure.

Instructions should be supplied by the manufacturer of the safety cabinet or hood to include specified 'clearance times' after the print has completed before opening the enclosure. This advice should be closely followed by the printer operator to avoid risks for inhalation and ingestion of particulates and VOC.

The instruction manuals provided by the manufacturers of some 3D printers do include health and safety information in relation to the melting plastic material. This often advises locating the printer in a 'well-ventilated area' due to the 'plastic odours' emitted. Independent Local Exhaust Ventilation (LEV) systems are commercially available, which claim to be designed for the specific application of controlling emissions from 3D printers e.g. Kora 3D SC-01 Safety Cabinet (Secure Micro Solutions)[1] and 3D PrintPRO range (BOFA International Ltd.)[2].

In considering the requirement for an effective enclosure to remove emissions from FFF desktop 3D printers is it important that suitable filters are selected to remove very small particles and VOC emissions. It is also essential that these filters are regularly replaced and this action is documented.

4.4 OTHER CONSIDERATIONS

4.4.1 Finishing techniques

The nature of 3D FFF printing can result in visible layers on the surfaces of the object produced, which could produce an undesirable appearance. Therefore, numerous techniques can be employed to 'finish' the object and smooth the surfaces. Anecdotally, this has included manual techniques, such as sanding and polishing but also the use of solvents. Investigation of these finishing techniques was outside of the scope of this project. However, it is important to advise users that risks to health resulting from these processes should also be considered when risk assessing the use of 3D printing equipment.

4.4.2 Extruding metal

A quick internet search revealed that 3D FFF printers using metal as the build material are quickly advancing but are not as widely available as their plastic equivalent. One such example is the Studio System™ (Desktop Metal Inc.), advertised as 'office-friendly' it functions by 'extruding metal rods'. There is established evidence from traditional industries that occupational exposure to metals, as particles, fumes or through skin contact, can cause various respiratory diseases. As metal 3D FFF

[1] Kora 3D [online] Available at http://www.kora3d.com/ (accessed 22 February 2019)

[2] BOFA [online] Available at http://www.bofa.co.uk/3D-printing-fume-extraction.asp (accessed 22 February 2019)

printers develop it is important to consider whether these machines could present potential harmful exposures.

4.5 RESEARCH LIMITATIONS

The emission measurements made throughout this research were carried out in controlled, laboratory tests. Measurements and observations of 3D printing practices within a 'real' environment, such as an office or classroom, would enable a validation of the results presented in this report and a better understanding how the findings could inform good exposure control practices. The findings could be further contextualised to estimate exposure to 3D printer emissions over a period of time where individuals are regularly working with these machines. The risks from these exposures could then be assessed in relation to any potential adverse health effects.

4.6 WORKING GROUP

The research findings described in this report and the control measures identified were shared as soon as they were available with the working group set up by HSE. Working group members identified evidence based safe working practices for schools using FFF desktop 3D printers. These findings contributed to the development by CLEAPSS of a good practice guide.

5 CONCLUSIONS

A working group was initiated by HSE including HSE scientific and regulatory colleagues and representatives from an advanced manufacturing catapult centre, from industry and the education sector. The working group shared knowledge and experience and identified the need for evidence based advice to schools on the safe use of desktop, 3D, FFF printers. HSE undertook laboratory experiments to characterise emissions from the printers and evaluate a potential exposure control.

Particle emissions:

- Emitted particles were in the size range to potentially enter the airways and lungs, and that emission rates when printing with ABS were higher than for PLA.
- Particle emission rates varied for different filament material on the same printer.
- Particle emission rates and size distributions for the same filament material varied for different printers.
- Particle emission rates increased and the average particle size decreased as the 3D printer nozzle temperature increased.
- TEM and EDX analysis identified metal particles emitted from heated filament containing embedded metals. These tests were simulated laboratory tests and it may be useful to investigate this further by collecting samples when printing with this type of filament.

Volatile emissions:

- The information provided by some suppliers of filament material was found to be unreliable and uninformative with respect to the release of hazardous volatile constituents.
- Pyrolysis testing was a repeatable method to test a wide range of filament materials for VOC emissions.
- Pyrolysis results indicated that both the temperature and heating time can affect the products released from filament material.
- When heated, some plastic filament materials released chemicals known to be hazardous to health and particulate and VOC emissions vary significantly between filament types.

Effectiveness of enclosing hood for controlling exposure

- Placing an enclosing hood over the 3D printer reduced particle emissions released to the room by 97% when exhausting air from the enclosing hood and by 99% in the recirculating air mode.
- Particulate and VOC emissions accumulated inside the enclosing hood during printing. The clearance time of the enclosing hood was approximately 20 minutes, therefore removing the hood before this time could result in personal exposure.

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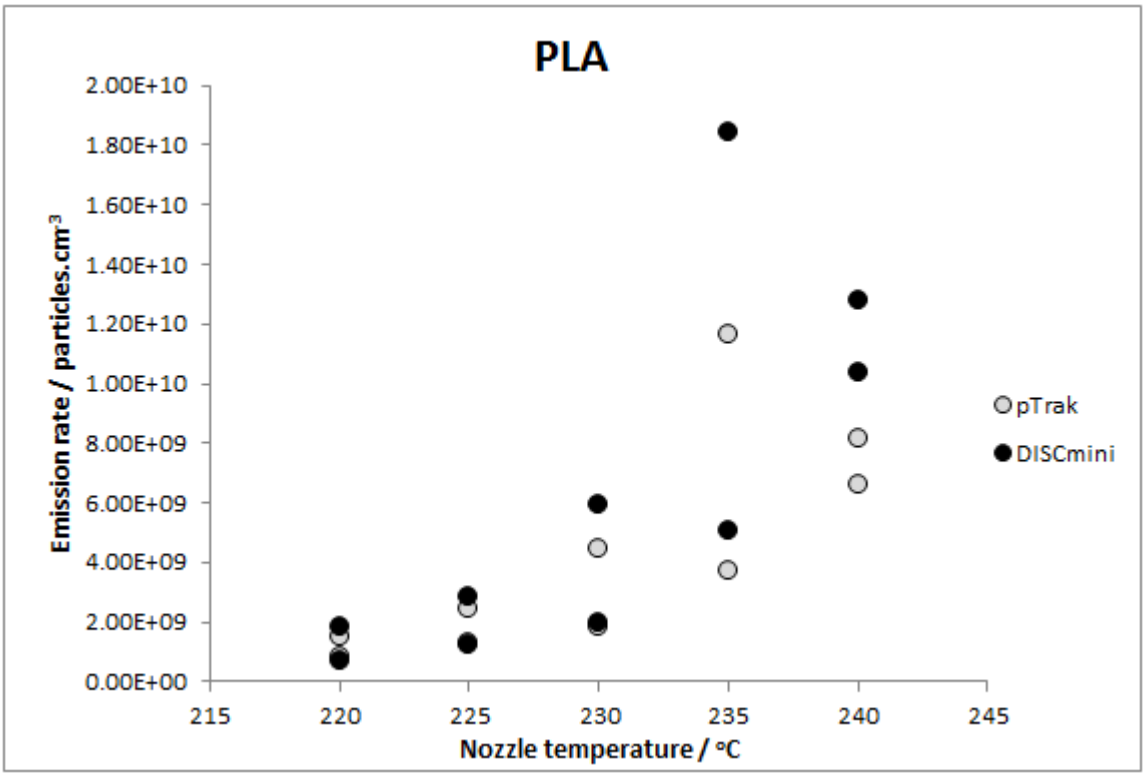
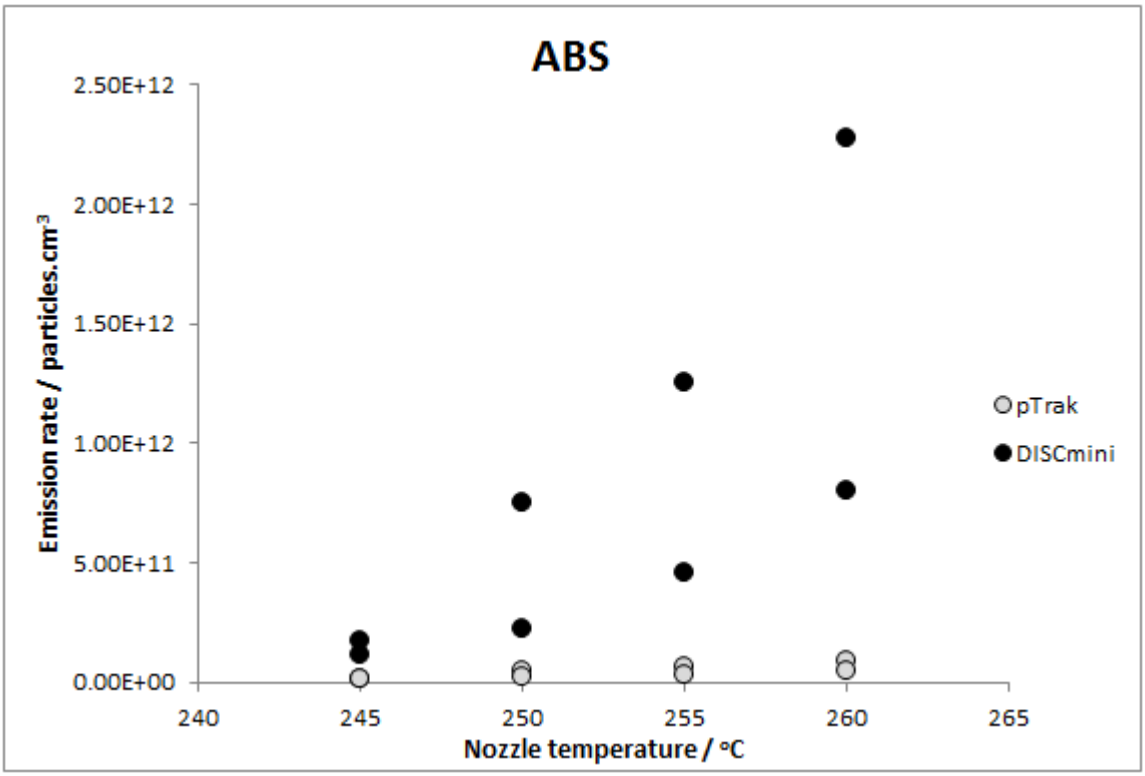
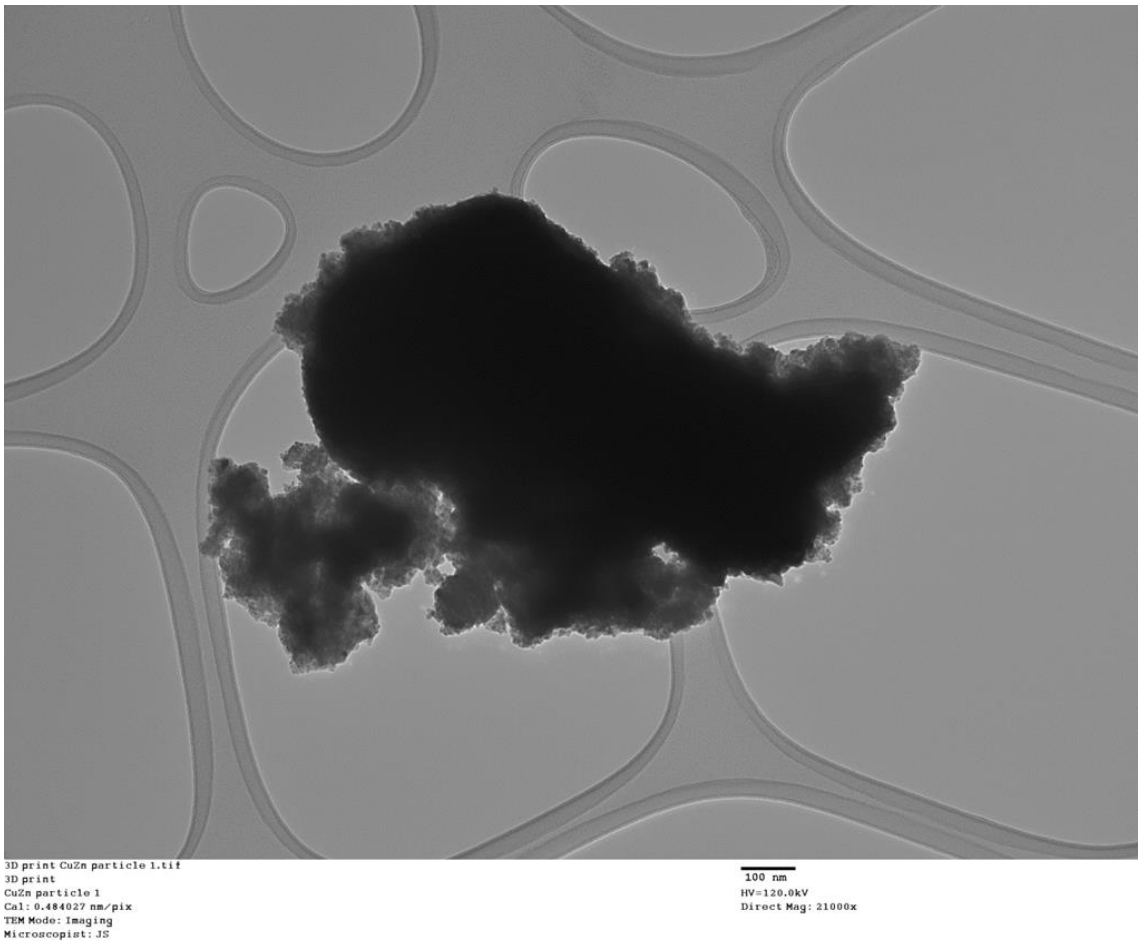
APPENDIX A PTRAK AND DISCMINI DATA COMPARISON

