JOINT CANADA-UNITED STATES
NATIONAL STANDARD

ANSI/CAN/UL 2904

STANDARD FOR SAFETY

Standard Method for Testing and Assessing Particle and Chemical Emissions from 3D Printers

Approved American National Standard
ANSI
ANSI/UL 2904-2019

Standards Council of Canada
Conseil canadien des normes

SCC FOREWORD

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UL Standard for Safety for Standard Method for Testing and Assessing Particle and Chemical Emissions from 3D Printers, ANSI/CAN/UL 2904

First Edition, Dated January 31, 2019

Summary of Topics

The First Edition of ANSI/CAN/UL 2904 has been issued to reflect the latest ANSI and SCC approval dates, and to incorporate the proposals dated August 31, 2018 and December 7, 2018.

The new requirements are substantially in accordance with Proposal(s) on this subject dated August 31, 2018 and December 7, 2018.

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JANUARY 31, 2019

ANSI/UL 2904-2019

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ANSI/CAN/UL 2904

Standard Method for Testing and Assessing Particle and Chemical Emissions from 3D Printers

First Edition

January 31, 2019

This ANSI/CAN/UL Safety Standard consists of the First Edition.

The most recent designation of ANSI/UL 2904 as an American National Standard (ANSI) occurred on January 31, 2019. ANSI approval for a standard does not include the Cover Page, Transmittal Pages, Title Page, Preface or SCC Foreword.

This standard has been designated as a National Standard of Canada (NSC) on January 31, 2019.

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Preface

This is the First Edition of the ANSI/CAN/UL 2904, Standard Method for Testing and Assessing Particle and Chemical Emissions from 3D Printers.

UL is accredited by the American National Standards Institute (ANSI) and the Standards Council of Canada (SCC) as a Standards Development Organization (SDO).

This Standard has been developed in compliance with the requirements of ANSI and SCC for accreditation of a Standards Development Organization.

This ANSI/CAN/UL 2904 Standard is under continuous maintenance, whereby each revision is approved in compliance with the requirements of ANSI and SCC for accreditation of a Standards Development Organization. In the event that no revisions are issued for a period of four years from the date of publication, action to revise, reaffirm, or withdraw the standard shall be initiated.

In Canada, there are two official languages, English and French. All safety warnings must be in French and English. Attention is drawn to the possibility that some Canadian authorities may require additional markings and/or installation instructions to be in both official languages.

Comments or proposals for revisions on any part of the Standard may be submitted to UL at any time. Proposals should be submitted via a Proposal Request in UL's On-Line Collaborative Standards Development System (CSDS) at http://csds.ul.com.

To purchase UL Standards, visit the UL Standards Sales Site at http://www. shopulstandards. com/ HowToOrder.aspx or call tollfree 1-888-853-3503.

This Edition of the Standard has been formally approved by the UL Standards Technical Panel (STP) on Chemical and Particle Emissions from 3D Printers, STP 2904.

This list represents the STP 2904 membership when the final text in this standard was balloted. Since that time, changes in the membership may have occurred.

STP 2904 Membership

Name	Representing	Interest Category	Region
Parham Azimi	Illinois Institute of Technology	General	USA
Christine Banks	Texas Campaign for the Environment	Consumer	USA
Marilyn S. Black	Underwriters Laboratories Inc.	Testing & Stds Org	USA
Becky Brooks	Natureworks LLC	Supply Chain	USA
Valerie Brown	Valerie Brown Writer	General	USA
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This Standard is intended to be used for conformity assessment.

The intended primary application of this standard is stated in its scope. It is important to note that it remains the responsibility of the user of the standard to judge its suitability for this particular application.

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INTRODUCTION

1 Scope

1.1 This standard presents methodologies for characterizing and quantifying coarse, fine, and ultrafine particles and volatile organic compound (VOC) emissions from operating three-dimensional (3D) printers under normal conditions of use in defined indoor environments including classroom, office, and residential scenarios.

1.2 This method primarily applies to the emissions of particles and volatile organic chemicals from 3D printers and feedstock which are widely used in classrooms, offices, libraries, residential settings, small and medium size enterprises, and other non-industrial indoor spaces. The 3D printers are operated with a variety of commercially available feedstock.

For environmental chamber tests under controlled conditions, a 3D printer's maximum size and format is limited.

For measurements, it is required that environmental chamber conditions are known and can be kept stable at least during the measurement.

1.3 The measurement protocols may be used to

a) compare emissions from different feedstock or adhesion materials operated by a specific 3D printer, (material impact)

b) compare emissions from printing objects of different shape, design, and size on a specific 3D printer (printed object impact)

c) compare emissions from different 3D printers operated under identical conditions i. e. same object, same feedstock (print media), same environmental conditions (3D printer hardware impact)

d) quantify emissions in a given specific exposure scenario – e.g. workshop, small production line, etc. (environmental impact)

e) obtain data for use in risk assessments or product claims

1.4 This method includes requirements on laboratory quality management systems and measurement uncertainty estimation.

1.5 This standard establishes emissions criteria for particles and certain chemicals based on existing standards, guidelines, and research data for the management of airborne gaseous and aerosol pollutants in indoor environments.

1.6 This standard may be utilized as the basis for product testing and for certification/verification programs.

1.7 This standard specifies the maximum allowable concentrations of target chemicals and particles. However, this standard does not purport to address all of the safety, health, comfort (e. g., odor) and performance concerns, if any associated with its use. Users of this standard may establish additional safety, health, comfort and other performance conditions, and determine the applicability of regulatory requirements prior to use.

1.8 This standard provides guidance for use of the measurement protocols as a basis for product claims or verifications.

2 Undated References

Any undated reference to a code or standard appearing in the requirements of this Standard shall be interpreted as referring to the latest edition of that code or standard.

3 Definitions

3.1 Accumulated Particle Number Concentration, $C_p(t)$ [cm^{-3}]

Time-dependent particle number concentration in a specified particle size range (at a minimum between 10 nm and 5 µm).

3.2 Aerosol

System of particles (solid and/or liquid) suspended in gas.

3.3 Aerosol Measurement Device

For the purposes of this test method, a device for determining the time-dependent particle number concentration of an aerosol within a defined particle size and concentration ranges and with a certain time resolution.

3.4 Air Exchange Rate (ACH), n [h^{-1}]

Ratio of the volume of clean air at room temperature (see 3.22) and pressure brought into the chamber per hour [$m^3\ h^{-1}$] to the unloaded chamber volume [m^3].

3.5 Air Flow Rate [$m^3\ h^{-1}$]

Air volume at room temperature and pressure entering the environmental chamber per unit time.

3.6 Air Velocity [$m\ s^{-1}$]

The air speed measured in the unloaded environmental testing chamber.

3.7 Aldehydes (ALD)

Aldehydes are low molecular weight organic compounds containing a functional group with the structure –CHO. The measured aldehydes are 2-butenal, acetaldehyde, benzaldehyde, 2,5-dimethylbenzaldehyde, 2-methylbenzaldehyde, 3 (and/or) 4-methylbenzaldehyde, butanal, 3-methylbutanal, formaldehyde, hexanal, pentanal, and propanal, individually calibrated to a compound specific standard via High-Performance Liquid Chromatography (HPLC) analysis.

3.8 Average Gas Emission Rate, $ER_{g,i}$ [µg h^{-1}]

Average mass of the analyte *i* (VOC or aldehyde) emitted from a tested 3D printer per unit time.

3.9 Average Particle Emission Rate, ER_p [h^{-1}]

Average number of particles emitted from a tested 3D printer per unit print time, calculated from total number of emitted particles (*TP*) divided by the total print time in hours.

3.10 Blank Value/ Empty Chamber background

Background concentration of the measuring system (environmental chamber, sampling media, and analyzer) for individual substances, total volatile organic compounds (TVOC) and particles including coarse, fine, and ultrafine particles.

3.11 Chamber Loading

Placing a tested 3D printer into the environmental chamber.

3.12 Clean Air

Air supplied to the chamber that meets requirements in 8.2 Chamber Parameters.

3.13 Coarse Particles

Particles having an aerodynamic diameter greater than 2.5 μm and less than or equal to 10 μm.

3.14 Condensation Particle Counter, CPC

Instrument that measures the particle number concentration of an aerosol by condensational growth to optical detection sizes using a working fluid such as water or butanol. For the measurement of total particle number concentration, a CPC with butanol as a working fluid is suggested.

3.15 Environmental Chamber

An enclosed test environment consisting of a known volume with controlled environmental parameters used for the purpose of providing accurate and reproducible particle and chemical emission measurements from defined product sources.

3.16 Emission Time [h]

Time between when 3D printer starts extruding (t_{start}) and 3D printer is no longer emitting new particles or 3D printer stops extruding, whichever comes after (t_{stop}).

3.17 Emission Yield, EY_i [μg g^{-1}]

This quantity gives the mass of the analyte *i* (VOC or aldehyde) or the number of particles, which is emitted from a tested 3D printer per unit of mass of feedstock used.

3.18 Feedstock

3D printer media consumed to create a printed object, for example, filament and liquid resin.

3.19 Fine Particles, FP

Particles having an aerodynamic diameter smaller than 2.5 μm and greater than 0.1 μm.

3.20 Load Factor

Quotient of the volume of the tested 3D printer (see 8.2) and the volume of the empty environmental chamber.

3.21 Mass/Number Concentration

Mass/number of particles or mass of VOC per unit air volume at room temperature and pressure.

3.22 Normal Environment

Environmental conditions: 23 ±1°C, 50 ±5% relative humidity as per ISO 554. Conditioning environment is the same as normal environment.

3.23 Particles

Small discrete solid or liquid objects that can be chemically homogeneous or heterogeneous, and are suspended in air or gas with specified physical parameters.

3.24 Particle Emission Rate, *PER(t)* [s^{-1}]

Time-dependent system-specific rate during the printing phase and post-operating phase.

3.25 Particle Loss Coefficient, β [s^{-1}]

Coefficient for describing particle loss in the environmental chamber.

3.26 Particle Size/Particle Diameter

The physical dimension of a particle. The term particle size is often used as a synonym for particle diameter. The term particle diameter is also used to classify particles in particle size classes.

3.27 Particle Size Spectrometer based on Electrical Mobility

Instrument that measures the particle number concentration of an aerosol in various particle size ranges, where particle size is determined by particle electrical mobility.

3.28 Printing Phase

Examination of the 3D printer during printing phase following pre-operating phase. The printing phase begins when the feedstock starts extruding and ends when the object is printed and the nozzle stops extruding and will not resume extruding.

3.29 Print Time [h]

The length of the printing phase.

3.30 Pre-operating Phase

Phase following the preparation phase. Experimental arrangement under normal environmental conditions where the 3D printer in the chamber is turned on (receiving electrical supply) and is waiting to start. Warming-up and energy saving modes are included. At the beginning of the pre-operating phase the 3D printer is switched on. Thereafter the 3D printer is operated with the default settings for the feedstock used.

3.31 Preparation Phase

First phase where the environmental chamber is prepared for testing. The phase includes chamber cleaning, unpacking test supplies, and confirming operatability of 3D printer system.

3.32 Post-operating Phase

Phase following the printing phase. Experimental arrangement in which the 3D printer is still in the chamber with the same air exchange rate as in the printing phase, but printing has already been completed.

3.33 Relative Humidity, RH [%]

The amount of water vapor present in air expressed as a percentage of the amount needed for saturation at the same temperature.

3.34 Sampling Interval

Time over which a single air sample is collected.

3.35 Sampling Period

Established time for collection of an air sample from the environmental chamber.

3.36 Temperature, T [°C]

Degree of hotness or coldness expressed in degrees Celsius.

3.37 Test Protocol

A defined process with specified materials, chemicals, application instructions and equipment for implementation in an environmental chamber.

3.38 Total Volatile Organic Compounds, TVOC

The sum value of all compounds within the C_6 to C_{16} range (those that elute between hexane and hexadecane) as measured by gas chromatography/mass spectrometry (GC/MS) techniques such as U.S. EPA Method TO-17 or ASTM D6196, and the concentrations of the converted areas of unidentified peaks using the toluene response factor.

3.39 Toluene Equivalent

Concentration of an unidentified compound determined from Toluene calibration. For GC/MS analysis, the TIC (total ion chromatogram) shall be used.

3.40 Total Particles, *TP* [-]

TP is calculated from the measured particle number concentration for a specified duration of particle emission sampling and quantifies the total number of emitted particles during a print job.

3.41 Ultrafine Particles, UFP

Particles having an aerodynamic diameter less than or equal to 0.1 µm. UFPs have a diameter larger than nominally 7 nm or the minimum size that the aerosol measurement instrument can detect, which should be at least 10 nm.

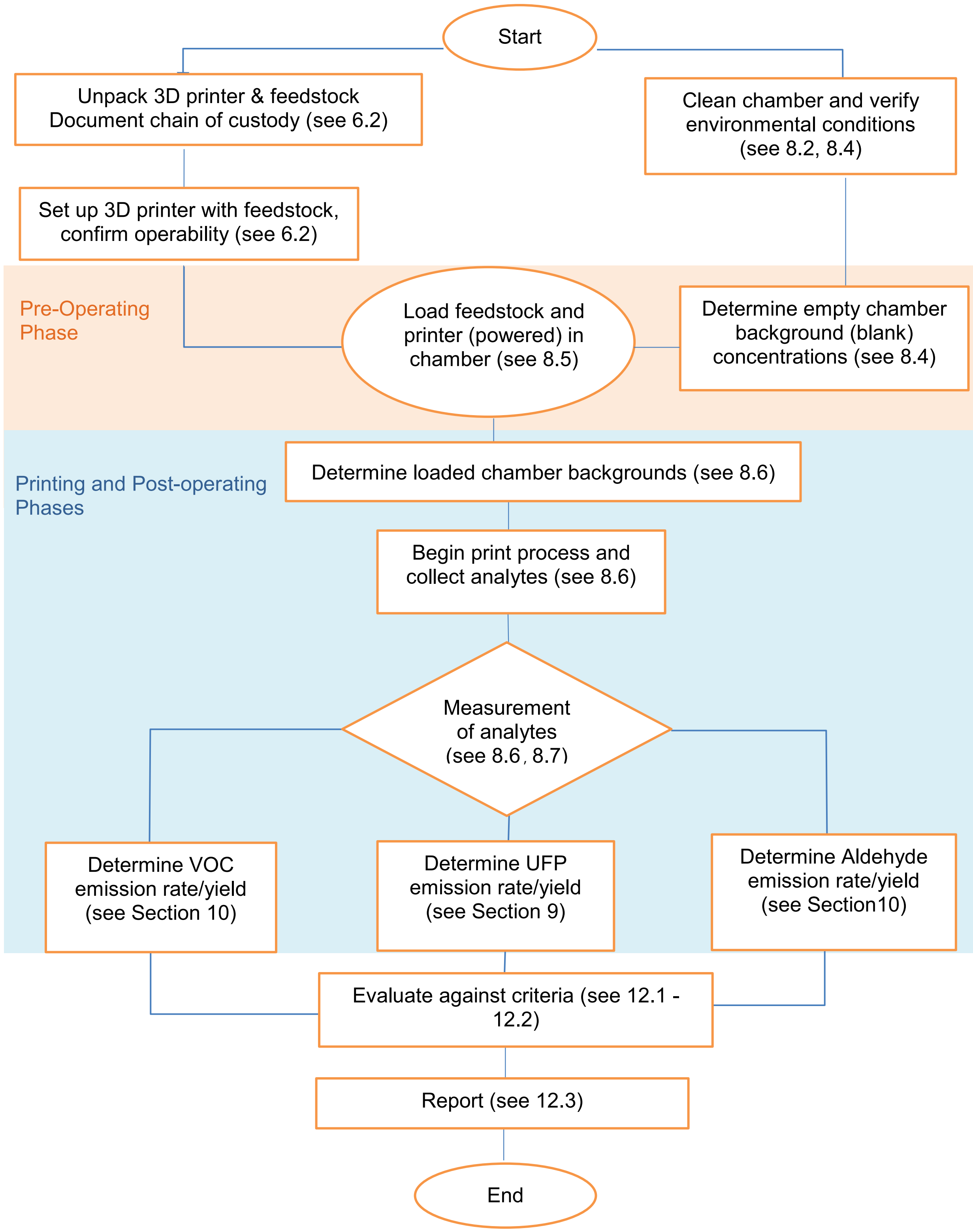
3.42 Volatile Organic Compounds, VOC

Those nonpolar and moderately polar organic chemicals with boiling points between 60ºC and 290ºC that are amenable to monitoring, based on sorbent collection/thermal desorption/GC/MS analysis. The volatility range of chemicals amenable to the method will depend on the sorbent cartridges and thermal desorption chromatographic system used by the laboratory.

