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Survey and Risk Assessment of 3D Pens

Survey of chemical substances in consumer products No. 173

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Editors: Danish Technological Institute
Sie Woldum Tordrup
Eva Jacobsen
Jeanette Schjøth-Eskesen
Christina Østerballe Pedersen

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Preface

The project ”Survey and Risk Assessment of 3D Pens” was carried out from April 2017 till November 2017.

Over the past years, several variations of handheld material extruders (3D pens) that can be used to create 3D objects have been sold to adults and children through Danish supliers. The Danish Environmental Protection Agency (the Danish EPA) wants to acquire greater knowledge of the content of chemical substances in 3D pens and accompanying material to assess if they pose a health risk for children.

The project forms part of the Danish Environmental Protection Agency’s program regarding surveys of chemical substances in consumer products and has been carried out by Danish Technological Institute (DTI) for the Danish Environmental Protection Agency.

The project was carried out by the following participants:

- Sie Woldum Tordrup, Project Manager, Danish Technological Institute
- Jeanette Schjøth-Eskesen, Danish Technological Institute
- Eva Jacobsen, Danish Technological Institute
- Christina Østerballe Pedersen, Danish Technological Institute
- Grete Lottrup Lotus, the Danish Environmental Protection Agency
- Shima Dobel, the Danish Environmental Protection Agency

The project was funded by the Danish Environmental Protection Agency.

Summary and conclusion

Survey and risk assessment of 3D pens for children

Background
3D pens are small handheld material extruders that can be used to make 3D objects. Today, several types of the 3D pens are sold by Danish supplies and the market is estimated to increase. At the same time, 3D pens are becoming even more user-friendly, and some types are designed to be used by children. Many of the 3D pens on the market today are based on well-known 3D printing techniques, but the chemical composition of the materials used for 3D pens has not previously been investigated. Therefore, the Danish EPA wants to acquire greater knowledge of the chemical substances in the materials for 3D pens in order to assess if the substances pose a health risk for children.

Objective
The objective of the project was to acquire greater knowledge of the specific chemical substances in the materials used for 3D pens; how children can expect to be exposed to the substances when using a 3D pen; and, if selected substances pose a health risk.

The project
In the project, a survey was carried out of the 3D pens for children that are available on the Danish market, and then selected 3D pens were purchased and analysed for content of chemical substances. On the basis of the analytical results, four substances were chosen. They have been assessed in relation to the health risk for children when they use 3D pens.

Survey
The survey was carried out mainly by searching for information about 3D pens via the websites of the distributors and manufacturers supplemented with a few inquiries to distributors and a single shop visit.

Under Danish domains (.dk) nine different 3D pens were identified on 12 different webshops that mainly comprise gadget and toy dealers. The marketed 3D pens use three techniques:
- The material cures with UV lighting
- The material hardens when the temperature is reduced
- The material hardens in the course of time

The two first techniques can be compared to well-known techniques within 3D printing: Stereolithography (SLA, UV curing) and Fused Deposition Modeling (FDM, temperature-dependent hardening). Some of the types of material used in 3D pens are based on polymer materials of the same type as used for 3D printing (ABS, PLA, UV reactive resins). Within 3D printing, there is no parallel to the third type of 3D pen where hardening takes place over time without any external stimulants. For that type, the texture of the accompanying material resembles play dough, but it has not been possible to identify the exact chemical composition of the material in connection with this survey.

Recommendations to the age group for using 3D pens varies from 5-18 years. Based on the limited data, there is no connection between the recommended age group and the hardening technique.

Play involving 3D pens is to a high degree expected to centre on the production process. The children sit alone and work with the 3D pens. They can come into direct contact with the un-

hardened material (when the material is placed in the 3D pen), and with the partly unhardened material after extrusion from the 3D pen. Unhardened materials are expected to contain reactive monomers (in the case of UV curing materials) or semifluid polymers (in the case of temperature-hardening materials), when the material comes out of the 3D pen.

The material is often workable when it comes out of the 3D pen, and it is possible to shape the material with the fingers. That gives direct skin contact with the material. For the temperature-hardening polymers that means that there is contact with the heated polymer material where migration is higher than at room temperature. For the UV reactive materials that means that there is contact with a material that is not completely polymerised, and therefore it can still contain reactive components.

Considerations about exposure

When using 3D pens, children can be exposed to chemical substances that potentially can be released from the material that is used in the 3D pen. For 3D pens it is expected that the production process itself will result in greater exposure than the subsequent use of the object that is created.

Children's exposure to chemical substances when using 3D pens will, i.a., depend on the materials, the chemical constituents and the design of the specific 3D pen. Exposure can potentially occur as skin contact (dermal) with the unhardened material before and after extrusion through the 3D pen, during intake (oral) of the material through hand-to- mouth transfer, by inhalation of volatile, chemical substances or of particles that are emitted to the air during use or in a combination of the above. The survey indicates that the target group is children from 5 years, and therefore direct oral intake is expected to constitute a less probable route of exposure. That is why focus is on children's exposure to chemical substances through skin contact and inhalation.

Analyses

Only content analyses were carried out on the selected materials. The materials are half-liquid and unhardened in the condition they have when children are exposed to them. Therefore, it is regarded as most relevant to carry out content analyses and to base the assessment of exposure and risk on those results.

Analyses were carried out on eight 3D pens with 12 accompanying materials that comprise UV reactive resins, ABS plastic, PLA plastic, Eco-Plastic and a material with a play dough-like texture. The analyses were carried out after the material had been extruded through the respective 3D pens.

Analyses were carried out for 15 metals/elements and a content of chromium, manganese, nickel, copper, zinc, strontium, molybdenum, tin, antimony and lead was detected. A content of cobalt, arsenic, selenium, cadmium or mercury was not detected. There is no clear tendency between the detected metals and the colour of the materials except for a high content of copper in the blue colour and in some of the dark colours. Based on the content analyses of metals and compared with the limit values for migration from toys, there might be a risk that they are exceeded for chromium and tin. However, that presupposes that the substances in question are hexavalent chromium and organic tin and that the substances migrate out of the materials. All in all, it is not regarded as probable that these conditions will be fulfilled, and it was chosen not to carry out further analyses of the metals.

The GC-MS screening analysis of the materials indicates a content of a wide range of chemical substances. The analysis identified the lowest number of substances for 3D pens that use a material with a play dough-like texture, PLA plastic or Eco-Plastic. They are succeeded by ABS plastic, whereas UV reactive resins contain the highest number of substances. There are

similarities between the results of the screening analyses and the results reported in the previous survey of 3D printed products for the Danish EPA, but there are also differences. In connection with 3D printed products, it was also the UV reactive resins that contained the highest number of different substances.

Quantitative analyses were carried out on 16 selected substances with various specific analytical methods. The substances were selected with a background in the classification of the substances. 10 of the selected substances were detected in the analysed samples, whereas six substances were not detected at a level above the detection limit of the methods (five isocyanates and bis(2-ethylhexyl) isophthalate). The table below shows the results that exceeded the detection limits of the methods.

Substance	CAS no.	Sample no., colour	Material type	Result
Acrylic acid	79-10-7	1, black 3, blue	UV resin	0.15 g/kg 0.31 g/kg
Methyl methacrylate	80-62-6	1, black 3, blue	UV resin	0.32 g/kg 0.29 g/kg
Methacrylic acid	79-41-4	3, blue	UV resin	0.34 g/kg
n-Butyl acrylate	141-32-2	3, blue	UV resin	120 g/kg
n-Butyl methacrylate	97-88-1	1, black 3, blue	UV resin	66 g/kg 20 g/kg
Pentaerythritol triacrylate	3524-68-3	1, black 3, blue	UV resin	>730* g/kg >250* g/kg
Toluene-2,6-diisocyanate	91-08-7	8, purple	UV resin	0.51 mg/kg
Benzyl chloride	100-44-7	3, blue	UV resin	330 mg/kg
Styrene	100-42-5	6, yellow	ABS plastic	1100 mg/kg
Vanillin	121-33-5	9, pink	Play dough-like	59 mg/kg

* It was not possible to obtain information about the purity of the reference material, which is a technical product. The purity of the technical product is assessed to be min. 50%, and the result was reported on the basis of this purity.

Styrene is hazardous when inhaled, and due to the high content in ABS plastic and the ascertained malodour when using the 3D pen, a headspace analysis was carried out of styrene. On the basis of the headspace analysis it is estimated that app. 10-20% of the total content of styrene in the material is emitted to the surrounding air.

Hazard and risk assessment

The ten substances that were detected above the detection limit of the analytical method were reviewed in relation to the toxicological effects by the DNEL reported by notifiers of the substances under REACH. Four of the substances were selected for hazard and risk assessment:

- Acrylic acid
- n-Butyl methacrylate
- Styrene
- Vanillin

The four substances were selected according to an initial assessment based on the determined threshold values of the substances and the calculation of the exposure level carried out on an exposure scenario for a 6-year-old child. Under the conditions used, acrylic acid, n-butyl methacrylate and styrene were the three substances that showed the highest risk (high RCR values), and they are therefore discussed in detail in the final part of the report.

In this connection, vanillin is an exception, because no DNEL value is reported in the REACH registration, but the substance is a known allergen. However, no data is available about the

specific threshold values regarding the health effect of vanillin. Therefore, the analysis results were compared to the general threshold value stated by the EU Scientific Committee on Consumer Safety (SCCS) for allergenic substances. This comparison shows that dermal exposure was exceeded considerably under the applied conditions. Therefore, the substance is included in the further discussions in this report.

Conclusion and future implications

The survey and analysis of selected materials for 3D pens has provided more knowledge of the techniques used in 3D pens, of the specific use situation and of the chemical content of the materials used. Based on the results of the screening analyses of the materials used in 3D pens as well as the knowledge of possible constituents, it was chosen to perform quantitative analyses of the content of 16 selected substances. In the tested materials, ten of the substances were detected above the detection limit of the method. Acrylic acid, styrene, n-butyl methacrylate and vanillin were subsequently selected for assessment of the health risk of the product during use.

Based on the developed and refined exposure scenarios, it is estimated that styrene is not expected to pose a risk. For acrylic acid and n-butyl methacrylate, the risk calculations indicate that it cannot be ruled out that the threshold values might be exceeded. However, at the same time the properties of the substances and the assumption of full migration mean that the calculation is likely to overestimate the risk. It has not been possible to verify the risk in this project due to lack of data. For vanillin, dermal exposure is above the general threshold value set by SCCS if full migration is assumed from the entire amount expected to come into contact with the skin. However, it is considered likely that the substance to a certain extent will be retained in the material that has a play dough-like texture. If instead, migration is calculated from a 0.01 cm thick layer in contact with the skin, then dermal exposure will be below the threshold value. Therefore, it is considered likely that vanillin does not pose a health risk in the product in question.

The screening analyses indicated a wide range of possible chemical substances. All of the substances have not been identified or reviewed in detail in this report. A more detailed review of the 151 identified substances as well as follow-up analyses and risk assessments of selected substances could provide increased knowledge of other relevant substances than the 16 selected for analysis in this project. The screening confirmed that the UV reactive materials contained far more different substances than the materials that harden without a light source, e.g., ABS and PLA. Combination effects – also called cocktail effects – that can change the health effects of chemical substances after simultaneous exposure to several different chemical substances, have not been discussed in this report.

This project focuses on exposure to the chemical substances. In previous reports on 3D printing, the problem related to particle generation connected with printing was elucidated. It has not been investigated whether particle generation also could pose a health risk when children use 3D pens. Likewise, no emission measurements were carried out on volatile substances in climate chambers or in use situations. They could give a more realistic picture of the exposure and provide increased knowledge of, for example, concentration levels in the immediate proximity of children during use.

Sammenfatning og konklusion

Kortlægning og risikovurdering af 3D-penne til børn

Baggrund
3D-penne er små, håndholdte materialeekstruders, der kan anvendes til at skabe 3D-objekter. Flere variationer af 3D-penne sælges i dag af danske forhandlere, og udbuddet vurderes at være stigende. Samtidig udvikles 3D-pennene, så de bliver stadig mere brugervenlige og rettet mod børn. Mange af de 3D-penne, som ses på markedet i dag, er baseret på kendte teknikker inden for 3D-printning, men den kemiske sammensætning af de anvendte materialer til 3D-penne er ikke tidligere undersøgt. Miljøstyrelsen ønsker derfor at få mere viden om indholdet af kemiske stoffer i de anvendte materialer til 3D-penne med henblik på at vurdere, om de kan udgøre en risiko for børns sundhed.

Formål
Projektets formål er at få større viden om de specifikke kemiske stoffer, som indgår i materialer, der anvendes til 3D-penne; hvordan børn kan forventes at blive eksponeret for disse stoffer under brug af 3D-pennen; og om udvalgte stoffer udgør en sundhedsmæssig risiko.

Projektet
I projektet er der gennemført en kortlægning af 3D-penne til børn på det danske marked, hvorefter udvalgte 3D-penne er indkøbt og analyseret for indhold af kemiske stoffer. På baggrund af analyseresultaterne er der udvalgt fire stoffer, som er vurderet i forhold til den sundhedsmæssige risiko for børns anvendelse af produkterne.

Kortlægning
Kortlægningen er gennemført primært ved søgning af information om 3D-penne via forhandleres og producenters hjemmesider suppleret med enkelte henvendelser til forhandlere samt et enkelt butiksbesøg.

Der blev under danske domæner (.dk) identificeret ni forskellige 3D-penne i 12 forskellige webshops, som hovedsagelig dækker gadget- og legetøjsforhandlere. De markedsførte 3D-penne anvender tre teknikker:
- Materialet hærder ved UV-belysning
- Materialet hærder ved reduktion af temperatur
- Materialet hærder over tid.

De to første teknikker anses for sammenlignelige med kendte teknikker inden for 3D-printning; Stereolithography (SLA, UV-hærdning) og Fused Deposition Modeling (FDM, temperature-afhængig hærdning). Materialetyperne anvendt i 3D-penne er for nogle typer baseret på polymermaterialer af samme type, som anvendes til 3D-printning (ABS, PLA, UV-reaktive resiner). Der findes ingen parallel inden for 3D-printning til den tredje type 3D-pen, hvor hærdning sker over tid uden nogen anden ydre stimuli. For denne type minder det anvendte materiales tekstur om modellervoks, men det har ikke været muligt at identificere den nærmere kemiske sammensætning af materialet i forbindelse med kortlægningen.

Anbefalinger til aldersgruppe for anvendelsen af 3D-penne varierer fra 5-18 år. Baseret på det begrænsede datagrundlag ses der ikke nogen sammenhæng mellem anbefalet aldersgruppe og hærdeteknik.

Leg med 3D-penne forventes i høj grad at være centreret om fremstillingsprocessen. Barnet sidder typisk selv og arbejder med 3D-pennen og kan komme i direkte kontakt med uhærdet materiale, når materialet monteres i 3D-pennen, samt med delvist uhærdet materiale efter ekstrudering fra 3D-pennen. Uhærdede materialer forventes at indeholde reaktive monomerer (for UV-hærdende materialer) eller bestå af smeltet polymer (for de temperaturhærdende materialer), når de forlader 3D-pennen.

Ofte er materialerne modellerbare, når de forlader 3D-pennen, og det er muligt at forme materialerne med fingrene, hvilket giver direkte hudkontakt med materialerne. For de temperaturehærdende polymerer betyder dette kontakt med opvarmet polymermateriale, hvor migrationen er højere end ved stuetemperatur. For de UV-reaktive materialer betyder det kontakt med et materiale, som ikke er færdigpolymeriseret, og som derfor stadig kan indeholde reaktive komponenter.

Overvejelser om eksponering
Ved anvendelse af 3D-penne kan børn blive eksponeret for kemiske stoffer, som potentielt kan frigives fra de materialer, der anvendes i 3D-pennen. For 3D-penne forventes det, at selve forarbejdningsprocessen medfører en større eksponering end den efterfølgende brug af det fremstillede objekt.

Børns eksponering for kemiske stoffer under anvendelsen af 3D-penne vil bl.a. afhænge af materialerne, de kemiske indholdsstoffer og designet af den enkelte 3D-pen. Eksponeringen vil potentielt kunne forekomme i forbindelse med hudkontakt (dermalt) med det uhærdede materiale før og efter ekstrudering gennem 3D-pennen, ved indtagelse (oralt) af materiale ved hånd-til-mund-overførsel, gennem indånding (inhalation) af flygtige, kemiske stoffer eller af partikler, som afgives til luften under brug, eller ved en kombination heraf. Da kortlægningen indikerer, at målgruppen er børn fra 5 år og opefter, forventes direkte oralt indtag at udgøre en mindre sandsynlig eksponeringsvej, og der er derfor fokuseret på børns eksponering for kemiske stoffer gennem hudkontakt og ved indånding.

Analyser
Der er udelukkende foretaget indholdsanalyse af de udvalgte materialer. Materialerne er halvflydende og uhærdede i den form, de antager, når barnet eksponeres for dem, derfor anses det som mest relevant at foretage indholdsanalyser og basere vurderingen af eksponering og risiko på disse resultater.

Der er foretaget analyser af otte 3D-penne med tilhørende 12 materialer, som omfatter UV-reaktive resiner, ABS-plast, PLA-plast, Eco-Plastic og et modellervokslignende materiale. Analyserne er foretaget, efter at materialerne har været ekstruderet igennem de tilhørende 3D-penne.

Der blev undersøgt for 15 metaller/grundstoffer og påvist indhold af krom, mangan, nikkel, kobber, zink, strontium, molybdæn, tin, antimon og bly. Der blev ikke påvist indhold af kobolt, arsen, selen, cadmium eller kviksølv. Der ses ingen klar tendens mellem de påviste metaller og materialernes farver udover et højt indhold af kobber i den blå farve og i nogle af de mørkere farver. Baseret på indholdsanalyserne af metaller sammenholdt med grænseværdier for migration fra legetøj kan der være en risiko for, at disse overskrides for krom og tin. Dette forudsætter, at der er tale om hexavalent krom og organisk tin, samt at stofferne migrerer ud af materialerne. Samlet set anses det ikke for sandsynligt, at disse betingelser vil være opfyldt, og det er valgt ikke at foretage yderligere analyser af metallerne.

GC-MS-screeningsanalyse af materialerne indikerer indhold af en lang række kemiske stoffer. Der er ved denne analyse set færrest stoffer for 3D-penne, som anvender modellervokslignende materiale, PLA-plast og Eco-Plastic. Derefter kommer ABS-plast, mens UV-reaktive

resiner indeholder det største antal stoffer. Der er lighedspunkter mellem resultaterne for screeningsanalyserne og resultater, som er rapporteret i en tidligere kortlægning af 3D-printede produkter for Miljøstyrelsen, men der ses også forskelle. Ved 3D-printede produkter var det ligeledes UV-reaktive resiner, som indeholdt flest forskellige stoffer.