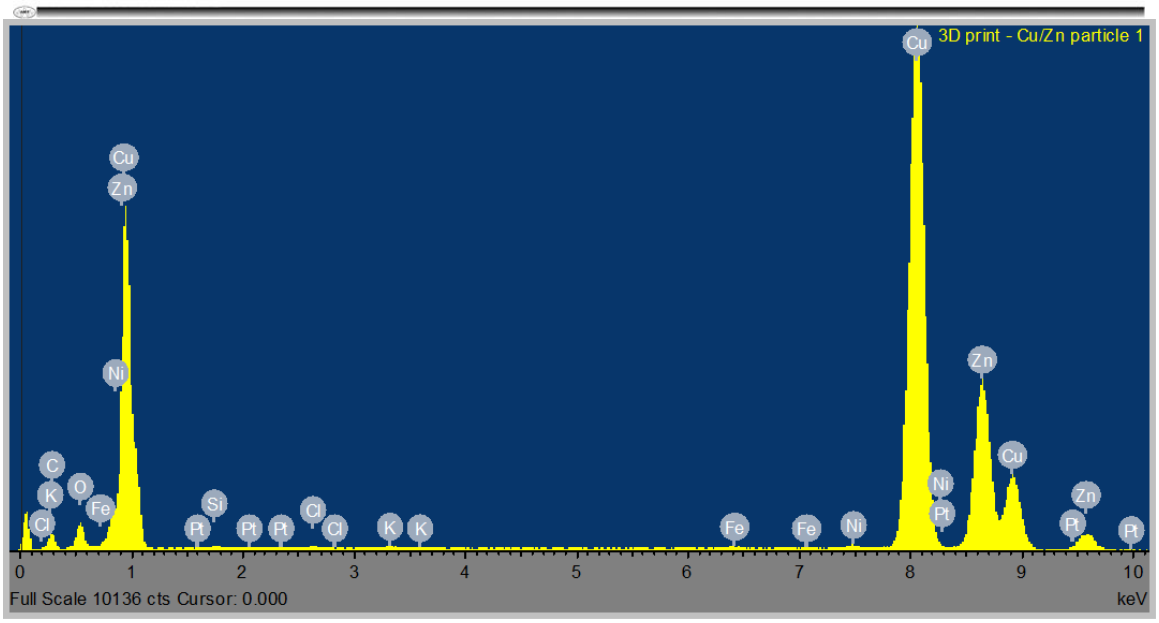


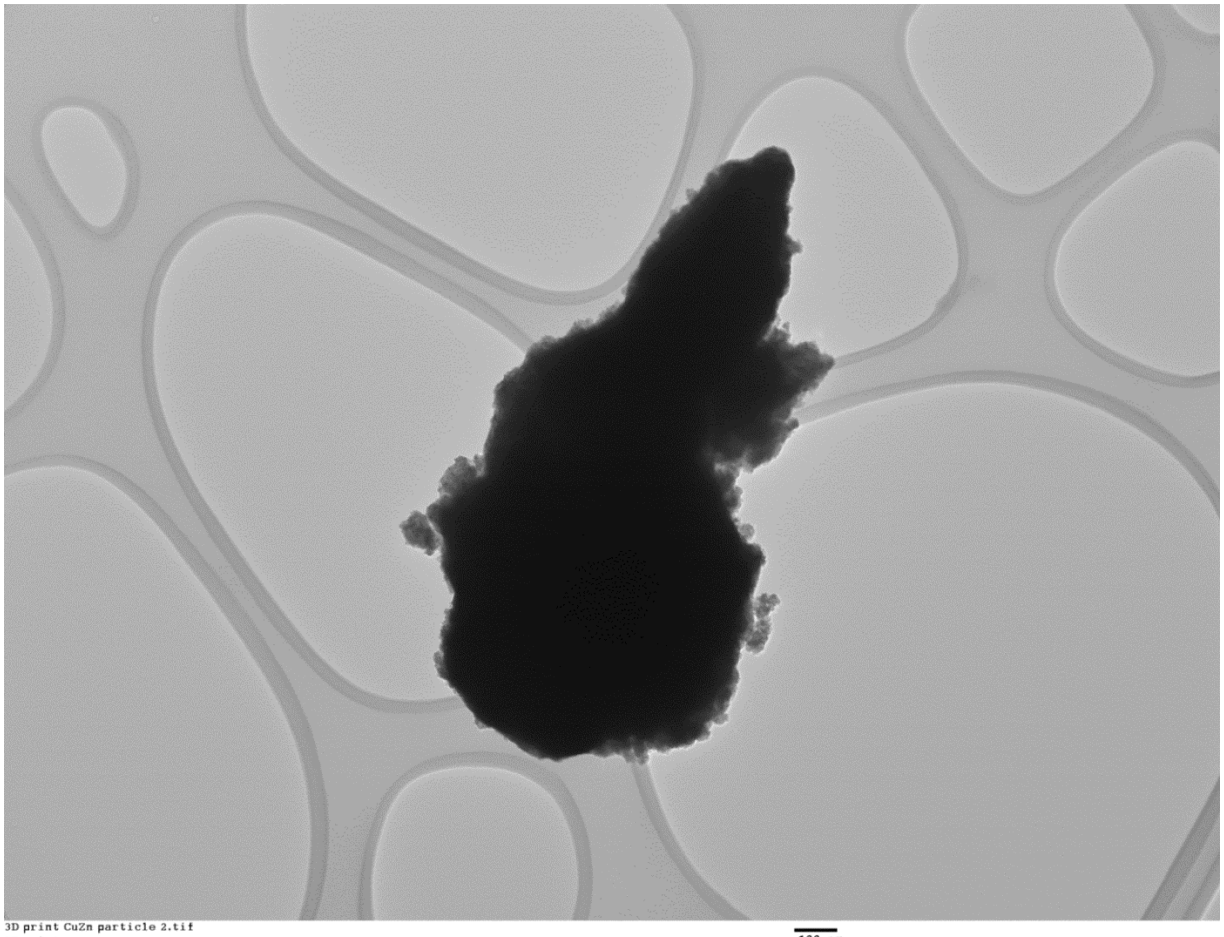


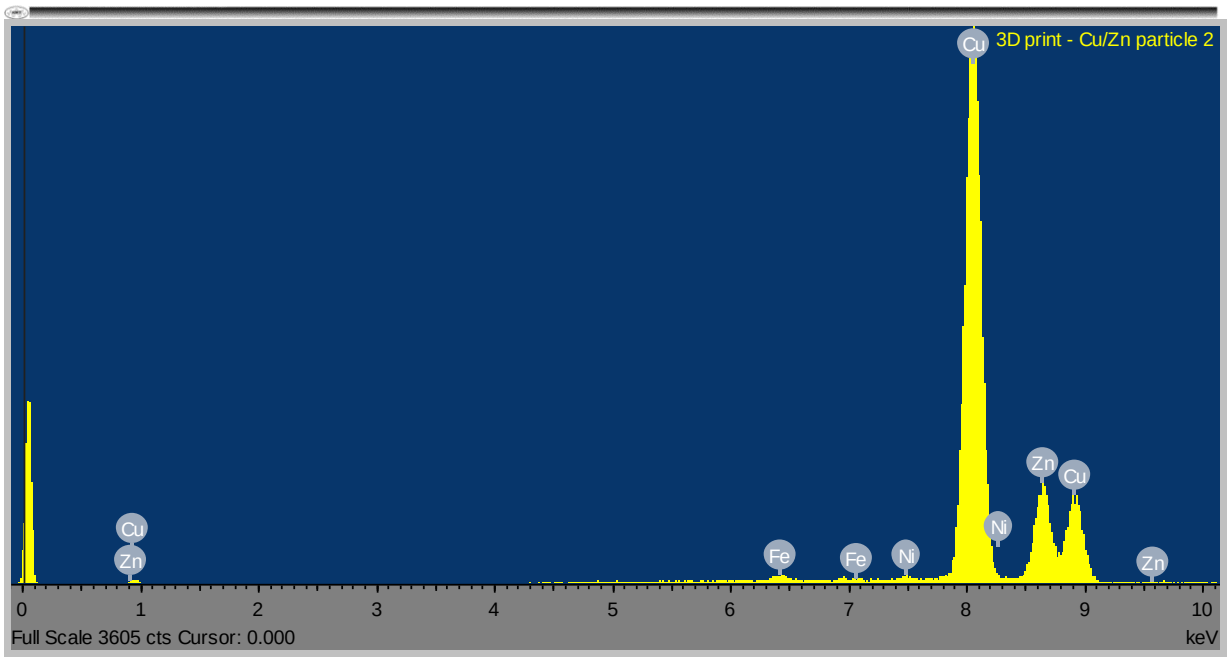
APPENDIX B TEM IMAGES AND EDX SPECTRA

B.1 ABS PRINTING IN THE TEST CHAMBER

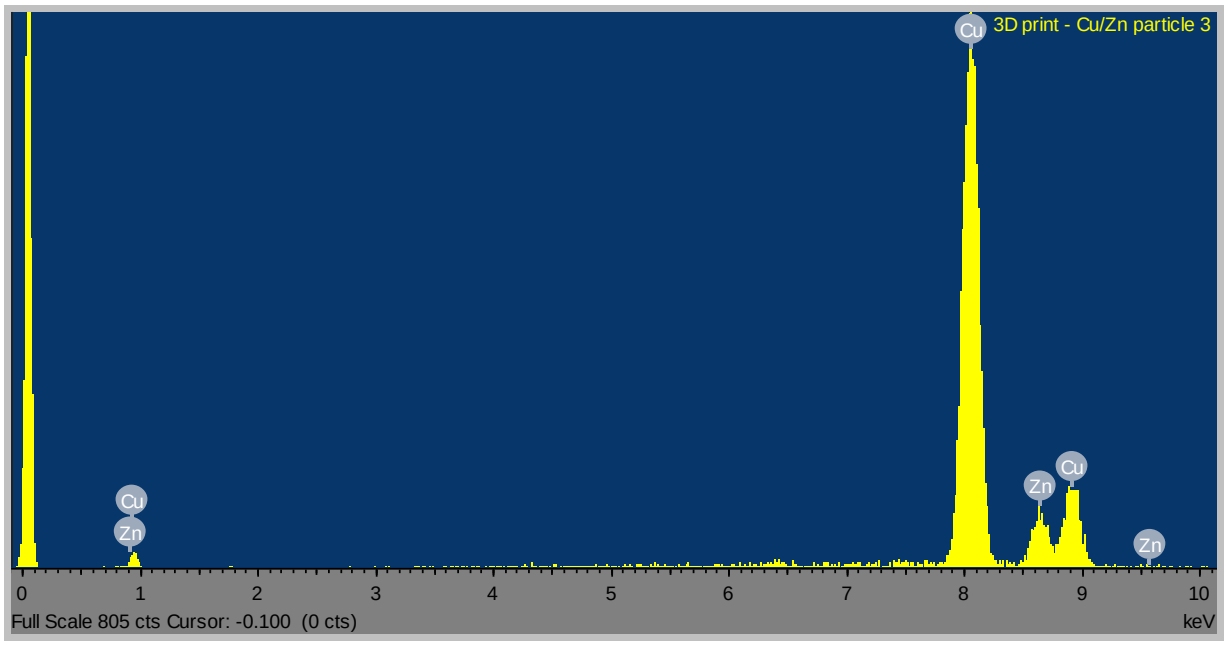


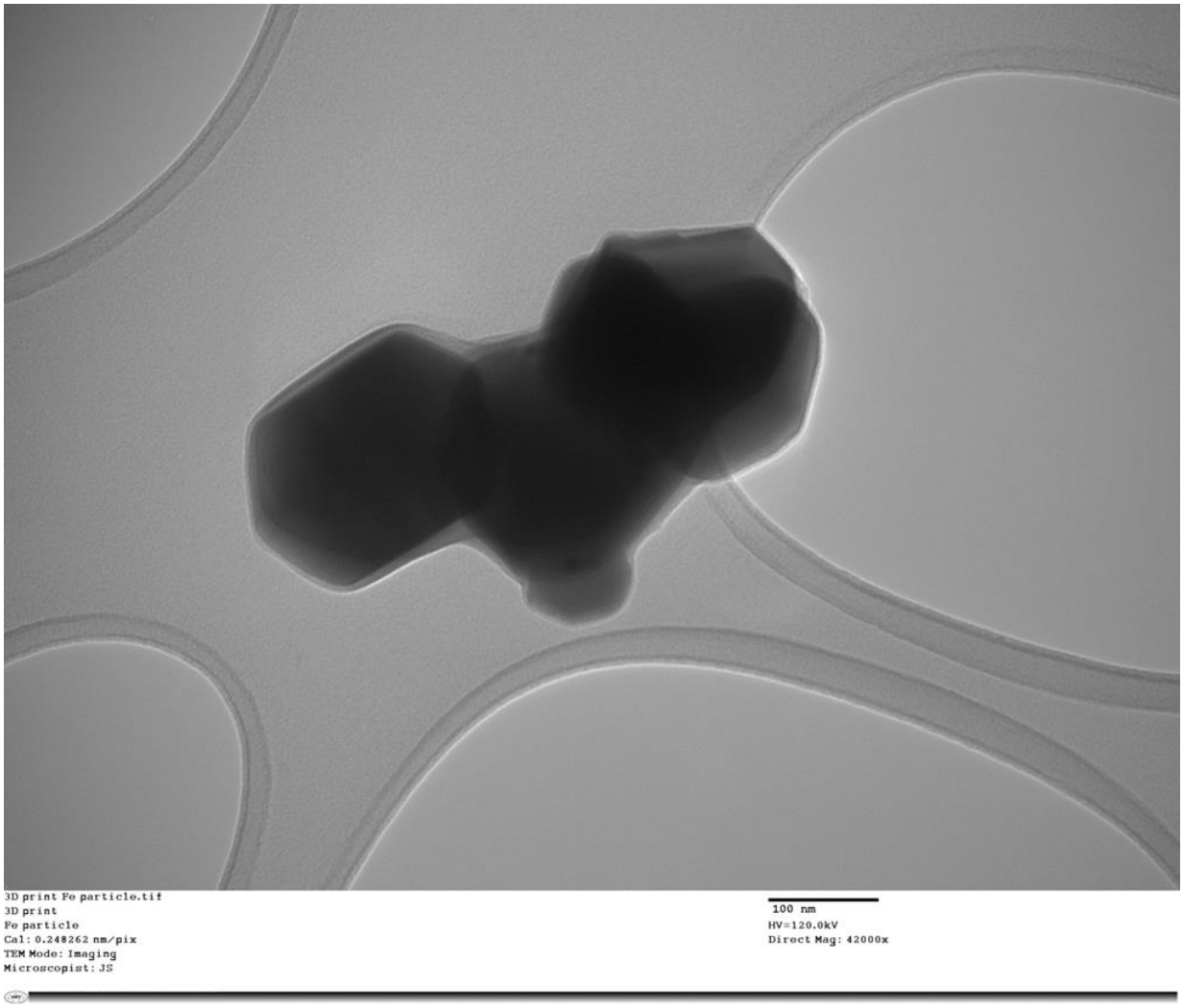


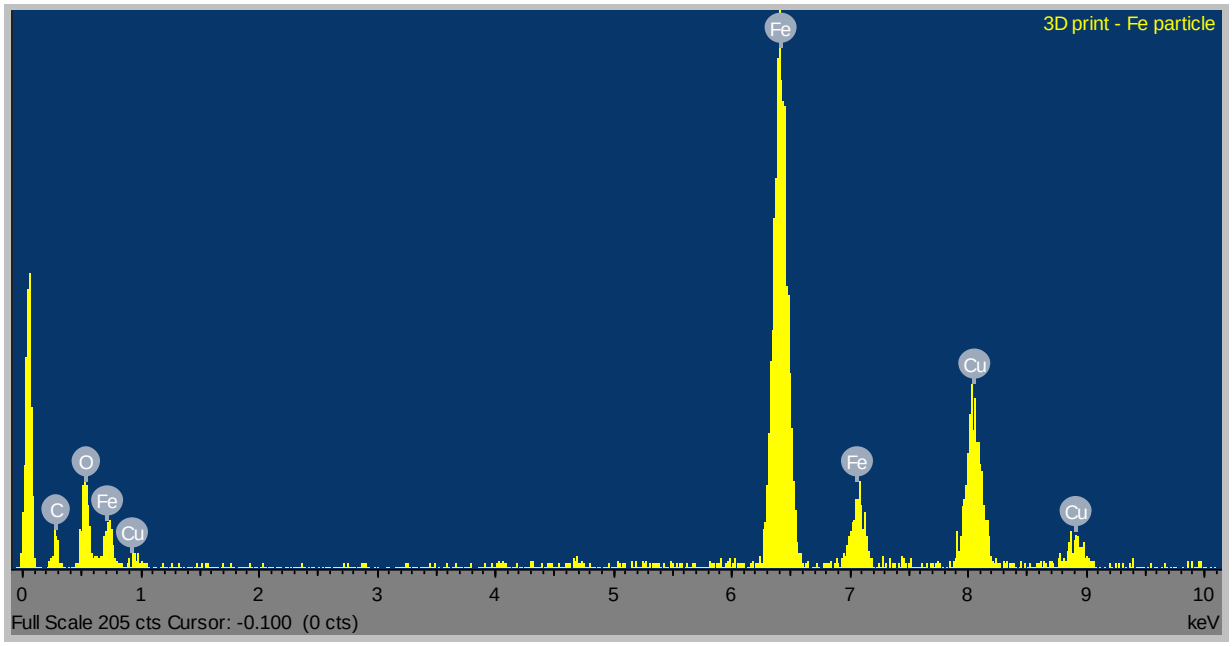

3D print CuZn particle 2.tif
3D print
CuZn particle 2
Cal: 0.659196 nm/pix
TEM Mode: Imaging
Microscopist: JS
100 nm
HV=120.0kV
Direct Mag: 15000x


3D print - Cu/Zn particle 2
Cu
Zn
Fe
Fe
Ni
Ni
Zn
Cu
Zn
0
1
2
3
4
5
6
7
8
9
10
Full Scale 3605 cts Cursor: 0.000
keV

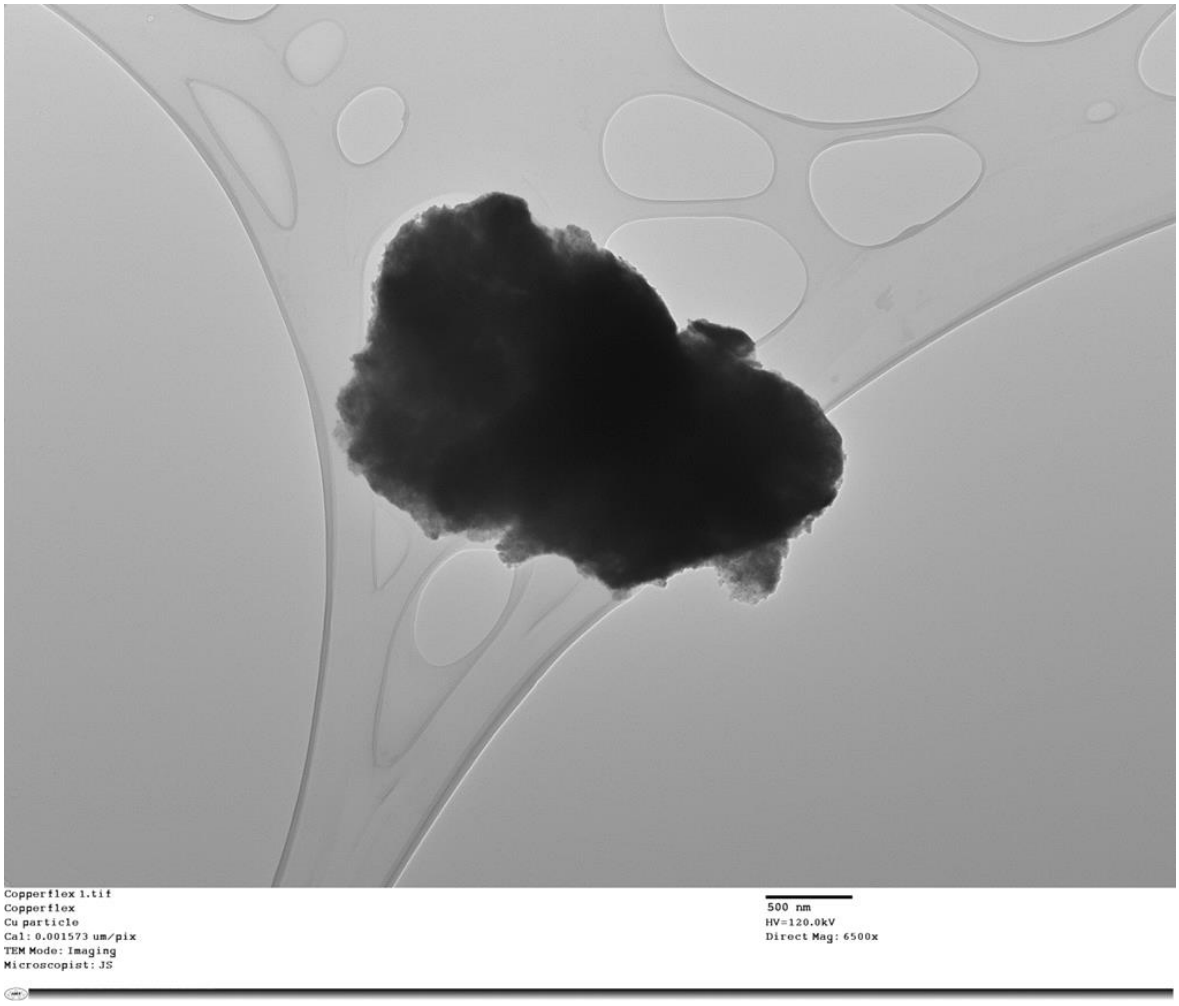

3D print CuZn particle 3.tif
3D print
CuZn particle 3
Cal: 0.155618 nm/pix
TEM Mode: Imaging
Microscopist: JS
20 nm
HV=120.0kV
Direct Mag: 67000x

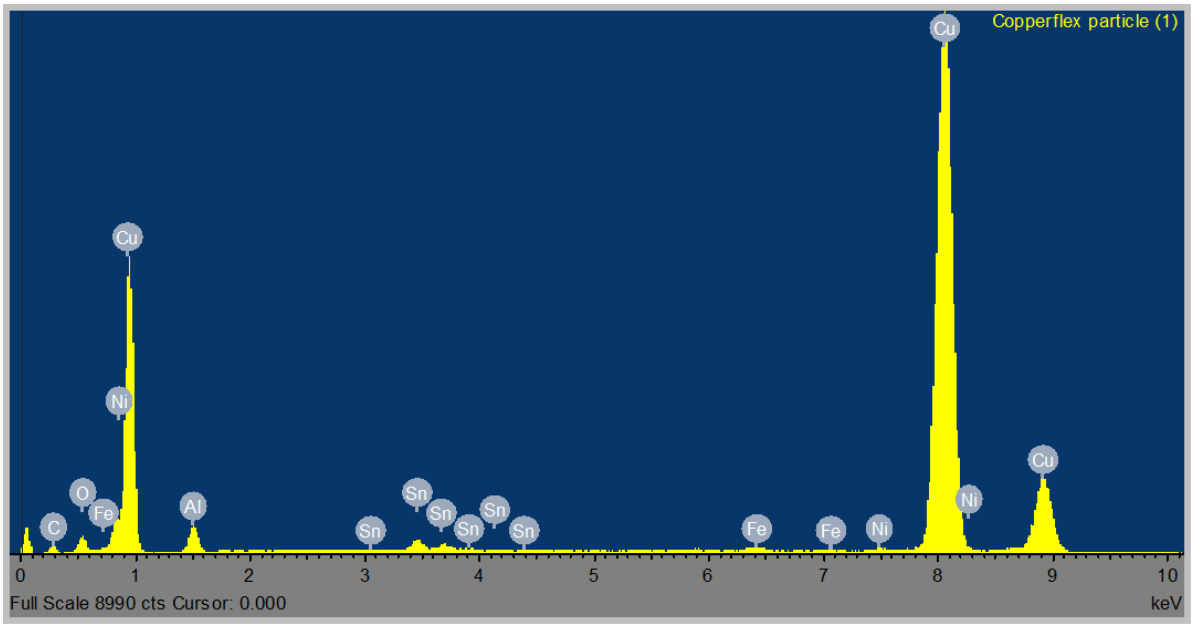

3D print - Cu/Zn particle 3
Cu
Zn
Cu
Zn
Cu
Zn
0
1
2
3
4
5
6
7
8
9
10
Full Scale 805 cts Cursor: -0.100 (0 cts)
keV