3.43 Very Volatile Organic Compounds, VVOC

For the purposes of this test method, identified and unidentified organic compounds which elute from a gas chromatographic separation on a nonpolar column before n-hexane (e. g. ethanol, isopropanol, acetone, pentane).

4 Method Overview



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TEST METHOD AND ANALYSIS

5 Instruments for Environmental Condition Measurements

5.1 Environmental Chamber

The chamber shall be constructed of stainless steel and non-adsorptive materials. Chambers shall have electropolished, or equivalent, interior surfaces to minimize wall loss. The chamber shall be designed and evaluated following ASTM D6670 guidance, UL 2823 (GREENGUARD Certification), ISO/IEC 28360, and ECMA-328. The chamber shall be designed as a single-pass system without recirculation of chamber air. The chamber shall be operated at a slightly positive pressure relative to the room to prevent the entrainment of room air. The chamber inlet and exhaust shall be positioned and designed to ensure complete mixing of chamber air. The chamber lid/door shall have a non-contaminating, non-sorbing gasket and a closure mechanism to create an airtight seal. Other materials introduced into to the chamber (e.g., racks and probes) shall be constructed of non-contaminating materials such as stainless steel. Tracer gas test procedure (ASTM E741 referenced through ASTM D6670) must also be performed on the chamber to ensure that the chamber air is well mixed with the supply air. The chamber is to be operated in accordance with 8.2.

5.2 Instruments for Environmental Measurement

For the test cycle and evaluation of the measurement results, the environmental data shall be recorded over the entire test procedure. For this purpose, a measuring system with an integral data logger is required. After performing the calibration, as a minimum, the following measurement accuracies shall be ensured:

- Temperature: ± 0.5°C
- Relative humidity: ± 5.0%

Electronic probes to measure temperature and relative humidity are to be placed inside the chamber or immediately at the chamber exhaust. The probes shall be calibrated periodically according to the laboratory's quality management system. At a minimum, these probes shall be calibrated on an annual basis against NIST traceable standards. Chamber inlet flow rates are also to be recorded weekly, as a minimum (and records are to be maintained).

5.3 Capillary Gas Chromatograph Mass Spectrometer with Thermal Desorption Unit

The thermal desorber (TD) desorption and inlet parameters shall be optimized to obtain quantitative recovery of VOCs in the range defined in 8.6.2.1. The GC column and oven temperature parameters shall be optimized for the analysis of volatiles. The MS shall be an electron impact instrument operated in the scanning mode over a mass range of at least m/z 35 – 350.

The analytical methods for individual VOCs shall be based on ASTM D6196, ASTM D7339, and U.S. EPA Methods TO-17 and TO-1, or equivalent methods. Standards and chamber samples shall be analyzed using identical conditions.

5.4 High-Performance Liquid Chromatography Equipped with a UV Detector

Formaldehyde, acetaldehyde, and other low molecular weight aldehydes samples shall be analyzed by HPLC equipped with a UV detector and an analytical column providing full resolution of the formaldehyde hydrazone derivative from unreacted 2,4-dinitrophenylhydrazine (DNPH) in a sample.

The analytical methods for formaldehyde, acetaldehyde, and other low molecular weight aldehydes shall be based on ASTM D5197 or an equivalent method. It is recognized that unsaturated low molecular weight aldehydes such as acrolein are not accurately determined by this method. Aldehydes with molecular weights equal or greater than that of butanal can be analyzed by TD-GC/MS.

5.5 Aerosol Measurement Instruments

A combination of aerosol instruments is needed in order to capture (1) particle count for particle size ranging at minimum between 10 nm and 5 µm, and (2) classification of particles by size. Data correlation between the two (or more) aerosol instruments must be proven (an example shown in Appendix D.4).

A Condensation particle counter (CPCs) may be used as a stand-alone aerosol measurement instrument for total particle number concentrations. CPCs can be calibrated for their specific counting efficiency according to ISO 27891. A CPC should have at least 50% detection efficiency for emitted particles greater than 10 nm in diameter, as specified by the CPC's particle detection efficiency (D_{50}) diameter. It should be recognized that the upper size detection limits of CPCs are not precisely specified and may be less than 5 µm (the upper limit of the recommended particle size spectroscopy range). Since the vast majority of particle in terms of numbers are in the fine and ultrafine range (i. e. have diameters less than 1 µm), variability in upper size limits among CPCs is not a significant issue. Particle contributions above 1 µm are considered negligible only for total particle number concentration measurements in this standard.

If the analysis of measured data indicates contributions of particle size fractions outside the instrument's size range to the emission, the aerosol instruments should be adapted accordingly. Such an indicator could be for example a cut-off of a particle size distribution at the upper size range of the instrument.

More details on aerosol measurement instruments and their readiness is in Appendix E.2.

Example
Online particle measurements using three instruments: a CPC measuring total number of particles with diameter larger than nominally 7 nm to nominally 3 µm; a particle size spectrometer based on electrical mobility measuring number distributions for particle electrical mobility diameter between 7 and 300 nm; and an optical particle counter (OPC) measuring particle number distributions for particle optical diameter of 300 nm to 25 µm. For CPCs, a typical lower particle number concentration detection limit is 0.01 cm^{-3} and a typical upper particle number concentration detection limit is 10^7 cm^{-3}. The minimum aerosol measurement time intervals vary from 0.1 seconds to 2 minutes.

5.6 Weight Scale

The printed object shall be weighed at the end of each test. The scale shall be accurate to second decimal place of gram (±0.01 g).

6 Test 3D Printer

6.1 Print Object

The test 3D printer is to print a template file called 40mmcube.stl. (This template file can be downloaded at https://www.thingiverse.com/thing:477.) A cube object will be printed (see Appendix D.3). The print time may vary with different 3D printers, therefore the file (print size) is to be adjusted to print for 4 hours using normal/manufacture recommended 3D printer settings. The finished printed object must weigh at least 45.0 g.

It is recommended to perform a rough calculation to predict the mass of finished product prior to the test using hardware and software parameters such as extrusion speed, density of the filament, filling percentage/density, and raft/skirt/brim options.

6.2 Preparation of the Test 3D Printer

The period of time between unpacking and preparation of the test 3D printer and feedstock shall be as short as practical, with exceptions reported. The time of placement of the test 3D printer in the conditioning environment shall be recorded.

A test 3D printer is conditioned in clean air at controlled conditions of temperature and RH mentioned in 8.2, which are the same air conditions as inside the chamber, for a defined minimum period of 12 hours before initiating a printing test.

A 4-hour test run with the same conditions as for the coming test is to be made prior to placement of the test 3D printer in the chamber to ensure complete operability of the 3D printer and equipment.

For this purpose, a maximum of two 4-hour print cycles is permitted.

Printed parts and residuals left on the 3D printer must be removed after each print job to ensure that there is no carry-over contamination. The cleaning instructions in the manual specific to the 3D printer should preferentially be followed, and feedstock residual must be mechanically removed inside and outside of the extrusion piece. In fused filament fabrication (FFF), “Cold pull” (also known as “Atomic method”) can be performed between changing the feedstock. It is a process where the feedstock inside the nozzle is melted, then cooled until nozzle temperature reaches around 100 to 140°C for ABS and Nylon, 90°C for PLA (temperature is dependent on filament material and is 3D printer specific), and the feedstock gets pulled from the top side to remove any blockage, dirt, and carbonized material out of the nozzle. If a nozzle can be taken apart, cleaning with acetone or ethyl acetate is also available, however these chemicals must be fully evaporated before loading the 3D printer. If none of the above methods is successful, the nozzle should be replaced. If the nozzle is replaced, the new nozzle is to be cleaned before use. The nozzle cleaning procedure or a nozzle replacement should be reported.

Placement of a test 3D printer in the conditioning environment establishes the beginning of the test period. This critical time shall be recorded and all subsequent times for transfer of the specimen to the test chamber and collection of air samples from the chamber shall be scheduled relative to this initial time. A ±2% deviation in transfer time and sampling times is allowed. Control and monitoring of the 3D printer and the printing process in the sealed environmental chamber is to be established and controlled from outside.

A 3D printer shall be tested with a configuration that allows a 4 hour printing time extruding feedstock from one or more nozzles. Additional tests are suggested for a 3D printer with multiple extruder nozzles, i.e., separate tests using one extruder nozzle each time with all the other settings the same. If applicable, recommended addons (such as devices to condition the feedstock), platform adhesives, or surface preparation should be applied prior to loading in an environmental chamber.

The 3D printer shall be tested with the default setting (standard print quality) to print in a manner a user is most likely/advised to print unless advised otherwise by the customer. Print settings are to be recorded and clearly identified in the report. Each 3D printer with any variation in the parameters listed above must be tested separately.

6.3 Feedstock

For each device, the feedstock in the device shall be as specified in the manufacture’s instruction manual or website. The testing laboratory shall be provided with the exact name, manufacture, color of the feedstock, For each device, the feedstock in the device shall be as specified in the manufacture’s instruction manual or website. The testing laboratory shall be provided with the exact name, manufacture, color of the feedstock, diameter, lot number, the minimum, maximum, and recommended nozzle temperatures, and recommended extrusion speed for that feedstock. A current Safety data sheet (SDS), CAS number(s), the country of origin of main polymer additives/dyes should be provided. Each feedstock with any variation in the parameters listed above must be tested separately. If applicable, recommended platform temperature and adhesives or surface preparation should be provided. In any case, reserve samples are highly recommended.

Examples of typical feedstock include, but are not limited to, polylactic acid (PLA), acrylonitrile butadiene styrene (ABS), thermoplastic polyurethane (TPU), nylon, and polycarbonate.

The feedstock shall be stored according to the manufacturer's instructions until the test, and the feedstock is to be provided in sufficient quantities

7 Quality Assurance Measures

Quality assurance when applying the test procedure is a necessary prerequisite for obtaining reliable emission data. ECMA-328 and ISO/IEC 28360 give an overview of this topic.

8 Environmental Chamber Testing and Analyses

8.1 Measured Variables

- Particle count as a function of particle size
- Total particle count within a defined size range (minimum required size range is 10 nm to 5 μm)
- Individual VOC concentration
- Individual aldehyde concentration
- Total VOC concentration

8.2 Chamber Parameters

Depending on the volume of the 3D printer to be studied, a chamber with the appropriate volume shall be selected (see Equation 1). The volume of a 3D printer is defined as the multiplication of the projected area and height of the 3D printer during a regular function with enclosure doors closed and not including unattached material feedstock if there are any. The chamber size needed for the test 3D printer is selected based on the criterion for the load factor in Equation 1:

$$0.01 < \frac{V_{3D\ printer}}{V_C} < 0.25 \tag{1}$$

where $V_{3D\ printer}$ is the volume of the 3D printer (m^3) and V_C is the volume of the empty test chamber (m^3). The smallest possible chamber shall be used by the testing institute since the volume dependent measured concentrations are greater and thus the uncertainty is reduced. During the test, only one 3D printer is to be in the environmental chamber. The chamber shall not be opened, and no people shall stay in it. When a fault (e.g. feedstock jam or print object not shaping, etc.) occurs, the test is to be repeated.

Test chambers shall have sufficient sealable bushings through the wall for passing power and control cables and allow the simultaneous sampling of VOCs and particles. Recommended test chamber conditions are listed below. Drier air may be required for extruding materials if they are susceptible to moisture (e.g., RH < 5%). RH used shall be reported.

- Temperature: 23 ± 1°C
- Relative humidity: 50 ± 5%
- Adjustable air exchange rate (in h^{-1})
  - Large chamber (V_C > 5 m^3): (1 < n < 2) ± 5%
  - Small chamber (V_C < 5 m^3): (1 < n < 5) ± 5%
- Air velocity: 0.1 – 0.3 m s^{-1} surface velocity is recommended

There shall be no condensation of water in the chamber as this would lead to an undue influence on the measurement results.

Chambers are to be regarded as suitable if, in addition to compliance with the above conditions, they have sufficiently low empty chamber background values for VOCs and particles.

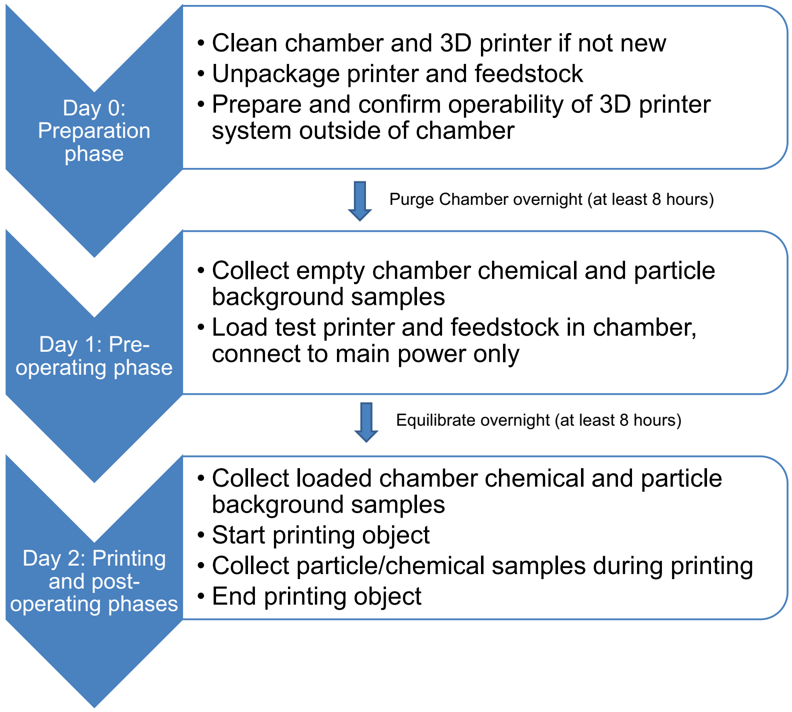
Before the chambers are first used, and repeatedly thereafter, they shall be cleaned and checked for compliance with the requirements. The empty chamber background values at an air exchange rate of n = 1 h^{-1} are to be less than the following values:

- Individual substances: 2 μg m^{-3}
- TVOC: 10 μg m^{-3}
- Total particle count concentration: 2000 cm^{-3} (e.g., CPC)
- Total particle mass concentration: 1 μg m^{-3} (e.g., particle size spectrometer and OPC)

The empty chamber background value for FP/UFP is to be checked by a sufficiently sensitive instrument (usually a CPC and/or particle size spectrometer).

The air exchange rates needed for the measurement shall be regularly checked and documented using an independent method, e.g. tracer gas method according to ASTM E741 for tracer gas application for an unloaded state.

8.3 Sampling Timeline



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8.4 Chamber Preparation/Preparation Phase

The chamber and components shall be washed with a dilute solution of laboratory detergent in water, and thoroughly rinsed with clean water and dried. Detergent should not interfere with the background measurements nor contaminate measurements. Alternative cleaning methods may be used provided that the background chamber concentrations can meet the requirements specified in 8.2.

The air exchange rate is to be adjusted within the range of acceptable air exchange rate for the particular chamber size (see 8.2).

The 3D printer shall be placed in the middle of the chamber, therefore adjust the particle and VOC sampling lines that are connected through sealable sampling ports on the walls and the ceiling of the chamber to extend approximately 10 cm away from the chamber walls and 10 to 20 cm from where the printer will be placed. All particle sampling lines shall be conductive (stainless steel or conductive silicon) to minimize electrostatic particle losses. Power and 3D printer control wires shall pass through sealed ports. Polytetrafluoroethylene (PTFE) tubing is recommended to VOCs. Sampling loss (inlet, tubing, and transport loss) should be less than 20%. Curvature of the sampling lines should be minimized. A diagram of the set-up is in Appendix D.1.