Der er foretaget kvantitative analyser for 16 udvalgte stoffer ved forskellige specifikke analysemetoder. Stofferne er udvalgt bl.a. med baggrund i stoffernes klassificering. Ti af de udvalgte stoffer blev påvist i de analyserede prøver, mens seks stoffer ikke blev påvist over metodernes detektionsgrænser (fem isocyanater samt bis(2-ethylhexyl) isoftalat). I tabellen nedenfor ses en oversigt over de resultater, som lå over metodernes detektionsgrænser.

Stof	CAS-nr.	Prøvenr., farve	Materialetype	Resultat
Acrylsyre	79-10-7	1, sort 3, blå	UV-resin	150 mg/kg 310 mg/kg
Methylmetacrylat	80-62-6	1, sort 3, blå	UV-resin	320 mg/kg 290 mg/kg
Methacrylsyre	79-41-4	3, blå	UV-resin	340 mg/kg
n-Butylacrylat	141-32-2	3, blå	UV-resin	120.000 mg/kg
n-Butylmethacrylat	97-88-1	1, sort 3, blå	UV-resin	66.000 mg/kg 20.000 mg/kg
Pentaerythritol-triacrylat	3524-68-3	1, sort 3, blå	UV-resin	>730.000* mg/kg >250.000* mg/kg
Toluen-2,6-diisocyanat	91-08-7	8, lilla	UV-resin	0,51 mg/kg
Benzylchlorid	100-44-7	3, blå	UV-resin	330 mg/kg
Styren	100-42-5	6, gul	ABS-plast	1100 mg/kg
Vanillin	121-33-5	9, lyserød	Modellervoks-lignende	59 mg/kg

* Det har ikke været muligt at få oplyst renheden for referencematerialet, som er en teknisk vare. Renheden af den tekniske vare estimeres til min. 50 %, og det er ud fra denne renhed, resultatet er afrapporteret.

Styren er farlig ved indånding, og pga. det høje indhold i ABS-plast, og da der blev registreret en ubehagelig lugt ved brug af 3D-pennen, blev der foretaget headspaceanalyse af styren, hvor ca. 10-20 % af det totale indhold af styren i materialet ses afgivet til den omkringliggende luft.

Fare og risikovurdering

De ti stoffer, som er påvist over analysemetodens detektionsgrænse, er gennemgået i forhold til stoffernes toksikologiske effekter. angivet med DNEL af registranter af stofferne under REACH. Fire stoffer blev udvalgt til fare- og risikovurdering:

- Acrylsyre
- n-Butylmethacrylat
- Styren
- Vanillin.

De fire stoffer er valgt på baggrund af en indledende vurdering baseret på fastsatte tærskelværdier for stofferne og en beregning af eksponeringsniveaet foretaget på et eksponeringsscenarie for et 6-årigt barn. Under de forudsætninger, som er anvendt, angiver beregningen en lav risiko ved anvendelse. Acrylsyre, n-butylmethacrylat og styren var de tre stoffer, som viste den højeste risiko (høje RCR-værdier) under de indledningsvis anvendte forudsætninger, og de er derfor behandlet mere detaljeret i den sidste del af rapporten. For vanillin findes ikke en tærskelværdi under REACH-registreringen, men stoffet er et kendt allergen. Der findes dog

ingen tilgængelig viden om specifikke tærskelværdier for den sundhedsmæssige effekt af vanillin, hvorfor resultater er sammenlignet med den generelle tærskelværdi angivet af EU's Videnskabelige Komite for Forbrugersikkerhed (Scientific Committee on Consumer Safety – SCCS) for allergene stoffer. Denne sammenligning viser, at den dermale eksponering er over den generelle tærskelværdi under de anvendte forudsætninger. Stoffet medtages derfor til videre diskussion i rapporten.

Konklusion og perspektivering

Kortlægning og analyse af udvalgte materialer til 3D-penne har givet øget viden om teknikkerne anvendt i 3D-penne, viden om den konkrete brugssituation og viden om de anvendte materialers kemiske indhold. Med udgangspunkt i resultater af screeningsanalyser af materialer anvendt i 3D-penne og kendskab til mulige indholdsstoffer blev det valgt at udføre kvantitative analyser af indhold af 16 udvalgte stoffer. Ti af stofferne blev påvist i de undersøgte materialer over metodens detektionsgrænse. Acrylsyre, styren, n-butylmethacrylat og vanillin blev herefter udvalgt til vurdering af den sundhedsmæssige risiko ved anvendelse af produktet.

Baseret på de opstillede og forfinede eksponeringsscenarier vurderes det, at styren ikke kan forventes at udgøre en risiko. For acrylsyre og n-butylmethacrylat indikerer risikoberegningerne, at det ikke kan afvises, at tærskelværdierne overskrides, men samtidig betyder stoffernes egenskaber og antagelsen om fuld migration, at beregningen sandsynligvis overestimerer risikoen. Det har ikke været muligt at verificere risikoen i nærværende projekt pga. manglende data. For vanillin ligger den dermale eksponering over den generelle tærskelværdi angivet af SCCS, hvis der antages fuld migration fra hele den mængde, der forventes at komme i kontakt med huden. Det anses dog for sandsynligt, at stoffet til en vis grad tilbageholdes i det materiale, som har en modellervokslignende tekstur. Hvis der i stedet beregnes på migration fra et 0,01 cm tykt lag i kontakt med huden, vil den dermale eksponering falde til under tærskelværdien, hvorfor det anses for sandsynligt, at også vanillin kan anses for ikke at udgøre en sundhedsmæssig risiko i det pågældende produkt.

Screeningsanalyserne pegede på en lang række af mulige kemiske stoffer, hvoraf ikke alle kunne identificeres og gennemgås i detaljer i dette projekt. En detaljeret gennemgang af de 151 identificerede stoffer samt opfølgende analyser og risikovurdering af udvalgte stoffer kunne give øget viden om andre relevante stoffer end de 16, der er udvalgt til analyse i dette projekt. Screeningen bekræftede, at der i de UV-reaktive materialer var langt flere forskellige stoffer end i de materialer, der hærder uden lyskilde, fx ABS og PLA. Kombinationseffekter, også kaldet cocktaileffekter, som kan ændre de sundhedsmæssige effekter af kemiske stoffer, når man eksponeres for dem på samme tid, er ikke behandlet i denne rapport.

Der er i dette projekt fokuseret på eksponering for de kemiske stoffer. I tidligere rapporter om 3D-printning er problemstillingen omkring dannelsen af partikler i forbindelse med printningen belyst. Det er ikke undersøgt, om partikeldannelse også kunne udgøre et sundhedsmæssigt problem under børns anvendelsen af 3D-penne. Der er ligeledes ikke foretaget emissionsmålinger på flygtige stoffer i klimakamre eller i brugssituationer, hvilket kunne give et mere realistisk billede af eksponeringen og give øget viden om fx koncentrationsniveauer i børns umiddelbare nærhed under anvendelse.

1. Introduction

1.1 Background

Several types of handheld material extruders can be used to create 3D objects. The products are sold as 3D pens, 3D fibre-tip pens, styling pistols etc., but in this report, they are jointly called 3D pens. Some types of 3D pens are spin-offs from 3D printers where the 3D printing techniques are used in small handheld units. The 3D pen can be used to make creative 3D objects within a few minutes, and previous technical knowledge, use of software or a computer are not needed. Compared to ordinary 3D printers, 3D pens are compact and easy to use, and a wide range of the products are also marketed to children and sold as toys for children.

During recent years, several variations of the 3D pen have been sold to children as well as adults by Danish distributors, often on the internet, and supplies are assessed to be on the increase. At the same time, the 3D pens are becoming even more user- friendly, and they are targeted at children.

Many of the 3D pens that are on the market today are based on two well-known techniques within 3D printing: Fused Deposition Modeling (FDM) and stereolithography (SLA).

Fused Deposition Modeling (FDM) is a process that is used by many desktop 3D printers. The technique is also used to create figures in several dimensions by means of handheld units such as 3D pens. The materials used for this technique come within the category of thermo-plastic polymers. The polymer chains have already in advance been created in the material and they are not degraded when heated. The applied materials are fed through a heated nozzle where the plastic melts so it can be extruded in liquid form. Afterwards, the material rapidly hardens at room temperature.

Stereolithography (SLA) is also known from 3D printers. The technique uses liquid polymers that cure when they are exposed to UV light. In 3D pens based on this technique, the liquid resin is ejected through a nozzle and it cures by means of a light source fixed to the tip of the pen. In this technique, the polymer itself is created under the influence of the light source. That means that the polymer chains are formed from smaller units (monomers), and the chemical composition changes significantly during the process. The nozzle remains cold, and therefore these 3D pens are regarded as safe for children as there are no burn risks[1].

The general knowledge of the more detailed chemical composition of 3D printing materials, their possible additives and migration from materials have been studied in two previous surveys for the Danish EPA (the Danish EPA, 2016A and 2017). In general, the information shows that a wide range of materials are used, and that, e.g., the additives in the materials come within the categories and substances/substance groups that also are used for a more traditional use of the polymers (colours, antioxidants, antistatic agents, release and processing aids). However, previous studies have shown that substances identified by content analysis of the applied materials for 3D printing in subsequent migration studies only were detected in very few cases and in low concentrations.

[1] Ammonista (2015), http://www.ammonista.com/archive/2015/8/21/3-d-printing-for-novice-hands

That means that a content of problematic substances was identified. However, under the applied test conditions it was also demonstrated that the substances did not migrate from the 3D printed products to an alarming degree.

In the previous survey projects, 3D pens were not reviewed. However, it is assumed that the materials that are used for 3D pens based on known 3D printing techniques are comparable to the printing material used for 3D prints.

In addition to the 3D pens based on known techniques and materials from 3D printing, some products use a material with a play dough-like texture to create 3D objects by means of a handheld unit, and they are targeted at children. The material is pressed out of the unit, and then it hardens over time at room temperature. The chemical constituents in that type of products and accompanying materials have not previously been investigated by the Danish EPA.

The Danish EPA wants to acquire greater knowledge of the chemical substances in the materials for 3D pens that are targeted at children to assess if the substances pose a health risk during use. It seems probable that children can be exposed to the substances in the materials before they have hardened.

1.2 Objective

The objective of this project was to acquire greater knowledge of:

- Chemical substances in the materials used for 3D pens and possible substances that are created when using the pens.
- The exposure of children to chemical substances that are released from 3D pens during use.
- Health risks for children when using 3D pens.

In this project, 3D pens comprise handheld units that can be used to create 3D objects. The project comprises 3D pens that are targeted at children and how children use 3D pens.

2. Survey of 3D pens for children

This chapter covers the survey of 3D pens for children. The applied method, delimitation and the achieved results are reported and discussed in relation to analyses and subsequent development of exposure scenarios.

2.1 Introduction

The objective of the survey was to collect available information about 3D pens that are sold to children on the Danish market. The survey was carried out in April 2017. The following gives a description and an overview of the techniques that are used in the various identified 3D pens: type of materials and possible content of chemical substances; how the material hardens after extrusion; in which shops 3D pens and accompanying materials were found. The country of origin is stated if the information was available. The recommended age of the children, whom the products were intended for, was also noted. That information was used to develop exposure scenarios and the subsequent risk assessment. The price of the 3D pens was also noted and included in the selection of products for analysis.

It is expected that the materials and techniques used in connection with 3D pens to a high degree will resemble the materials and techniques that are used for 3D printing. Therefore, it is anticipated that information about the content of chemical substances and their properties was covered in previous surveys and analyses carried out for the Danish EPA:

- *Kortlægning samt fare- og ressourcevurdering af 3D-printere og 3D-printede artikler* (Survey and Risk & Resource Assessment of 3D printers and 3D Printed Products) (the Danish EPA, 2016A).
- Risk Assessment of 3D Printers and 3D Printed Products (the Danish EPA, 2017).

In consultation with the Danish EPA and on the basis of the survey it was decided which 3D pens were to be purchased and analysed. The purchase represents the supply of 3D pens sold to children on the Danish market, and it covers the techniques and materials that are assumed to give rise to the highest exposure.

2.2 Survey method

The general objective of the survey was to collect available information about 3D pens that are marketed to children. A 3D pen is regarded as being intended for children if a recommended age interval of 0-14 years is stated; if the marketing material and/or packaging depicts children who are using the product; and, if the product is found on the website under the product category “toys”.

The supply of 3D pens and accompanying material was investigated when visiting Danish web-based distributors and event managers/course organisers who work with 3D pens and who offer events intended for children. When possible, information has been collected about:

- Manufacturer (’brand’)
- Country of origin or where the product was imported from
- Distributor (in case of several distributors, all have been mentioned)
- Price

- Recommended age of the children to whom the products are marketed
- 3D printing technique and possible description of the process
- Material types and constituents

A starting point was taken in the information that can be found on the internet, and a preliminary screening of distributors and event managers was carried out. Subsequently, three distributors were chosen and contacted by phone to obtain additional information about the products that each distributor offers on the internet. The inquiry was based on a questionnaire (see Enclosure 1), and subsequently an attempt was made to collect the information listed above. Priority was given to distributors with several types of 3D pens in order to increase the output of the inquiry.

In addition, two event managers/course organisers were contacted by e-mail. The e-mail inquiry consisted of several questions that to a high degree resembled the questions put to the distributors; however, the questions regarding the use of 3D pens were more detailed so light could be shed on the target group (age group) and realistic user scenarios. Information about use was applied for later development of exposure scenarios connected with the risk assessment.

In the project, shop visits had low priority as it was assumed that the information available in the shops often could be found via the shop websites. However, one shop visit was carried out to investigate, which products are available in an ordinary toy shop, how the products are presented, and how the individual products are labelled.

In addition, one of the contacted distributors forwarded an inquiry to one of the manufacturers to collect further information about 3D pens. The specific manufacturer is accountable for the most common brands. A starting point was taken in the questionnaire that was used to contact the distributors, but it was expanded with more questions, e.g.: about which measures were taken during the design of the 3D pen, and the experience the manufacturer might have with how children use 3D pens (see Enclosure 1).

In connection with the shop visit, the Danish app called "*Tjek Kemien*" was used to scan the bar code on the two 3D pens that were found in the shop in order to collect information about a possible content of substances on the Candidate List. The Candidate List covers substances of very high concern under REACH. Companies that use the substances have a special obligation to procure information and distribute information about the substances in the supply chain (Regulation 1907/2006).

2.3 Results of the survey

A general overview of the 3D pens registered in connection with the survey appears in Table 1.

Table 1 Overview of the registered 3D pens in the survey and the distributors who market the products. All of the 3D pens that were found are CE marked. However, it does not appear from the CE marking whether it applies to the product as a toy or as another product type, e.g., electronics that also may require CE marking.

Product	Technique	Materials and colours	Distributor	Recommended age	Price (DKK) of 3D pen	Country of origin	Remark
Atmosflare	SLA-based (UV cured)	No material type stated #I[2]: Pink (70 DKK) Purple, yellow, black, white, green (119.95 DKK) #II: Purple, blue, brown, orange, white, red, grey, yellow, pink, green, black (99 DKK)	#I: Toys'R'us #II: www.coolshop.dk	#I: 14-18 years #II: 10+ years	#I: 329 #II: 499 Incl. 2 cartridges	China	Meets standard EN-71 (stated on the packaging) Content of allyl aliphatic urethane (oligomers) and ethylphenyl(2,4,6-trimethyl-benzoyl)-phosphinate (stated on the packaging)
3Doodler Start	FDM-based (temperature-dependent hardening)	Eco-Plastic #I: Red, white, yellow, orange, mint green, blue, grey, green, luminous and sets with four different colours (59.95 DKK) #II3: White, red, yellow, blue, green, grey and sets with four (59.95 DKK)	#I: www.monito.dk #II: www.legeakademiet.dk #III: www.coolstuff.dk	#I: 8+ years #II: 8+ years #III:8+ years	#I: 1099.95 #II: 1,129.95 #III: 499.00 Incl. 8 colours	China	Meets standard ASTM F963-11 (Stated on the packaging) "environmentally-friendly material basd on rice flour (and therefore can be eaten). The rice flour strands have no chemicals, they are BPA-free and completely biodegradable" (Legeakademiet.dk). Translation from Danish.

[2] https://www.toysrus.dk/atmosflare-3d

[3] https://www.legeakademiet.dk/pi/3Doodler-tilbeh%C3%B8r-Milj%C3%B8venlige-rismelsstave_2739379_60308.aspx

Product	Technique	Materials and colours	Distributor	Recommended age	Price (DKK) of 3D pen	Country of origin	Remark
		#III4: Blue, green, grey, mint, orange, red, white, yellow and sets with four (59 DKK) luminous (79 DKK)					"Plastic hardens in 10 – 15 seconds" (Coolstuff.dk). Translation from Danish.
IDO3D	SLA-based (UV cured)	No material type stated #I: No range of colours stated #II[5]: Changes colour when applied to cold/warm water	#I: www.coop.dk #II: www.jollyroom.dk	#I: 8-14 years #II: 8+ years	149.95-249.95 E.g. set with 2-4 colours	Not stated	Meets standard ASTM D4236 (stated on the packaging)
3Doodler Create	FDM-based (temperature-dependent hardening)	ABS/PLA/Flexy #I: ABS – Luminous, orange, light blue, dark blue, purple, red, yellow, turquoise, brown, neon green, green (79 DKK) PLA – Luminous, black, grey, cream-coloured, light purple,	#I: www.3dprinthuset.dk #II: www.coolstuff.dk #III: www.bilka.dk	#II: 12+ years	885.00-894.00 ABS included	China	Meets standard EN-71 (stated on the packaging) "two temperature ranges, two speeds" (Coolstuff.dk). Translation from Danish "The tip of the pen becomes very hot during use and must not be touched"

[4] https://www.coolstuff.dk/3Doodler-Start-Plast

[5] http://www.jollyroom.dk/legetoj/kreativt-legetoj/ovrigt/ido3d-3d-pen-color-change

Product	Technique	Materials and colours	Distributor	Recommended age	Price (DKK) of 3D pen	Country of origin	Remark
		white, yellow, orange, Bordeaux-red, gold, brown, blue, silver, light blue, dark blue, purple, salmon-coloured, pink, mint green, mint blue, forest green, lime green (79 DKK) #II[6]: ABS – Black, yellow, white, blue, red, green Flexy – turquoise, black, silver, purple, yellow and sets with four colours (79 DKK) PLA – red, green, white, yellow, blue, black and sets with four colours (79 DKK) #III: ABS - Neon green, yellow, brown, neon yellow, lime green, red, purple, turquoise (70 DKK) PLA – Light blue, dark blue,					(Coolstuff.dk). Translation from Danish. "3Doodler is not a toy and should not be used by children under the age of 12" (Coolstuff.dk). Translation from Danish.