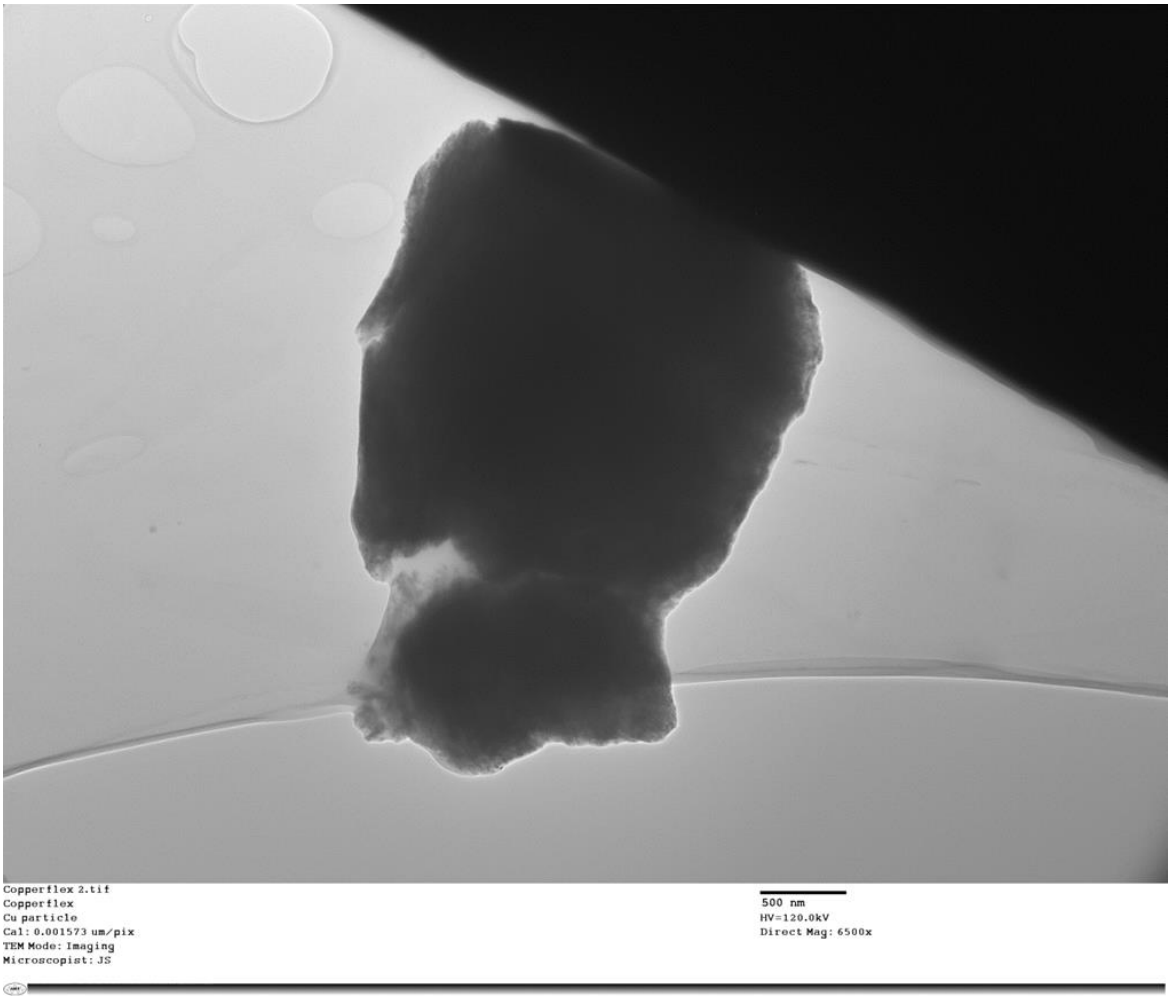

3D print Fe particle.tif
3D print
Fe particle
Cal: 0.248262 nm/pix
TEM Mode: Imaging
Microscopist: JS
100 nm
HV=120.0kV
Direct Mag: 42000x

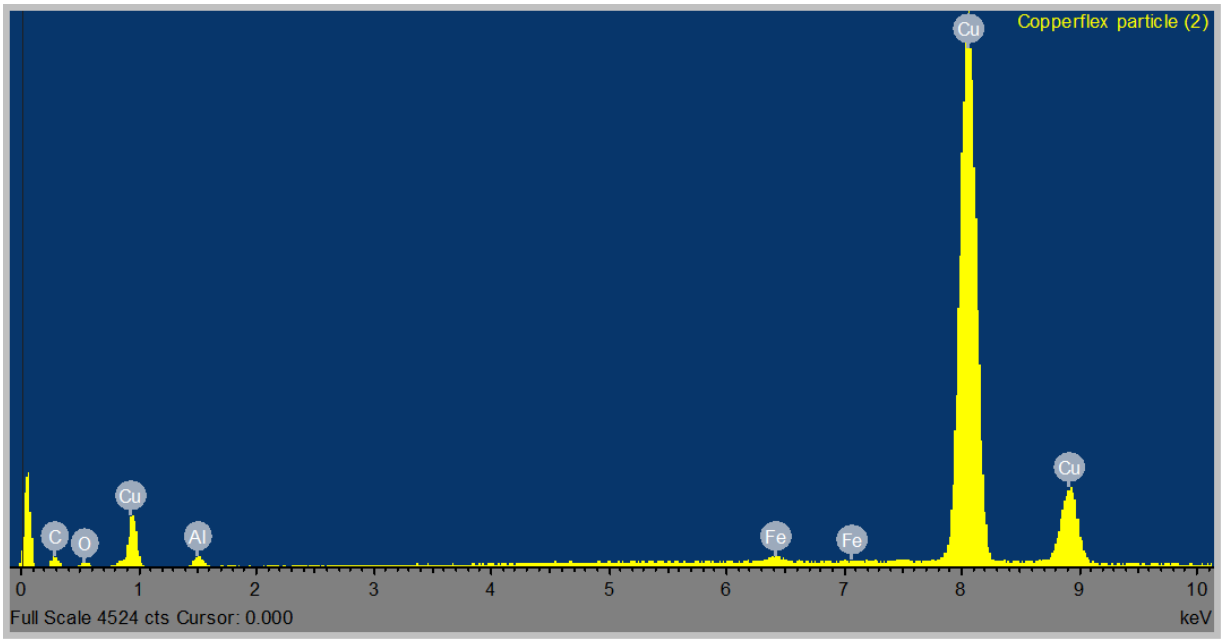

3D print - Fe particle
Fe
Cu
O
Fe
C
Cu
Fe
Cu
0
1
2
3
4
5
6
7
8
9
10
Full Scale 205 cts Cursor: -0.100 (0 cts)
keV