The clean chamber shall be operated at the test conditions overnight or for a minimum of 8 hours prior to introducing the test 3D printer.

8.5 3D Printer Loading/Pre-operating Phase

The test 3D printer, loaded with enough feedstock to print for a minimum of 4 hours as well as adhesives and tapes on the platform if needed, shall be placed into the test chamber. Only the main power to the 3D printer should be turned on, and the platform and nozzle heater should not be heated the day before the printing phase. Test 3D printer is to be placed in the middle of the chamber, therefore it may need to be elevated using a stainless steel table. If the 3D printer comes with a removable cover or door, then those parts should be installed on the machine and testing should be performed using the machine as intended by the manufacture. There shall be sufficient space for chamber air to circulate freely around the exposed face of the specimen. The loaded chamber is to be equilibrated overnight or for a minimum of 8 hours prior to taking loaded background measurements. An example of setup inside a chamber can be seen in Appendix D.2. If the test 3D printer is not capable of being left on overnight, the test 3D printer is to be loaded with the power switch in the "on" position but with the power cord outside of the chamber not connected to the power supply. The power supply shall be plugged in prior to loaded chamber background sampling.

This test method could be applied to measure emissions from platform preparation/adhesives. If testing for platform preparation emissions, a blank sample of the 3D printer without filament and platform preparation is required.

8.6 Air Sampling

The environmental data record begins with empty background chamber sampling period and resumes with the start of the pre-operating phase when the 3D printer is loaded and powered. Loaded background measurements are taken during the pre-operating phase before the 3D printer starts to operate its print function. The printing phase is the time between when extrusion starts and then stops, and it does not include the warm up stage where a 3D printer requires a few minutes to initiate (transfer file, find position and heat up extruder and build plate if needed). End of printing marks the beginning of the post-operating phase. The post-operating phase runs over a maximum period of four air exchanges [four hours at 1 air exchange rate (h^{-1})].

Testing is carried out using the template in accordance with 6.1.

8.6.1 Particles

Coarse, fine, and ultrafine particle measurements shall be recorded during pre-operating phase, printing phase, and post-operating phase. To begin the test, particle measurements are started at least 30 minutes before print started (i.e., start of feedstock extrusion). The particle measurements are to continue after the print had stopped for at least 1 full air change, or until concentrations return to near-background level (e.g., less than 2 times the average of the concentration measured during the 30 minutes pre-operating phase).

8.6.2 VOCs and Aldehydes

The VOC/aldehyde loaded chamber background samples are collected for 30 to 60 minutes during pre-operating phase before printing starts. Sampling time is to be optimized by the laboratory for its analysis parameters. The VOC/aldehyde samples during printing phase are collected for an hour before printing ends (from Hour 3 to Hour 4 for a 4-hour print project).

Air samples shall be collected directly from inside the chamber. The total sampling flow rate at any time shall not exceed 75% of the inlet flow rate. The start and stop times and the sampling flow rates shall be recorded. A unique identification number shall be assigned to each air sample.

Sampling flow rates shall be regulated with electronic mass flow controllers, or equivalent, with an accuracy of ±2% of full scale, or better, and capable of continuously maintaining the flow during sampling within ±5% of the specified value.

At least one measurement duplicate shall be collected for every ten VOC/aldehyde samples collected. Real-time TVOC measurement is also recommended (Appendix E.1).

8.6.2.1 Sampling Media

VOC sampling media for individual VOCs and TVOC shall consist of thermally desorbed, solid-phase sorption tubes. Refer to ASTM D6196 and D6345, and U.S. EPA Methods TO-1 and TO-17 for guidance. The samplers shall be capable of quantitatively collecting VOCs with a broad range of functional groups and volatilities approximately within the volatility range of n-pentane through n-heptadecane (C_5 – C_{17}). Minimal losses of analytes (i.e., < 5%) due to breakthrough shall occur. This can be accomplished by the use of sampling tubes containing two or more sorbent materials in series, with the highest surface area material used as the backup to prevent the breakthrough of the most volatile compounds. Typical sorption tubes contain Tenax-TA as the primary sorbent backed up by carbonaceous sorbent (s). Before use, samplers shall be conditioned by thermal desorption. Samplers taken from refrigerated storage shall be warmed to room temperature prior to use.

Sampling media for formaldehyde, acetaldehyde and other low molecular weight aldehydes through butanal (C_4 aldehydes) shall consist of cartridges containing a solid support material (e. g., silica gel) treated with an acid solution of DNPH as a derivatizing reagent. Refer to ASTM D5197 for guidance. Samplers shall be warmed to room temperature prior to use.

Following collection, air samples shall be sealed in clean airtight containers (e.g. sealable plastic bag such as zip lock® bags) and stored at reduced temperature in a dedicated refrigerator or freezer. Samples shall be analyzed as soon as practical after collection. Use unexposed samplers as storage blanks. If sampled tubes are to be sent to another laboratory for analysis, a travel blank shall be shipped with the sampled tubes to address shipping contamination.

8.7 Instrumental Analysis

8.7.1 Chemical Analyses

Chamber air samples are analyzed using instrumental methods that are capable of positively identifying individual VOCs and quantifying them using multi-point calibrations prepared using pure standards. The methods provide sufficient sensitivity and accuracy to reliably quantify individual VOCs at concentrations of 2 µg m^{-3} or less.

8.7.2 VOCs and TVOC

All target VOCs shall be quantified by GC/MS based on multipoint calibrations prepared using pure compounds. If possible, other positively identified VOCs shall be quantified by the same method. An internal standard calibration method is recommended. A minimum of four points shall be used. Target analytes shall be introduced onto sorbent tubes as gas or liquid standards and then analyzed using methods identical to those used for the analysis of chamber samples. Analyze at least one calibration standard with each batch of samples. Perform full calibrations no more than three months prior to testing to ensure accuracy for the analyses.

Recommended target VOCs to be calibrated are listed in Appendix A, Table A.2. Appendix A, Table A.2 represents chemicals known to be carcinogenic, those found in The California Department of Public Health Standard Method v1.2-2017 for VOC emission testing (CDPH SM, previously known as CA 01350) as Chronic Reference Exposure Level (CREL), and appeared greater than 50% frequency in research measurements.

Individual VOCs not positively identified as target VOCs by GC/MS shall be quantified using toluene as the reference compound for calculating compound mass. VOCs quantified by this surrogate method shall be clearly indicated.

8.7.3 Aldehydes

Aldehydes analyzed by HPLC shall be quantified based on multipoint calibrations prepared from hydrazone derivatives of the pure compounds. Standards and samples shall be analyzed using identical methods. At least one standard shall be analyzed with each batch of samples.

DATA ANALYSIS

9 Particle Data Analysis

The data analysis methods follow Seeger et. al. (2018), Zhang et al. (2017) and RAL-UZ-205 Appendix S-M 4.9, section discussing fine and ultrafine (nanoparticle) particle measurements in environmental chambers. Total particle emissions (*TP*) from the complete print job and average particle emission rate (ER_p) shall be calculated based on measured accumulated particle number concentration $C_p(t)$. Evaluation steps are described in order below.

9.1 Preprocessing of Particle Measurement Data

Particle measurement data should be checked for accuracy before proceeding to data analysis. Irregular data (e.g. abnormal individual spike or when instrument reports errors) should be corrected or removed. Data should be smoothed for instruments with high sampling frequency (e. g. particle number concentrations reported by the CPC with high recording frequency (e.g., 0.5 Hz) should be averaged over nominally 1 minute using an algorithm for floating mean value).

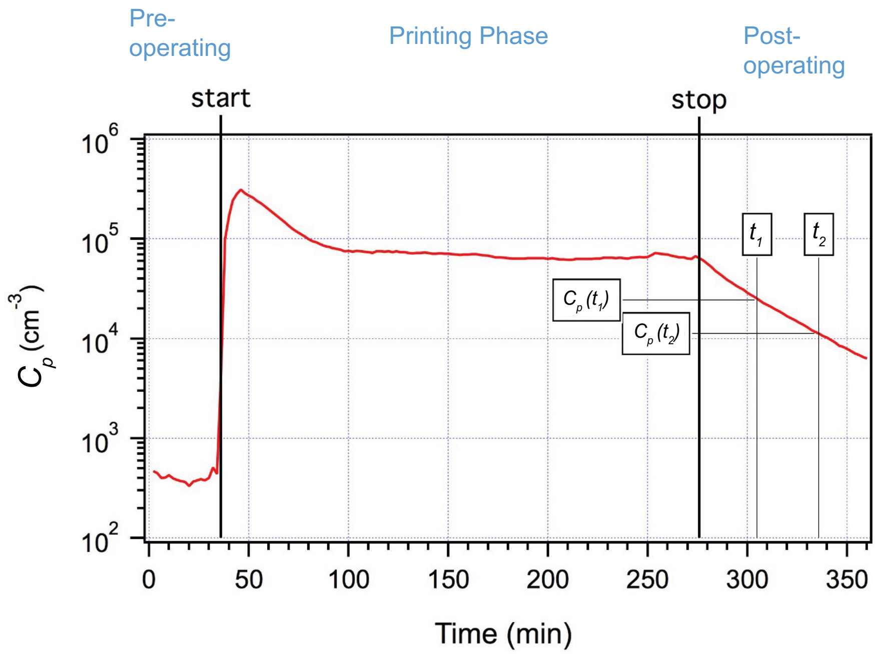
For a particle size distribution measurement, a combination of different instruments with overlapping size ranges should preferentially be used, given limited particle size ranges each instrument can measure. In this case, measurement data from multiple instruments must be combined and corrected before further analysis. In general, the particle size distribution data from multiple aerosol sizing instruments should be combined into one size distribution over the entire size range (example in Appendix D.4). A particle size distribution measurement is recommended for a detailed analysis of the time dependent emission process.

9.2 Particle Concentrations (C_p)

Particle concentrations can refer to particle number, surface area or mass concentrations, for size-resolved or total concentrations; in the following, total particle concentration (i. e. integrated particle concentrations over the entire particle size range) is shown as an example. Particle surface and mass (or volume) are inferred from the measured number distribution which involves a number of assumptions, such as, that the particles are spherical with no surface irregularities and that the density is known.

The accumulated particle number concentration (C_p), or corrected and combined particle concentration (scanning mobility particle sizer (SMPS) plus OPC for below), is shown in a graph as a function of time (Figure 1). This time series plot is used to determine $C_p(t_1)$, $C_p(t_2)$, t_1, t_2, to calculate particle loss coefficient.

Figure 1
Example of accumulated particle number concentration as a function of time. Start and stop marks the times the printing started and ended. The time before start is the pre-operating phase, time between start and stop is the printing phase, and time after stop is the post-operating phase.



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9.3 Particle Loss Coefficient (*β*)

Particles removed from the air in the chamber due to transport out of the chamber associated with the continuous air exchange, instrument sampling and loss to the walls are calculated based on the exponential decay of particles after printing stopped (stop of emission). It is assumed that the particle loss rates are constant and applied for both the printing phase and post-operating phase. Particle loss rate is calculated by:

(2)

$$\beta = \frac{l_n\left(C_p(t_1)/C_p(t_2)\right)}{t_2 - t_1}$$

where t_1 (s) is at least 15 min after the end of the printing phase and t_2 (s) is at least 25 min after t_1. $C_p(t_1)$ (cm^{-3}) and $C_p(t_2)$ (cm^{-3}) are the corresponding particle concentrations. The unit for β is s^{-1} for number concentration. Loss rates used in this standard do not consider particle size-dependent losses.

9.4 Particle Emission Rate (*PER(t)*)

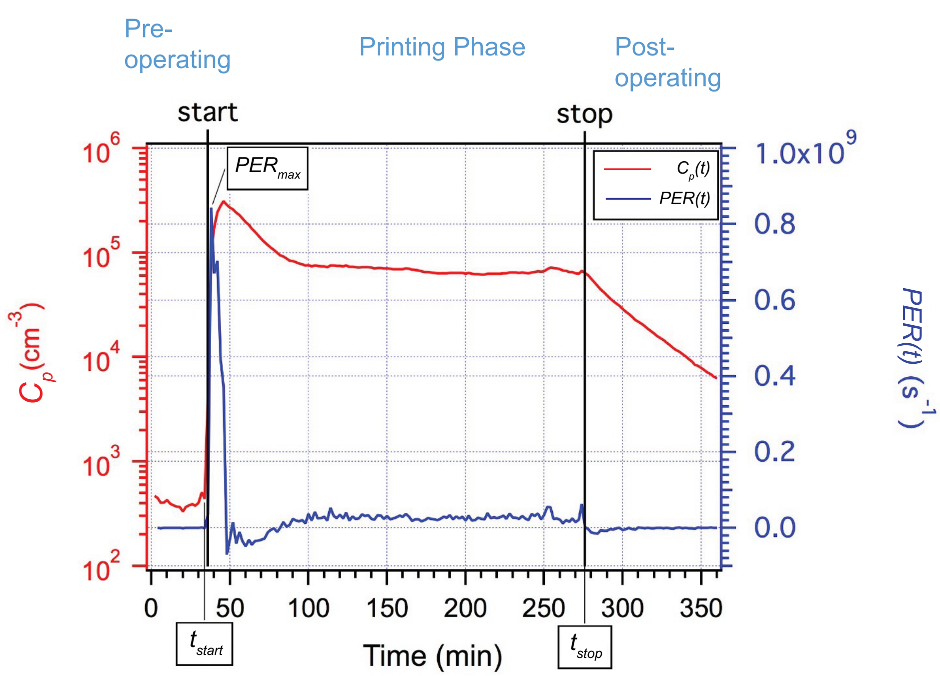
Particle emission rates as a function of time are calculated using C_p (corrected with β) based on a mass balance and is given by:

(3)

$$PER(t) = V_c\left(\frac{C_p(t) - C_p(t-\Delta t)exp(-\beta \cdot \Delta t)}{\Delta t\ exp(-\beta \cdot \Delta t)}\right)$$

where Δt (s) is the time interval between two successive data points. Unit for *PER(t)* is s^{-1} for number concentration. Figure 2 is an example of particle emission rate and accumulated particle number concentration plotted as a function of time.

Figure 2
Example of concentration (in red from Figure 1) and particle emission rate (in blue) as a function of time. Start and stop marks the times the printing started and ended. The time before start is the pre-operating phase, time between start and stop is the printing phase, and time after stop is the post-operating phase.



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In some cases, the calculated emission rate *PER(t)* may assume negative values due to influences which cannot be considered in the calculations. For before and after the print phase, the absolute values of the negative *PER(t)* values should not exceed 5% of the maximum value of *PER(t)* (PER_{max}) below the zero line (RAL-UZ-205).

9.5 Total Particle Emission (*TP*)

Total particle emission (*TP*) over the complete print job is the integral of *PER(t)* over the emission phase:

(4)

$$TP = \int_{t_{start}}^{t_{stop}} PER(t) \quad dt = \sum_{t_{start}}^{t_{stop}} PER(t) \cdot \Delta t$$

where t_{start} is the time when extrusion begins or C_p begins to increase. t_{stop} is defined as below,

If $t_{1\%\ PERmax} \leq t_{print\ end}$
$t_{stop} = t_{print\ end}$

else

$t_{stop} = t_{1\%\ PERmax}$

$t_{1\%\ PERmax}$: time when *PER(t)* remains steady, i.e. at least over the next 10 minutes, below 1% of PER_{max}.
$t_{print\ end}$: time when extrusion ends.

TP is unitless and is used to calculate average particle emission yield and rate.

9.6 Particle Yield

Particle yield was developed specifically for 3D printers to evaluate the particle emissions from a specific 3D printer and feedstock combination. It is defined as the total particles (*TP*) emitted for a given print job, divided by the printed object mass, including object supports (i. e., the mass of feedstock used for the complete print job).