[6] https://www.coolstuff.dk/3Doodler-Plast

Product	Technique	Materials and colours	Distributor	Recommended age	Price (DKK) of 3D pen	Country of origin	Remark
		purple, salmon-coloured, pink, black, grey, beige, white, orange, yellow, pastel green (70 DKK)					
3D Magic Styling pistol	SLA-based (UV cured)	No material type stated TOY'R'US[7]: Red, yellow, green, purple, orange, blue (two colours for 100 DKK)	TOY'R'US/ Fætter BR	6-12 years	249.95 Incl. 2 cartridges	China	Meets RoHS (stated on the packaging)
3D Magic 3D Maker	SLA-based (UV cured)	No material type stated TOY'R'US[8]: Red, yellow, green, purple, orange, blue (two colours for 100 DKK)	TOYS'R'US /Fætter BR	6-14 years	399.00	China	"Fill the molds with jelly, and place them in the 3D-Maker for a few minutes" (ToysRUs.dk). Translation from Danish.
DOHVINCI	Play dough-like material	No material type stated TOY'R'US[9]: Orange, pink, purple, yellow, green, blur, turquoise, white, peach, purple with glitter (four colours for 60 DKK)	#I:TOYS'R'US #II: Fætter BR #III: Legekæden	#I: 6-12 years #II: 6-12 years #III: 6+	119.95-398 Incl. 3 tubes (yellow, blue, pi k)	China	"press and design your own master piece" (Legekaeden.dk). Translation from Danish.

[7] https://www.toysrus.dk/3d-magic

[8] https://www.toysrus.dk/3d-magic

[9] https://www.toysrus.dk/dohvinci

Product	Technique	Materials and colours	Distributor	Recommended age	Price (DKK) of 3D pen	Country of origin	Remark
		Glitter colours: Red, turquoise, blue, purple, pink, yellow (6 colours for 90 DKK)	#IV: Bilka (sælges også i Føtex og Netto)	years #IV: 5+ years			
3D-RAW	FDM-based (temperature-dependent hardening)	No material type stated	www.happyroom.dk	8+ years	1,289.00 Incl. 6 colours (black, white, red, blue, yellow, green)	China	
3D Stereo drawing pen RP-100B	FDM-based (temperature-dependent hardening)	PLA, ABS PLA – Red, white (299 DKK) 10 mixed colours, each 10 metres for 199 DKK 20 mixed colours, each 10 metres for 349 DKK	www.getgadget.dk	Not stated	499.95 Incl. 3 colours	Not stated	”recommends PLA filament as it is made of plant-based material” (Getgadget.dk). Translation from Danish.

Nine products from eight different manufacturers were identified and registered. The products are under Danish domains (.dk) and were found on 12 different webshops that mainly comprise gadget and toy dealers. Many of the products are sold by several distributors, but one specific brand is not sold by all of the identified distributors.

Several variations of each brand are often sold by each distributor. Variations within the products i.a. comprise different types of material (PLA[10], ABS[11], Flexy[12] and Eco-Plastic) and material colours, as well as different design topics for products with ancillary 3D moulds/ shapes (designs such as butterflies, fish and buildings have been seen). Finally, the 3D pen itself is available in different colours, which makes it possible for the children in the target group to purchase the 3D pen in their favourite colour. The colour of the material that is used in the 3D pen can be relevant for the assessment of the health risks. The content of chemical substances will typically vary according to the colour of the 3D pen itself and the accompanying material (the Danish EPA, 2014A). This survey only focuses on which implication the colour of the material used in the 3D pen can have and not on variations in the colour of the 3D pen itself or variations within the design/theme of the individual 3D pens. That is believed to be less important for the exposure of children to chemical substances.

The price levels of the registered products range from DKK 120 to DKK 1,289. The inexpensive products are single-use products, whereas it is possible to separately purchase material for the more expensive 3D pens. How much material comes with the starter set differs from product to product.

2.3.1 Techniques used in 3D pens

The registered products come within the following three categories:

- Products that cure by means of a light source
- Products where heated material is extruded and hardens at room temperature
- Products where the material is extruded and hardens at room temperature

Products that cure by means of a light source

The technique used in this product category can be compared to the technique used for SLA-based 3D printing where the material that is used in the 3D pen consists of a viscous liquid that cures by means of a UV source. In the 3D pens based on this technique, the material cures by means of a diode placed at the tip of the 3D pen. In the following, this category will be called SLA-based 3D pens, and four of the registered products are based on this technique.

The registered 3D pens that are identified as SLA based use LED light to cure the material (polymerisation). In several of the identified 3D pens, the light source can be turned on or switched off during use. If the light source is switched off, the curing process will be slow, and the child will be exposed to uncured material from the 3D pen. LED light diodes emit radiation in a more limited spectrum than traditional light bulbs, and they emit a minimum amount of ultraviolet (UV) light[13]. UV light that is used for 3D printing with the SLA technique covers a wavelength from 10 nm to 380 nm. For 3D printing with the SLA technique, powerful light sources are used, and special safety measures are connected with the design of 3D printers

[10] polylactic acid

[11] acrylonitrile-butadiene-styrene

[12] Flexy is a flexible and elastic material for 3D pens and 3D printing; further information about the polymer type has not been found.

[13] http://www.kunstkonserveringen.dk/nyt/arkiv/nyheder-details/led-lys-paa-museerne.html, accessed 2017.05.01

as the UV radiation from the powerful sources is harmful to humans. Safety-wise, it is therefore an advantage to use a weak LED source in a 3D pen for curing, as it only emits a limited amount of UV light. Therefore, it meets the toy requirements (the Danish Safety Technology Authority, 2015). However, a weaker light source for curing could mean that the content of chemical substances that contributes to the curing of the material in 3D pens could deviate from the content in the printing material that is used for SLA-based 3D printing. However, in this survey a possible deviation has neither been confirmed nor ruled out.

Products where heated material is extruded and hardens at room temperature
Another category of products uses a technique where a solid plastic material is heated, extruded at increased temperature through the 3D pen and subsequently hardens at room temperature when the material has been pressed out. The technique can be compared to the FDM technique that is used for 3D printing. The material that is used in 3D pens consists of a solid material, and the survey confirms that some 3D pens use materials of PLA and ABS plastic that are well-known from 3D printing. However, it has not been possible to confirm if the material composition has been adjusted to the use in 3D pens. In the following, this category will be called FDM-based 3D pens, and three of the registered products are based on this technique.

Products where the material is extruded and hardens at room temperature
This technique uses more solid materials with a play dough-like texture that can be shaped with a pistol or with the fingers, and it hardens within a couple of hours. This technique is not used for 3D printing. In the following, this category will be called play dough-based 3D pens. One registered product is based on this technique.

2.3.2 Materials and chemical content

Limited knowledge has been acquired in the survey of materials for 3D pens. However, a few 3D pens use the same type of material as used for 3D printing.

In connection with the shop visit, bar codes were scanned on two 3D pens based on the SLA technique via the Danish app called "*Tjek Kemien"*. Only one of the two bar codes were recognised in the app. For this 3D pen and the accompanying material, an inquiry concerning the content of candidate list substances was sent via the app. No reply was received.

One distributor of FDM-based 3D pens pointed out that known materials used for 3D printing based on the FDM technique are also sold for 3D pens. The distributor assumes that the materials for the 3D pen are comparable with the corresponding plastic materials for 3D printing. The materials for the registered 3D pens that use the FDM technique are based on ABS, Flexy or PLA plastic. ABS and PLA materials for 3D printing and their chemical content were analysed in two previous projects carried out for the Danish EPA (the Danish EPA, 2016 and 2017), and therefore they are not reviewed in this report. One distributor pointed out that one specific 3D pen, targeted at small children, solely uses a material based on rice flour (Eco-Plastic). According to the manufacturer, the thickness of the plastic strand should exclude other types of plastic from being used as they cannot be fed into the 3D pen. Further information about that material has not been found.

In one of the registered SLA-based products that cure by UV light, a content of allyl aliphatic urethane (oligomers) and ethyl phenyl(2,4,6-trimethylbenzoyl)-phosphinate was stated on the product packaging. According to ECHA's register, ethyl phenyl(2,4,6-trimethylbenzoyl)-phosphinate, CAS No. 84434-11-7, is self-classified by industry as skin sensitising (Skin sens 1B). Neither of the two substances were mentioned specifically in the previous surveys that were carried out for the Danish EPA (the Danish EPA, 2016A and 2017). However, the Danish EPA report from 2016 does stress that liquids used for SLA printing might contain urethanes, but that type of liquid is not the most commonly used (the Danish EPA, 2016A).

One distributor mentioned that he obtained information from the supplier about the content of chemical substances when purchasing goods. However, the information is subject to an agreement on confidentiality. In relation to chemical substances, this distributor studies the hazard assessment and classification of the chemical substances in 3D pens and accompanying material, but not the risk or exposure regarding children. The same distributor mentions that according to the supplier of the distributor there is no content of substances of very high concern (SVHC) in the 3D pens. The distributor has opted out other 3D pens on the market that appeared to contain substances that can be regarded as problematic (allergens as specific example). Pigments can be a problem within plastics as they can contain substances that have problematic health effects, e.g., substances that are on the candidate list (the Danish EPA, 2014A). However, the distributor could not remember if pigments were a problem in the particular 3D pens, the distributor had obtained information about when purchasing the 3D pens.

One distributor emphasized that impurities in the printing material for 3D printers often appear if unoriginal printing material is purchased. The same is expected to apply to material for 3D pens. The distributor knows that several users purchase material strands for 3D printers with a suitable diameter and use them for 3D pens (e.g., inexpensive material made in China).

One distributor has chosen to only sell FDM-based 3D pens, as he believes those pens are safer than SLA-based pens, due to the potential risk of chemical vapours from the viscous materials. The distributor sells FDM-based 3D printers and 3D pens, and in general recommends PLA for both product types for private and schools/children. He considers PLA to be the better alternative to ABS due to the health effects. ABS is a polymer based on the three monomers: acrylonitrile, butadiene and styrene. The three monomers of ABS have many undesired toxicological effects such as acute toxicity, inflammable, harmful to specific organs, toxic to reproduction, mutagenic, carcinogenic, skin sensitising, suspected of having endocrine disruptive effects and of being poisonous to aquatic organisms with prolonged effects[14]. However, normally the concentration of residue monomers in ABS plastic will be very low, and the fully hardened plastic is not regarded as problematic.

According to the report from the Danish EPA from 2017 it is assessed that there might be a risk of inconvenience due to respiratory or eye irritation caused by the emission of substances and particles from the printing process connected with 3D printing with PLA or ABS (the Danish EPA, 2017). Therefore, there might also be a risk when using 3D pens that use similar materials.

Very often, the materials are still workable when they come out of the nozzle of the 3D pen, and the object can be shaped with the hands[15]. However, the material can be sticky on the surface and stick to the fingers during use, which has been emphasized by one distributor. Sticky material can indicate that the material is not fully hardened. Therefore, potential exposure to the applied monomers in the material could take place if a polymer is not fully hardened. In relation to health effects, a polymer that is not completely hardened is more problematic than a fully hardened polymer.

[14] Classification by ECHA.

[15] 3Doodler video tutorial, http://the3doodler.com/videos/, accessed 2017.04.30

2.3.3 Age group of users

During the survey, 3D pens that are not immediately targeted at children were identified. Those pens were not registered during the survey, and they are regarded as a creative tool for adults. Their product descriptions recommend that children always should use this type of 3D pen under adult supervision. One distributor mentioned that not all 3D pens are classified as toys by the manufacturer, but nevertheless they are expected to be used by children.

The 3D pens that are registered in this survey and regarded as being intended for children have a recommended age group that ranges from 5 years and up to 18 years. One distributor recommends a specific 3D pen for the age group five years and older, whereas the three other distributors of the same product recommend an age group from six years and up. In general, there is not always agreement among the identified distributors regarding the recommended age group for a given 3D pen.

On their websites, several distributors recommend that 3D pens should be used by older children. That has been confirmed by the contacted event managers, and they explain that certain motoric skills are required by the children to make creative 3D designs with a 3D pen. If the motoric skills are not sufficiently developed, children quickly loose interest in the pen.

One of the contacted distributors (who also arranges events and courses at schools), emphasizes that they solely recommend teaching children from grade 2 and up. Having contacted the supplier, the distributor has chosen to take special precautions at events for children. For instance, only FDM-based printers and PLA-based 3D pens and materials are chosen, as it is assumed that the exposure of children to possible health hazardous vapours will be minimised. In addition, the size of the room and the possibility to air the room are also considered in connection with events.

2.3.4 Possible risks when using 3D pens

One distributor deliberately chose not to include 3D pens based on the FDM technique in his range of products due to the safety risk of the hot material when toys are in question. However, another distributor stressed that the manufacturer of the FDM-based 3D pens had taken design-related measures when designing the pen. The heated nozzle is not directly accessible and there are no burn risks. This distributor emphasized the possibility to choose a bio based polymer (PLA) for FDM-based 3D pens. PLA requires a lower temperature than, e.g., ABS to beworkable, and therefore the risk of burns is reduced.

Several distributors state that a material that is used in one of the registered products is based on rice flour. One distributor mentions that a test of the product revealed that the material is tepid when it comes out of the nozzle, but it does not have a sticky surface or emit odour during use.

One of the registered 3D pens based on the FDM technique can adjust the temperature, depending on whether ABS or PLA is used. A webinar shows how it is possible to distinguish the various materials from each other, and how the temperature can be adjusted accordingly[15]. That could give rise to incorrect adjustment of the pen, which perhaps could result in an increased migration from the material if, e.g., PLA is heated to a higher temperature than intended.

According to one distributor, some manufacturers regard 3D pens as toys and some do not. That is especially the case for 3D pens that are intended for older children (from 14 years of age) or adults. The Toy Safety Directive defines toys as products that are used by children under the age of 14 when playing. The recommended age limit of 14 years for using 3D pens indicates that the product does not come within the definition of toys (Directive 2009/48/EF).

One manufacturer emphasizes that it is necessary to work carefully with the 3D pen. If material is left on the hands, then alcohol-based agents such as ethanol or hand disinfectants are recommended to clean the hands[16].

One distributor has tested several products within the category of 3D pens because the category is new. Focus was especially on 3D pens with a built-in light source. In toys with built-in laser and LED lamp, the light source must not pose a risk for the child. According to the explanatory guidance document for the Toy Safety Directive (European Commission, 2016) the technical requirements must follow the international standard IEC 60825-1 (IEC, 2014).

Another distributor stresses that 3D pens typically give rise to uneven surfaces, but the objects are not treated with solvents such as acetone to improve the appearance of the surface. The report of the Danish EPA from 2016 states that such treatment at times is recommended for 3D printed products (the Danish EPA, 2016A). When 3D pens are used, the risk of exposure to solvents is reduced substantially compared to 3D printing. The distributor mentions that the production process often is in focus when children use the 3D pen.

2.4 Summary of survey

Distributors of 3D pens for children were identified on Danish websites, and the marketing of various 3D pens was observed. The marketed 3D pens use three techniques: UV curing, temperature-dependent hardening and hardening over time. The two first techniques can be compared to known techniques within 3D printing: SLA (UV cure) and FDM (temperature-dependent hardening). In some cases, the material types used in 3D pens are based on the same polymer materials as used for 3D printing. That is especially the case for materials for 3D pens with temperature-dependent hardening where ABS and PLA are used.

The polymer type is not stated in the same way for materials for 3D pens with UV curing, but it is assumed that they could be comparable to the UV reactive resins used for 3D printing. However, it has not been possible to confirm that in connection with this survey.

There is no parallel within 3D printing to the third type of 3D pen where hardening takes place over time without any external stimulant. The texture of the material resembles play dough, but it has not been possible to identify the detailed chemical composition of the applied materials in connection with this survey.

Recommendations related to the age groups of the individual 3D pens vary from 5 to 18 years. Only one single 3D pen is recommended down to 5 years of age, and only one distributor recommends an interval up to 18 years of age. However, the recommendations to age often vary from distributor to distributor and from 3D pen to 3D pen. Based on the limited data, no connection is seen between the recommended age group and the hardening technique.

Play involving 3D pens is to a high degree expected to centre on the production process. That is why focus should be on the production process when the risk is assessed. It is important to include a few parameters in the further considerations regarding exposure:

- The children sit alone and work with the 3D pens. They can come into direct contact with the unhardened material (when the material is placed in the 3D pen), with the partly unhardened material containing, e.g., reactive monomers (in the case of UV curing materials) or with semifluid polymers (in the case of temperature-hardening materials), just when the material exits the 3D pen.

[16] Ido3D video tutorial, http://www.ido3dart.com/tips-and-tricks-vertical/, accessed 2017.04.30

- The design and functions of the 3D pens can be of great importance, as, e.g., the temperature of the nozzle can result in burns, the increased temperature of the material can result in increased migration or emission of volatile substances, and the efficiency of UV light can be decisive for the reaction rate and thus the chemical composition of the material when it exits the 3D pen.
- The materials are often workable when they exit the 3D pen, and many distributors of 3D pens state that it is possible to continue shaping the material with the fingers.

3. Development of exposure scenarios

This chapter discusses and develops exposure scenarios for children who use 3D pens. The exposure scenarios are developed for subsequent assessment of children's exposure to concentrations of chemical substances that might pose a health risk.

3.1 Introduction and method

When using 3D pens, children can be exposed to chemical substances that can be released from the materials used in 3D pens. In connection with 3D pens, it is expected that the production process itself will result in greater exposure than subsequent use of the object that is created. Therefore, focus is on exposure during the production of objects with 3D pens. During the production of objects, the materials are extruded through the 3D pen and they harden by cooling, UV light or over time.

Children's exposure to chemical substances when using 3D pens will i.a. depend on the materials, the chemical constituents and the design of the individual 3D pen. Potentially, exposure can occur in connection with skin contact (dermal) with the unhardened material before and after extrusion through the 3D pen, during intake (oral) of the material through hand-to-mouth transfer, by inhalation of volatile chemical substances or of particles that are emitted to the air during use or in a combination of the above.

A starting point is taken in the models that are described in the guidance document of the European Chemicals Agency (ECHA) for assessment of consumer exposure (ECHA, 2016). It is stated, which mathematic equations are used for the subsequent calculations (CHAPTER 5), and which significant parameters form part of the calculations. Some parameters depend on the product that is used, meaning the 3D pen (e.g., the amount of material that is used, and the concentration of the substances in the material), whereas other parameters depend on the use situation. The last-mentioned parameters will be assessed according to the information about use obtained in the survey that was carried out (e.g., about the material properties, handling and duration of the activity).

The calculations also comprise several anatomic and physiological parameters that depend on the age groups that are most relevant in relation to using 3D pens. A number of determined default values are included, e.g., for skin area of body parts and volume of inhaled air per day for children in various age groups.

As far as possible, default values and other parameters for calculation are determined with reference to relevant guidelines and recommendations from ECHA (ECHA, 2016), the Nordic Council of Ministers (Norden, 2011), previous exposure scenarios in reports published by the Danish EPA and relevant publications from the Dutch research institute RIVM (Bremmer and Van Veen, 2002).

The models and default values will together with the actual analysis results be used to calculate children's exposure to specific substances in selected materials used in 3D pens and marketed to children. As a starting point, the applied models and default values will be used to calculate a realistic worst case exposure scenario.