B.2 COPPER FLEX FILAMENT

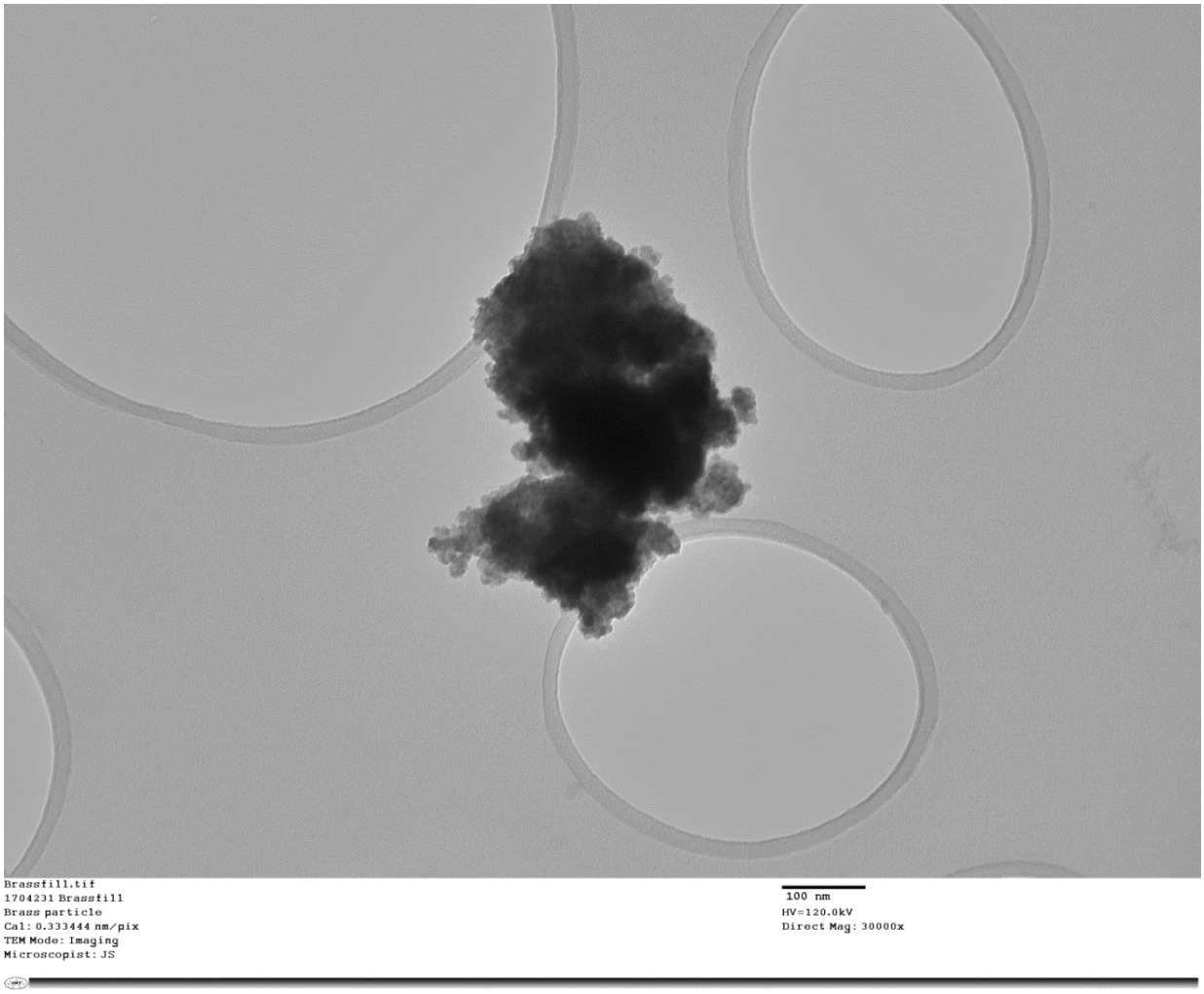


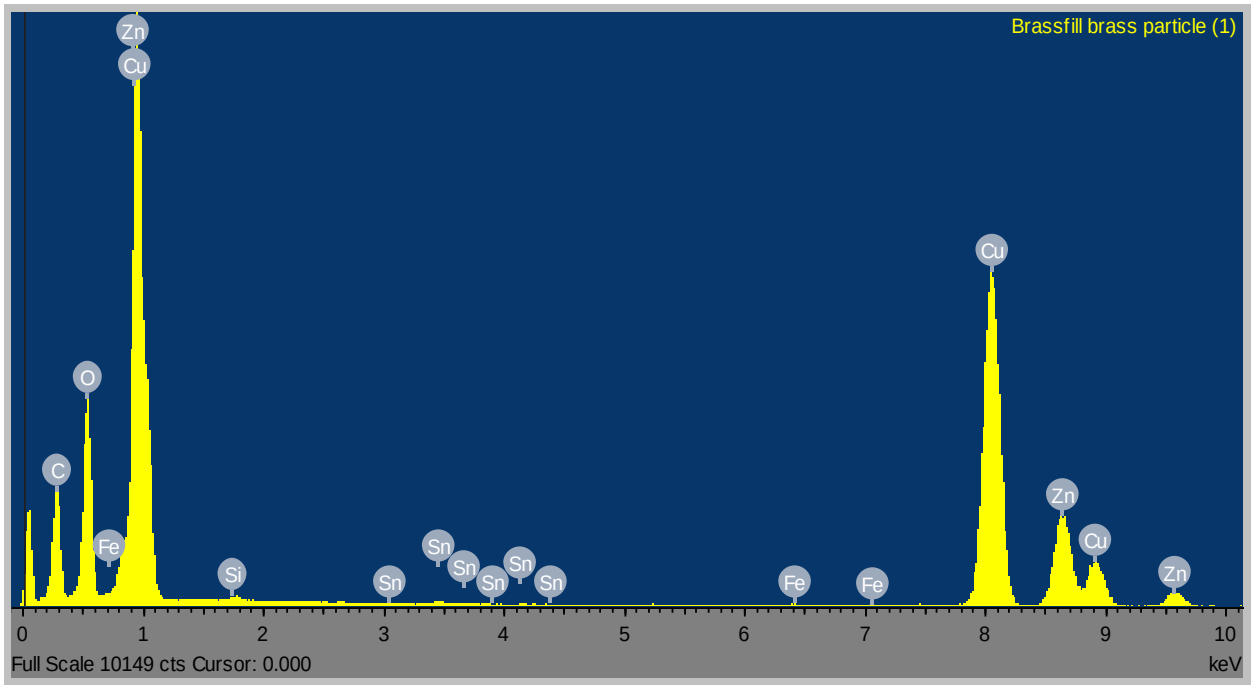


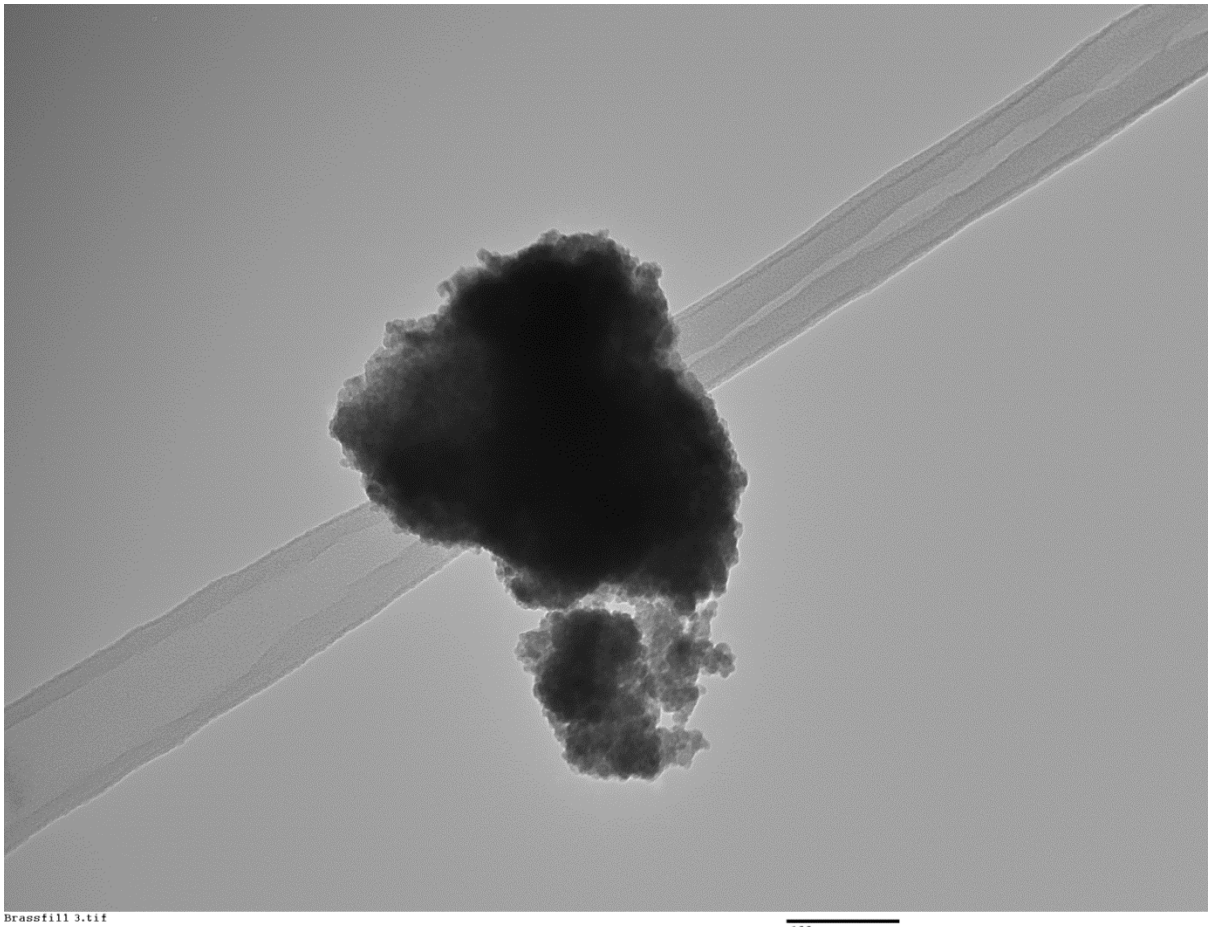

Copperflex 2.tif
Copperflex
Cu particle
Cal: 0.001573 um/pix
TEM Mode: Imaging
Microscopist: JS
500 nm
HV=120.0kV
Direct Mag: 6500x

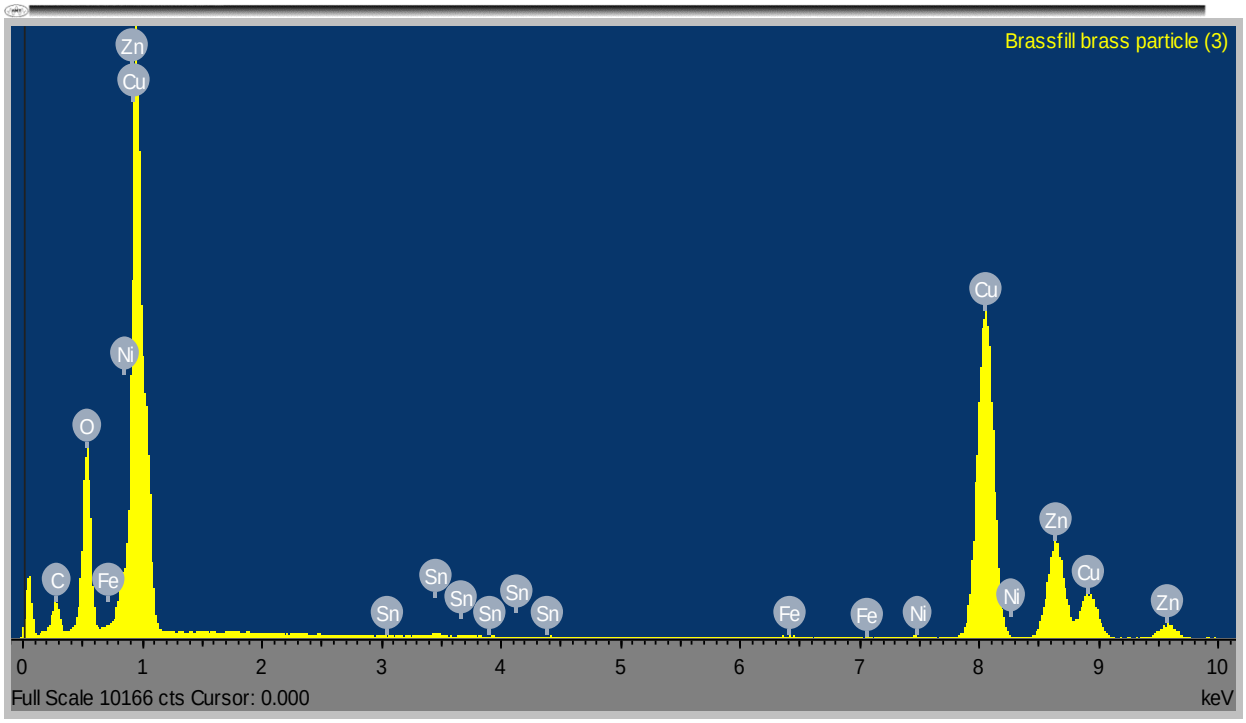

Copperflex particle (2)
Cu
C
O
Cu
Al
Fe
Fe
Cu
0
1
2
3
4
5
6
7
8
9
10
Full Scale 4524 cts Cursor: 0.000
keV