9.7 Average Particle Emission Rate (ER_p)

The average particle emission rate, ER_p (h^{-1}), is total particles (*TP*) divided by the total print time in hours.

10 VOC and Aldehyde Data Analysis

10.1 Average VOC Emission Rate (ER_g)

Similar to particle calculation, VOC and aldehyde measurements are used to derive emission rates using a mass conservation equation derived for environmental chamber with 1st order decay. The average gas emission rate, $ER_{g,i}$ (µg h^{-1}), of chemical *i* shall be calculated using Equation 5:

(5)

$$ER_{g,i} = \frac{Q\left(C_{it} - C_{i0} \cdot exp\left(-\frac{Q}{V}\left(t - t_0\right)\right)\right)}{1 - exp\left(-\frac{Q}{V}\left(t - t_0\right)\right)}$$

The inlet flow rate, *Q* (m^3 h^{-1}), is the measured flow rate of air into the chamber. The chamber concentration, C_{it} (µg m^{-3}), is the concentration of a target VOC_i, formaldehyde, and other carbonyl compounds measured at time *t* (the middle of the collection time). The chamber background concentration, C_{i0} (µg m^{-3}), is the corresponding chamber concentration measured without a 3D printer operating.

10.2 VOC Yield

Similar to the Particle Yield calculation described in Section 9.6, VOC yield is calculated to compare VOC emissions from a specific 3D printer and feedstock combination. The VOC yield is the total individual VOC_i emitted for a given print job ($ER_{g,I} \cdot t_{print}$), divided by the printed object mass ($m_{printed}$), including object supports (Equation 6).

$$Yield_{g,i} = \frac{ER_{g,i} \cdot t_{print}}{m_{printed}} \quad (6)$$

TARGET CHEMICALS AND PARTICLES, AND EXPOSURE MODELING

11 Target Analytes

11.1 Target Particles

Target particles are all particles including UFP and FP that can be measured by the aerosol measurement instruments used for the testing, which should cover a wide range of particle sizes normally from less than 10 nm to larger than 5 µm.

Allowable maximum particle emission rate and yield as certification/verification requirements are given in 12.1.

11.2 Volatile Organic Compounds (VOCs)

VOCs emitted during the print process that are considered known or probable human carcinogens; those listed with non-cancer chronic reference exposure levels by CDPH SM; those with published occupational exposure threshold values (TLV®s) by American Conference of Governmental Industrial Hygienists (ACGIH®); those with Lowest Concentration of Interest (LCI) published by the German Ausschuss zur gesundheitlichen Bewertung von Bauprodukten (AgBB) program (AgBB, 2015) and other VOCs found in abundance in 3D printer emissions with irritation/odor or other unknown health impact are considered target VOCs for testing under this method (Appendix A, Table A.1).

A TVOC criterion considers all emitting VOCs as achievable for the test method.

Non listed VOCs that are abundant in the emissions are also to be quantified and reported, including as a minimum, the 5 VOCs having the highest measured emissions.

Target VOCs and their allowable maximum emission rate levels as required by certification/verification requirements are given in 12.2.

Data attained from this method can be used for risk assessment analysis using exposure models presented in this standard method or other documented exposure models if required.

12 Evaluation and Test Report

Evaluation of the 3D printer emissions for certification and verification is done by comparing the measured VOC and particle values to those listed in 12.1 and 12.2. Currently, the particle ER and yield criteria are based on a value for 80th percentile performance as determined from the research data (Appendix F). VOC ER criteria are derived from Exposure Modeling (Appendix B) and Maximum Allowable

Concentrations (Appendix A) defined specifically for indoor air use in typical non-industrial environments (such as residential settings, classrooms, offices, libraries etc.). These approaches are used today to define and qualify the indoor air quality (IAQ) acceptability of products for use in high performing Green buildings as defined by two IAQ standards and other building management and product procurement requirements. The standards are American National Standards Institute (ANSI)/ American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE)/ U.S. Green Building Council (USGBC)/ Illuminating Engineering Society (IES) Standard 189.1, and CDPH SM (which is referenced in ASHRAE 189.1). The lowest criteria in 1/10 TLV®, AgBB LCI, and CDPH SM's ½ CREL are used to derive ERs in 12.2 (office environment only). The recommended default setting is set as an office environment with the use of one 3D printer. This corresponds to one 3D printer in a single person office with a volume of 30.6 m^3 (12 ft (l) * 10 ft (w) * 9 ft (h)) and effective outdoor air change rate of 0.68 hr^{-1}, as based on ASHRAE 62.1 for offices.

The data obtained from this test method can be used for bench marking and for exposure modeling in other defined environments. Classroom, Office, and Residential environments presented in this standard are those commonly used in Green and IAQ standards mentioned above. The volumes and the air change rates of the rooms are the primary differences (Appendix B). Appendix A, Table A.3 lists the derived ERs for classroom, office, and residential environments. 3D printers used in high throughput manufacturing occupational environments may be subject to specific OSHA regulations and permissible concentrations of specific chemical and particles under set conditions. More complete risk assessments must be performed for Proposition 65 evaluation or other regulatory purposes.

Based on research data mentioned previously, the average coefficient of variation (CV) for particles was 23.8% (over 18 different sets of repeated tests done using ABS, PLA, nylon, and HIPS) and TVOC CV of 20% with individual VOC CV being less due to direct calibration.

The TP emission data obtained from a single test is assumed to have a Gaussian distribution, and the data point is treated as if it falls in the lower 2.5 percentile.

Requirements for using test data for product claims, verifications, or certifications are given in Section 13.

12.1 Maximum Allowable Particle Emission Rates

Total Particles	Particle Yield = 2 × 10^{10} particles g^{-1} feedstock Particle Emission Rate = 3 × 10^{11} particles h^{-1}

These are performance-based criteria and are not health criteria. These criteria are based on FFF technology only (Appendix F), and may be applicable to other technologies based on other data.

12.2 Maximum Allowable VOC Emission Rates

CAS Number	Chemical	Office mg hr^{-1}	Source
	Total VOC (TVOC)	10.4	ASHRAE 189.1
107-21-1	1,2-Ethanediol (Ethylene glycol)	4.16	CDPH SM
71-36-3	1-Butanol (N-Butyl alcohol)	62.4	AgBB
104-76-7	1-Hexanol, 2-ethyl	6.24	AgBB
71-23-8	1-Propanol (Propyl alcohol)	512	ACGIH® 1/10
78-83-1	1-Propanol, 2-methyl (Isobutyl alcohol)	64.5	AgBB
96-48-0	2(3H)-Furanone, dihydro (Butyrolactone)	56.2	AgBB

CAS Number	Chemical	Office mg hr^{-1}	Source
25265-77-4	2,2,4-Trimethyl-1,3-pentanediol monoisobutyrate (Texanol Ester Alcohol)	12.5	AgBB
128-37-0	2,6-Di-tert-butyl-4-methylphenol (BHT)	2.08	AgBB
78-93-3	2-Butanone (Methyl ethyl ketone, MEK)	104	AgBB
4170-30-3	2-Butenal	0.0208	AgBB
112-07-2	2-Butoxyethyl acetate	27.1	AgBB
110-43-0	2-Heptanone	485	ACGIH® 1/10
591-78-6	2-Hexanone	41.6	ACGIH® 1/10
123-42-2	2-Pentanone, 4-hydroxy-4-methyl-	20.0	AgBB
79-06-1	2-Propenamide	0.0624	ACGIH® 1/10
107-13-1	2-Propenenitrile (Acrylonitrile)**	0.0520	½ CREL
126-98-7	2-Propenenitrile, 2-methyl-	5.62	ACGIH® 1/10
79-41-4	2-Propenoic acid, 2-methyl	146	ACGIH® 1/10
88-12-0	2-Pyrrolidinone,1-ethenyl- (1-Vinyl-2-pyrrolidinone)	0.479	ACGIH® 1/10
141-79-7	3-Penten-2-one, 4-methyl	125	ACGIH® 1/10
4994-16-5	4-Phenylcyclohexene	6.24	AgBB
75-07-0	Acetaldehyde	1.46	CDPH SM
79-20-9	Acetate, methyl (Acetic acid, methyl ester)	1260	ACGIH® 1/10
64-19-7	Acetic acid	26.0	AgBB
103-09-3	Acetic acid, 2-ethylhexyl ester	7.28	AgBB
67-64-1	Acetone	25.0	AgBB
98-86-2	Acetophenone (Ethanone, 1-phenyl)	10.2	AgBB
100-52-7	Benzaldehyde	1.87	AgBB
71-43-2	Benzene*	0.0312	CDPH SM
95-63-6	Benzene, 1,2,4-trimethyl	9.36	AgBB
99-62-7	Benzene, 1,3-diisopropyl	15.6	AgBB
98-82-8	Benzene, 1-methylethyl (Cumene)	10.4	AgBB
637-50-3	Benzene, 1-propenyl-	49.9	AgBB
108-90-7	Benzene, chloro	10.4	CDPH SM
100-41-4	Benzene, ethyl	17.7	AgBB
103-65-1	Benzene, propyl	19.8	AgBB
100-51-6	Benzyl alcohol (Benzenemethanol)	9.16	AgBB
123-72-8	Butanal	13.5	AgBB
141-32-2	Butyl acrylate (2-Propenoic Acid, butyl ester)	2.29	AgBB
105-60-2	Caprolactam (2H-Azepin-2-one, hexahydro)	6.24	AgBB
540-97-6	Cyclohexasiloxane, dodecamethyl	25.0	AgBB
120-92-3	Cyclopentanone	18.7	AgBB
541-02-6	Cyclopentasiloxane, decamethyl	31.2	AgBB
556-67-2	Cyclotetrasiloxane, octamethyl	25.0	AgBB
112-31-2	Decanal	18.7	AgBB
111-46-6	Diethylene glycol (2,2'-oxybisethanol)	9.16	AgBB
117-81-7	Diethylhexyl phthalate	10.4	ACGIH® 1/10
1119-40-0	Dimethyl glutarate	1.04	AgBB
123-91-1	Dioxane (1,4-)	1.52	AgBB

CAS Number	Chemical	Office mg hr^{-1}	Source
107-06-2	Ethane, 1,2-dichloro	4.16	½ CREL
111-76-2	Ethanol, 2-butoxy	22.9	AgBB
50-00-0	Formaldehyde	0.187	CDPH SM
68-12-2	Formamide, N,N-dimethyl	0.312	AgBB
107-31-3	Formic acid, methyl ester (Methyl formate)	512	ACGIH® 1/10
111-71-7	Heptanal (Heptaldehyde)	18.7	AgBB
111-14-8	Heptanoic acid	11.4	AgBB
66-25-1	Hexanal	18.7	AgBB
110-54-3	Hexane	72.8	CDPH SM
78-59-1	Isophorone (2-Cyclohexen-1-one, 3,5,5-trimethyl-)	20.8	CDPH SM
98-83-9	Methylstyrene (iso-Propenylbenzene; (1-Methylethenyl)benzene)	52.0	AgBB
80-62-6	Methyl methacrylate (2-Propenoic acid, 2-methyl-, methyl ester)	43.7	AgBB
78-94-4	Methyl vinyl ketone (3-Buten-2-one)	1.25	ACGIH® 1/10
75-09-2	Methylene chloride (Dichloromethane)	4.16	CDPH SM
111-84-2	Nonane	2190	ACGIH® 1/10
124-19-6	Nonyl aldehyde (Nonanal)	18.7	AgBB
124-13-0	Octanal	18.7	AgBB
527-84-4	o-Cymene (2-Isopropyltoluene)	20.8	AgBB
110-62-3	Pentanal	16.6	AgBB
109-52-4	Pentanoic acid (Valeric acid)	8.74	AgBB
108-95-2	Phenol	0.208	AgBB
85-44-9	Phthalic anhydride (1,3-Isobenzofurandione)**	0.208	½ CREL
123-38-6	Propanal	99.9	ACGIH® 1/10
79-09-4	Propanoic acid	6.45	AgBB
75-98-9	Propanoic acid, 2,2-dimethyl	8.74	AgBB
138-22-7	Propanoic acid, 2-hydroxy-, butyl ester	62.4	ACGIH® 1/10
110-86-1	Pyridine	6.45	ACGIH® 1/10
100-42-5	Styrene	5.20	AgBB
1576-87-0	t-2-Pentenal	0.250	AgBB
3333-52-6	Tetramethylbutanedinitrile	5.83	ACGIH® 1/10
108-88-3	Toluene (Methylbenzene)	3.12	CDPH SM
25551-13-7	Trimethylbenzene (All Isomers)	256	ACGIH® 1/10
6846-50-0	TXIB (2,2,4-Trimethyl-1,3-pentanediol diisobutyrate)	9.36	AgBB
100-40-3	Vinyl cyclohexene (Cyclohexene, 4-ethenyl-)	0.916	ACGIH® 1/10
106-42-3	Xylene (para and/or meta)	7.28	CDPH SM
95-47-6	Xylene, ortho	7.28	CDPH SM

Values above are for one 3D printer.

* Benzene has a CREL of 3 µg m^{-3} (June 2014); guidance value established by this Standard Method at 30 µg m^{-3} before March 31st, 2017 and at 1.5 µg m^{-3} starting from April 1st, 2017.

** Additional VOCs of concern found frequently in emissions and not listed by CDPH Standard Method.

12.3 Test Report

The full test and the complete evaluation for the tested 3D printer shall be recorded in the test report. In particular, the following data are to be included:

12.3.1 Data on the Test Laboratory

- Name and full address
- Name of the responsible person

12.3.2 Data on the Tested 3D Printer and Feedstock

- Precise product specification, indicate of the desk-top or standalone device, model number, print speed specified by the manufacturer, etc. If 3D printer information is unobtainable, the testing laboratory should keep a retention sample.
- 3D printer parameters used for the test. If applicable, recommended platform material, platform temperature, and adhesives or surface preparation as well.
- Feedstock type and product specifications: The exact name, manufacture, color of the feedstock, lot number, diameter, minimum, maximum, and recommended nozzle temperatures, and recommended extrusion speed for that feedstock. A current SDS, CAS number(s), the country of origin of main polymer, additives/dyes should be reported.
- Production date of 3D printer and feedstock
- Date of receipt
- Type of packaging
- Storage time before the test for 3D printer and feedstock
- Study date / period
- Volume or external dimensions of the tested 3D printer
- The nozzle cleaning procedure or a nozzle replacement
- Number of prints performed, total hours printed, filaments used prior to testing
- Chain of custody

12.3.3 Data on the Test

- Study date / period
- Experimental conditions (type and size of the chamber, temperature, relative humidity, air exchange, and air flow rate)
- Compliance with the condition of the load factor (see Equation 1)
- Description of the aerosol measurement instruments used:
  - ○ Manufacturer, type and serial number
  - ○ Name and version of the software

- ○ Date of last calibration or maintenance
- ○ Currently used equipment settings, including particle size range that are detected
- ○ Type and dilution factor if an aerosol dilution stage was used
- ○ Result of measures to ensure the readiness of the aerosol measuring instrument according to 5.5 and Appendix E.2.

- Start, end, and duration of preparation, pre-operating, printing, and post-operating phases
- Printing/extrusion speed during the test
- Printing mode during the test (low / normal / high quality, etc.)
- The mass of printed object
- Timing and duration of air sampling. Additionally, volume and volumetric flow rate for 3 sets of VOC and aldehyde sampling
- VOC, aldehyde sample identifications
- Identification and location of the files with continuously recorded readings (environment, uncorrected and, if necessary, corrected particle number concentration)
- Pictures of 1) the tested 3D printer inside a chamber, 2) finished/printed object

12.3.4 Data on Evaluation

- Total particle emission rate and yield
- Assumed particle density if particle mass concentration is calculated
- Particle emission rate by size and the associated collection size range by each collection bin
- Proof of correlation between aerosol instruments if more than one aerosol measurement instruments are used
- Name, CAS-No., and concentration of identified VOCs, and concentration of unidentified VOCs in the pre-operating phase and printing phase, and calculated emission rates. Target VOCs to be listed separately in any case
- TVOC value as the sum of the quantified and unidentified compounds during pre-operating phase and printing phase as well as calculated emission rates (relevant value for award basis)
- Specification of VVOCs with CAS-No., if any
- Specification of detection and determination limits for VOC and aldehyde emission rates
- Particle concentration diagram according to 9.2, similar to Figure 1
- PER(t) diagram according to 9.4, similar to Figure 2
- Table of values for auxiliary variables determined in accordance with Particle Data Analysis, Section 9: t_1, t_2, $C_p(t_1)$, $C_p(t_2)$, β, PER_{max}, t_{start}, $C_p(t_{start})$, t_{stop}, $C_p(t_{stop})$, and $PER(t_{stop})$
- A report of any malfunctions and deviations from test algorithms

- Summary of the results by the test institute in view of the criteria (if necessary, an indication that the emission characteristics determined only apply in conjunction with the tested type of feedstock)

- Signature under the summary which shall again include the exact device identification

- If different models are used for additional exposure modeling, the models and parameters must be specified for consistency.