The choice of the most relevant route of exposure and model for calculation will depend on how children use the 3D pen, and of the specific substances that are identified and their adverse health effects. Therefore, the calculation models for exposure by inhalation, skin contact and oral intake are briefly described in the following (Section 3.3). Based on the survey, the considerations related to exposure are also reviewed in the following (SECTION 3.2). In general, the survey shows that the target group is children from 5 years of age and up, where direct oral intake is expected to constitute a minor source of exposure. Therefore, focus has especially been on children's exposure to chemical substances through skin contact and by inhalation, whereas oral intake is expected to play a minor role.

3.2 Exposure considerations connected with the use of 3D pens

In order to calculate children's exposure to chemical substances when using 3D pens, a number of parameters have to be used, and they are estimated on the basis of information collected in the survey. Those parameters are reviewed in the following.

3.2.1 Body weight, skin area and inhalation volume

Information collected from the websites of the distributors during the survey has shown that the age group for 3D pens for children depends on the type of 3D pen. However, in general the target group is children from 5 years and up. The default values recommended by the Nordic Council of Ministers (Norden, 2011) are intended for age intervals that separate at 6 years, and there is a significant difference between the values for the two age groups. Therefore, the average values that are stated in the recommendations from the Nordic Council of Ministers for 3-<6 years and 6-<11 years, respectively, have been included, as the target group for using 3D pens covers both age groups. The values appear in Table 2. Which values are used in the actual exposure calculations for the risk assessment in Chapter 6 will depend on the recommended age group of the specific pen. As default, the youngest recommended age is used as a realistic worst case consideration.

To calculate dermal exposure, it is assumed that the hands are the relevant skin area for exposure when 3D pens are used. That is because direct contact with the material and hands might occur during printing and possible subsequent modelling of the soft material. It is assessed that a skin area corresponding to the outer part of the finger tips typically will be exposed. That corresponds to exposure of app. 1/8 of the area of the hands.

To calculate exposure by inhalation, the volume of inhaled air daily or for a shorter period of time, respectively, during varied physical activity, can be used. In that connection, the use of a 3D pen is considered to be creative work with slight physical activity (the Danish EPA, 2015A). The values are shown as average values in Table 2.

Table 2 Recommended physiological default values for children (Norden, 2011).

Parameter	Description	Age	Value
BW	Body weight, average	3-<6 years	18.6 kg
		6-<11 years	31.8 kg

A_{ge}	Surface area of hands*	3-<6 years	0.037 m^2
		6-<11 years	0.051 m^2
IH air	Volume of inhaled air, average, daily basis	3-<6 years	10.1 m^3/d
		6-<11 years	12. 0 m^3/d
	Volume of inhaled air, average, light activity	3-<6 years	0.011 m^3/min
		6-<11 years	0.011 m^3/min

* Values for total surface area of hands are stated. An exposure of app. 1/8 of the area of the hands is considered realistic when children use 3D pens.

3.2.2 Duration, frequency and amount of product

The user frequency is assumed to be lower than for play dough, in which case RIVM assumes one weekly use of the product and a contact time of 60 min. For the 3D pen it is assumed that the product is used 30 min. for the 3-6-year-olds and 60 min. for the 6-11-year-olds, respectively, and that the user frequency in average is once a month and max. once per day. In other words, the time of use is expected to be shorter for children in the lower age group, as they compared to the older children (6-11 years) often are not occupied with a game for very long. The low user frequency was based on the price that is substantially higher for materials for 3D pens than for play dough.

To calculate exposure, realistic estimates are used of the amount of material that it is probable that children (in the two relevant age groups) would use and come into direct skin contact with when using 3D pens.

Amount of material that is used

Some of the material used in 3D pens can be compared to material with a play dough-like texture. In RIVM's fact sheets on toys (Bremmer and Ven Veen, 2002) an amount of 350 g of play dough per use is recommended as default in connection with exposure calculations. For other material types for 3D pens, e.g., the UV cured material, the texture is compared to, e.g., finger paint before curing.

In their fact sheets on toys, RIVM estimates that 20 g finger paint is used per exposure (Bremmer and Ven Veen, 2002). The survey has shown that the material units for 3D pens are much smaller than for play dough (app. 1-40 g, and most of them are 20 g or less, see Enclosure 2). In the 3D pen, the material is extruded and led through a small opening. Tests with the 3D pens have shown that the extrusion rate in average is 1.7 g/min. (for all tested 3D pens the interval 0.4-3.3 g/min. is covered, see Enclosure 2). It is assumed that the child will not extrude material the entire time the 3D pen is used, but that the child also will spend time mounting material, changing colours and possibly collecting/shapingthe extracted material with the hands without using the 3D pen.

The amount of material that is applied when using the 3D pen will probably vary according to the age of the child. Children who are a bit older are expected to use the 3D pen for longer periods of time, and therefore they extrude more material out of the pen, causing the total amount that is used to increase. The applied amount will vary from pen to pen, but on the basis of a measured average extrusion rate of 1.7 g/min., and the assumption that material is actively extruded during half of the use period, an applied amount of 25 g for 3-6-year-olds and 50 g for children in the age group of 6-11-years is assumed to constitute a realistic worst case scenario.

Amount of material that comes into contact with the skin
In the information that was reviewed during the survey, several manufacturers stated that the material still is workable when it exits the 3D pen. That means that children might have skin contact with the material during hardening. However, if a comparison is made with other types of semifluid products, such as finger paint or play dough, it is expected that less skin contact occurs when a 3D pen is used. Therefore, it is assumed that the material mainly is applicated when using the pen, and that children who use finger paint or play dough often will be younger, and that their fine motoric skills will not be as developed as the fine motoric skills of the youngest children who use 3D pens. In addition, the material will become less workable over time as the material hardens, and therefore it is expected that children will have direct skin contact with the unhardened material for a limited period of time.

In a report about children's exposure to different preservatives in toys (the Danish EPA, 2014B) a starting point was taken - for other types of children's paint than finger paint (hobby paint, window/glass paint and glue) - in the amount stated for finger paint. However, due to expected reduced skin contact an amount is used to calculate dermal exposure corresponding to 20% of the amount of material that is used. That will correspond to a value of 5 g (20% of 25 g). The applied amount is assumed to be higher for the 6-11-year-olds (50 g), but it is expected that the relative amount that comes into direct contact with the skin is lower for that age group due to improved fine motoric skills and the utilization of the 3D pen as a tool. Therefore, it is assumed that the child will come into direct contact with 10% of the material, corresponding to 5 g.

Amount of material - oral intake
To calculate the oral intake, the amount of material that is taken in is estimated. When determining the migration limits of metals, the guideline of the Toy Safety Directive states that children can be expected to consume up to 100 mg from pliable toy material and 400 mg from liquid or sticky toy material. These values are based on RIVM's recommendations for default values for children under 3 years of age, who suck on the toys or put the toys into their mouth for longer periods of time (Van Engelen, 2008). Intake via hand-to-mouth must be assumed to be substantially lower than 100-400 mg, also when the age group that uses 3D pens is considered. However, there are no recommendations from RIVM for default values for hand-to-mouth exposure. That is why this report uses a value for oral intake of 100 mg as a worst case amount (0.1 g) (the European Commission, 2016).

3.2.3 Physical parameterss during use
As stated in ECHA's guideline (ECHA, 2016), a standard room of **20 m^3** is used to calculate exposure via inhalation, which is considered to be a realistic worst case scenario. However, it is regarded as likely that children from the chosen age group (5 years) often are under adult supervision when they use the 3D pen, and therefore the 3D pen might be used in a larger room – such as a kitchen/family room. One of the distributors who was contacted in connection with the survey pointed out that the children often are very concentrated when they use a 3D pen, and that they sit close to the material during use. Therefore, the concentration of possible substances can locally be expected to be higher than the average room concentration (peak load). This is assumed to be especially relevant in relation to substances that elicit local effects during inhalation. In a previous survey for the Danish EPA, volumes of between 0.095 m^3 to 3.6 m^3 were believed to constitute a realistic volume in relation to the assessment of peak load (the Danish EPA, 2017). In the guideline from ECHA on exposure (ECHA, 2016) it is suggested to use a room of e.g. **2 m^3**. Therefore, that value is used to assess the peak load in the calculations regarding acute effects.

In calculations of exposure during inhalation, an air change of, e.g., 0.5 times per hour can be assumed. That is equivalent to admitting an amount of outdoor air every hour corresponding to half of the volume of the room. In a survey for the Danish EPA about chemical substances in

carpets it was noted that air change in children's rooms actually can be much lower (the Danish EPA, 2016B). Therefore, it was chosen to not include the effects of ventilation in the exposure calculations carried out in this report. That means that the real exposure via inhalation will be lower than estimated here.

3.3 Models for calculation of exposure

A starting point is taken in simple calculation models to calculate exposure, and they will be explained in the following. If calculations with the simple models suggest a risk when using 3D pens, then it is possible to use more complex models and to refine the exposure scenario.

3.3.1 Exposure to a substance via inhalation

Assessing exposure via inhalation is relevant if the analysis of materials for 3D pens shows substances that, e.g., cause irritation during inhalation or cause harmful effects after absorption into the blood.

3.3.1.1 Calculation of the concentration in the air

The concentration of a substance in the air is especially relevant if exposure to the substance results in local effects in the respiratory tract such as irritation. Those effects are often highly dependent on the concentration.

Calculation model

Exposure via inhalation is estimated from the concentration of a substance in the air and is expressed in mg/m^3. The method stated in the guidelines from ECHA (ECHA, 2016) can be used on all substances, no matter if the chemical substance in the air occurs as gas or as airborne particles.

The model requires knowledge about the used amount of a material (stated in gram), the concentration of the substance in the material (stated in mg/g material), and several parameters that have to be set on the basis of the specific application and default values in the tables of the ECHA guidance document (ECHA 2016).

The parameters and equations of the model are shown here:

Air concentration of the substance in the room, C_{inh} [mg/m^3] is calculated as:

$$Cinh\left[\frac{mg}{m^3}\right] = \frac{Qprod\ [g] * Fc\ prod\ [\frac{mg}{g}]}{Vroom\ [m^3]} \qquad (1)$$

C_{inh} is the air concentration of the substance in the room (meaning in the inhaled air) and is stated as mg substance/m^3 air. C_{inh} is calculated from the following parameters:

Q_{prod}: Amount of material in gram
F_{cprod}: Concentration of the substance in the material in mg substance/g material
V_{room}: Volume of the room where exposure takes place, in m^3

Assumptions when using this model

The calculation model represents a worst case situation where it is assumed that 100% of the substance in the product amount (Qprod) that is used is emitted to the room instantaneously, that the child is exposed to the substance in the corresponding concentration in the room (meaning a homogenous distribution in the room), and that the effect of ventilation is not taken into account. This simple model is used in this report, and it is expected to give a worst case assessment of the risk via inhalation as it is expected that the substances are not emitted

instantaneously, but instead migrate from the material over time in combination with a certain ventilation – both resulting in a lower concentration in the room.

It is regarded as likely that the concentration of the substances in the air emitted from the materials when the 3D pen is used locally can be higher than when a standard room size is used for the calculation. To assess peak loads, a smaller room volume (Vroom) can be used.

Applied parameters
For this calculation, a material amount of 25 g for the 3-6-year-olds and 50 g for the 6-11-year-olds is used, as, i.a., volatile substances are in question. In worst case, they might migrate out of the entire amount that is used when playing with the 3D pen.

Depending on which effects are most critical for the substances that are assessed, the room concentration can be calculated in a limited room (2 m^3) to assess the peak load and local effects or in a standard room (20 m^3), respectively, to assess the long-term effects.

3.3.1.2 Calculation of exposure via inhalation

On the other hand, if the substance causes harmful effects after absorption into the blood, e.g., damages to the liver or kidneys, then the inhaled amount of substance per day per kg body weight is calculated according to D_{inh} [mg/kg BW/day], as the total inhaled amount will often be decisive for these types of effects.

Calculation model
Exposure via inhalation is estimated on the basis of the concentration of the substance in the air, C_{inh} and a number of parameters that have to be set according to the specific application and default values stated by, i.a., the Nordic Council of Ministers (Norden, 2011).

The parameters and equations of the model are shown here:

The inhaled amount of substance per day per kg body weight, D_{inh} [mg/kg BW/day], is calculated as (ECHA, 2016):

$$\mathrm{Dinh}\left[\frac{\mathrm{mg}}{\mathrm{kg\ day}}\right] = \frac{\mathrm{Cinh}\left[\frac{\mathrm{mg}}{\mathrm{m^3}}\right] * \mathrm{IH\ air}\left[\frac{\mathrm{m^3}}{\mathrm{t}}\right] * \mathrm{T\ [t]} * \mathrm{n}[\frac{1}{\mathrm{day}}]}{\mathrm{BW\ [kg]}} \qquad (2)$$

Where:

C_{inh}:	Air concentration of the substance in the room in mg substance/m^3
IH-air:	Inhaled air stated in m^3/hour
T:	Exposure time per exposure in hours
n:	Number of exposures per day
BW:	Body weight in kg

Assumptions when using this model
The model comprises the concentration of the substance in the room, C_{inh}, calculated with equation (1) above, and therefore the basic assumptions are the same: The model represents a worst case situation where it is assumed that 100% of the substance in the product amount (Qprod) that is used is emitted instantaneously in the room, that the child is exposed to the substance in the corresponding concentration in the room (meaning a homogenous distribution in the room), and that the effect of ventilation is not taken into account. This simple model is therefore expected to give a worst case assessment of the risk via inhalation.

Applied parameters
The parameters mentioned in the above section are used to calculate the concentration in the air.

For that calculation, an exposure time of 30 min. for 3-6-year-olds and 60 min. for 6-11-year-olds, respectively, are used. In addition, a frequency per day (n) corresponding to one application per day is used, and that is regarded as a realistic worst case scenario for application based on the survey carried out in this report.

Default values for inhaled air are used as stated by the Nordic Council of Ministers (see Table 2) and the model assumes that all substance that is accessible in the inhaled air is absorbed (100% absorption). In that case, the calculation can be regarded as worst case, as absorption typically will take place over time, and the substances are often decomposed in and eliminated from the body.

3.3.2 Dermal exposure to a substance

Assessment of exposure via skin contact (dermal exposure) is relevant if the analysis of the materials for 3D pens discloses substances that are skin irritating or that have sensitizing properties, and substances that can be absorbed through the skin giving rise to other adverse effects.

3.3.2.1 Calculation of the concentration on the skin

The concentration of substances that have local effects, e.g. skin irritating or sensitizing, are calculated as the amount of substance per surface area.

Calculation model

By means of the models that are stated in the ECHA guidance documents (ECHA, 2016), dermal exposure can be estimated as the amount of substance per surface (in mg/cm^2).

L_{der} is skin exposure expressed as mg substance/cm^2 skin and is calculated as:

$$Lder\left[\frac{mg}{cm^2}\right] = \frac{Qprod\ [g] * Fc\ prod\left[\frac{mg}{g}\right]}{Ader[cm^2]} \quad (3)$$

Where:

Q_{prod}: Amount of material in gram
F_{cprod}: Concentration of the substance in the material in mg substanc/g material
A_{der}: Skin area that is exposed, in cm^3

Assumptions when using this model

Equation 3 assumes that all substance in the amount of material that is expected to come into direct contact with the skin will be accessible on the skin instantaneously (100% migration and accessibility), and that a person is exposed to the total amount, which often will not be the case. In the materials investigated in this project, the chemical substances are expected to be more or less fixed in the material, when it comes into contact with the skin. According to information collected in the survey, the materials are expected to start curing immediately after they exit the 3D pen. Therefore, skin exposure will depend on the extent and the rate at which the substance is released (migrate) from the used material. Therefore, this simple model is expected to give a worst case assessment of the risk during skin contact.

With knowledge of the migration rate (if it is accessible for the specific substance in the material) and of the size of the contact area and contact duration, skin exposure can be calculated more realistically by using more complex models. That has not been done in this report.

Applied parameters
In the calculation, it is assumed that app. 1/8 of the skin area on the hands can come into direct contact with the material, which corresponds to the finger tips. Therefore, 1/8 of the default values for the skin area on the hands stated by the Nordic Council of Ministers is used as area (see Table 2) for the two age groups.

The amount of material used for calculations with this model is the amount the child in the specified age group is expected to be in direct skin contact with. Therefore, a product amount of 5 g for both age groups is used.

3.3.2.2 Calculation of exposure via skin contact

For substances that can be absorbed through the skin and elicit effects on the internal organs, it is the total amount of the substance that is available for skin absorption that is calculated in relation to the body weight.

Calculation model
The exposure stated as the concentration of the substance in the body, D_{der} (in mg/kg BW/day) is calculated as (ECHA, 2016):

$$Dder\left[\frac{mg}{kg\ day}\right] = \frac{Lder\left[\frac{mg}{cm^2}\right] * Ader\ [cm^2] * n\ [\frac{1}{day}]}{BW\ [kg]} \qquad (4)$$

Where:

L_{der}: Skin exposure in mg substance per cm^2
A_{der}: Skin area that is exposed, in cm^2
n: Number of exposures per day
BW: Body weight in kg

Assumptions when using this model
The model comprises skin exposure of the substance, L_{der}, calculated with equation (3) in the above, and therefore the basic assumptions are the same: It is assumed that all of the substances in the material that is in direct contact with the skin will be accessible on the skin instantaneously (100% migration and accessibility), which is not regarded as realistic for the investigated materials. The skin exposure will depend on the extent of the release of the substance from the material that is used.

In addition, the model assumes that the substance is absorbed completely, and it is not taken into account that absorption typically will take place over time, and that all substances often are decomposed in and eliminated from the body after absorption. This simple model is expected to give a worst case assessment of the risk by dermal intake.

Applied parameters
The parameters described in the above section are used to calculate skin exposure.

In addition, an exposure frequency per day (n) of 1 corresponding to one application per day is used for this calculation, which is regarded as a realistic worst case scenario for application based on the survey carried out in this project.

The default values for body weight as stated by the Nordic Council of Ministers are used (see Table 2).

3.3.3 Oral exposure to a substance

In general, oral exposure is mainly assumed to occur with children under 3 years of age (Van Engelen, 2008). However, due to the texture of the materials it cannot be completely excluded for children who are somewhat older, as hand-to-mouth exposure might take place. For children who use 3D pens it is regarded as possible that a small intake of the materials might occur due to deposit of slightly sticky materials on the fingers that subsequently are put into the mouth with resulting oral intake.

The model is used for substances where, e.g., systemic, chronic effects are identified where the effect of exposure appears after use of long duration.

Calculation model

According to the REACH guideline on consumer exposure (ECHA, 2016), the oral intake, *Doral* (mg/kg BW/day) of a substance can be found by using the following equation:

$$D_{Oral} = \frac{Q_{prod} * FC_{prod\ intake} * n * 1000}{BW} \qquad (5)$$

Where:

Qprod intake: Amount of product that is taken in, in g
Fcprod: Weight fraction of the substance in the product
n: Number of incidents per day
BW: Body weight in kg

Assumptions when using this model

In this model, it is assumed that all of the substance in the material will be released when consumed (100% migration), which is regarded as a worst case scenario. In addition, the model assumes that the substance is completely absorbed. It is not taken into account that absorption typically will take place over time and that it might not be complete, or that the substances often will be decomposed in and eliminated from the body after absorption. This simple model is expected to give a worst case assessment of the risk connected with oral intake.