B.3 BRASSFILL FILAMENT

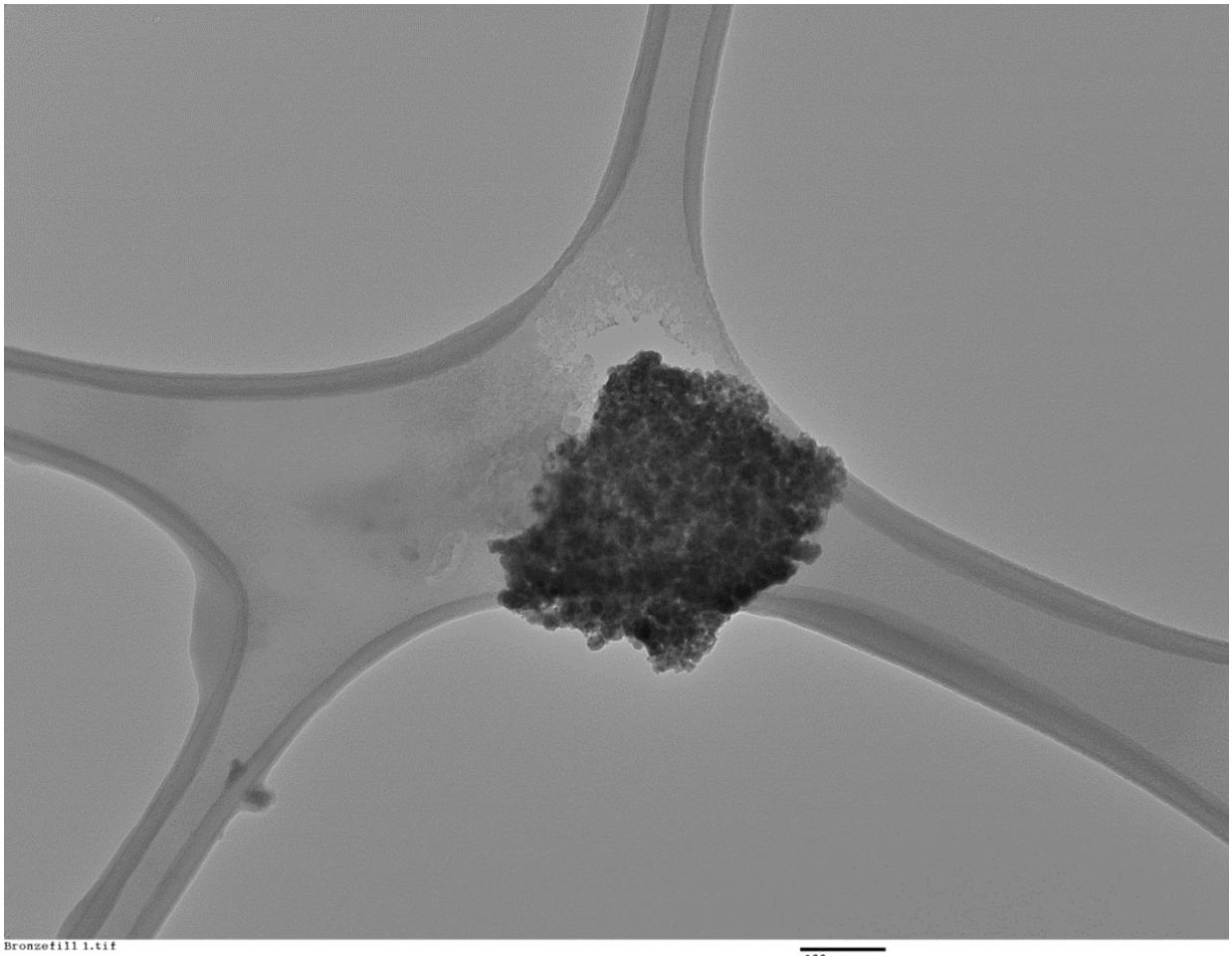


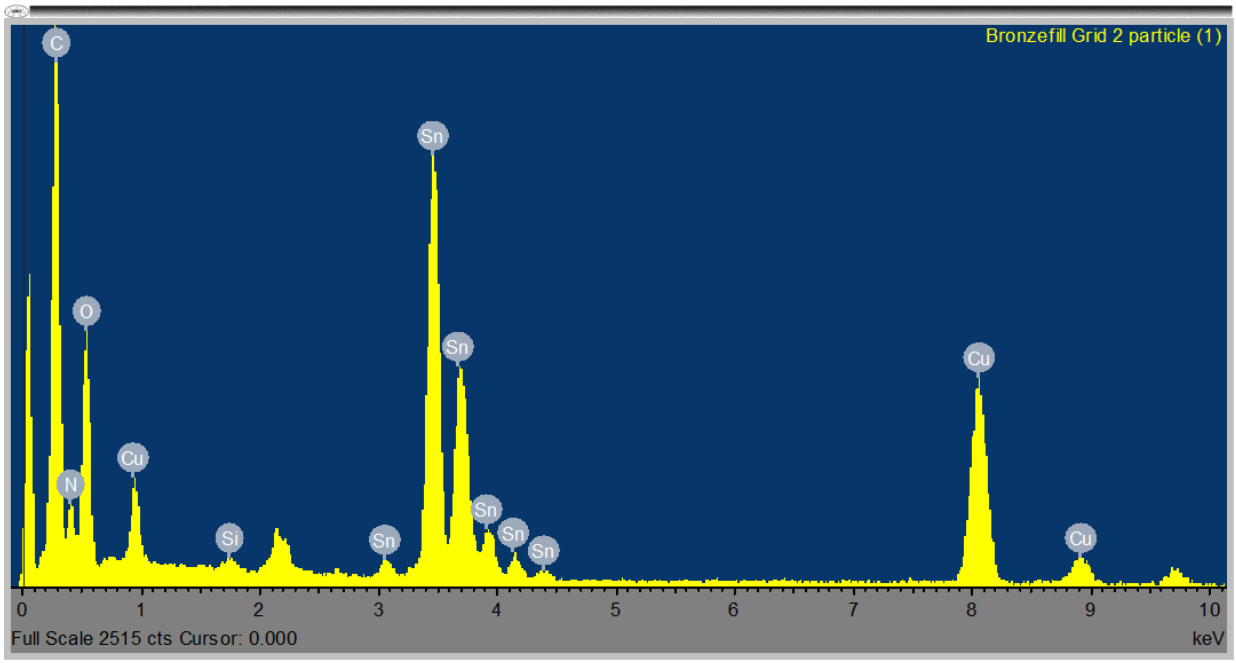


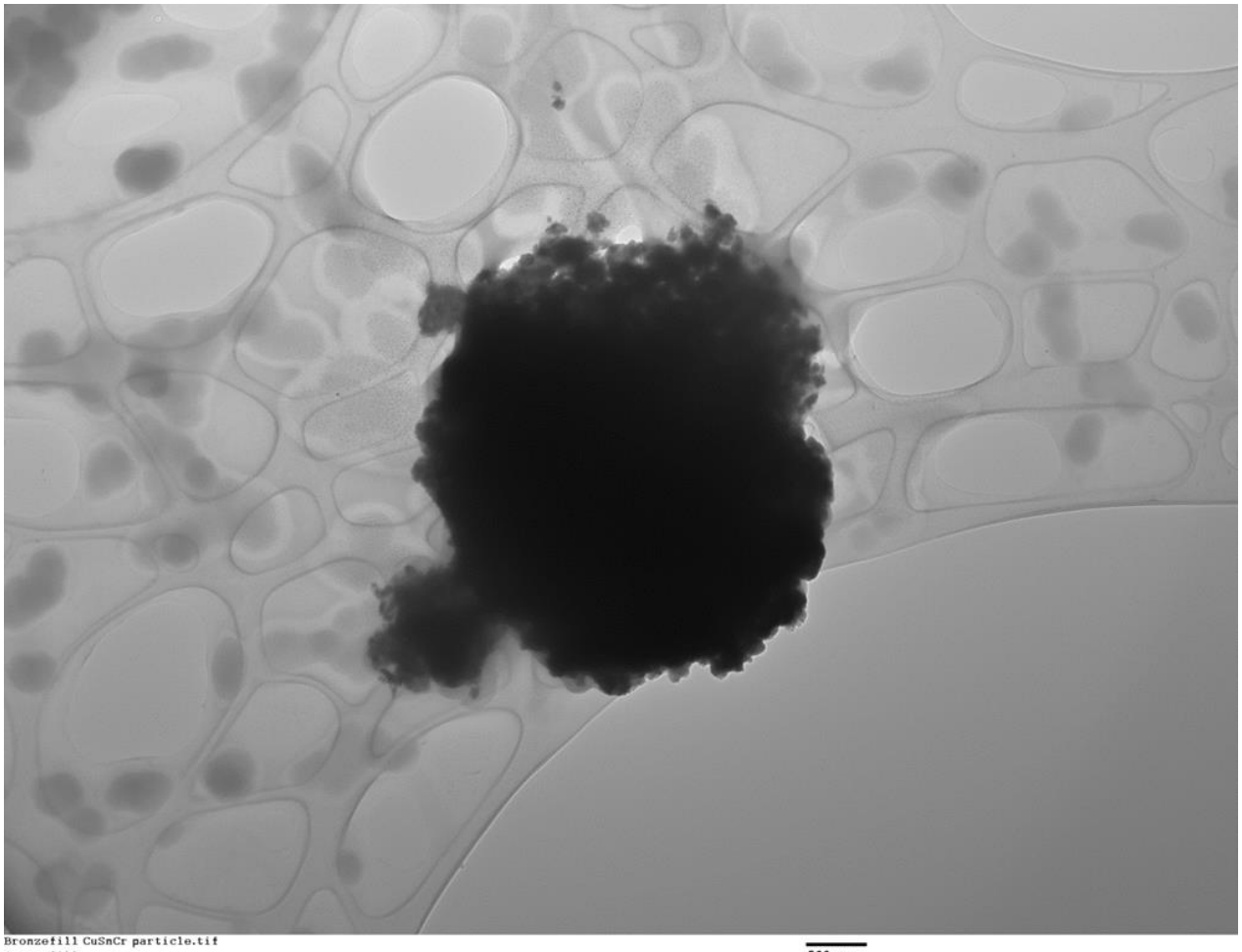

Brassfill 3.tif
1704231 Brassfill
Brass particle 3
Cal: 0.248262 nm/pix
TEM Mode: Imaging
Microscopist: JS
100 nm
HV=120.0kV
Direct Mag: 42000x


Brassfill brass particle (3)
Zn
Cu
Ni
O
C
Fe
Sn
Sn
Sn
Sn
Sn
Fe
Fe
Ni
Cu
Ni
Zn
Cu
Zn
0
1
2
3
4
5
6
7
8
9
10
Full Scale 10166 cts Cursor: 0.000
keV

B.4 BRONZEFILL FILAMENT



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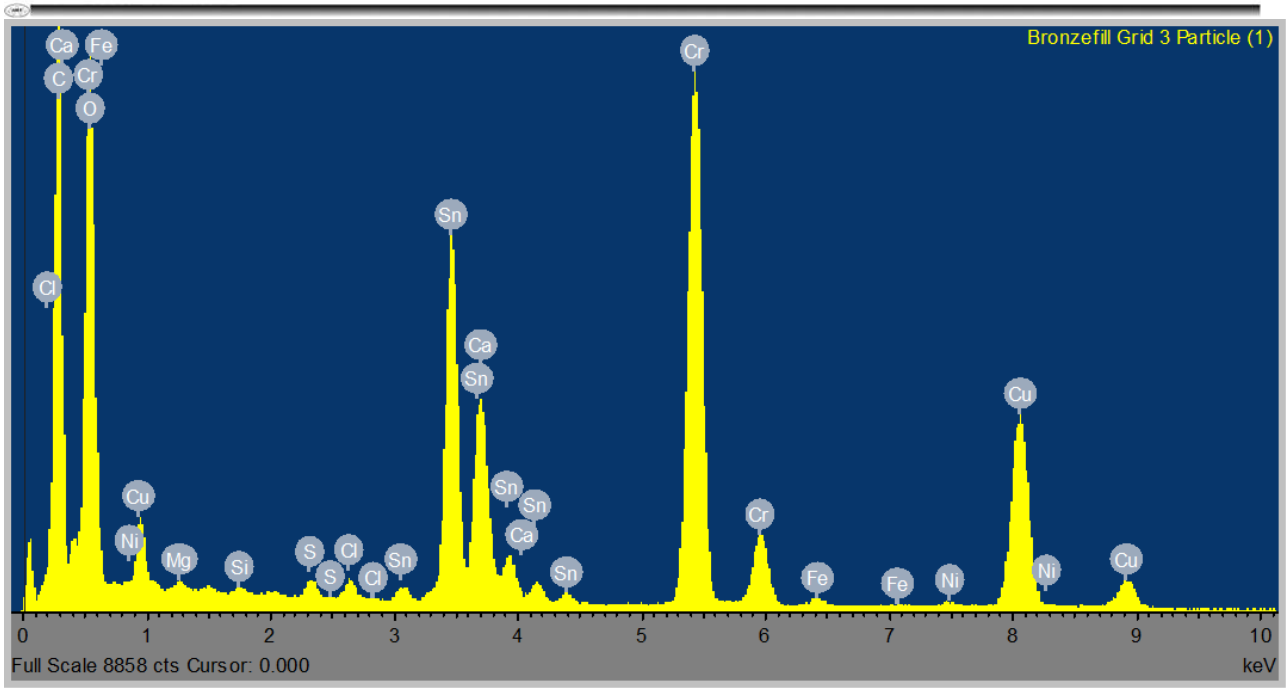
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Sn
Cr
Cr
Fe
Fe