13 Requirements for Use of Standard as Basis for a Product Claim, Verification, or Certification

Whenever this *Standard Method for Testing and Assessing Particle and Chemical Emissions from 3D Printers* is to be used to make, certify, or verify a product claim, the following guidelines shall be followed.

13.1 Manufacture and Third-Party Claims

Certification or verification organizations substantiating manufacturers' claims or providing verification/certification compliance to this standard method shall operate in accordance with ISO/IEC 17065, Conformity Assessment – Requirements for the Bodies Certifying Products, Processes and Services. This ensures resulting certifications or verifications are impartial, consistent with the standard method, and are based on accurate and objective data.

Claims made by manufactures regarding their own products shall follow the principles of ISO 14021 for self-declared environmental labels and declarations. These requirements include that such claims be: based on scientific evidence; accurate; verifiable; and updated if circumstances alter their accuracy. All information on methods, criteria, and data used to support a claim shall be made available.

For product verification or certification, products should be newly manufactured and the required default exposure model is the use of one 3D printer in the single person office environment with the office VOC criteria defined in Section 12.2 and particle criteria in Section 12.1. This exposure model corresponds to the standard industry acceptance environment for indoor products for green high performing building programs. The particle criteria in Section 12.1 shall be met based on direct measurement.

Labeling of verified or certified products shall have noted on all market facing materials "Meets Certification Requirements of UL 2904".

Approved certified bodies can be found by ANSI or other accrediting body websites, for example https://www.ansi.org/Accreditation/who-is-accredited.

13.2 Laboratory Selection

Manufacturers or certification/verification organizations shall utilize only laboratories demonstrating competency to perform the standard method. Laboratories with direct connection to the manufacturer of the 3D printer or feedstock shall be subject to independent verification. They should be accredited to ISO/IEC 17025:2017, General Requirements for the Competence of Testing and Calibration Laboratories, and have UL 2904 and accompanying quality program within their accredited scope. Elements of the required test report are in 12.3.

Approved testing laboratories can be found by A2LA or other accrediting body websites, for example https://portal.a2la.org/search/.

Appendix A – Target VOCs and Their Allowable Maximum Concentration Levels

Table A.1
VOCs with ACGIH® TLV®s, AgBB LCIs, and CDPH SM CRELs and Allowable Criteria

CAS Number	Chemical	ACGIH® 1/10 TLV® (TWA) µg m^{-3}	ACGIH® 1/10 TLV® (STEL) µg m^{-3}	AgBB LCI µg m^{-3}	CDPH SM ½ CREL µg m^{-3}
107-21-1	1,2-Ethanediol (Ethylene glycol)		10000	260	**200**
71-36-3	1-Butanol (N-Butyl alcohol)	6100		**3000**	
104-76-7	1-Hexanol, 2-ethyl			**300**	
71-23-8	1-Propanol (Propyl alcohol)	24600		VVOC	
78-83-1	1-Propanol, 2-methyl (Isobutyl alcohol)	15200		**3100**	
96-48-0	2(3H)-Furanone, dihydro (Butyrolactone)			**2700**	
25265-77-4	2,2,4-Trimethyl-1,3-pentanediol monoisobutyrate (Texanol Ester Alcohol)			**600**	
128-37-0	2,6-Di-tert-butyl-4-methylphenol (BHT)	200		**100**	
78-93-3	2-Butanone (Methyl ethyl ketone, MEK)	59000	88500	**5000**	
4170-30-3	2-Butenal		86	**1 (5)**	
112-07-2	2-Butoxyethyl acetate	13000		**1300**	
110-43-0	2-Heptanone	**23300**			
591-78-6	2-Hexanone	**2000**	4000		
123-42-2	2-Pentanone, 4-hydroxy-4-methyl-	23800		**960**	
79-06-1	2-Propenamide	**3**			
107-13-1	2-Propenenitrile (Acrylonitrile)	430			**2.5****
126-98-7	2-Propenenitrile, 2-methyl-	**270**			
79-41-4	2-Propenoic acid, 2-methyl	**7000**			
88-12-0	2-Pyrrolidinone,1-ethenyl- (1-Vinyl-2-pyrrolidinone)	**23**			
141-79-7	3-Penten-2-one, 4-methyl	**6000**	10000		
4994-16-5	4-Phenylcyclohexene			**300**	
75-07-0	Acetaldehyde		4500	1200	**70**
79-20-9	Acetate, methyl (Acetic acid, methyl ester)	**60600**	75700	VVOC	
64-19-7	Acetic acid	2500	3700	**1250**	
103-09-3	Acetic acid, 2-ethylhexyl ester			**350**	
67-64-1	Acetone	59400	118700	**1200**	
98-86-2	Acetophenone (Ethanone, 1-phenyl)	4900		**490**	
100-52-7	Benzaldehyde			**90**	
71-43-2	Benzene	160	800		**1.5***
95-63-6	Benzene, 1,2,4-trimethyl	12300		**450**	
99-62-7	Benzene, 1,3-diisopropyl			**750**	
98-82-8	Benzene, 1-methylethyl (Cumene)	24600		**500**	
637-50-3	Benzene, 1-propenyl-			**2400**	
108-90-7	Benzene, chloro	4600			**500**
100-41-4	Benzene, ethyl	8700	54300	**850**	1000
103-65-1	Benzene, propyl			**950**	
100-51-6	Benzyl alcohol (Benzenemethanol)			**440**	

Table A.1 Continued on Next Page

Table A.1 Continued

CAS Number	Chemical	ACGIH® 1/10 TLV® (TWA) µg m^{-3}	ACGIH® 1/10 TLV® (STEL) µg m^{-3}	AgBB LCI µg m^{-3}	CDPH SM ½ CREL µg m^{-3}
123-72-8	Butanal			**650**	
141-32-2	Butyl acrylate (2-Propenoic Acid, butyl ester)	1100		**110**	
105-60-2	Caprolactam (2H-Azepin-2-one, hexahydro)	**500**		**300**	
540-97-6	Cyclohexasiloxane, dodecamethyl			**1200**	
120-92-3	Cyclopentanone			**900**	
541-02-6	Cyclopentasiloxane, decamethyl			**1500**	
556-67-2	Cyclotetrasiloxane, octamethyl			**1200**	
112-31-2	Decanal			**900**	
111-46-6	Diethylene glycol (2,2'-oxybisethanol)			**440**	
117-81-7	Diethylhexyl phthalate	500			
1119-40-0	Dimethyl glutarate			**50**	
123-91-1	Dioxane (1,4-)	7200		**73**	1500
107-06-2	Ethane, 1,2-dichloro	4000			**200**
111-76-2	Ethanol, 2-butoxy	9700		**1100**	
50-00-0	Formaldehyde		37	100	**9**
68-12-2	Formamide, N,N-dimethyl	3000		**15**	40
107-31-3	Formic acid, methyl ester (Methyl formate)	**24600**	36800		
111-71-7	Heptanal (Heptaldehyde)			**900**	
111-14-8	Heptanoic acid			**550**	
66-25-1	Hexanal			**900**	
78-59-1	Isophorone (2-Cyclohexen-1-one, 3,5,5-trimethyl-)		2800		**1000**
98-83-9	Methylstyrene (iso-Propenylbenzene; (1-Methylethenyl) benzene)	4800		**2500**	
80-62-6	Methyl methacrylate (2-Propenoic acid, 2-methyl-, methyl ester)	20500	41000	**2100**	
78-94-4	Methyl vinyl ketone (3-Buten-2-one)		**60**		
75-09-2	Methylene chloride (Dichloromethane)	17400			**200**
111-84-2	Nonane	**105000**			
124-19-6	Nonyl aldehyde (Nonanal)			**900**	
124-13-0	Octanal			**900**	
527-84-4	o-Cymene (2-Isopropyltoluene)			**1000**	
110-62-3	Pentanal	17600		**800**	
109-52-4	Pentanoic acid (Valeric acid)			**420**	
108-95-2	Phenol	1900		**10**	100
85-44-9	Phthalic anhydride (1,3-Isobenzofurandione)	610			**10****
123-38-6	Propanal	**4800**		VVOC	
79-09-4	Propanoic acid	3000		**310**	
75-98-9	Propanoic acid, 2,2-dimethyl			**420**	
138-22-7	Propanoic acid, 2-hydroxy-, butyl ester	**3000**			
110-86-1	Pyridine	**310**			
100-42-5	Styrene	8500	17000	**250**	450

Table A.1 Continued on Next Page

Table A.1 Continued

CAS Number	Chemical	ACGIH® 1/10 TLV® (TWA) µg m^{-3}	ACGIH® 1/10 TLV® (STEL) µg m^{-3}	AgBB LCI µg m^{-3}	CDPH SM ½ CREL µg m^{-3}
1576-87-0	t-2-Pentenal			**12**	
3333-52-6	Tetramethylbutanedinitrile	**280**			
108-88-3	Toluene (Methylbenzene)	7500		2900	**150**
25551-13-7	Trimethylbenzene (All Isomers)	**12300**			
6846-50-0	TXIB (2,2,4-Trimethyl-1,3-pentanediol diisobutyrate)			**450**	
100-40-3	Vinyl cyclohexene (Cyclohexene, 4-ethenyl-)	**44**			
106-42-3	Xylene (para and/or meta)	43400	65100	500	**350**
95-47-6	Xylene, ortho	43400	65100	500	**350**

Bolded values are the allowable criteria (the lowest value across the risk tables).

* Benzene has a CREL of 3 µg m^{-3} (June 2014); guidance value established by this Standard Method at 30 µg m^{-3} before March 31st, 2017 and at 1.5 µg m^{-3} starting from April 1st, 2017.

** Additional VOCs of concern found frequently in emissions and not listed by CDPH Standard Method.

Table A.2
Recommended Target VOCs to be Authentically Calibrated

Chemical	CAS No.
1,2-Ethanediol (Ethylene glycol)	107-21-1
1-Butanol (N-Butyl alcohol)	71-36-3
1-Hexanol, 2-ethyl	104-76-7
2-Propenenitrile (Acrylonitrile)	107-13-1
Acetaldehyde	75-07-0
Acetophenone (Ethanone, 1-phenyl)	98-86-2
Benzaldehyde	100-52-7
Benzene	71-43-2
Benzene, 1-methylethyl (Cumene)	98-82-8
Benzene, chloro	108-90-7
Benzene, ethyl	100-41-4
Caprolactam (2H-Azepin-2-one, hexahydro)	105-60-2
Decanal	112-31-2
Dioxane (1,4-)	123-91-1
Ethane, 1,2-dichloro (Ethylene dichloride)	107-06-2
Formaldehyde	50-00-0
Formamide, N,N-dimethyl	68-12-2
Hexanal	66-25-1
Hexane	110-54-3
Isophorone (2-Cyclohexen-1-one, 3,5,5-trimethyl-)	78-59-1
Methylene chloride (Dichloromethane)	75-09-2
Nonyl aldehyde (Nonanal)	124-19-6
Phenol	108-95-2
Phthalic anhydride (1,3-Isobenzofurandione)	85-44-9

Table A.2 Continued on Next Page

Table A.2 Continued

Chemical	CAS No.
Styrene	100-42-5
Toluene (Methylbenzene)	108-88-3
Xylene (para and/or meta)	106-42-3
Xylene, ortho	95-47-6

Table A.3 Maximum Allowable VOC Emission Rates Derived for Classroom, Office, and Residential Models in Appendix B

CAS Number	Chemical	Classroom mg hr^{-1}	Office mg hr^{-1}	Residen-tial mg hr^{-1}	Source
	Total VOC (TVOC)	94.7	10.4	3.25	ASHRAE 189.1
107-21-1	1,2-Ethanediol (Ethylene glycol)	37.9	4.16	1.30	CDPH SM
71-36-3	1-Butanol (N-Butyl alcohol)	568	62.4	19.5	AgBB
104-76-7	1-Hexanol, 2-ethyl	56.8	6.24	1.95	AgBB
71-23-8	1-Propanol (Propyl alcohol)	4660	512	160	ACGIH® 1/10
78-83-1	1-Propanol, 2-methyl (Isobutyl alcohol)	587	64.5	20.1	AgBB
96-48-0	2(3H)-Furanone, dihydro (Butyrolactone)	511	56.2	17.5	AgBB
25265-77-4	2,2,4-Trimethyl-1,3-pentanediol monoisobutyrate (Texanol Ester Alcohol)	114	12.5	3.90	AgBB
128-37-0	2,6-Di-tert-butyl-4-methylphenol (BHT)	18.9	2.08	0.650	AgBB
78-93-3	2-Butanone (Methyl ethyl ketone, MEK)	947	104	32.5	AgBB
4170-30-3	2-Butenal	0.189	0.0208	0.00650	AgBB
112-07-2	2-Butoxyethyl acetate	246	27.1	8.44	AgBB
110-43-0	2-Heptanone	4410	485	151	ACGIH® 1/10
591-78-6	2-Hexanone	379	41.6	13.0	ACGIH® 1/10
123-42-2	2-Pentanone, 4-hydroxy-4-methyl-	182	20.0	6.24	AgBB
79-06-1	2-Propenamide	0.568	0.0624	0.0195	ACGIH® 1/10
107-13-1	2-Propenenitrile (Acrylonitrile)**	0.474	0.0520	0.0162	½ CREL
126-98-7	2-Propenenitrile, 2-methyl-	51.1	5.62	1.75	ACGIH® 1/10
79-41-4	2-Propenoic acid, 2-methyl	1330	146	45.5	ACGIH® 1/10
88-12-0	2-Pyrrolidinone,1-ethenyl- (1-Vinyl-2-pyrrolidinone)	4.36	0.479	0.149	ACGIH® 1/10
141-79-7	3-Penten-2-one, 4-methyl	1140	125	39.0	ACGIH® 1/10
4994-16-5	4-Phenylcyclohexene	56.8	6.24	1.95	AgBB
75-07-0	Acetaldehyde	13.3	1.46	0.455	CDPH SM
79-20-9	Acetate, methyl (Acetic acid, methyl ester)	11500	1260	394	ACGIH® 1/10
64-19-7	Acetic acid	237	26.0	8.12	AgBB
103-09-3	Acetic acid, 2-ethylhexyl ester	66.3	7.28	2.27	AgBB