Applied parameters

Consumption via hand-to-mouth is assumed to be low when the age group that uses 3D pens is taken into consideration. There are no recommendations from RIVM for default values for hand-to-mouth exposure, and a value of 100 mg is used for oral intake as worst case amount (0.1 g).

For this calculation, an exposure frequency per day (n) of 1, corresponding to 1 application per is assumed. That is regarded as a realistic worst case scenario for application based on the survey carried out in this report.

The default values for body weight as stated by the Nordic Council of Ministers are used (see Table 2).

4. Analyses

This chapter concerns the selection of 3D pens and materials for chemical analyses, a description of the chosen analytical methods and results of the analyses that were carried out.

4.1 Selection of 3D pens and accompanying material

The selection of 3D pens and accompanying material and the subsequent analytical program were determined on the basis of the survey of 3D pens for children.

In co-operation with the Danish EPA, eight different 3D pens and accompanying material were selected from the following criteria:

1. Popularity and accessibility: The selected 3D pens were found at several distributors on the Danish market.
2. Techniques: The selected 3D pens cover techniques where the accompanying material hardens with or without a LED light source, including material with a play dough-like texture.
3. Material for 3D pens: The materials have different colours and cover several types of materials within each technique.
4. It has to be possible to create upright 3D structures simply by using the 3D pen.

A total of 12 materials were selected for the eight 3D pens. Only materials that were developed for the particular 3D pen, which means they were of the same brand as the 3D pen and were marketed together with the pen, were tested. All purchased 3D pens are CE marked, but it does not appear from the label if it covers the product type toys or another product type that requires CE marking, such as, e.g., some types of electronic products. Information about CE marking and types of plastic was not available for all 3D pens during the survey. However, when the products were purchased it became available (stated on the packaging or in the enclosed papers). 3D pens selected for analysis, material types and colours are stated in Table 3. According to the information on the packaging, all 3D pens were made in China except for one 3D pen (materials with samples no. 3 and 4) for which the country of origin was not stated.

Table 3. Overview of selected material for 3D pens for analysis. For several of the 3D pens, material was purchased in two colours (but the same type of material). That is the case for 3-4, 5-6, 7-8, 9-10 and 11-12, respectively.

Sample no.	Colour	Material type
1	Black	UV resin
2	Blue	Eco-Plastic
3	Blue	UV resin
4	Red	
5	Black	ABS plastic
6	Yellow	
7	Green	UV resin
8	Purple	
9	Pink	Play dough-like material

Sample no.	Colour	Material type
10	Green	
11	Red	PLA plastic
12	Brown	

Products that were identified in the survey and required moulds and a separate oven with integrated light for curing were assessed to be on the verge of the definition of a 3D pen, and therefore they were not included in the further analyses.

The selected 3D pens cover three different techniques distributed on three 3D pens with UV reactive materials, four 3D pens where the material is heated and hardens when cooled, and a 3D pen that neither uses a certain temperature nor UV light in connection with hardening.

The materials selected for analysis comprise: Eco-Plastic, ABS plastic, PLA plastic, UV reactive resins and a material with a play dough-like texture for the selected 3D pens (see Table 3). Some pens can use several types of material (e.g., PLA plastic and ABS plastic), but for each 3D pen only one material type was chosen for analysis (the one that is included in the starter set).

For each material type, 1-2 colours were tested. The selected colours represent as many colours as possible. The dark colours are prioritized for the analyses, as a previous survey for the Danish EPA regarding 3D printed products (the Danish EPA, 2017) analysed a number of colours and pointed out that black and dark colours seemed to contain higher concentrations of metals than brighter colours.

4.2 Analysis program

The materials for 3D pens are often partly liquid immediately when they exit the 3D pen, and the user (child) can therefore be exposed to the liquid, unhardened materials. The materials that are used for 3D pens are expected to be developed especially for use in 3D pens, and there can be significant differences in the chemical composition compared to materials for 3D printing that previously were analysed. Therefore, it is assumed that the users of 3D pens are not necessarily exposed to the same substances as they would be if material for 3D printing was in question. In addition, traditional migration analyses cannot be used to calculate exposure, as this is a question of exposure to substances from an unhardened material. Therefore, it must solely be regarded as realistic that the users are exposed to the substances in the unhardened material. On that background, an analysis program that solely comprises content analyses of unhardened material was developed.

When determining the analysis program for 3D pens, the following challenges were identified:

- Hardening of the materials for 3D pens is expected to start immediately after the material exits the container. That means that the chemical composition of the sample will change in the course of time for the reactive materials.
- It is expected that the greatest exposure will take place immediately after the material exits the 3D pen, and the child is able to shape the material with the fingers. Therefore, the analyses should be carried out on unhardened material.
- Several parameters can be important for the analyses, such as the temperature and the relative humidity in the analysis laboratory. The parameters can be important for hardening as well as for migration, and thus for the analysis result.

As direct contact with the unhardened materials used in 3D pens pose the greatest risk for exposure, an analysis program was carried out in two steps. The first step consisted of content analyses of 15 metals/elements by ICP-MS and a semi quantitative screening analysis by GC-MS for substances. The content analyses were carried out by extracting samples immediately

after they exit the 3D pen. That method does not make it possible to distinguish between substances that originate from the material and substances that originate or are created during extrusion through the 3D pen. Analysis of the materials was carried out on the completely new 3D pens, and a possible release of substances from the 3D pen itself is assumed to decrease over time. That has not been investigated in detail.

The results of the semi quantitative determinations of the substances identified by the screening analysis were used in the second step where products were selected for quantitative determination of selected constituents on the basis of the initial hazard assessment, see the selected products in chapter 4.5. The quantitative determinations confirm a content of selected substances from the screening analysis, and data is obtained to carry out the exposure assessment.

The 15 metals/elements were selected on the basis of previous analyses in the survey for the Danish EPA within 3D printing due to the overlap between material types for 3D printing and in 3D pens (the Danish EPA, 2017). By choosing the same metals/elements a comparison can be made of the materials used in 3D pens and for 3D printing.

4.3 Analysis for selected metals by ICP-MS

By means of microwave induced heating, accurately weighed sub samples were prepared with a mixture of concentrated nitric acid (HNO_3) and hydrogen peroxide (H_2O_2). The resulting solution was diluted with Milli-Q water.

Double determinations were carried out.

The digest was analysed for the selected metals and half-metals by ICP-MS with CCT in KED mode and with helium as collision gas. Germanium, rhodium and rhenium were used as internal standards. The quantification by ICP-MS was carried out against traceable external standards of the elements.

The calibrations were verified against independent traceable control solutions.

Blanks of the liquids were analysed correspondingly.

The results are reported as an average of the double determinations of the analyses.

Analysis uncertainty: 10% RSD for values that are 10 times the detection limit.
Detection limit of the method: 0.1-0.13 mg/kg (however, 0.5 mg/kg for zinc).

4.3.1 Results of the analysis for selected metals

Double determinations were carried out, and both results are stated in Table 4. For some of the samples, the relative standard deviation of the double determination is higher than 20%.

Table 4. Results from analyses of selected metals and elements.

Unit: mg/kg	Sample number, colour, material											
Metal	**1, black UV resin**	**2, blue Eco-Plastic**	**3, blue UV resin**	**4, red UV resin**	**5, black ABS plastic**	**6, yellow ABS plastic**	**7, green UV resin**	**8, purple UV resin**	**9, pink "Play dough"**	**10, green "Play dough"**	**11, red PLA plastic**	**12, brown PLA plastic**
Chromium, Cr	0.24	0.18	-	3.4	2.0	0.75	-	-	-	1.1	0.62	0.68
	0.16	0.18	-	1.9	1.4	0.84	-	-	-	1.3	0.94	0.71
Manganese, Mn	0.21	0.43	0.14	0.33	0.20	-	-	-	2.6	2.1	-	-
	0.10	0.43	0.14	0.20	0.15	-	-	-	2.5	2.6	-	-
Nickel, Ni	0.31	0.28	-	0.88	0.63	0.31	-	-	-	0.36	0.23	0.23
	0.28	0.13	-	0.46	0.49	0.32	-	-	-	0.44	0.31	0.22
Copper, Cu	1.0	190	52	75	60	25	3.3	-	0.65	8.4	5.1	5.7
	1.6	190	51	41	36	27	3.7	-	0.61	10	6.2	5.9
Zinc, Zn	34	16	0.50	122	85	33	<0.13	0.18	7.7	44	24	63
	59	8.9	0.50	68	45	58	0.50	0.21	7.6	54	37	57
Strontium. Sr	0.34	0.25	0.72	0.63	0.32	0.48	0.23	-	11	7.8	-	0.40
	0.38	0.25	0.74	0.41	0.14	0.46	<0.13	-	11	9.0	-	0.39
Molybdenum, Mo	-	-	-	0.86	0.53	-	-	-	-	0.38	0.16	0.14
	-	-	-	0.48	0.29	-	-	-	-	0.45	0.24	0.14
Tin, Sn	1.2	2.8	2.5	5.4	-	-	-	-	-	-	41	33
	1.9	2.2	3.2	3.1	-	-	-	-	-	-	44	28
Antimony, Sb	-	-	-	-	-	<0.13	-	-	-	-	-	-
	-	-	-	-	-	0.37	-	-	-	-	-	-
Lead, Pb	1.4	0.48	-	-	0.24	0.40	-	-	-	-	-	-
	2.4	0.21	-	-	0.30	1.7	-	-	-	-	-	-

-: means less than the detection limit of 0.13 mg/kg (however, 0.5 mg/kg for zinc)

No content of cobalt, arsenic, selenium, cadmium or mercury was detected in the analysed samples.

Below, the individual material types are reviewed, see results in Table 4.

UV Resin, samples no. 1. 3, 4, 7 and 8
All of the five samples contain zinc as the only common denominator in amounts of 0.2-122 mg/kg, and four of the samples contain copper in amounts from 1-190 mg/kg. The blue colour has the highest content of copper. In addition, chromium, manganese, nickel, strontium, molybdenum, tin and lead (0.14-5.4 mg/kg) were detected. One product (sample no. 7 and 8) differs from the other two products (samples 1, 3 and 4, respectively) as only copper, zinc and strontium were detected in rather low concentrations in the product compared to the other products.

Eco-Plastic, sample no. 2
The sample has a high content of zinc amounting to 8.9-16 mg/kg and of copper amounting to 190 mg/kg, which is due to the blue colour. In addition, the sample contains low concentrations of chromium, manganese, nickel, strontium, tin and lead (0.13-2.5 mg/kg).

ABS plastic, samples no. 5 and 6
In general, the two samples contain low amounts (0.14-2.0 mg/kg) of chromium, manganese, nickel, strontium, molybdenum, antimony and lead. For copper a content of 26-60 mg/kg was detected and for zinc a content of 33-85 mg/kg was detected. The two samples are from the same type of 3D pen, and there is only minor difference in the content except for copper and zinc, which presumably is due to the colours.

Material with a play dough-like texture, samples no. 9 and 10
Both samples contain manganese in an amount of 2.4-2.5 mg/kg and strontium in an amount of 8.4-11 mg/kg. The green colour has a high concentration of copper amounting to 9.4 mg/kg. In addition, the green colour contains chromium, nickel and molybdenum, which have not been detected above the detection limit in the pink colour.

PLA plastic, samples no. 11 and 12
Both samples contain tin in amounts of 30-42 mg/kg, zinc in amounts of 24-60 mg/kg, and copper in amounts of 5.6-5.8 mg/kg. The content of other metals (chromium, nickel, strontium and molybdenum) is rather low (0.14-0.94 mg/kg).

In general, the most frequently occurring metals are copper and zinc. In 11 of the 12 samples, copper was detected with a content of 0.6-190 mg/kg, and zinc was detected in all 12 samples with a content of 0.13-122 mg/kg. In general, the content of copper and zinc is higher in materials for 3D pens than for 3D printers. The highest content of copper appears in 4 samples in the colours blue, red and black. The blue colour has the highest content, which also is the case in previous analyses of materials for 3D printing (the Danish EPA, 2017). Another black sample only contains a minor amount of copper, indicating that the manufacturers must use different types of dyes for the materials.

None of the samples contain cadmium or mercury in amounts above the detection limit, and for lead the content is between 0.2-2.4 mg/kg in four of the samples (material types UV resin and ABS plastic). Eight of the samples contain chromium, which can indicate a content of hexavalent chromium. For chromium, the highest content appears to be 1.9-3.4 mg/kg in a red UV resin. In six of the samples (material types UV resin, Eco-Plastic and PLA plastic) tin was detected, which might indicate a content of organic tin. For tin, the highest content appears to be 30-42 mg/kg in red and brown PLA plastic.

The uncertainties are higher in the analysis results for materials used in 3D pens compared to materials used in 3D printers. That might be because the materials for 3D pens are not quite homogeneous when they exit the 3D pen. Another reason for the high uncertainty might be that the pen itself emits metals during use. The 3D pens used in this project were completely new when purchased and it is assumed that possible emissions of metal from the pen itself would be highest at the beginning. In this project, it has not been possible to further analyse the inhomogeneity of the materials or the emission of metals from the 3D pen itself.

4.3.2 Toxicity of metals

If focus is on the most critical metals in relation to toxicity, then none of the samples contain cadmium or mercury in amounts exceeding the detection limit, and for lead the contents are between 0.2-2.4 mg/kg. Several samples contain chromium (0.16-3.4 mg/kg) and tin (1.2-42.3 mg/kg), which might indicate a content of hexavalent chromium and organic tin, respectively. For chromium, the highest amount appears in a red UV resin (-4), whereas the highest tin content appears in a red PLA filament (-11), see Table 4.

The migration limits for metals, determined in the Toy Safety Directive for ”liquid or sticky toy material” are stated in Table 5 together with the interval of the content of the individual metals that were found in the analysed samples. The migration limits of the liquid or sticky toy materials are stated. When the material exits the 3D pen, it can in worst case be regarded as liquid or sticky. The screening analysis for metals that was carried out in this survey does not determine to what extent hexavalent chromium or organic tin, respectively, are present. Their limit values are substantially lower than the limit values for chromium or tin. If it is assumed that hexavalent chromium or tin are present, and that the entire content migrates out, then the limit values in the Toy Safety Directive have been exceeded. However, it is not expected that the entire amount of chromium is hexavalent chromium, or that the entire amount of tin is organic tin. In addition, it is expected that the migration of the substances to some extent is limited by the materials, and therefore complete migration is not regarded as realistic.

In sample 2 (blue, Eco-Plastic) copper was determined in a higher content than the limit value for migration. Therefore, a high copper content can be expected in blue samples as it originates from the colour. Eco-Plastic is used in 3D pens and it is a thermoplastic. The material melts in 3D pens and re-hardens when the temperature declines, but polymerization does not take place during the process. That means that the chemical bonds in the polymer remain intact. Therefore, it is expected that the migration of copper out of the material is limited, and it is not expected that the limit value will be exceeded.

Table 5. Overview of the results from analysis of metal and limit values indicated for migration of toys stated in the Toy Safety Directive (Directive 2009/48/EC).

Metal	Content found by analysis (min-max in mg/kg)	Limit values, directive 2009/48 (mg/kg in liquid or sticky toy material)
Chromium, Cr	0.16-3.4	9.4 for Cr III; 0.005 for Cr VI
Manganese, Mn	0.1-253	300
Nickel, Ni	0.13-0.88	18.8
Copper, Cu	0.63-190	156
Zinc, Zn	<0.13-122	938
Strontium, Sr	<0.13-11.23	1125
Molybdenum, Mo	0.14-0.86	Not stated
Tin, Sn	1.2-42.31	3750; organic tin 0.2
Antimony, Sb	<0.13-0.37	11.3
Lead, Pb	0.27-2.4	3.4

4.4 Screening analysis by GC-MS

The screening analyses by GC-MS cover a considerable number of volatile and semi-volatile organic substances, but the method is not suited for all substances. The method cannot detect acrylates or volatile aldehydes (including C1- to C4-aldehydes). Acrylonitrile is a monomer in ABS plastic, and it also requires a specific analytical method. The analysis for specific substances is described in the chapter on quantitative content analyses (chapter 4.6).

As the content of all substances was calculated against the same internal standard, the results from the GC-MS screening are regarded as semi-quantitative. In the analysis, some of the response factors of the substances were close to the response factor of the internal standard, whereas the response factor of other substances differs a lot. That will result in a more uncertain determination of the concentration in the sample.

Analytical method – volatile and semi-volatile organic substances by GC-MS
Sub samples of app. 0.5 gram were extruded directly into the extraction liquid and extracted with 5 mL dichloromethane. Extraction took place by shaking and was succeeded by ultrasound. Subsequently, methanol (1:5) was added to the extract to make the polymer precipitate. A deuterated internal standard of DEHP-d_4 was used.

The analyses of the extracts were carried out by capillary gas chromatography with mass selective detection (GC-MS).

Blanks of the liquids were analysed correspondingly.

The detection limits are estimated from internal standards and previous experience and can vary between 1 and 50 mg/kg depending on the matrices and the response of the substances.

All reported volatile and semi-volatile organic substances were determined semi-quantitatively against the response factor for DEHP-d_4.

Phenol-d_6, Naphthalene-d_8 and Phenanthrene-d_{10} had also been added as internal standards, but they were not used for the quantification. A reporting limit of 10 mg/kg was chosen.

Each substance was identified by comparing the actual mass spectra with the mass spectra from the NIST library[17]. The NIST library is a database with mass spectra for more than 500.000 chemical compounds. A hit rate in percent has been stated for all substances, and it indicates how probable the identifications are. However, verification against reference substances is necessary to obtain a probable identification; please refer to the quantitative analyses.

For certain substances, the hit rate can be low, and therefore the identification can be misleading as the set-up of a screening program by GC-MS cannot be optimum for all substances. All identifications with hit rates greater than 50% from the NIST library were reported, and so were a few identifications with lower hit rates if regarded relevant, e.g., at high concentrations. The identifications from the NIST library should only be regarded as indicative. They should be used as basis for deciding whether or not additional verification of the substances against relevant reference substances is necessary, and whether or not it is relevant to continue the migration tests for volatile and semi-volatile organic substances.

Constituents in materials used for 3D pens and 3D printers are difficult to identify as some of them are not disclosed by the manufacturers due to confidentiality. Therefore, it must be

[17] National Institute of Standards and Technology (NIST), USA.

assumed that the NIST library does not necessarily include all relevant mass spectra of the substances in these materials. The screening analysis by GC-MS can only include volatile and semi-volatile substances. That means that very polar and less volatile substances cannot be detected by this method as HPLC-UV or LC-MS must be applied. These techniques require knowledge of possible constituents and access to relevant reference substances, and therefore they were not included in the screening analyses in this project.