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8
9
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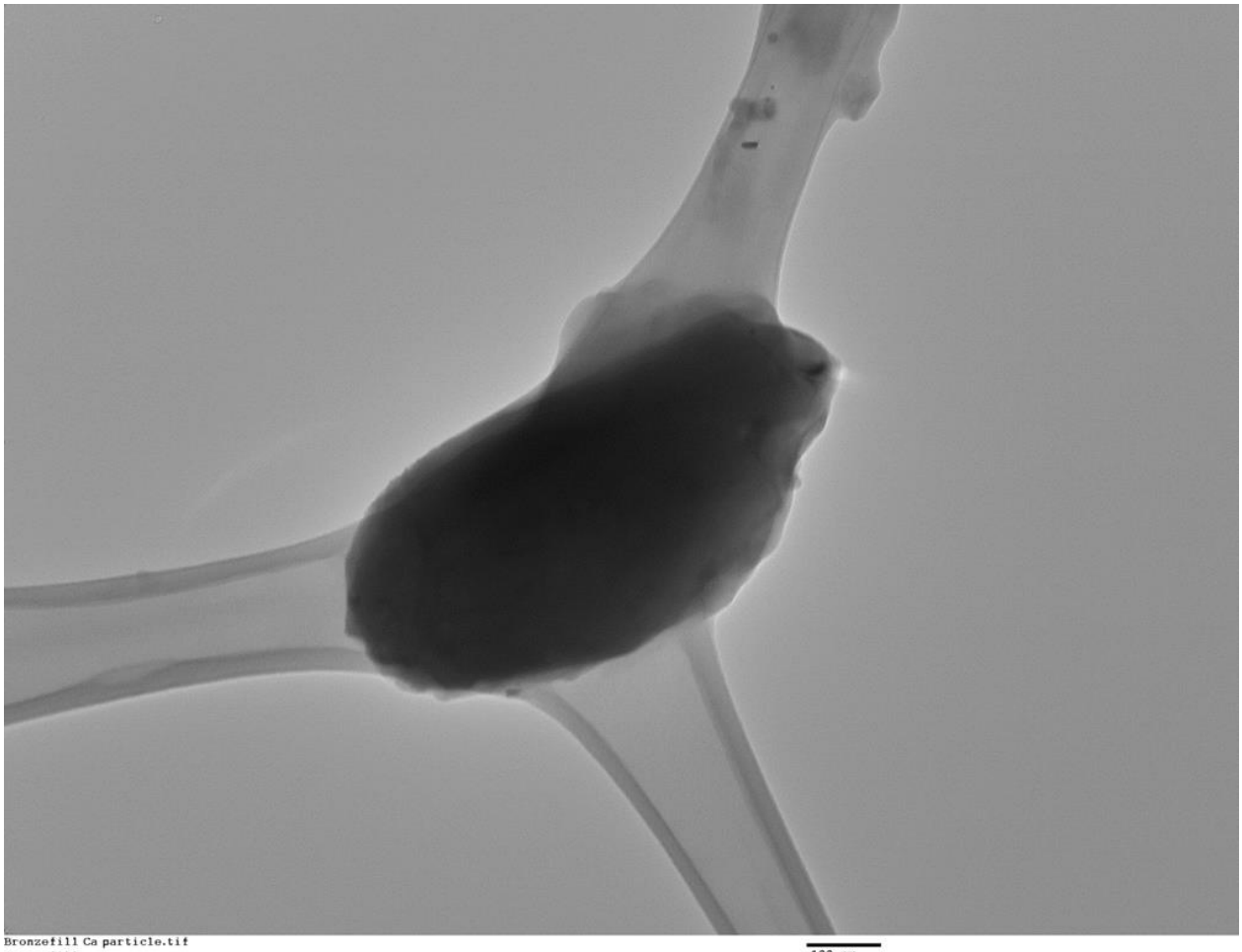
Full Scale 8858 cts Cursor: 0.000
keV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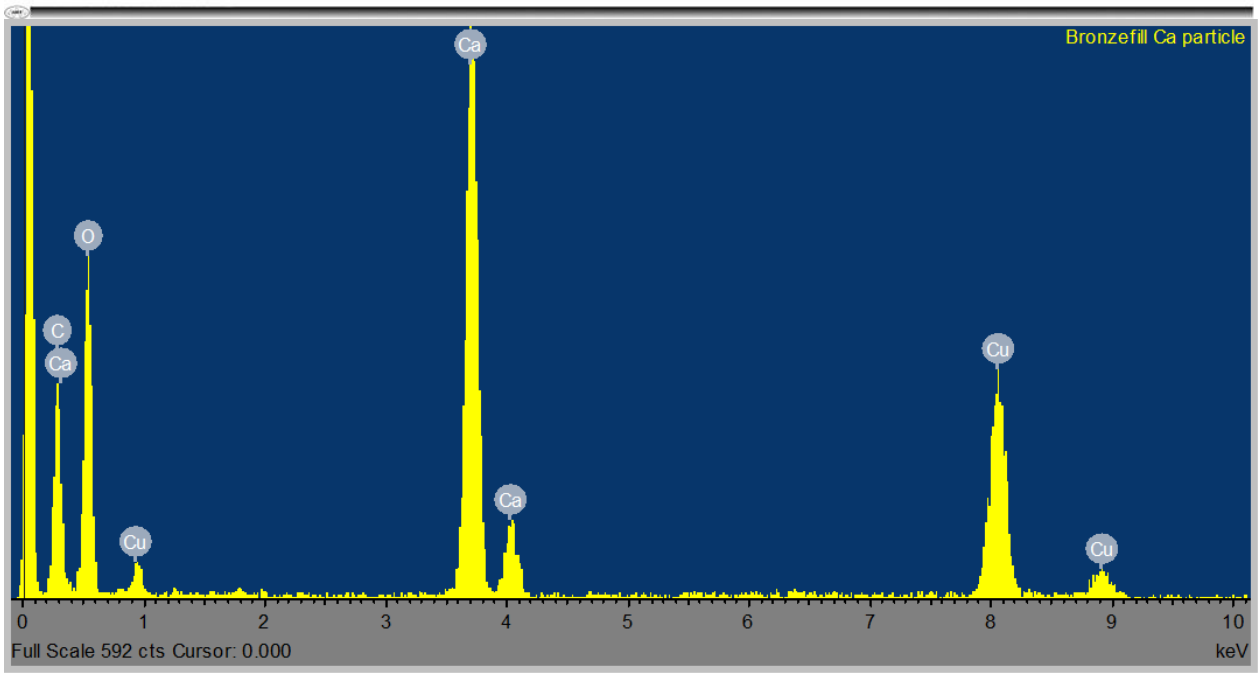
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Full Scale 592 cts Cursor: 0.000
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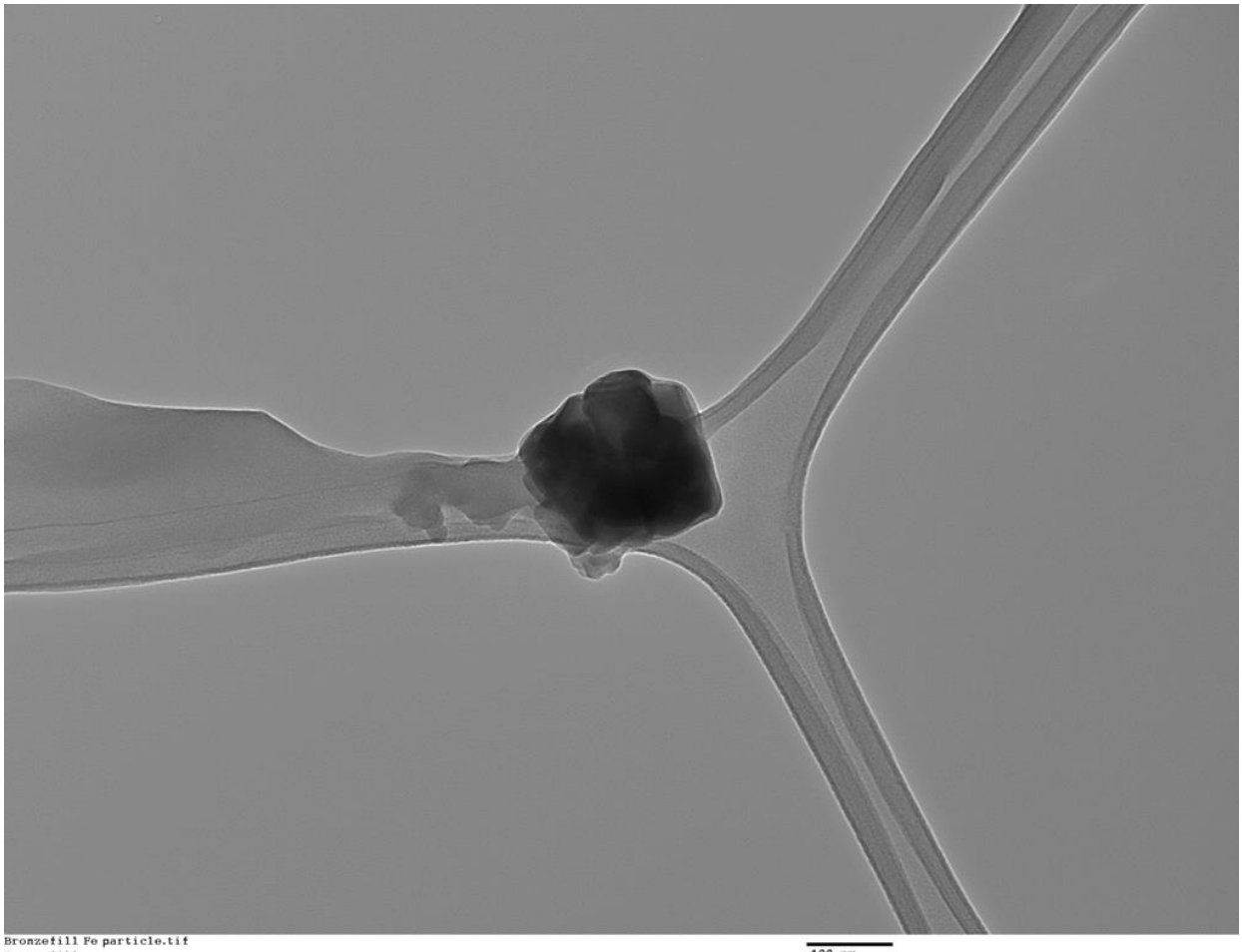
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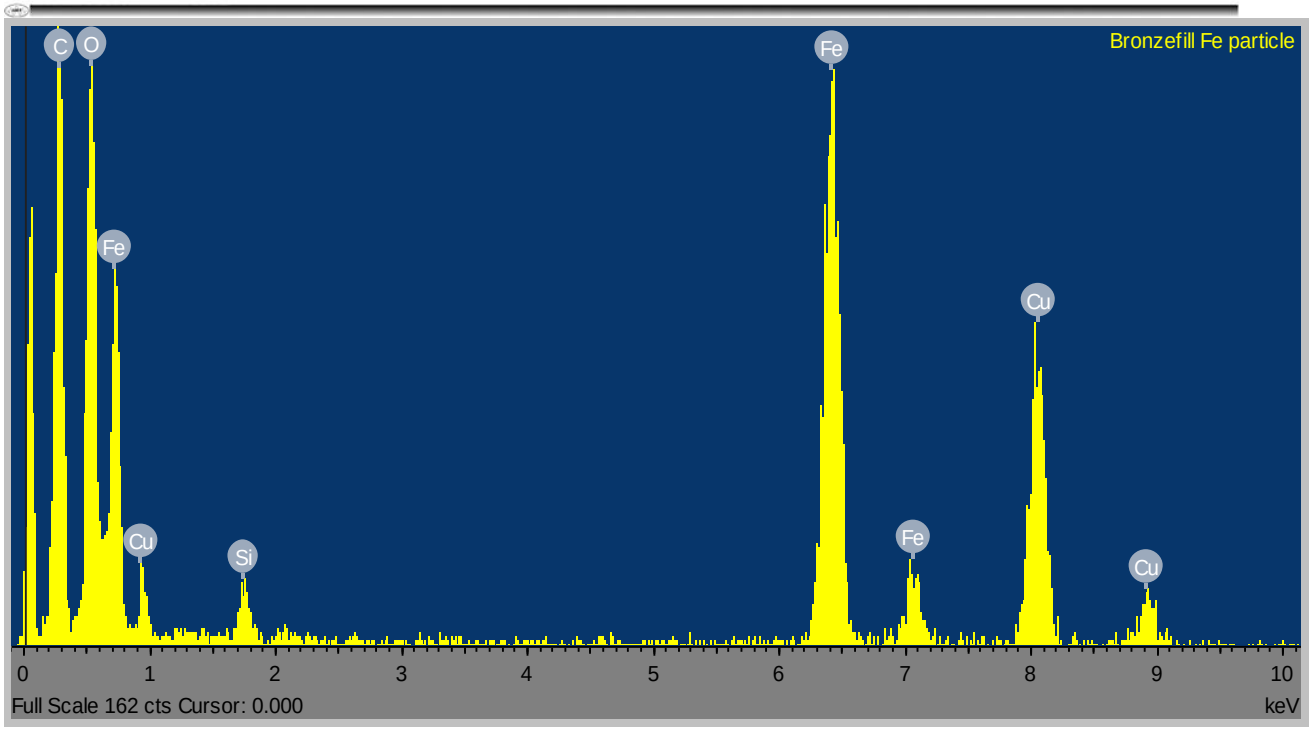
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10
Full Scale 162 cts Cursor: 0.000
keV