Table A.3 Continued on Next Page

Table A.3 Continued

CAS Number	Chemical	Classroom mg hr^{-1}	Office mg hr^{-1}	Residential mg hr^{-1}	Source
67-64-1	Acetone	227	25.0	7.79	AgBB
98-86-2	Acetophenone (Ethanone, 1-phenyl)	92.8	10.2	3.18	AgBB
100-52-7	Benzaldehyde	17.0	1.87	0.585	AgBB
71-43-2	Benzene*	0.284	0.0312	0.00974	CDPH SM
95-63-6	Benzene, 1,2,4-trimethyl	85.2	9.36	2.92	AgBB
99-62-7	Benzene, 1,3-diisopropyl	142	15.6	4.87	AgBB
98-82-8	Benzene, 1-methylethyl (Cumene)	94.7	10.4	3.25	AgBB
637-50-3	Benzene, 1-propenyl-	455	49.9	15.6	AgBB
108-90-7	Benzene, chloro	94.7	10.4	3.25	CDPH SM
100-41-4	Benzene, ethyl	161	17.7	5.52	AgBB
103-65-1	Benzene, propyl	180	19.8	6.17	AgBB
100-51-6	Benzyl alcohol (Benzenemethanol)	83.3	9.16	2.86	AgBB
123-72-8	Butanal	123	13.5	4.22	AgBB
141-32-2	Butyl acrylate (2-Propenoic Acid, butyl ester)	20.8	2.29	0.714	AgBB
105-60-2	Caprolactam (2H-Azepin-2-one, hexahydro)	56.8	6.24	1.95	AgBB
540-97-6	Cyclohexasiloxane, dodecamethyl	227	25.0	7.79	AgBB
120-92-3	Cyclopentanone	170	18.7	5.85	AgBB
541-02-6	Cyclopentasiloxane, decamethyl	284	31.2	9.74	AgBB
556-67-2	Cyclotetrasiloxane, octamethyl	227	25.0	7.79	AgBB
112-31-2	Decanal	170	18.7	5.85	AgBB
111-46-6	Diethylene glycol (2,2'-oxybisethanol)	83.3	9.16	2.86	AgBB
117-81-7	Diethylhexyl phthalate	94.7	10.4	3.25	ACGIH® 1/10
1119-40-0	Dimethyl glutarate	9.47	1.04	0.325	AgBB
123-91-1	Dioxane (1,4-)	13.8	1.52	0.474	AgBB
107-06-2	Ethane, 1,2-dichloro	37.9	4.16	1.30	½ CREL
111-76-2	Ethanol, 2-butoxy	208	22.9	7.14	AgBB
50-00-0	Formaldehyde	1.70	0.187	0.0585	CDPH SM
68-12-2	Formamide, N,N-dimethyl	2.84	0.312	0.0974	AgBB
107-31-3	Formic acid, methyl ester (Methyl formate)	4660	512	160	ACGIH® 1/10
111-71-7	Heptanal (Heptaldehyde)	170	18.7	5.85	AgBB
111-14-8	Heptanoic acid	104	11.4	3.57	AgBB
66-25-1	Hexanal	170	18.7	5.85	AgBB
110-54-3	Hexane	663	72.8	22.7	CDPH SM
78-59-1	Isophorone (2-Cyclohexen-1-one, 3,5,5-trimethyl-)	189	20.8	6.50	CDPH SM
98-83-9	Methylstyrene (iso-Propenylbenzene; (1-Methylethenyl) benzene)	474	52.0	16.2	AgBB
80-62-6	Methyl methacrylate (2-Propenoic acid, 2-methyl-, methyl ester)	398	43.7	13.6	AgBB
78-94-4	Methyl vinyl ketone (3-Buten-2-one)	11.4	1.25	0.390	ACGIH® 1/10
75-09-2	Methylene chloride (Dichloromethane)	37.9	4.16	1.30	CDPH SM

Table A.3 Continued on Next Page

Table A.3 Continued

CAS Number	Chemical	Classroom mg hr^{-1}	Office mg hr^{-1}	Residen-tial mg hr^{-1}	Source
111-84-2	Nonane	19900	2190	682	ACGIH® 1/10
124-19-6	Nonyl aldehyde (Nonanal)	170	18.7	5.85	AgBB
124-13-0	Octanal	170	18.7	5.85	AgBB
527-84-4	o-Cymene (2-Isopropyltoluene)	189	20.8	6.50	AgBB
110-62-3	Pentanal	152	16.6	5.20	AgBB
109-52-4	Pentanoic acid (Valeric acid)	79.6	8.74	2.73	AgBB
108-95-2	Phenol	1.89	0.208	0.0650	AgBB
85-44-9	Phthalic anhydride (1,3-Isobenzofurandione)**	1.89	0.208	0.0650	½ CREL
123-38-6	Propanal	909	99.9	31.2	ACGIH® 1/10
79-09-4	Propanoic acid	58.7	6.45	2.01	AgBB
75-98-9	Propanoic acid, 2,2-dimethyl	79.6	8.74	2.73	AgBB
138-22-7	Propanoic acid, 2-hydroxy-, butyl ester	568	62.4	19.5	ACGIH® 1/10
110-86-1	Pyridine	58.7	6.45	2.01	ACGIH® 1/10
100-42-5	Styrene	47.4	5.20	1.62	AgBB
1576-87-0	t-2-Pentenal	2.27	0.250	0.08	AgBB
3333-52-6	Tetramethylbutanedinitrile	53.0	5.83	1.82	ACGIH® 1/10
108-88-3	Toluene (Methylbenzene)	28.4	3.12	0.974	CDPH SM
25551-13-7	Trimethylbenzene (All Isomers)	2330	256	79.9	ACGIH® 1/10
6846-50-0	TXIB (2,2,4-Trimethyl-1,3-pentanediol diisobutyrate)	85.2	9.36	2.92	AgBB
100-40-3	Vinyl cyclohexene (Cyclohexene, 4-ethenyl-)	8.33	0.916	0.286	ACGIH® 1/10
106-42-3	Xylene (para and/or meta)	66.3	7.28	2.27	CDPH SM
95-47-6	Xylene, ortho	66.3	7.28	2.27	CDPH SM

Values above are for one 3D printer.

* Benzene has a CREL of 3 µg m^{-3} (June 2014); guidance value established by this Standard Method at 30 µg m^{-3} before March 31st, 2017 and at 1.5 µg m^{-3} starting from April 1st, 2017.

** Additional VOCs of concern found frequently in emissions and not listed by CDPH Standard Method.

Appendix B – Exposure Modeling

Indoor air quality concentration modeling is done on VOCs to convert measured emission rates to an estimated room concentrations for potential inhalation exposure of building occupants. Indoor air concentration resulting from the tested 3D printer is calculated based on a steady state mass balance model with the assumption that the emission is well mixed within the model room. The exposure concentration is used to determine compliance with the maximum allowable levels.

The estimated exposure concentration, C_i (µg m^{-3}), of a target emission for a particular room model, *i*, is derived using Equation 7.

$$C_i = ER_i(\frac{A}{V_m})(\frac{1}{N_m}) \tag{7}$$

where emission rate, ER_i, is multiplied by the number of 3D printers in modeled room, *A*, and divided by the volume of the model room, V_m (m^3), and the modeled room's air exchange rate, N_m (h^{-1}). *A*, V_m, and N_m are specific to the three standardized scenarios: office, classroom, and residential setting.

B.1 Office Model for Exposure Modeling

The office model is based on an enclosed office in a public/commercial building that is assumed to be occupied by a single individual (ASHRAE 62.1). The office ventilation rate is based on the ASHRAE parameters of 5 CFM per person and 0.06 CFM ft^{-2} for office spaces in commercial buildings. These parameters are applied to the office size (V_m = 30.6 m^3) for a single occupant, which results in a ventilation rate (N_m) of 0.68 h^{-1}. The number of 3D printers installed in the office is to be defined. The default number will be one 3D printer per office.

B.2 Classroom Model for Exposure Modeling

Classroom modeling uses the requirements and parameters in CDPH SM. These parameters are applied to a typical classroom [12 m x 7.3 m x 2.6 m (40' x 24' x 8.5') or V_m = 231 m^3] with an occupancy of 27 students and ventilation rate (N_m) of 0.82 h^{-1}. The number of 3D printers installed in a classroom (*A*) is to be defined. The default number will be one 3D printer per classroom.

B.3 Residential Model for Exposure Modeling

An informative Appendix B for a new single-family residence scenario can be found in the 2017 update of the CDPH SM (Standard Method for the Testing and Evaluation of VOC Emissions from Indoor Sources Using Environmental Chambers, Version 1.2). Although not a formal part of the required elements of the test method, Appendix B was added for informational data for a residential model. Data for the informative Appendix B single-family residence was gathered from the 2008 DOE Buildings Energy Data Book, which summarized statistics collected by the National Association of Home Builders (NAHB) on materials used in the construction of a 211 m^2 (2,272 ft^2) single-family home, similar in size to the average 2008 home. The CDPH SM "home" is proposed to be a four bedroom, two bath residence with a floor space area of 211 m^2 and a simple total volume (floor space area times ceiling height) of 547 m^3.

The average statistical data from the CDPH SM "home" was used to develop a usable model using a computer-aided design (CAD) program and the residential parameters presented in the CDPH SM informative Appendix B. The use of CAD allowed for reliable estimation of volumes, surface areas and product loadings, building from the floor area of the CDPH home. Details are provided in the attached Tables and Figures. Table B.1 presents summary information about the home model. Table B.2 presents calculated areas (in m^2) and loadings (in m^2 m^{-3}) of key construction materials/products for the home, with data for each individual floor also provided. Table B.3 presents the room volumes of key areas of the house. Figure B.1 and Figure B.2 are the CAD floor-plan drawings of the first and second floors of the home, respectively and Figure B.3 and Figure B.4 include room dimensions. A ventilation rate (*n*) of 0.23

h^{-1} will be used as representative of a modern energy efficient home, based on a ventilation flow rate of 127 m^3 h^{-1} (75 cfm) using Table 4.1a of ASHRAE 62.2. The default loading will be one 3D printer per bedroom/hobby room.

Table B.1
Summary Information for the Single-Family Residence Model Home

Parameter	Unit of Measure	Parameter Value
Floor space	m^2	(124 and 117) 241[1]
Ceiling height	m	2.74 and 2.44[2]
Volume	m^3	621 and 579[3]
No. Bedrooms[4]	Unit	4
No. Full Baths[4]	Unit	2
No. Other Rooms[4]	Unit	3 + Garage

1. Floor space based on exterior dimensions, measurements taken to the outside of the exterior walls, and does not include a garage, carport, porch, unfinished attic or utility room, or any unfinished area of the basement. The numbers in parentheses represent the first and second floors areas, respectively.

2. A 9-ft ceiling (2.74-m) height is used for the first floor and an 8-ft (2.44-m) ceiling height is used for the second floor.

3. The first volume provided is a simple calculation of floor space area times ceiling height. The second volume provided uses the floor space area inside the home minus the interior walls times the ceiling height; this represents the volume of air that circulates throughout the house.

4. Due to incomplete data, it is necessary to estimate the home configuration. The most frequent number of bedrooms is three, but many floor plans for homes of this size contain a fourth bedroom or bedroom/den. This home is assumed to consist of four bedrooms, two full baths, and three other rooms.

Table B.2
Residential Scenario Parameters and Derived Values for the 15% Window Ratio CAD2 Simulated Single Family Residence with Loading Ratios

		CAD2 Home (Volume = 579 m^3)				
Product Type	**Area Unit[1]**	**Quantity[1]**	**1st Floor Area**	**2nd Floor Area**	**Total Area**	**L (m^2 m^{-3})**
Flooring (all types)	**m^2**	NA	108	101	209	0.366
Ceiling	**m^2**	NA	112	107	219	0.378
Walls and wallcoverings	**m^2**	NA	235	270	505	0.872
Interior wallboard paint[2]	**m^2**	NA	347	377	724	1.250
Ceiling/Floor Thermal Insulation	**m^2**	NA	102	109	211[2]	0.364
Wall Thermal Insulation	**m^2**	NA	68.1	71.1	139	0.240
Thermal insulation[3]	**m^2**	NA	170	180	350	0.605
Ceiling/Floor Acoustic Insulation	**m^2**	NA	0	85.1	85.1	0.147
Wall Acoustic Insulation	**m^2**	NA	105	149	254	0.439
Acoustic insulation (comprehensive acoustic upgrade)[4]	**m^2**	NA	105	234	339	0.586
Windows[5]	**m^2**	19	19.9	12.6	32.5	0.056

Table B.2 Continued on Next Page

Table B.2 Continued

		CAD2 Home (Volume = 579 m³)				
Product Type	Area Unit[1]	Quantity[1]	1st Floor Area	2nd Floor Area	Total Area	L (m^2 m^{-3})
Exterior doors[6]	m^2	4 (4/0)	7.6	0	7.6	0.013
Interior doors[7]	m^2	12 (6/6)	12.2	15.7	27.9	0.048
Closet doors[7]	m^2	6 (2/4)	14.8	24.8	39.6	0.068

1. Material areas or quantities are taken from the Buildings Energy Data Book (U.S. DOE, 2008) accessible at http://buildingsdatabook.eren.doe.gov/.

2. The value is calculated as sum of ceiling and wall area.

3. The sum of ceiling/floor and wall thermal insulations.

4. For optional comprehensive acoustic upgrade only. The value is calculated as sum of insulation required for partition walls and floors.

5. The surface area is estimated for a window-to-floor area ratio of 18%, assuming the total window area is three times of the operable window area and using the measured media operable window area/floor area of 0.06 taken from the recent CA home study (Offerman, 2009).

6. The surface area is estimated for interior surface only exposed.

7. The surface area is estimated for both faces exposed.

Table B.3
Area and Volume of Single-Family Residential Model

First Floor						
Room	Dimensions (m)	Dimensions	Area (m^2)	Area (ft^2)	Volume (m^3)	Volume (ft^3)
Garage	6.5 x 6.4	21’-4’’ x 21’-0’’	41.62	448	114.17	4032
Kitchen	6.0 x 3.1	19’-8’’ x 10’-3’’	18.73	201.58	51.37	1814.22
Pantry	2.9 x 3.7	9’-6’’ x 12’-1’’	10.66	114.79	29.25	1033.11
Hallway	0.91 x 2.6	3’-0’’ x 8’-5’’	2.35	25.25	6.44	227.25
Laundry Closet	2.0 x 0.89	6’-6’’ x 2’-11’’	1.76	18.96	4.83	170.64
Laundry	2.0 x 1.5	6’-6’’ x 4’-10’’	2.92	31.41	8.00	282.69
Bath	1.7 x 1.7	5’-6’’ x 5’-6’’	2.81	30.25	7.71	272.25
Dining	4.2 x 3.4	13’-8’’ x 11’-0’	13.97	150.33	38.31	1352.97
Living	6.5 x 9.1	21’-4’’ x 30’-0’’	59.46	640	163.11	5760
Second Floor						
Room	Dimensions (m)	Dimensions	Area (m^2)	Area (ft^2)	Volume (m^3)	Volume (ft^3)
Master Bedroom	4.7 x 3.4	15’-6’’ x 11’-1’’	15.96	171.79	38.92	1374.32
Master Bath Hall	0.91 x 2.3	3’-0’’ x 7’-8’’	2.14	23	5.21	184
Master Toilet Room	0.91 x 1.7	3’-0’’ x 5’-6’’	1.53	16.5	3.74	132
Master Closet	1.0 x 2.1	3’-5’’ x 6’-11’’	2.19	23.63	5.35	189.04
Master Bath Shower	0.91 x 0.91	3’-0’’ x 3’-0’’	0.84	9	2.04	72
Master Bath	2.4 x 3.5	8’-0’’ x 11’-4’’	8.42	90.67	20.54	725.36
Second Floor Hall	3.8 x 2.4	12’-6’’ x 8’-0’’	9.29	100	22.65	800

Table B.3 Continued on Next Page

Table B.3 Continued

Second Floor Bath	1.5 x 2.4	5'-0'' x 8'-0''	3.72	40	9.06	320
Bedroom 2	5.9 x 3.0	19'-6'' x 10'-0''	18.12	195	44.17	1560
Bedroom 2 Closet	2.0 x 1.2	6'8'' x 3'-10''	2.37	25.56	5.79	204.48
Bedroom 3	4.8 x 3.5	15'-8''x 11'-4''	16.49	177.56	40.22	1420.48
Bedroom 3 Closet	2.0 x 1.2	6'8'' x 3'-10''	2.37	25.56	5.79	204.48
Bedroom 4	3.4 x 3.5	11'-0' x 11'-4''	11.58	124.67	28.24	997.36
Bedroom 4 Closet	0.66 x 2.1	2'-2'' x 7'-0''	1.41	15.17	3.44	121.36

Figure B.1
First Floor Floor-Plan for the CAD2 15% Window Ratio Single Family Residential Model