Not all materials were completely dissolved when dichloromethane was added. That might be due to a content of inorganic dyes, for instance Cu, but some very polar additives cannot be identified by the screening analysis. After one night of standing, some of the materials swelled up and absorbed all the dichloromethane and became a jelly-like substance that could not be injected on GC. Therefore, the GC analysis had to be carried out within few hours after the extraction of certain materials.

4.4.1 Results of the screening analyses

The detailed results of the screening analyses by GC-MS are presented in Table 6 to Table 10. The results were reported according to increasing retention time. A hit rate has been stated for all substances. The hit rate in percent indicates how probable the identification is in relation to the comparison of the actual mass spectra with the mass spectra from the NIST library. Please also refer to the method description of the screening analysis.

Table 6. Results from analysis of 3D pens, materials of UV reactive resin.

Unit: mg/kg			Sample number		
Substance	**CAS no.**	**Hit rate %**	**1**	**3**	**4**
Propylene glycol	57-55-6	65	106	2180	1880
2-Hydroxyethyl 2-propenoic acid ester, sum of two peaks	818-61-1	98	n.d.	1020	880
Benzyl chloride	100-44-7	65	n.d.	110	72
N,N-dimethyl-benzenemethanamine	103-83-3	87	n.d.	160	130
Ethenyl 2-propenoic acid ester, sum of two peaks	2177-18-6	43	n.d.	150	130
Oxybis(2,1-ethanediyloxy-2,1-ethanediyl)2-propenoic acid ester, sum of two peaks	17831-71-9	75	n.d.	130	110
Mequinol, sum of one to two peaks	150-76-5	67	413	80	63
2,4,5-Trimethyl-Benzaldehyde, sum of two peaks	5779-72-6	46	n.d.	180	160
2,4,6-Trimethyl-benzoic acid methyl ester	2282-84-0	54	183	43	24
Ethyl-2,4,6-trimethylbenzoate, sum of two peaks	1754-55-8	94	330	180	120
Benzoic acid, 2,4,6 trimethyl	480-63-7	77	n.d.	n.d.	75
Phenylphosphinic acid	1779-48-2	57	290	150	150
Tri (propylene glycol) diacrylate	42978-66-5	70	49	n.d.	n.d.
Phenyl-phosphonic acid diethyl ester, sum of two peaks	1754-49-0	95	230	180	170
Phenyl-phosphonous acid diethyl ester	1638-86-4	83	n.d.	10	10
2-Oxo-pentanedioic acid dimethyl ester, sum of two peaks	13192-04-6	50	n.d.	77	66

Unit: mg/kg			Sample number		
Substance	**CAS no.**	**Hit rate %**	**1**	**3**	**4**
Tri(propylenglycol), sum of two peaks	1638-16-0	63	2080	n.d.	n.d.
Pentaerythritol triacrylate, sum of four to six peaks	3524-68-3	41	10710	3350	2720
N-ethyl-N-(2-methoxyethyl)-benzenamine	-	63	n.d.	95	100
Parbenate (4-(dimethylamino)-benzoic acid ethyl ester), sum of two peaks	10287-53-3	98	2930	1350	1210
Tetradecanoic acid 2-[(Z)-1-octadecenyloxy]ethyl ester, sum of two peaks	30760-01-1	28	310	115	89
Tri-(propylene glycol) propyl ether	96077-04-2	29	3110	n.d.	n.d.
2-(2(3H)-Oxo-4H-1,4-benzoxazin-4-yl)acetic acid	6243-07-8	54	n.d.	84	92
Hexadecanoic acid methyl ester	112-39-0	67	n.d.	50	70
Succinic acid ethyl 2-phenoxyethyl ester	-	39	n.d.	21	18
(7,7-Dimethyl-1-oxo-2,3,4,5,6,7-hexahydro-1H-inden-2-yl) acetic acid methyl ester, sum of two peaks	55085-50-2	26	n.d.	110	120
3-[N-phenylsulfonylamino] benzamide	-	29	n.d.	n.d.	17
4,8,12,16-Tetraoxaeicosan-1-ol, sum of four peaks	-	53	10280	n.d.	n.d.
4-Oxo-pentanoic acid phenylmethyl ester	6939-75-9	19	n.d.	210	170
3-Octyl-2-oxiraneoctanoic acid methyl ester	2500-59-6	69	n.d.	n.d.	43
Mesity-isopropyllketon	2040-22-4	35	3980	640	460
Ethyl mesitylglyoxylate	5524-57-2	32	n.d.	1470	1370
9,12-Diepoxy ethyl stearate	-	48	n.d.	29	25
Pentaerythritoltetraacrylate	4986-89-4	49	290	n.d.	n.d.
Hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl)ethyl ester	23470-00-0	82	n.d.	190	170
Bis(2-ethylhexyl) isophthalate	137-89-3	48	50	n.d.	n.d.
Substances with low hit rate: number of peaks, concentration interval			3, 25-240	14, 10-140	14, 10-60

n.d. means not detected

Table 7. Results from analysis of 3D pens, materials of ABS plastic.

Unit: mg/kg			Sample number	
Substance	**CAS no.**	**Hit rate %**	**5**	**6**
1,3-Dimethyl-benzene	108-38-3	45	520	110
Styrene	100-42-5	46	1100	2150
4-Cyanocyclohexene	100-45-8	57	n.d.	73
Acetophenone	98-86-2	69	n.d.	280
α,α-Dimethyl-benzenemethanol	617-94-7	43	n.d.	280
2,2'-azobis (2-methylpropionitrile)	78-67-1	76	n.d.	56
(1-Methylethyl)-benzene	98-82-8	35	29	n.d.
Propyl-benzene	103-65-1	78	29	n.d.
Cis-1,1'-(1,2-Cyclobutanediyl)bis-benzene, sum of two peaks	7694-30-6	21	300	570
Dodecyl acrylate	2156-97-0	59	59	n.d.
Isophorone diisocyanate	4098-71-9	91	n.d.	58
1,1'-(1,3-Propanediyl)bis-benzene	1081-75-0	94	42	n.d.
Trans-1,1'-(1,2-cyclobutanediyl)bis-benzene	20071-09-4	73	100	n.d.
Hexadecanoic acid methyl ester	112-39-0	78	67	n.d.
Hexadecanoic acid ethyl ester	628-97-7	86	31	n.d.
3-Cyclohexen-1-yl-benzene, sum of two peaks	4994-16-5	43	116	n.d.
2-[1-(4-Cyano-1,2,3,4-tetrahydronaphthyl)]propanenitrile, sum of two peaks	57964-69-3	81	3700	4000
Octadecanoic acid ethyl ester	111-61-5	76	0	n.d.
3-[1-(4-Cyano-1,2,3,4-tetrahydronaphthyl)]propanenitrile, sum of two peaks	57964-40-6	94	820	830
Cyclopentanecarboxylic acid pentadecyl ester	-	24	100	89
Substances with low hit rate: number of peaks, concentration interval			10, 40-160	11, 70-330

n.d. means not detected

Table 8. Results from analysis of 3D pens, materials of UV reactive resin.

Unit: mg/kg			Sample number	
Substance	**CAS no.**	**Hit rate %**	**7**	**8**
Acetic acid, butyl ester	123-86-4	93	14	24
Cyclohexanone	108-94-1	53	7	17
4-Acetyl-morpholine	1696-20-4	84	17	140
N-Acryloylmorpholine	5117-12-4	98	8800	10100
2,4,5-Trimethyl-benzaldehyde	5779-72-6	49	n.d.	87
2,4,6-Trimethyl-benzoic acid methyl ester	2282-84-0	71	370	440
Tetrahydropyrrolo[2,1-c][1,4]oxazin-4-	101250-37-7	72	34	n.d.

Unit: mg/kg			Sample number	
Substance	**CAS no.**	**Hit rate %**	**7**	**8**
one				
2,4,6-Trimethyl-benzoic acid	480-63-7	82	880	2400
2,6-bis(1,1-Dimethylethyl)-4-hydroxy-4-methyl-2,5-cyclohexadien-1-one	-	89	160	n.d.
2,6-bis(1,1-Dimethylethyl)-2,5-cyclohexadiene-1,4-dione	719-22-2	72	33	n.d.
Butylated hydroxytoluene	128-37-0	71	230	380
2,4,6-Trimethyl-benzoic acid	480-63-7	79	34	51
Ethyl-2,4,6-trimethylbenzoate	1754-55-8	32	n.d.	55
Isophorone diisocyanate, sum of two peaks	4098-71-9	89	150	230
Phenyl cyclohexyl ketone	712-50-5	74	70	160
(1-Hydroxycyclohexyl)phenyl-methanone, sum of two peaks	947-19-3	97	5250	7050
Diphenyl-phosphinic methyl acid ester	1706-90-7	97	85	140
Ethyl mesitylglyoxylate	5524-57-2	31	770	1550
Mesity-isopropyllketon, sum of three peaks	2040-22-4	38	6140	6540
4-(Diphenylphosphinyl)-butanesulfonic acid methyl ester	-	87	270	160
Substances with low hit rate: number of peaks, concentration interval			16, 20-220	20, 30-230

n.d. means not detected

Table 9. Results from analysis of 3D pens, material with a play dough-like texture.

Unit: mg/kg			Sample number	
Substance	**CAS no.**	**Hit rate %**	**9**	**10**
Glycerine	56-81-5	92	7500	7580
Glycerol 1,2-diacetate, sum of two peaks	102-62-5	76	70	n.d.
1,2,3-Propanetriol 1-acetate	106-61-6	51	n.d.	61
Vanillin	121-33-5	64	36	42
2-Methyl-benzenesulfonamide	88-19-7	98	470	n.d.
4-Methyl-benzenesulfonamide	70-55-3	70	470	n.d.
Sum of alkanes	-	-	25900	24890

n.d. means not detected

Table 10. Results from analysis of 3D pens, materials of Eco-Plastic and PLA plastic.

Unit: mg/kg			Sample number		
Substance	**CAS no.**	**Hit rate %**	**2**	**11**	**12**
2-Hydroxy-propanoic acid methyl ester	2155-30-8	82	150	n.d.	n.d.
(2-Methylpropyl)-hydrazine	42504-87-0	65	200	n.d.	n.d.
3,6-Dimethyl-1,4-dioxane-2,5-dione, sum af to til tre toppe	95-96-5	57	780	3200	4800
2-Oxepanone	502-44-3	89	290	n.d.	n.d.
2-Isocyanato-1,3-bis(1-methylethyl)-benzene	28178-42-9	95	31	n.d.	n.d.
Isophorone diisocyanate	4098-71-9	92	120	n.d.	n.d.
Cyclopentanecarboxylic acid heptyl ester	-	8	810	n.d.	n.d.
Cyclopentanecarboxylic acid pentadecyl ester	-	22	630	n.d.	n.d.
Stoffer med lav hitrate: antal toppe, koncentrationsinterval			10, 30-90	9, 40-250	9, 45-270

n.d. means not detected

Many different volatile and semi-volatile substances were detected in the samples. The constituents of the samples are almost identical for the 3D pens where several types of material were chosen.

The lowest number of substances was detected for the 3D pens that use a material with a play dough-like texture, PLA plastic or Eco-Plastic. Then comes ABS plastic, whereas the highest number of different substances were found in UV reactive resins.

Below is a list of comments to each material type, see Table 6 to Table 10. The identifications from the NIST library should only be regarded as indicative.

UV reactive resin, samples no. 1, 3, 4, 7 and 8
Different UV reactive resins are used for 3D pens as the material from one 3D pen (sample no. 7 and 8) differs from the two other products (sample no. 1 and sample no. 3 and 4). Samples no. 1, 3 and 4 contain high concentrations of pentaerythritol triacrylate, whereas sample no. 7 and 8 contain N-Acryloylmorpholine and hydroxycyclohexyl phenyl ketone. An isophthalate was only detected in sample no. 1.

ABS plastic, samples no. 5 and 6
Samples no. 5 and 6 are ABS plastic and contain a high amount of styrene. That corresponds with the results in the project on 3D printed products, and with the fact that styrene is a monomer that is used in ABS plastic (the Danish EPA, 2017).

Material with a play dough-like texture, samples no. 9 and 10
The samples 9 and 10 resemble play dough and smell of vanilla, and the screening analyses did detect a content of vanillin. The samples mainly consist of alkane compounds and glycerine. Sample no. 9, pink, contains 4-Methyl-benzenesulfonamide (toluene-4-sulfonamide) that is used in the surface treatment of metal, glue, sealant, ink and toner[18].

[18] ECHA – open brief profile for toluene-4-sulfonamide, accessed 2017-08-26

Eco-Plastic, sample no. 2
The highest concentrations were found for a number of aliphatic esters and the substance 3,6-Dimethyl-1,4-dioxan-2,5-dion (DL lactide). The latter also exists in PLA plastic and is assumed to be a monomer of the plastic (the Danish EPA, 2017).

PLA plastic, samples no. 11 and 12
In general, the samples had poor identification of the constituents in low concentrations. The highest constituents were identified as 3,6-Dimethyl-1,4-dioxane-2,5-dion (DL lactide) that is a monomer of the plastic. In sample no. 12 (brown) 2-(3-Hydroxy-2-quinolinyl)-1H-indene-1,3(2H)-dion was detected. The substance is a yellow dye (Disperse Yellow 54) that is used as colour in polymer and textiles and also in ink and toner[19].

A content of isophorone diisocyanate was detected in Eco-Plastic (sample no. 2), ABS plastic (sample no. 6) and UV reactive resin (sample no. 7 and 8). Isocyanates are, i.a., used for polyurethane coatings (monomer), glue, sealant, play dough and polymers[20].

4.4.2 Initial hazard assessment in connection with GC-MS screening analysis

The substance identification that was carried out in connection with the GC-MS screening resulted in the detection of 151 substances that subsequently have been assessed. Out of them, sixteen substances were selected for quantitative analysis. Substances that only have been identified with a very low hit rate have not been analysed further.

Out of the 151 identified substances, 61 are registered on the list of the European Chemicals Agency (ECHA) on classification and labelling of chemical substances (C&L Inventory); 44 have been classified by the industry (self-classified), and 17 have a harmonised classification[21]. The 17 substances that have a harmonised classification have been reviewed in detail, see Table 11. Several of the substances have effects such as: acute toxic, skin irritating or corrosive, eye irritation, carcinogenic and mutagenic, and effects on specific organs. Six of the substances have been classified as skin sensitising (skin sens 1), and one substance is also sensitising if inhaled (Resp. Sens 1).

With 151 identified substances, it has not within the framework of this project been possible to review all classifications in detail. Therefore, the comments in the following cover:

- The 17 substances that have a harmonised classification
- Substances for which the self-classification states CMR effects (carcinogenic, mutagenic and toxic for reproduction)
- Substances that come within relevant chemical substance groups in relation to the polymer materials, such as: acrylates, phthalates and isocyanates

In addition, a comparison was carried out between the substances that were found in comparable material types in previous analyses of 3D printed products (the Danish EPA, 2017).

Sample 1 (UV resin) contains bis(2-ethylhexyl) isophthalate (CAS no. 137-89-3) that, i.a., has been self-classified as toxic for reproduction in category 1B (self-classification). Sample 1 also contains acrylates, i.a., pentaerythritol triacrylate (CAS no. 3524-68-3) that is classified as

[19] ECHA – open brief profile for 3-hydroxy-2-(3-hydroxy-2-quinolyl)-1H-inden-1-one, accessed 2017-08-26

[20] ECHA – open brief profile for 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate, accessed 2017-08-26

[21] ECHA – search for chemicals: https://echa.europa.eu/da/home

“causing eye and skin irritation” and “may cause allergic skin reaction” (harmonised classification).

Sample 2 (Eco-Plastic) contains several isocyanates (CAS no. 28178-42-9, self-classification, CAS no. 4098-71-9, harmonised classification) that have several adverse health effects such as skin and eye irritation and skin sensitisation.

Samples 3 and 4 (UV resin, are very comparable) contain benzyl chloride (CAS no. 100-44-7) that, i.a., is classified as carcinogenic in category 1B (harmonised classification). In addition, the samples contain 2-Propenoic acide, oxybis(2,1-ethanediyloxy-2,1-ethanediyl) ester (CAS no. 17831-71-9), an acrylate that does not have a harmonised classification. However, most notifiers have classified it as acute toxic, skin irritating, sensitising and harmful to the eyes. In a few self-classifications, it is also suspected of being mutagenic (Muta 2) (self-classification).

As expected for ABS, samples 5 and 6 (ABS plastic, are comparable) contain styrene (CAS no. 100-42-5). The samples also contain nitrile compounds in large amounts (i.a., CAS no. 57964-39-3, not in the CLP database). However, the nitrile compound with the likely CAS no. 78-67-1 is only detected in sample 6 (harmonised classification). In addition, the samples contain m-xylene (CAS no. 108-38-3) that also is detected in 3D pens and 3D printed products of ABS. The substance m-xylene is classified as causing skin irritation and being acute toxic (harmonised classification). Various benzene derivatives (CAS no. 20071-09-4 and 4994-16-5 do not exist in the C&L Inventory) were only detected in sample 5, but are correspondingly found in 3D printed products of ABS (comparison with (the Danish EPA, 2017)).

Samples 7 and 8 (UV resin, are comparable) contain 4-acetyl-morpholine that most notifiers have self-classified as skin sensitising (skin sens 2) and suspected of being toxic for reproduction (Repr. 2) (self-classification). In addition, the samples contain several ketones (e.g., CAS no. 947-19-3, self-classification) that also are the main content in 3D printed products made with UV resin. However, other main components are different. CAS no. 712-50-5 (self-classification) was detected in this UV resin used for 3D pens and in 3D printed products of UV resins. Besides ketones, the samples contain cyclohexanone (CAS no. 108-94-1) that is detected in much smaller amounts in 3D pens compared to 3D printed products. Cyclohexanone has a harmonised classification stating that the substance is harmful if inhaled.

Samples 9 and 10 (material with a play dough-like texture, are comparable) contain vanillin (CAS no. 121-33-5), and most notifiers self-classify them as causing eye irritation, whereas others self-classify them as skin sensitising (skin sens 1) (self-classification). Product 9 also contains two toluene derivatives that some self-classify as suspected of being toxic for reproduction (Repr 2) (CAS no. 70-55-3, only few) and suspected of being carcinogenic (Carc 2) (CAS no. 88-19-7, the main part).

Samples 11 and 12 (PLA, are comparable) contain none of the 17 substances with harmonised classification or other substances that are regarded relevant to examine in connection with this screening.

Table 11. Overview of the 17 identified substances with harmonized classification. Content is stated as an estimate from the screening analysis of the individual samples.