APPENDIX C PYROLYSIS RESULTS

NATURAL POLYLACTIC ACID (NAT-PLA-1.75 mm)

Tube (mg)	104.252
Tube + Sample (mg)	104.545
Tube After 250°C Test (mg)	104.551
Tube After 300°C Test (mg)	104.529

Mass of Sample (µg)	293	
Sample Loss at 250°C (µg/%)	-6	-2.05%
Sample Loss at 300°C (µg/%)	22	7.51%
Total Sample Loss (µg/%)	16	5.46%

COMPOUNDS	RT (min)	TEST AT 250°C (150°C) PLA-008s.D		TEST AT 300°C (200°C) PLA-009s.D		TOTAL COMBINED		TOTAL CALCULATED MASS LOSS (mg/g)
		TIC PEAK AREA	PROPORTION	TIC PEAK AREA	PROPORTION	TIC PEAK AREA	PROPORTION	
Lactide (Isomer 1)	10.24	18700	2.6%	202500	15.5%	221200	10.9%	5.9
Lactide (Isomer 2)	10.81	245500	33.8%	887900	68.0%	1133400	55.8%	30.5
Aliphatic Hydrocarbon Oil	18 - 25	461200	63.6%	35300	2.7%	496500	24.4%	13.4
Other (mainly lactide oligomers)	-	0	0.00%	179700	13.8%	179700	8.8%	4.8
TOTAL		725400	100%	1305400	100%	2030800	100%	54.6

CLEAR WATER NINJAFLEX (NIN-FLX-CWA-1.75 mm)

Tube (mg)	104.260
Tube + Sample (mg)	104.575
Tube After 250°C Test (mg)	104.574
Tube After 300°C Test (mg)	104.509

Mass of Sample (µg)	315	
Sample Loss at 250°C (µg/%)	1	0.3%
Sample Loss at 300°C (µg/%)	65	20.6%
Total Sample Loss (µg/%)	66	21.0%

COMPOUNDS	RT (min)	TEST AT 250°C (150°C) NIN-003s.D		TEST AT 300°C (200°C) NIN-004s.D		TOTAL COMBINED		TOTAL CALCULATED MASS LOSS (mg/g)
		TIC PEAK AREA	PROPORTION	TIC PEAK AREA	PROPORTION	TIC PEAK AREA	PROPORTION	
Tetrahydrofuran	2.52	21000	3.2%	86000	0.9%	107000	1.0%	2
Butanediol	7.20	25000	3.8%	775000	7.9%	800000	7.7%	16
Diisopropenylbenzene	12.42	5000	0.8%	45000	0.5%	50000	0.5%	1
Other Aromatic Isocyanates	14.9/17.0	28000	4.2%	79000	0.8%	107000	1.0%	2
C12 Cyclic Diester	16.11	41000	6.2%	18000	0.2%	59000	0.6%	1
Aliphatics (cyclic/unsaturated)	18.5/24.2/31.0	155000	23.4%	133000	1.4%	288000	2.8%	6
MDI (mainly 4,4-)	21.3/21.9	386000	58.4%	8648000	88.4%	9034000	86.5%	181
TOTAL		661000	100%	9784000	100%	10445000	100%	210

WHITE HIPS (SMS 1.75 mm)

Tube (mg)	104.250
Tube + Sample (mg)	104.673
Tube After 250°C Test (mg)	104.664
Tube After 300°C Test (mg)	104.668

Mass of Sample (µg)	423	
Sample Loss at 250°C (µg/%)	9	2.13%
Sample Loss at 300°C (µg/%)	-4	-0.95%
Total Sample Loss (µg/%)	5	1.18%

COMPOUNDS	RT (min)	TEST AT 250°C (150°C) HIP-002s.D		TEST AT 300°C (200°C) HIP-003s.D		TOTAL COMBINED		TOTAL CALCULATED MASS LOSS (mg/g)
		TIC PEAK AREA	PROPORTION	TIC PEAK AREA	PROPORTION	TIC PEAK AREA	PROPORTION	
Ethylbenzene	5.75	8200	0.8%	0	0.0%	8200	0.5%	<0.1
Styrene	6.26	42300	4.3%	22700	3.3%	65000	3.9%	0.5
Cyanonaphthalenes	15.58/15.90	4500	0.5%	0	0.0%	4500	0.3%	<0.1
Diphenylpropane	17.33	2900	0.3%	2600	0.4%	5500	0.3%	<0.1
Styrene Dimers	17.8 - 18.8	124100	12.6%	3300	0.5%	127400	7.6%	0.9
Phenanthrene	18.96	19000	1.9%	0	0.0%	19000	1.1%	0.1
Phenylnaphthalenes	19.70/20.87	12700	1.3%	0	0.0%	12700	0.8%	<0.1
Styrene Trimer	24.98	139100	14.2%	110400	15.9%	249500	14.9%	1.8
Styrene Oligomers	25.8 - 26.3	524600	53.4%	493500	71.2%	1018100	60.8%	7.2
Other (mainly aromatic)	-	104900	10.7%	60200	8.7%	165100	9.9%	1.2
TOTAL		982300	100%	692700	100%	1675000	100%	11.8