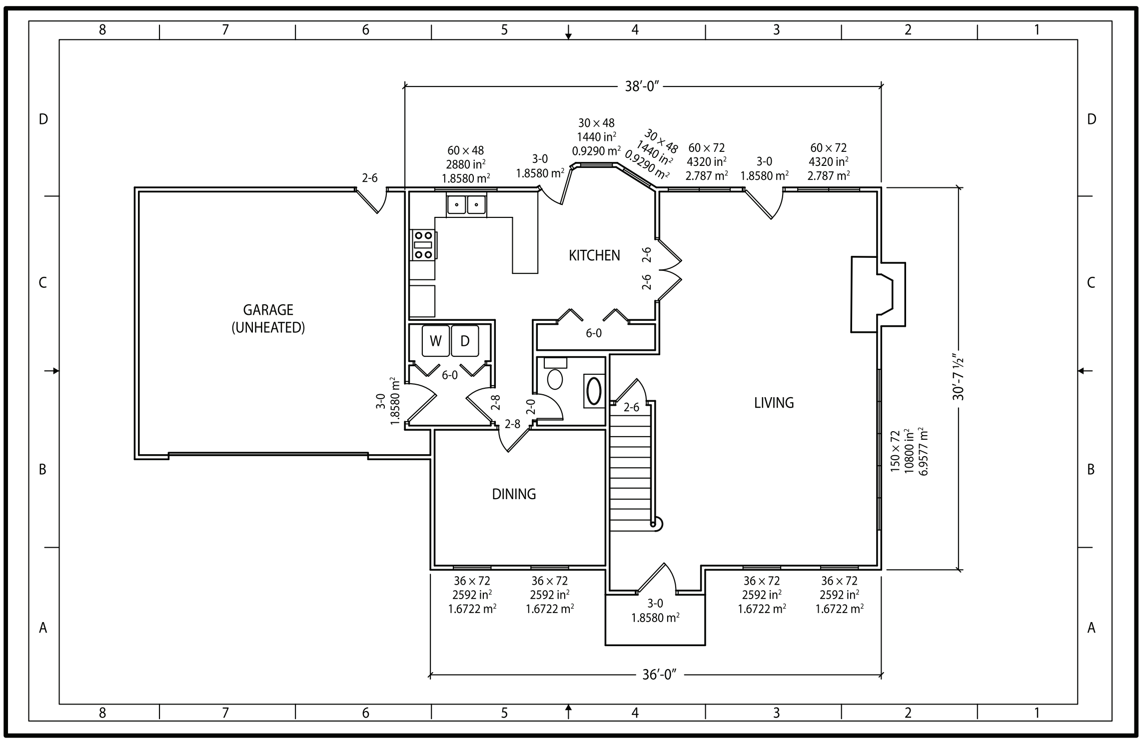

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Figure B.2
Second Floor Floor-Plan for the CAD2 15% Window Ratio Single Family Residential Model

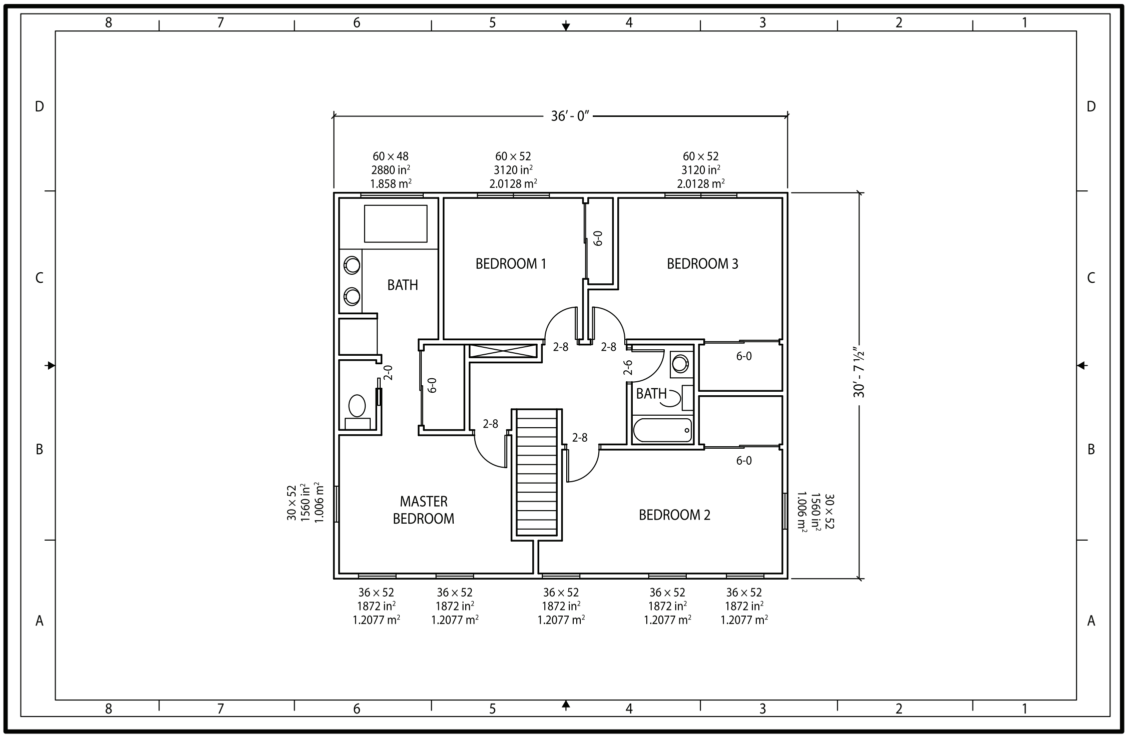

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Figure B.3
First Floor Room Dimensions for the CAD2 15% Window Ratio Single Family Residential Model

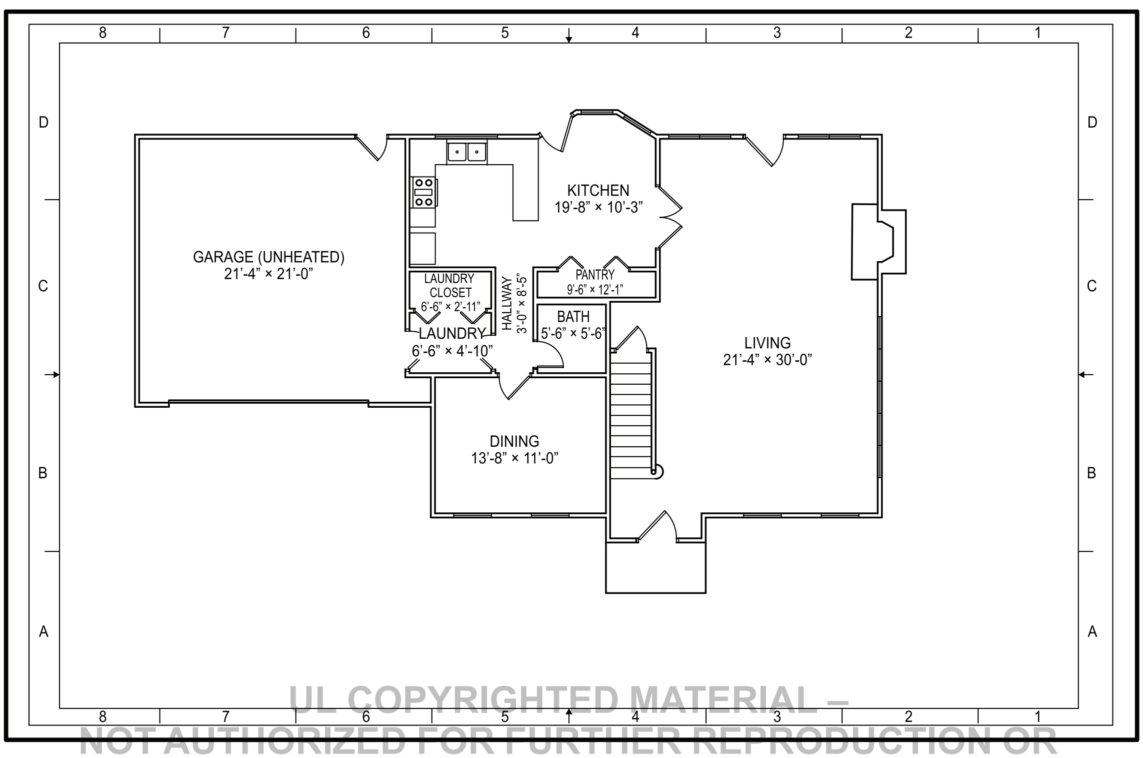

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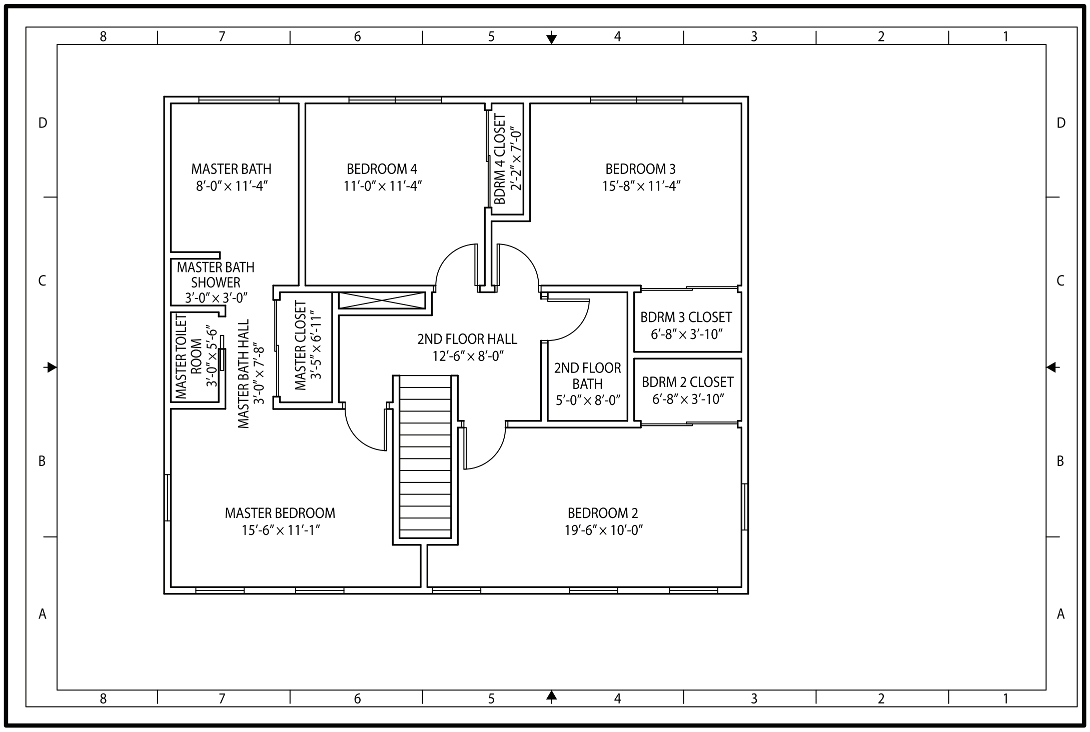
Figure B.4
Second Floor Room Dimensions for the CAD2 15% Window Ratio Single Family Residential Model



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Appendix C – References and Documents

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ASTM D6196-15, Standard Practice for Selection of Sorbents, Sampling, and Thermal Desorption Analysis Procedures for Volatile Organic Compounds in Air

ASTM D6345-10, Standard Guide for Selection of Methods for Active, Integrative Sampling of Volatile Organic Compounds in Air

ASTM D5197-16, Standard Test Method for Determination of Formaldehyde and Other Carbonyl Compounds in Air (Active Sampler Methodology)

ASTM D7339-18, Standard Test Method for Determination of Volatile Organic Compounds Emitted from Carpet using a Specific Sorbent Tube and Thermal Desorption / Gas Chromatography

ASTM E741-11, Standard Test Method for Determining Air Change in a Single Zone by Means of a Tracer Gas Dilution

ASHRAE 189.1, Standard for the Design of High-Performance Green Buildings

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ASHRAE 62.2, Ventilation and Acceptable Indoor Air Quality in Low-Rise Residential Buildings

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EPA Method TO-17: Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling onto Sorbent Tube.

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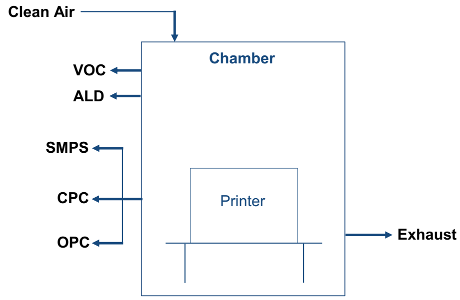
Appendix D – Examples

D.1 An Example of Chamber Setup



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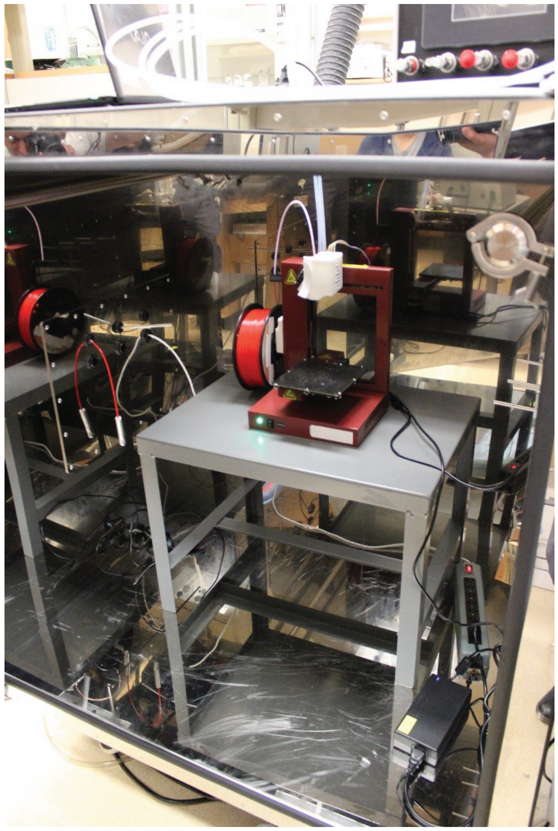
D.2 An Example of the Inside of a Test Chamber



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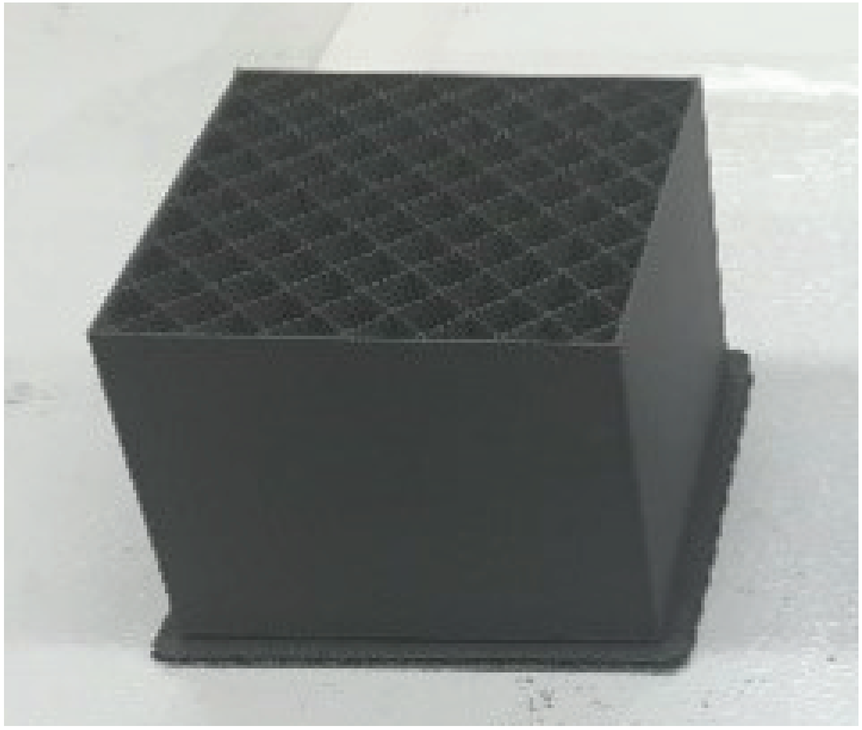
D.3 Template for a Print Object (https://www.thingiverse.com/thing:477)