Substance	CAS no.	Sample no.	Content mg/kg	Harmonised classification
Benzyl chlorid	100-44-7	3 4	113 72	Acute Tox. 4 (H302), Skin Irrit. 2 (H315), Eye Dam. 1 (H318), Acute Tox. 3 (H331), STOT SE 3 (H335), Carc. 1B (H350), STOT RE 2 (H373)
Styrene	100-42-5	5 6	1097 2148	Flam. Liq. 3 (H226), Skin Irrit. 2 (H315), Eye Irrit. 2 (H319), Acute Tox. 4 (H332), STOT RE 1 (H372), Repr. 2 (H361d)
2-Propenoic acid, (1-methyl-1,2-ethanediyl)bis[oxy(methyl-2,1-ethanediyl)] ester	42978-66-5	1	49	Skin Irrit. 2 (H315), Eye Irrit. 2 (H319), Skin Sens. 1 (H317), STOT SE 3 (H335), Aquatic Chronic 2 (H411)
2-Propenoic acid, 2-hydroxyethyl ester	818-61-1	3 4	1071* 878*	Acute tox. 3 (H311), Skin Corr. 1B (H314), Skin Sens. 1 (H317), Aquatic Acute 1 (H400)
Acetic acid, butyl ester	123-86-4	7 8	14 24	Flam. Liq 3 (H226), STOT SE 3 (H336)
Acetophenone	98-86-2	6	276	Acute tox 4 (H302), Eye irritant 2 (H319)
(1-Methylethyl)-benzene	98-82-8	5	29	Flam. Liq 3 (H226), Asp. Tox. 1 (H304), STOT SE 3 (H335), Aquatic Chronic 2 (H411)
1,3-Dimethyl-benzene	108-38-3	5 6	520 108	Flam. Liq 3 (H226), Acute Tox. 4 (H312), Skin Irrit. 2 (H315), Acute Tox. 4 (H332)
propyl-Benzene	103-65-1	5	29	Flam. Liq. 3 (H226), Asp. Tox. 1 (H304), STOT SE 3 (H335), Aquatic Chronic 2 (H411)
N,N-dimethyl-Benzenemethana-mine	103-83-3	3 4	155 127	Flam. Liq. 3 (H226), Acute Tox. 4 (H302), Acute Tox. 4 (H312), Skin Corr. 1B (H314), Acute Tox. 4

Substance	CAS no.	Sample no.	Content mg/kg	Harmonised classification
				(H332), Aquatic Chronic 3 (H412)
Cyclohexanone	108-94-1	7 8	7 17	Flam. Liq 3 (H226), Acute Tox. 4 (H332)
Pentaerythritol triacrylate	3524-68-3	1 3 4	10710* 3349* 2804*	Skin Irrit. 2 (H315), Eye Irrit. 2 (H319), Skin Sens. 1 (H317)
Pentaerythritol tetraacrylate	4986-89-4	3	137	Skin Irrit. 2 (H315), Eye Irrit. 2 (H319), Skin Sens. 1 (H317)
Isophorone diisocyanate	4098-71-9	2 6 7 8	120 58 147* 233*	Skin Irrit. 2 (H315), Eye Irrit. 2 (H319), Skin Sens. 1 (H317), Acute Tox. 3 (H331), STOT SE 3 (H335), Resp. Sens 1 (H334), Aquatic Chronic 2 (H411)
4-Methoxyphenol	150-76-5	1 3 4	413 81* 63*	Acute Tox. 4 (H302), Eye Irrit. 2 (H319), Skin Sens. 1 (H317)
2,2'-Azobis (2-methylpropionitrile)	78-67-1	6	56	Self-react. C (H242), Acute Tox. 4 (H302), Acute Tox. 4 (H332), Aquatic Chronic 3 (H412)
2-Hydroxy-propanoic acid methyl ester	2155-30-8	2	153	Flam. Liq. 3 (H226), Eye Irrit. 2 (H319), STOT SE 3 (H335)

4.5 Choice of products and substances for quantitative analyses

A total of six materials were chosen for quantitative analyses for selected substances.

In general, the metal analyses state a low content in relation to limit values for migration in toys. There can be uncertainty on the presence of organic tin and hexavalent chromium, but further metal analyses were not carried out.

The GC-MS screening that was carried out gave an overall impression of the chemical composition and pointed at specific substances and substance groups of interest in relation to the later risk assessment. The GC-MS screening can give a deceptive impression of the chemical composition in relation to which substances and especially amounts children actually are exposed to when playing with 3D pens, and it cannot form the basis of the risk assessment. Therefore, the substance groups isocyanates, acrylates as well as isophthalate, styrene, vanillin and benzyl chloride are chosen for quantitative analysis where individual substances within each substance group are analysed quantitatively by using a more specific method

(e.g., HPLC, see Table 12). The substance groups were chosen on the basis of the initial hazard assessment and subsequent prioritisation in co-operation with the Danish EPA. It is expected that migration from materials that melt in the 3D pen and subsequently harden at room temperature (ABS, PLA, Eco-Plastic) is lower than from the UV resins that are not fully polymerized when they exit the 3D pen. Several substances were found by GC-MS screening, and the corresponding classifications are in general assessed to be more problematic than the classifications of the materials that harden without the influence of UV. Therefore, more quantitative analyses are carried out on UV resins than on materials that harden without the influence of UV.

The products selected for quantitative analyses cover UV reactive resin, Eco-Plastic, ABS plastic and material with a play dough-like texture.

Table 12. Overview of selected quantitative analyses and samples

Quantitative analysis for	Sample no.	Material type
Acrylic acid, methyl methacrylate, methacrylic acid, n-butylacrylate, 2-ethylhexyl acrylate, n-butylmethacrylate and pentaerythritol triacrylate. HPLC.	1 3	UV resin UV resin
Isophorone diisocyanate (CAS no. 4098-71-9), other isocyanates that are included within the same analytical method: 2,4-Toluene diisocyanate (2,4-TDI, CAS no. 584-84-9), 2,6-Toluene diisocyanate (2,6-TDI, CAS no. 91-08-7), 4,4'-Diphenylmethane diisocyanate (MDI, CAS no. 101-68-8), Hexamethylene diisocyanate (HDI, CAS no. 822-06-0) and 4,4'-Methylene-bis(cyclohexyl isocyanate), (HMDI, CAS no. 5124-30-1). HPLC	2 6 8	Eco-Plastic ABS plastic UV resin
Styrene (CAS no.100-42-5), GC-MS and headspace	6	ABS plastic
Vanillin, GC-MS	9	Play dough-like
Isophthalate identified in screening as CAS no. 137-89-3, GC-MS	1	UV resin
Benzyl chloride (CAS no. 100-44-7)	3	UV resin

Acrylic acid and other smaller acrylates were not detected by the GC-MS screening analysis. The screening analysis identified a possible content of pentaerythritol triacrylate, and therefore two materials of UV reactive resin, samples 1 and 3, respectively, were chosen for further analysis by HPLC for acrylic acid, selected acrylates and pentaerythritol triacrylate.

The screening analysis detected a possible content of isophorone diisocyanate in samples no. 2, 6 and 8 (Eco-Plastic, ABS plastic and UV resin, respectively). It was decided to carry out further analyses and include possible analysis of content of other selected isocyanates by HPLC that cannot be detected by GC-MS analysis.

Sample no. 6 (ABS plastic) was chosen for quantitative determination of styrene. When ABS is used in 3D pens, direct exposure to the heated material can result in a risk of exposure to styrene during use. That is because the migration of possible residue monomers increases at higher temperature (and not because polymerisation has not been terminated). The analysis determines the total amount of the monomer styrene in the ABS material. It was chosen not to analyse for acrylonitrile as no migration of acrylonitrile was detected in 3D printed products (the Danish EPA, 2017).

Sample no. 9 (material with a play dough-like texture) was chosen for quantitative analysis for vanillin, as the substance is regarded as relevant in relation to exposure of children due to the classification of the substance as eye irritating and skin sensitising (self-classification).

A content of isophthalate was detected in sample no. 1 (UV resin). The hit rate was only 50% for bis(2-ethylhexyl) isophthalate, and therefore an analysis was carried out to verify if this specific substance was in question or if it was a different phthalate.

4.6 Quantitative content analyses

In the following, the methods used for quantitative analyses are described.

Acrylic acid and acrylates (samples no. 1 and 3, UV resin)
A sub sample was extracted with acetonitrile and analysed by HPLC with UV detection (HPLC/UV). The quantification was carried out by using the calibration curves of each reference substance. Blanks of the liquids were analysed correspondingly. Triple determination was carried out.
Detection limit of the method: 0.05 mg/g
The detection limit was determined from the lowest calibration point.
Recovery percent (component dependent): 80-120%
Uncertainty: 15% RSD

Two solutions were tested in connection with the analysis for acrylates. Acetonitrile is a much better extraction agent than THF. It cannot be excluded that other solvents can have a different extraction efficiency, but that has not been examined in this project. In connection with extraction with THF it was not possible to determine acrylic acid or several of the acrylates due to interference from other substances in the material. It was not possible to analyse for 2-ethylhexylacrylate due to interference from pentaerythritol triacrylate in both solvents.

It was only possible to purchase a technical material as reference substance for pentaerythritol triacrylate. It consists of several isomers that result in several peaks in the chromatogram. That makes the quantification uncertain as no certificate can be obtained that describes the distribution between the isomers. All analysed samples contain isomers, but it appears that the relation between the isomers in the samples differ from the reference substance. It has not been possible to receive information about the purity of the technical material, but it is estimated to min. 50%, and the results are reported on the basis of a purity of 50%.

Isocyanates (samples no. 2, 6 and 8, Eco-Plastic, ABS plastic and UV resin, respectively)
A sub sample was extracted with dichloromethane added internal standard, derivatized and analysed by HPLC with fluorescence detection (HPLC/FLD). The quantifications were carried out by using the calibration curves of each reference substance. Blanks of liquids were analysed correspondingly. Triple determination was carried out.
Detection limit of the method: 0.1 ug/g
The detection limit was determined from the lowest calibration point.
Recovery percent (component dependent): 50-105% (detection limit is increased for isocyanate with low recovery)
Uncertainty: 25% RSD

Styrene (sample no. 6, ABS plastic), benzyl chloride (sample no. 3, UV resin), vanillin (sample no. 9, material with a play dough-like texture) and phthalates and isophthalate (sample no. 1, UV resin)
A sub sample was extracted with dichloromethane added internal standards and analysed by GC with MS detection (GC/MS). The quantifications were carried out by using the calibration curves of each reference substance. Blanks of the liquids were analysed correspondingly. Triple determination was carried out.
Detection limit of the method (component dependent): 5-25 ug/g
The detection limit was determined from the lowest calibration point.
Recovery percent (component dependent): 80-120%

Uncertainty: 15% RSD

The reference substance bis(2-ethylhexyl) isophthalate, CAS no. 137-89-3, was included for the analysis of phthalate. The substance had a suggested hit rate of 50% according to the NIST library.

4.6.1 Results of quantitative content analyses

The following tables state the results of the quantitative analyses. All analyses were carried out on the materials after they had been fed through the 3D pens.

Table 13. Results from analyses of acrylic acid and selected acrylates

Unit: mg/kg		Sample no., colour, material	
Substance	**CAS no.**	**1, black, UV resin**	**3, blue, UV resin**
Acrylic acid	79-10-7	150	310
Methyl methacrylate	80-62-6	320	290
Methacrylic acid	79-41-4	<50	340
n-Butyl acrylate	141-32-2	<50	120.000
n-Butyl methacrylate	97-88-1	66.000	20.000
Pentaerythritol triacrylate	3524-68-3	>730,000*	>250,000*

< Means less than the stated detection limit. *It has not been possible to receive information about the purity of the reference material, which is a technical grade. The purity of the technical grade is estimated to min. 50% and it is from that purity the result is reported.

Table 14. Results from analyses of isocyanates

Unit: mg/kg		Sample no., colour, material		
Substance	**CAS no.**	**2, blue Eco-Plastic**	**6, yellow, ABS plastic**	**8, purple, UV resin**
Toluen-2,4-diisocyanate	584-84-9	<0.1	<0.1	<0.1
Toluen-2,6-diisocyanate	91-08-7	<0.1	<0.1	0.51
Hexamethylene diisocyanate	822-06-0	<0.2	<0.2	<0.2
4,4'-Methylenbis(phenyl isocyanate) – mixture of cis and trans	101-68-8	<0.1	<0.1	<0.1
4,4'-Methylenbis(cyclohexyl isocyanate) – mixture of cis and trans	5124-30-1	<0.1	<0.1	<0.1
Isophorone diisocyanate	4098-71-9	<0.1	<0.1	<0.1

In the GC-MS screening, the NIST library stated that several of the samples could have a content of isophorone diisocyanate in several of the samples. The subsequent quantitative analysis by HPLC did not detect a content of isophorone diisocyanate (the same extraction agents were used in the two analyses). That might be due to differences in the two analysis techniques, and based on previous experience with the methods it is probable that substances can be created when the sample is heated by injection on the GC-MS equipment. Afterwards they can be detected in the analysis. That does not happen in the quantitative method on HPLC, and therefore it gives a better impression of the substances and amounts a child is actually exposed to during use.

Sample no. 3 (blue, UV resin) was analysed for benzyl chloride, CAS no. 100-44-7.
The sample contains 330 mg/kg.

Sample no. 6 (yellow, ABS plastic) was analysed for styrene, CAS no. 100-42-5.
The sample contains 1100 mg/kg.

Sample no. 9 (pink, play dough-like) was analysed for vanillin, CAS no. 121-33-5.
The sample contains 59 mg/kg.

Sample no. 1 (black, UV resin) was analysed for bis(2-ethylhexyl) isophthalate, CAS no. 137-89-3. The analysis showed that sample no. 1 did not contain bis(2-ethylhexyl) isophthalate, but it probably contained another phthalate, which it has not been possible to identify in this project. The GC-MS screening detected a content of 50 mg/kg when calculated against the internal standard DEHP-d_4.

4.7 Headspace analysis of styrene

When using 3D pens it was observed that some pens became very hot and malodorous. Therefore, a decision was made to carry out a headspace analysis for styrene in order to estimate how much styrene the user can be exposed to by inhalation when a 3D pen that uses ABS plastic is in question. Sample no. 6 was chosen for the analysis. According to the manufacturer, the ABS plastic is heated to between 230 and 240 degrees when the 3D pen is used.

Before a headspace analysis, the sub sample is heated, and it can be heated up to 120 degrees. In the laboratory, heating takes place over a longer period of time, and therefore it cannot be ruled out that the heating process might influence the composition of the ABS plastic differently in a 3D pen. However, the risk is assessed to be limited as the temperature is lower than the temperature in a 3D pen.

Two headspace analyses were carried out on the ABS plastic before and after the plastic had been fed through the 3D pen to examine if the process is of importance. When sampling a material that has been fed through a 3D pen, drawing takes place directly into the sample vial. Part of the styrene might have time to evaporate in connection with the sampling. Therefore, it cannot be ruled out that the analysis underestimates the actual emission of styrene from ABS plastic, immediately after it exits the 3D pen.

App. 0.01 g was weighed in a sample vial before heating to 120 degrees.
Styrene was detected by GC-MS.
The detection limit of the method: 50 ug/g
The detection limit was determined from the lowest calibration point
Recovery percent: 109-120%
Uncertainty: 20% RSD

4.7.1 Results of headspace analysis of styrene

The results of the headspace analysis of sample no. 6 are stated in Table 15.

Table 15. Results of headspace analysis of styrene

Unit: mg/kg	Sample no. 6, yellow, ABS
Base material, 120 degrees	120
After the 3D-pen, 120 degrees	270

Sample 6 was analysed after it had been fed through a 3D pen, and a content of styrene of 1,100 mg/kg was quantified. By headspace, app. a tenth of that content was measured in the

material before it was fed into the 3D pen, and app. a fifth was measured after the material had been fed through the 3D pen.

4.8 Summary of analysis results

Analyses were carried out on 8 3D pens with 12 accompanying materials consisting of UV reactive resins, ABS plastic, PLA plastic and Eco-Plastic and a material with a play dough-like texture. The analyses were carried out after the materials had been fed through the respective 3D pens.

Analyses were carried out for 15 metals/elements, and a content of chromium, manganese, nickel, copper, zinc, strontium, molybdenum, tin, antimony and lead was detected. No content of cobalt, arsenic, selenium, cadmium or mercury was detected. The detected metals and elements in the materials that had been fed through the 3D pens correspond to the analysis results that were reported in a previous project for the Danish EPA where analyses were carried out on 3D printed products (the Danish EPA, 2017). More metals/elements and higher concentrations were detected in this project - especially in UV reactive resins. There is no clear tendency between the detected metals and the colour of the materials except for a high content of copper in the blue colour and in some of the dark colours. Based on the content analyses of metals and compared to the limit values for migration of toys, there might be a risk that they are exceeded for chromium and tin. However, that presupposes that hexavalent chromium and organic tin are in question, and that the substances migrate out of the materials. All in all, it is not regarded as probable that these conditions will be fulfilled, and it was chosen not to carry out a similar analysis in this project.

The GC-MS screening analysis of the materials indicates a content of a wide range of chemical substances. This analysis identified the lowest number of substances for 3D pens that use a material with a play dough-like texture, PLA plastic or Eco-Plastic. Then comes ABS plastic, whereas UV reactive resins contain the highest number of different substances. There are similarities between the results of the screening analyses and the results reported in the previous survey of 3D printed products. However, there are also differences in the constituents. In connection with 3D printed products, the UV reactive resins also contained most different substances. Substances were identified that come within the relevant chemical substance groups, meaning substance groups that can be expected in polymer materials, such as acrylates, isocyanates, styrene and nitrile compounds. In one UV reactive resin (sample no. 1), an indication of a possible content of an isophthalate was detected in the screening analysis. Correspondingly, a content of phthalates was only detected in 3D printed products of UV resin in the previous survey (the Danish EPA, 2017). In this project, it has not been possible to confirm the identity of the substance. In addition, the screening identified vanillin in one type of material. The stated hit rates of identification indicate a large uncertainty on the identifications for certain substances, which also was the case in the previous project.

Quantitative analyses were carried out on 16 selected substances with various specific analytical methods. Table 16 gives an overview of the results of the 10 substances for which the quantitative results were above the detection limits of the methods. The remaining six substances (five isocyanates and bis(2-ethylhexyl) isophthalate) were not detected at a level above the detection limit, and therefore a content of those substances cannot be confirmed.

Table 16. Overview of quantitative results.

Substance	CAS no.	Sample no., colour	Material type	Result
Acrylic acid	79-10-7	1, black 3, blue	UV resin	0.15 g/kg 0.31 g/kg
Methyl methacrylate	80-62-6	1, black 3, blue	UV resin	0.32 g/kg 0.29 g/kg
Methacrylic acid	79-41-4	3, blue	UV resin	0.34 g/kg
n-Butyl acrylate	141-32-2	3, blue	UV resin	120 g/kg
n-Butyl methacrylate	97-88-1	1, black 3, blue	UV resin	66 g/kg 20 g/kg
Pentaerythritol triacrylate	3524-68-3	1, black 3, blue	UV resin	>730* g/kg >250* g/kg
Toluene-2,6-diisocyanat	91-08-7	8, purple	UV resin	0.51 mg/kg
Benzyl chloride	100-44-7	3, blue	UV resin	330 mg/kg
Styrene	100-42-5	6, yellow	ABS plastic	1100 mg/kg
Vanillin	121-33-5	9, pink	Play dough-like	59 mg/kg

The quantitative results for benzyl chloride and vanillin are a factor 2-3 higher than the calculated semi-quantitative results from the initial GC-MS screening, whereas styrene is a factor 2 lower.