NATURAL ABS (ABS-NAT-1.75 mm)

Tube (mg)	104.251
Tube + Sample (mg)	104.592
Tube After 250°C Test (mg)	104.579
Tube After 300°C Test (mg)	104.572

Mass of Sample (µg)	341	
Sample Loss at 250°C (µg/%)	13	3.8%
Sample Loss at 300°C (µg/%)	7	2.1%
Total Sample Loss (µg/%)	20	5.9%

COMPOUNDS	RT (min)	TEST AT 250°C (150°C) ABS-006s.D		TEST AT 300°C (200°C) ABS-007s.D		TOTAL COMBINED		TOTAL CALCULATED MASS LOSS (mg/g)
		TIC PEAK AREA	PROPORTION	TIC PEAK AREA	PROPORTION	TIC PEAK AREA	PROPORTION	
Butadiene Dimer	5.27	3300	0.2%	3500	0.5%	6800	0.3%	<1
Ethylbenzene + Xylene	5.75 - 5.85	11300	0.6%	0	0.0%	11300	0.4%	<1
Styrene	6.26	168700	8.4%	8000	1.2%	176700	6.6%	4
Styrene Oligomers	14.5 - 18.5	48000	2.4%	0	0.0%	48000	1.8%	1
Styrene-Nitrile Oligomers	20.6 - 21.2	995300	49.7%	322900	47.8%	1318200	49.2%	29
Styrene-Nitrile Oligomers	21.5 - 22.0	236000	11.8%	112100	16.6%	348100	13.0%	8
Aromatic Compounds	23.2 - 23.7	371500	18.5%	120600	17.8%	492100	18.4%	11
Aromatic Compounds	24.0 - 24.6	52100	2.6%	25400	3.8%	77500	2.9%	2
Other (mainly aromatic)	-	117600	5.9%	83700	12.4%	201300	7.5%	4
TOTAL		2003800	100%	676200	100%	2680000	100%	59

FLUORESCENT YELLOW ABS (ABS-FLYEL-1.75 mm)

Tube (mg)	103.833
Tube + Sample (mg)	104.247
Tube After 250°C Test (mg)	104.216
Tube After 300°C Test (mg)	104.205

Mass of Sample (µg)	414	
Sample Loss at 250°C (µg/%)	31	7.5%
Sample Loss at 300°C (µg/%)	11	2.7%
Total Sample Loss (µg/%)	42	10.1%

COMPOUNDS	RT (min)	TEST AT 250°C (150°C) ABS-009s.D		TEST AT 300°C (200°C) ABS-010s.D		TOTAL COMBINED		TOTAL CALCULATED MASS LOSS (mg/g)
		TIC PEAK AREA	PROPORTION	TIC PEAK AREA	PROPORTION	TIC PEAK AREA	PROPORTION	
Butadiene Dimer	5.27	1300	0.2%	0	0.0%	1300	0.1%	<1
Ethylbenzene + Xylene	5.75 - 5.85	7000	1.1%	0	0.0%	7000	0.7%	<1
Styrene	6.26	122000	19.5%	2000	0.5%	124000	12.0%	12
Styrene Oligomers	14.5 - 18.5	21700	3.5%	0	0.0%	21700	2.1%	2
Styrene-Nitrile Oligomers	20.6 - 21.2	276600	44.2%	220300	53.6%	496900	48.0%	49
Styrene-Nitrile Oligomers	21.5 - 22.0	48500	7.8%	65700	16.0%	114200	11.0%	11
Aromatic Compounds	23.2 - 23.7	98600	15.8%	82100	20.0%	180700	17.4%	18
Aromatic Compounds	24.0 - 24.6	10500	1.7%	14800	3.6%	25300	2.4%	2
Other (mainly aromatic)	-	38900	6.2%	25800	6.3%	64700	6.2%	6
TOTAL		625100	100%	410700	100%	1035800	100%	101

WHITE NYLON (NYL-WHI-1.75 mm)

Tube (mg)	103.635
Tube + Sample (mg)	103.876
Tube After 250°C Test (mg)	103.860
Tube After 300°C Test (mg)	103.839

Mass of Sample (µg)	241	
Sample Loss at 250°C (µg/%)	16	6.6%
Sample Loss at 300°C (µg/%)	21	8.7%
Total Sample Loss (µg/%)	37	15.4%

COMPOUNDS	RT (min)	TEST AT 250°C (150°C) NYL-009s.D		TEST AT 300°C (200°C) NYL-010s.D		TOTAL COMBINED		TOTAL CALCULATED MASS LOSS (mg/g)
		TIC PEAK AREA	PROPORTION	TIC PEAK AREA	PROPORTION	TIC PEAK AREA	PROPORTION	
Caprolactam	2.52	34500	94.3%	47300	81.0%	81800	86.1%	132
Caprolactam Dimer	7.20	2100	5.7%	11100	19.0%	13200	13.9%	21
TOTAL		36600	100%	58400	100%	95000	100%	154

NYLON - TAULMAN 645 (NYL-645-1.75 mm)

Tube (mg)	104.027		Mass of Sample (µg)	164
Tube + Sample (mg)	104.191		Sample Loss at 250°C (µg/%)	29	17.7%
Tube After 250°C Test (mg)	104.162		Sample Loss at 300°C (µg/%)	25	15.2%
Tube After 300°C Test (mg)	104.137		Total Sample Loss (µg/%)	54	32.9%

COMPOUNDS	RT (min)	TEST AT 250°C (150°C) NYL-007s.D		TEST AT 300°C (200°C) NYL-008s.D		TOTAL COMBINED		TOTAL CALCULATED MASS LOSS (mg/g)
		TIC PEAK AREA	PROPORTION	TIC PEAK AREA	PROPORTION	TIC PEAK AREA	PROPORTION	
Caprolactam	2.52	1386000	99.7%	5400	19.5%	1391400	98.1%	323
Caprolactam Dimer	7.20	4100	0.3%	22300	80.5%	26400	1.9%	6
TOTAL		1390100	100%	27700	100%	1417800	100%	329

NYLON - TAULMAN 618 (NYL-TAU-1.75 mm)

Tube (mg)	103.873
Tube + Sample (mg)	104.072
Tube After 250°C Test (mg)	103.993
Tube After 300°C Test (mg)	103.967

Mass of Sample (µg)	199	
Sample Loss at 250°C (µg/%)	79	39.7%
Sample Loss at 300°C (µg/%)	26	13.1%
Total Sample Loss (µg/%)	105	52.8%

COMPOUNDS	RT (min)	TEST AT 250°C (150°C) NYL-011s.D		TEST AT 300°C (200°C) NYL-128s.D		TOTAL COMBINED		TOTAL CALCULATED MASS LOSS (mg/g)
		TIC PEAK AREA	PROPORTION	TIC PEAK AREA	PROPORTION	TIC PEAK AREA	PROPORTION	
Caprolactam	2.52	2364600	99.7%	25500	46.7%	2390100	98.5%	520
Caprolactam Dimer	7.20	7300	0.3%	29100	53.3%	36400	1.5%	8
TOTAL		2371900	100%	54600	100%	2426500	100%	528

BRONZE FILL by COLORFAB (1.75 mm)

Tube (mg)	104.907
Tube + Sample (mg)	105.629
Tube After 250°C Test (mg)	105.569
Tube After 300°C Test (mg)	105.454

Mass of Sample (µg)	722	
Sample Loss at 250°C (µg/%)	60	8.3%
Sample Loss at 300°C (µg/%)	115	15.9%
Total Sample Loss (µg/%)	175	24.2%

COMPOUNDS	RT (min)	TEST AT 250°C (150°C) BZF-001s.D		TEST AT 300°C (200°C) BZF-002s.D		TOTAL COMBINED		TOTAL CALCULATED MASS LOSS (mg/g)
		TIC PEAK AREA	PROPORTION	TIC PEAK AREA	PROPORTION	TIC PEAK AREA	PROPORTION	
Crotonic Acid	5.70	1300	8.1%	582900	20.9%	584200	20.8%	50
Lactide (Isomer 1)	10.24	700	4.3%	211500	7.6%	212200	7.6%	18
Lactide (Isomer 2)	10.81	15400	95.7%	1664300	59.7%	1679700	59.9%	145
Acrylic/Crotonic Esters	12.3 - 13.5	0	0.0%	149800	5.4%	149800	5.3%	13
Unknown (aliphatic)	20.08	0	0.0%	74400	2.7%	74400	2.7%	6
Other	-	0	0.0%	107200	3.8%	107200	3.8%	9
TOTAL		16100	100%	2790100	100%	2806200	100%	242

BRASS FILL by COLORFAB (1.75 mm)

Tube (mg)	105.387
Tube + Sample (mg)	105.877
Tube After 250°C Test (mg)	105.793
Tube After 300°C Test (mg)	105.684

Mass of Sample (µg)	490	
Sample Loss at 250°C (µg/%)	84	17.1%
Sample Loss at 300°C (µg/%)	109	22.2%
Total Sample Loss (µg/%)	193	39.4%

COMPOUNDS	RT (min)	TEST AT 250°C (150°C) BSF-001s.D		TEST AT 300°C (200°C) BSF-002s.D		TOTAL COMBINED		TOTAL CALCULATED MASS LOSS (mg/g)
		TIC PEAK AREA	PROPORTION	TIC PEAK AREA	PROPORTION	TIC PEAK AREA	PROPORTION	
Crotonic Acid	5.70	1300	8.1%	582900	20.9%	584200	20.8%	82
Lactide (Isomer 1)	10.24	700	4.3%	211500	7.6%	212200	7.6%	30
Lactide (Isomer 2)	10.81	15400	95.7%	1664300	59.7%	1679700	59.9%	236
Acrylic/Crotonic Esters	12.3 - 13.5	0	0.0%	149800	5.4%	149800	5.3%	21
Unknown (aliphatic)	20.08	0	0.0%	74400	2.7%	74400	2.7%	10
Other	-	0	0.0%	107200	3.8%	107200	3.8%	15
TOTAL		16100	100%	2790100	100%	2806200	100%	394

COPPER FLEX by REPRAPPER TECH (1.75 mm)

Tube (mg)	104.441
Tube + Sample (mg)	104.807
Tube After 250°C Test (mg)	105.793
Tube After 300°C Test (mg)	105.454

Mass of Sample (µg)	366	
Sample Loss at 250°C (µg/%)	-986	-269.4%
Sample Loss at 300°C (µg/%)	339	92.6%
Total Sample Loss (µg/%)	-647	-176.8%

COMPOUNDS	RT (min)	TEST AT 250°C (150°C) BSF-001s.D		TEST AT 300°C (200°C) BSF-002s.D		TOTAL COMBINED		TOTAL CALCULATED MASS LOSS (mg/g)
		TIC PEAK AREA	PROPORTION	TIC PEAK AREA	PROPORTION	TIC PEAK AREA	PROPORTION	
Crotonic Acid	5.70	1300	8.1%	582900	20.9%	584200	20.8%	<0.1
Lactide (Isomer 1)	10.24	700	4.3%	211500	7.6%	212200	7.6%	<0.1
Lactide (Isomer 2)	10.81	15400	95.7%	1664300	59.7%	1679700	59.9%	<0.1
Acrylic/Crotonic Esters	12.3 - 13.5	0	0.0%	149800	5.4%	149800	5.3%	<0.1
Unknown (aliphatic)	20.08	0	0.0%	74400	2.7%	74400	2.7%	<0.1
Other	-	0	0.0%	107200	3.8%	107200	3.8%	<0.1
TOTAL		16100	100%	2790100	100%	2806200	100%	<1

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HSE
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Measuring and controlling emissions from polymer filament desktop 3D printers

Affordable desktop 3D printers are being widely used in businesses, schools and colleges. Some of these printers use filaments to deposit polymer through a heated nozzle to build three dimensional objects. This type of desktop printer is generally unenclosed and some published studies have raised concerns that they may release potentially harmful fumes and particles. The scientific evidence base on exposures and potential health endpoints is being developed internationally.

This report describes initial research in a laboratory setting to a) measure emissions of particulates and volatile organic compounds from desktop 3D printers and b) investigate the effectiveness of control measures to reduce these printer emissions. Two common filament materials were investigated: polylactic acid (PLA) which is generally used in schools, and acrylonitrile butadiene styrene (ABS).

The research found that the heated filaments emitted large numbers of very small particles and volatile organic chemicals which could be breathed in. However, more research is required to establish if under real use conditions these printers release sufficient concentration of emissions to cause harm. The research identified that exposures are significantly reduced by: (1) setting a lower printer nozzle temperature; (2) using a filament with a lower emission rate; (3) placing the printer in a clear enclosing hood fitted with an extraction fan and particulate filter and (4) maintaining a hood 'clearance time' of about 20 minutes.

These findings have informed the development of a new good practice guide for schools published by CLEAPSS in 2019. This guide provides advice about precautionary measures for safe use of desktop 3D printers and measures to minimise health risks for students and school employees.

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