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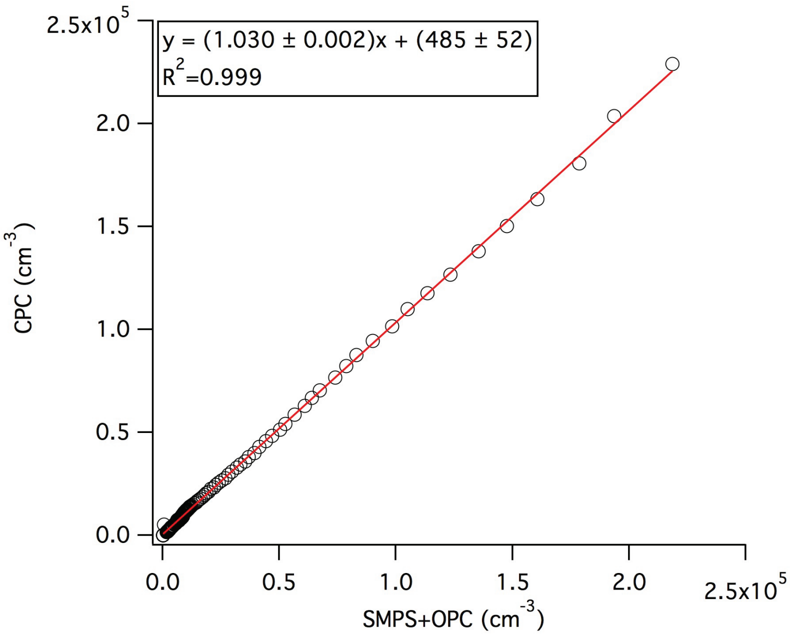
40mmcube.stl

D.4 Correlation between Aerosol Measurement Instruments

Consistency between different aerosol measurement instruments must be proven. An example (Figure D.4) checks for accurately measuring particle count with various combination of aerosol instruments. Total particle number concentration from CPC is compared against that from scanning mobility particle sizer (SMPS) and OPC combined. The measured particle size range for SMPS is 7 nm to 300 nm (103 channels), and that for OPC is 300 nm to 25 µm (6 channels), therefore integrating SMPS and OPC data covers the size range between 10 nm and 5 µm (the required size range in this standard). In this example, the 3D printer emitted particles were found to be generally smaller than 3 µm, thus the CPC data and SMPS and OPC combined data are comparable.

Figure D.4
An Example of Comparing Particle Number Counts from Different Aerosol Measurement Instruments



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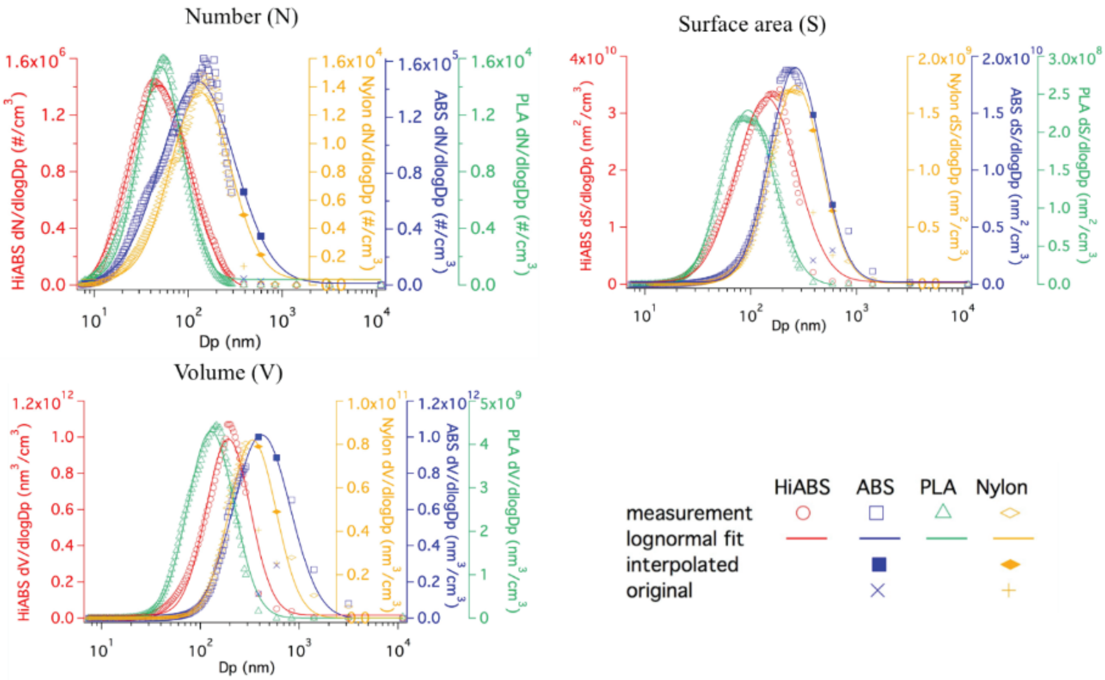
Size resolved particle measurements must also be correlated. If the particle distribution is not smooth, the data may require interpolation. Particle size distribution is assumed to have a lognormal distribution (as observed in the examples, Figure D.5). If the particle data from different instruments overlap in size ranges and/or fall under uncertain range on the instrument, the data points that fit closer along the lognormal distribution should be accepted for the particle data analysis, and those that do not fit along the lognormal distribution should be omitted.

Otherwise if a data merging software is available/applicable, a software provided by the aerosol instrument manufacture can be used to deal with overlapped data points.

Example
In below figures (Figure D.5), each particle size distribution is combined using SMPS and OPC number distribution data. Since the measurement of the lower two channels of the OPC used was not accurate due to large measurement noise, those data points (blue X and yellow +) are removed and replaced with the values intersecting the lognormal fit interpolated over the entire data set (blue solid square and yellow solid diamond).

Figure D.5
An Example of Particle Concentration Distributions



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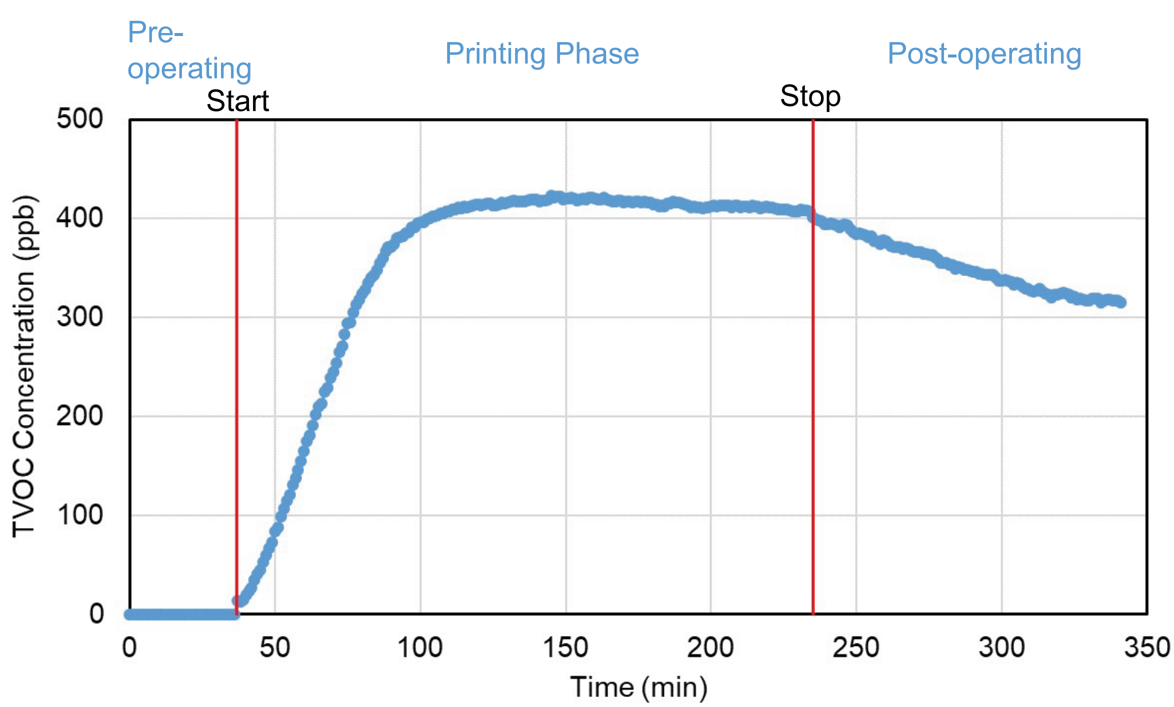
Appendix E – Technical Information on Measurement Instrumentations

E.1 Real Time TVOC

It is suggested to continuously monitor the real-time speciated VOC and TVOC concentrations inside the environmental chamber during the experiments using an advanced VOC monitor that uses photoionization detector (PID) or flame ionization detector (FID) and have built-in correction factors for several (i.e. not necessary all) target VOCs listed in Appendix A with detection limit of one parts-per-billion (ppb) and response time of less than one minute. Monitoring the real-time speciated VOC and TVOC concentrations have several advantages. First, it would verify if the VOC concentrations achieve approximately steady state by the time air sampling for VOC analysis is conducted. In a case that the VOC concentrations do not achieve approximately steady state, it is suggested to adjust (reduce in most of the cases) the air exchange rate of the emission test chamber within the recommended ranges in Section 8.2. The other advantage of real-time VOC monitoring is to be able to observe the real-time changes in speciated VOC and TVOC concentrations during the printing phase and potentially roughly estimate the speciated VOC emission rates if they are varied. Figure E.1 shows an example of TVOC concentration as a function of time.

Figure E.1
Example of TVOC Concentration as a Function of Time



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Start and stop marks the times the printing started and ended. The time before start is the pre-operating phase, time between start and stop is the printing phase, and time after stop is the post-operating phase.

E.2 Aerosol Instruments

Particle size range

The lower detection limit of the particle size is the smallest particle diameter where the counting efficiency of an aerosol measurement device is at least 50%.

The corresponding upper detection limit is the largest particle diameter, where the counting efficiency of an aerosol measurement device is at 50%.

Particle number concentration range

The lower detection limit of the particle number concentration is the concentration which can be distinguished from the measured background concentration with a statistical probability of 95% (due to the device-specific error-count rate). The error count rate (usually below 0.1 cm^{-3} for CPC) is a count rate which is not caused by particles.

Dilution step

A measurements is limited by the lowest concentration limit of the instrument used. See the manufacturer's manual for precise information.

For CPCs, the upper particle number concentration detection limit – usually in the order of 10^7 cm^{-3} – must not be exceeded. It may be necessary to use a calibrated aerosol dilution stage with a specified dilution factor to cover very high particle number concentrations.

When a dilution step is used, $C_P(t)$ must be corrected accordingly by the dilution factor. The corrected data set and/or file with the corrected values should be clearly labelled. The corrected data set in this case is the basis for the subsequent calculation.

Readiness of aerosol measurement instruments

This appendix describes the mandatory measures to ensure the readiness of aerosol measurement instruments. The measures described should be performed in addition to periodic maintenance.

Instrument set up

The following steps should be executed in sequence:

1. After the aerosol measurement instrument and the connecting hoses are checked for cleanliness, the instrument is switched on and warmed-up.

2. Instrumental operating parameters (e.g., temperature, pressure, fullness of the reservoir of the CPC) are checked according to the manufacturer's instructions.

3. The sampling flow rate of the aerosol measurement instrument is checked. An internal flow meter should preferably be used for this. Otherwise, an externally calibrated flow meter must be used. The measured flow rate of the aerosol measurement instrument must not deviate by more than ± 10% of the specified set point in the calibration certificate.

4. A zero check is performed with the inlet of the aerosol measurement instrument connected to a HEPA filter (filter efficiency ≥ 99.99%) according to the manufacturer's instructions. For CPC, if particle number concentrations are > 1 cm^{-3} over a period of 1 min (after any leaks between the HEPA filter and aerosol inlet were eliminated), there is a malfunction in the CPC.

5. The particle number concentration in ambient air outside the test chamber is measured. Readings should exceed 1 cm^{-3}. Aerosol sources with sufficiently high output may be used for this test. A zero readout indicates a malfunction of the aerosol measurement instrument.

6. The aerosol measurement instrument is connected to the sampling port of the emission test chamber via a conductive material (e.g. conductive silicone or stainless steel tube); the connection is as straight as possible with a maximum length of 3 m.

7. Time and date of the aerosol measurement instrument, software and laboratory clock are synchronized.

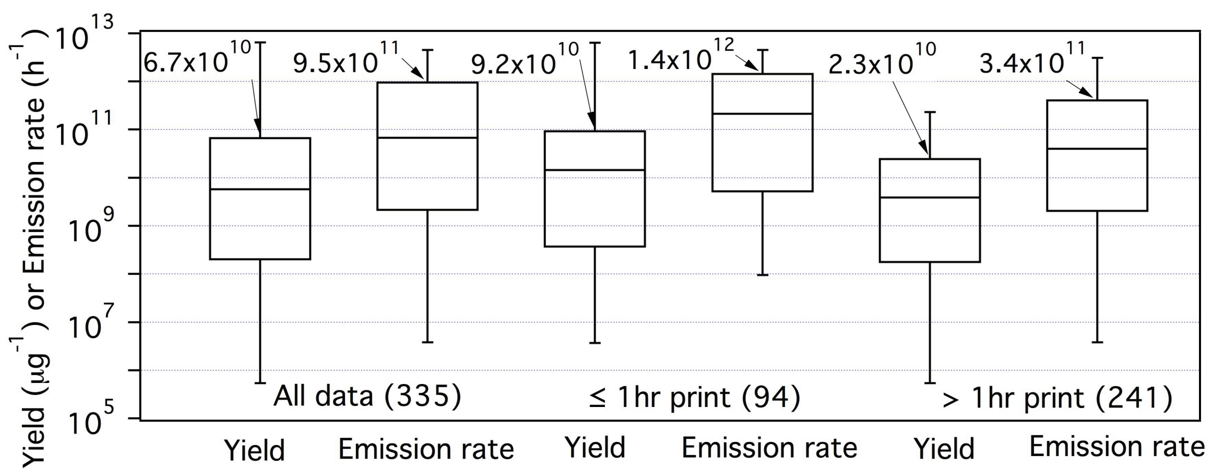
8. The particle background concentration in the emission test chamber is measured. The background concentration shall not exceed the specified values under 8.2.

9. The correct function of the measuring instrument will be certified in the test report.

Appendix F – Rationale for the Particle Criteria

The recommended performance-based criterion is developed from the Georgia Tech research measurement database. The criteria development is similar to the process taken to determine particle criteria for laser printers under RAL-UZ 205. As shown in the figure below, there were 335 experimental tests including various 3D printer brands, filament materials, brands and print conditions that were randomly chosen from what is available in the market at the time. A majority of the tests were obtained with ABS and PLA materials. The total particle emissions during printing are normalized to either mass of filament used (i.e., yield) or print time (i.e., emission rate). Research found that a print time less than 1 hour gives a higher yield or emission rate, due to the emissions being dominated by the initial peak in concentration through the process of new particle formation without preexisting particle present. In order to not bias the results and given that 3D printing normally last several hours, the criteria were set using the data with print times of 1 hour or longer. This includes 241 print runs as shown in the right two box plots in Figure F.1. Regarding the values for the recommended criteria, the data were sorted from the smallest to the highest and the 80 percentiles were selected as the criteria. This means that if emissions are higher than 80% of the dataset, it will be considered unacceptable.

Figure F.1
Particle Emission Rate and Yield Obtained from Georgia Tech Research



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Note, the lines in the boxes indicate the medians; the top and bottom of the boxes indicate the 80% and 20% quartiles; the top and bottom of whiskers indicate the maximum and minimum values, the 80 percentile values are shown on the graph.

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