The content of pentaerythritol triacrylate is very high in the two analysed UV reactive materials. That indicates that it is one of the main components in the polymer material.

The quantitative analyses could not identify one phthalate, and one isocyanate could not be recovered by HPLC analysis as it might have been created in the injector of the GC-MS. That supports the fact that GC-MS screenings are a splendid tool to obtain an impression of the complexity of substances and the estimated content in a material that is unknown. However, they have to be followed up by further analyses with specific methods and reference substances to be sure of the correct identity and exact concentration.

Styrene is dangerous if inhaled, and due to the high content in ABS plastic and the ascertained malodour when using the 3D pen, a headspace analysis was carried out of styrene. On the basis of the headspace analysis it is estimated that app. 10-20% of the substance is emitted to the surrounding air.

5. Hazard assessment of 3D pens

5.1 Choice of substances for hazard and risk assessment

The results of the quantitative analyses for 16 selected substances on six materials for 3D pens show a content of ten substances above the detection limit of the applied methods (see Table 16, which sums up the results of the quantitative analysis).

The toxicological effects of the ten substances, as stated by notifiers of substances under REACH[22], are listed in Table 17. As shown in the table, DNEL values (Derived No Effect Level) have not been stated for users for all substances. In this project, it was decided that substances for which no DNEL value was stated will not be discussed further.

Four substances were selected for review in this report:

- Acrylic acid
- n-Butyl methacrylate
- Styrene
- Vanillin

The four substances were selected according to an introductory risk assessment based on the indicated DNEL in Table 17, and the exposure calculation performed on scenarios for a 3-6-year-old child, as described in CHAPTER 3, and with the exposure model that corresponds to the declared effects. This means that the calculation distinguishes between the following routes of exposure: inhalation, dermal or oral exposure, and whether acute or long-term effects are concerned. The risk characterization ratio (RCR) for substances in this realistic worst case assessment were below 1, which indicates a low risk upon usage (data not shown). Acrylic acid, n-butyl methacrylate and styrene were the three substances that showed the highest RCR values according to the conditions described in CHAPTER 3. They are therefore discussed in detail in the following sections.
In this connection, vanillin is an exception, because ECHA does not report a DNEL value, but the substance is a known allergen (SCCS, 2012). However, no data is available on the specific threshold values for vanillin. Therefore, the analysis result was used to calculate a dermal exposure, which is compared to the general threshold value reported by SCCS for allergenic substances (SCCS, 2012). This comparison shows that the threshold value was exceeded considerably under the applied conditions. Therefore, the substance is included in the discussion in the following sections.

Table 17. Overview of substances analysed quantitatively with results above the detection limit and the threshold values (DNEL) for users stated by notifiers of the substance at ECHA.

Substance	CAS no.	DNEL (ECHA)
Acrylic acid	79-10-7	**Inhalation:** Long-term: (DNEL) 3.6 mg/m³ irritation (respiratory tract) Acute /short term: (DNEL) 3.6 mg/m³ irritation (respiratory tract) **Dermal:**

[22] https://echa.europa.eu/

		Acute /short term: (DNEL) 1 mg/cm² skin irritation/corrosion
Methyl metacrylate	80-62-6	**Inhalation:** Long-term, systemic: (DNEL) 74.3 mg/m³ (repeated dose toxicity) Long-term, local: (DNEL) 104 mg/m³ (repeated dose toxicity) **Dermal:** Long-term, systemic (DNEL) 8.2 mg/kg BW/day Long-term, local (DNEL) 1.5 mg/cm2 (sensitizing) Acute /short term, local (DNEL): 1.5 mg/cm2 (sensitizing)
Methacrylic acid	79-41-4	**Inhalation:** Long-term, systemic: (DNEL) 6.3 mg/m³ irritation (respiratory tract) Long-term, local: (DNEL) 6.55 mg/m³ irritation (respiratory tract) **Dermal:** Long-term, systemic (DNEL) 2.55 mg/kg BW/day irritation (respiratory tract)
n-Butylacrylate	141-32-2	-
n-Butylmethacrylate	97-88-1	**Inhalation:** Long-term, systemic: (DNEL) 66.5 mg/m³ (repeated dose toxicity) Long-term, local: (DNEL) 366.4 mg/m³ irritation (respiratory tract) **Dermal:** Long-term, systemic (DNEL) 3 mg/kg BW/day (repeated dose toxicity)
Pentaerythritol triacrylate	3524-68-3	-
Toluen-2,6-diisocyanat	91-08-7	No threshold values stated at ECHA for the general population, but for workers the following is stated: **Inhalation:** Long-term, systemic(DNEL) 0.035 mg/ m³ Long-term, local (DNEL) 0.035 mg/ m³ Acute, systemic (DNEL) 0.14 mg/ m³ Acute, local (DNEL) 0.14 mg/ m³
Benzyl chloride	100-44-7	-
Styrene	100-42-5	**Inhalation:** Long-term, systemic: (DNEL) 10.2 mg/m³ (repeated dose toxicity) Acute/short term, systemic: (DNEL) 174.25 mg/m³ (acute toxicity) Acute/short term, local: (DNEL) 182.75 mg/m³ (acute toxicity) **Dermal:** Long-term, systemic (DNEL) 343 mg/kg BW/day (repeated dose toxicity) **Oral:** Long-term, systemic (DNEL) 2.1 mg/kg BW/day (repeated dose toxicity)
Vanillin	121-33-5	**Dermal:** Acute, local: SCCS: 0.8 ug/cm² (SCCS, 2012)

5.2 Hazard assessment of the four selected substances

The following section provides an overview of the hazardous health effects, which are generally attributed to the selected substances. The information is based on the threshold value assessments stated in the public part of the REACH-register dossier of the substance, where mainly studies based on the established OECD test guideline, mainly are carried out according to the GLP standard (Good Laboratory Practice), create a foundation for the determined threshold value. Furthermore, the risk assessment reports from the EU and other international organizations (e.g., OECD) are used. Great emphasis will be put on the routes of exposure that in previous chapters were emphasized as especially important when using 3D pens: dermal contact and inhalation, but all effects of these substances will be included in the assessment.

Each substance will be assessed according to:

- Identification, classification and physicochemical properties
- Absorption and distribution
- Local effects: irritation and allergy (skin/eyes/respiratory irritation, corrosiveness and sensitization)
- Systemic effects: acute and chronic effects
- Identification of critical effect and determination of a safe dose (DNEL)

CLP classification and hazard classes are applied, and hazard statements have been given for the analysed substances. For vanillin, which does not have a harmonized classification, but on the other hand is self-classified by industry, aggregated hazard classes and statements are used, which have been notified for the respective substance. In case of coinciding classification within the relevant categories (e.g., Acute Tox. 2 and Acute Tox. 3), the most conservative is highlighted (worst case). To emphasize the relative frequency of the self-classified categories, the number of notifications for each category is given in relation to the total number of notifications for the respective substance.

Irritation and allergy, and acute and chronic effects will be assessed according to the CLP classification (self-classification or harmonized classification) of the substances. Where possible, the derived no-effect level (DNEL) will be identified for the relevant routes of exposure (primarily dermal contact and inhalation).

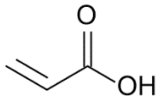
5.2.1 Acrylic acid

Identification, classification and physicochemical properties

Physicochemical properties and the classification of the substance from the ECHA substance profile are shown in Table 18.

Table 18. Physicochemical properties stated in ECHA's published registration data for this substance as well as the classification of the substance in ECHA's CLP database.

Chemical name	Acrylic acid
Synonyms	2-hydroxyethyl methacrylate 2-Propenoic acid ACRYLIC ACID Acrylic Acid (stabilized with MEHQ) acrylic acid, acrylic acid glacial, acrylic acid technical Acrylic acid; prop-2-enoic acid Acrylicacid Acrylsäure prop-2-enoate

	Prop-2-enoic acid propenoic acid
CAS no.	79-10-7
EC no.	201-177-9
Chemical structure	
Classification Harmonised CLP classification	Flam. Liq. 3, H226 – Flammable liquid and vapour Acute Tox. 4, H302 - Harmful if inhaled, H312 - Harmful in contact with skin, H332 - Harmful if inhaled Skin Corr. 1A, H314 – Cases severe skin burns and eye damage Aquatic Acute 1, H400 – Very toxic to aquatic life STOT SE 3, H335 May cause respiratory irritation: C ≥ 1%
Physical condition	Liquid
Molecular weight	72.06 g/mol
Melting point	13 °C
Boiling point	141 °C
Vapour pressure	5.29 hPa
Distribution coefficient (log Pow)	0.46
Water solubility	1000 g/L

Absorption and distribution

According to the toxicokinetic study referred to in the published part of the registration data of the substance at ECHA[23], acrylic acid is quickly absorbed and eliminated in rats (Fischer 344) after a single oral dose of 150 or 40 mg/kg body weight. Exhalation was stated to be the most important elimination route with app. 80-90% of the administered dose recovered after dosage. The process is fast and almost complete within 8 hours after a dosage of 40mg/kg, and within 24 hours after a dosage of 150 mg/kg. 88-95% of the administered dose was recovered at the completion of the study. The incomplete recovery can most likely be explained by the volatility of acrylic acid and its inclination to bind itself to materials such as plastic or glass, which may result in the loss of substance during the chemical analysis. No information exists on the distribution after dermal absorption or inhalation of the substance. For a hydrophilic substance such as acrylic acid, an almost quantitative absorption (100%) via inhalation can probably be assumed (EU RAR, 2002). In case of dermal exposure, part of the acrylic acid can be expected to evaporate due to the vapour pressure of the substance, whereas the remaining part is absorbed fast as observed in studies on mice and rats. However, dermal absorption is very dependent on i.a. the pH value of the dosage of the solution (EU RAR, 2002).

Local effects: Irritation and allergy

DNEL values for several local effects were declared in the toxicological summary of the registration of the substance at ECHA[23].

For irritation of the respiratory tract, a DNEL of 3.6 mg/m³ is stated for both acute and chronic irritation. A rat study (Sprague-Dawley), carried out according to a method that is considered comparable with the OECD Guideline 403 for determination of the acute inhalation toxicity, is stated as key study. Test animals (10 of each sex) were exposed to saturated vapours with the substance in two concentrations of 4.25 and 5.12 mg/L, respectively, over a period of 4 hours.

[23] https://echa.europa.eu/da/registration-dossier/-/registered-dossier/15803/7/2/2

It is not stated how the declared DNEL was reached, or which safety factors were used to determine the DNEL value.

A DNEL of 1 mg/cm² is stated for acute irritation/corrosion of skin. A rabbit test (New Zealand White) was indicated as the key study, and it was carried out according to GLP guidelines (standard acute method). The test animals (5 of each sex) were exposed to a dermal dose of 2000 mg/kg body weight by exposure to the substance in a 20% aqueous solution for a period of 24 hours. Irritation, discoloration, rupture and/or mechanical damage were observed in places where the substance was dosed on the skin during the entire observation period (14 days). Another rabbit test (New Zealand White) is referred to, and it was carried out according to the OECD Guideline 404 for determination of acute dermal irritation/damage. In this test, five test animals were exposed to the substance for only 3 minutes (load is not indicated), after which the animals developed eczema, which spread over the contact area within an hour. Based on this test, it was concluded that the substance is highly corrosive. It is not stated how the given DNEL was reached or which safety factors were applied. A repeated administration of a 4% solution on the skin of mice over a period of 13 weeks with 3 dosages per week caused irritation, whereas the administration of a 1% solution for 13 weeks or throughout the entire lifetime did not cause any effects (EU RAR, 2002).

Systemic effects: Acute and chronic effects
No systemic effects for acrylic acid were stated in relation to the registration of the substance. In the EU risk assessment of the substance from 2002, it has been concluded that acrylic acid is neither carcinogenic, mutagenic nor toxic for reproduction (EU RAR, 2002).

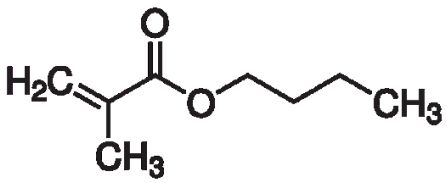
Identification of critical effect and determination of safe dosage
In general, the toxicological profile of acrylic acid is dominated by the local irritation effects, which are also highly relevant in relation to the expected user pattern regarding the use of 3D pens with expected skin contact and risk of evaporation of volatile substances during the production of 3D objects. Therefore, the critical effect in the risk assessment of this substance is regarded to be irritation (dermal and inhalation). DNEL for users, as stated by the notifier of the substance, is used for the risk assessment.

5.2.2 n-Butyl methacrylate

Identification, classification and physicochemical properties
Physicochemical properties and the classification of the substance from the ECHA substance profile (brief profile) appear in Table 19.

Table 19. Physicochemical properties stated in ECHA's published registration data for the substance as well as the classification of the substance in ECHA's CLP database.

Chemical name	n-Butyl methacrylate
Synonyms	2-Propenoic acid, 2-methyl-, butyl ester butyl 2-methylprop-2-enoate BUTYL METHACRYLATE Butyl Methacrylate (stabilized with HQ) butyl-methacrylate- N-BUTYL METHACRYLATE n-Butylmetacrylat n-Butylmethacrylat
CAS no.	97-88-1
EC no.	202-615-1

Chemical structure	
Classification Harmonised CLP classification	Flam. Liq. 3, H226 – Flammable liquid and vapour Skin Irrit. 2, H315 – Causes skin irritation Eye Irrit. 2, H319 – Causes serious eye irritation Skin Sens. 1, H317 - May cause an allergic skin reaction STOT SE 3, H335 - May cause respiratory irritation
Physical condition	Liquid
Molecular weight	142.20 g/mol
Melting point	-50 °C
Boiling point	163 °C
Vapour pressure	2.12 hPa
Octanol/water distribution coefficient (log Pow)	3
Water solubility	360 mg/L

Absorption and distribution

n-butyl methacrylate is absorbed more or less via all routes and then quickly hydrolyzes with carboxylesterases to methacrylic acid and the respective alcohol (n-Butanol). The original acrylate disappears from the body within few minutes. The primary degradation products – methacrylic acid and the corresponding alcohol are also quickly removed from the blood via the physiological routes, where the largest part of the dosage substance is exhaled as CO_2. For the decomposition product methacrylic acid the decay period in rats is only 1.7 minutes[24].

Local effects: Irritation and allergy

n-butyl methacrylate is classified as skin irritating and sensitizing. According to the published part of the REACH registration of the substance, LLNA data (Local Lymph Node Assay) is not available, which means that the induction-specific DNEL has not been derived for skin sensitizing. As the notifier believes the substance has low allergy-inducing potential, also reported earlier (ECETOX, 1996), a sensitization DNEL of 1% is assumed in solution.[25]

The substance can also cause irritation of the respiratory tract (locally), and notifiers under REACH have set a DNEL for chronic irritation of the respiratory tract of 366.4 mg/m³ irritation (respiratory tract). That was based on a 28-day inhalation study on rats of both sexes, which was carried out according to applicable GLP rules and OECD guidelines (OECD 412, Sub-acute Inhalation Toxicity: 28-Day Study), where the histopathological changes in the nasal cavity were detected. In the study, NOAEC (No Observed Adverse Effect Concentration) for this local effect was set to 310 ppm (corresponding to 1832 mg/m³). That is consistent with the structurally similar methyl methacrylate, which just as n-butyl methacrylate forms methacrylic acid at decomposition. For the calculation of DNEL, a joint safety factor of 5 is applied, by means of which the differences between humans (intraspecies)[25] are taken into consideration.

[24] https://echa.europa.eu/da/registration-dossier/-/registered-dossier/15151/7/2/1

[25] https://echa.europa.eu/da/registration-dossier/-/registered-dossier/15151/7/1

Systemic effects: Acute and chronic effects
The substance can cause chronic irritation of the respiratory tract (systemic), and noifiers under REACH have determined a DNEL for chronic irritation of the respiratory tract of 66.5 mg/m³ irritation (repeated dose toxicity). This was determined according to a 28-day inhalation study on rats of both sexes, which was carried out according to applicable GLP rules and OECD guidelines (OECD 412, Subacute Inhalation Toxicity: 28-Day Study), where histopathological changes in the nasal cavity were detected. In the study, NOAEC (No Observed Adverse Effect Concentration) for the systemic effect was set to 1891 ppm (corresponding to 11,175 mg/m³). For the calculation of DNEL, a joint safety factor of 168 is used, where the length of the applied study (sub-acute to chronic; factor 6), differences between humans (intraspecies, factor 5), and that the exposure time is assumed to be considerably longer for the general population than for workers (factor 5,6)[25].

In case of oral ingestion, the notifiers of the substance have set a DNEL for chronic effects to 3 mg/kg BW/day (repeated dose toxicity). That was determined according to signs of general systemic toxicity at a dose exceeding 120 mg/kg BW/day (NOAEC) both for male and female rats in a sub-chronic 90-day probe study carried out according to OECD Guideline 408 (Repeated Dose 90-Day Oral Toxicity in Rodents). The effects include affected liver activity (increased liver weight, prolonged prothrombin time, decreased serum globuline and triglyceride levels) and kidney weight (increased absolute weight). For the calculation of DNEL, a joint safety factor of 40 is applied, by means of which the differences between species (rats to humans, factor 4), differences between humans (intraspecies, factor 5) and the length of the study (sub chronic to chronic, factor 2) are taken into consideration[25].

No CMR effects (carcinogenicity, mutagenicity and reproductive toxicity) have been reported for n-butyl methacrylate (ECETOC, 1996).

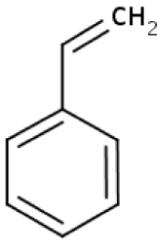
Identification of critical effect and determination of safe dose
As oral ingestion connected with the use of 3D pens by children is considered to be very limited, and as the allergy inducing potential is low, the most critical effect is considered to be irritation of the respiratory tract with a DNEL of 66.5 mg/m^3.

5.2.3 Styrene

Identification, classification and physicochemical properties
Physicochemical properties and the harmonized CLP classification reported on ECHA's website are shown in Table 20.

Table 20. Physicochemical properties stated in ECHA's published registration data for the substance as well as the classification of the substance in ECHA's CLP database.

Chemical name	Styrene
Synonyms	Styreen Styren Styrene Styrene monomer Styrol Styrole Styrolene
CAS no.	100-42-5
EC no.	202-851-5

Chemical structure	
Classification Harmonised CLP classification	Repr. 2, H361d – Suspected of damaging the unborn child Acute Tox. 4, H332 – Harmful if inhaled STOT RE 1, H372 – Causes damage to organs (auditory organ) through prolonged or repeated exposure Skin Irrit. 2, H315 – Causes skin irritation Eye Irrit. 2, H319 – Causes serious eye irritation Flam. Liq. 3, H226 – Flammable liquid and vapour
Physical condition	Liquid
Molecular weight	104.151 g/mol
Melting point	-31 °C
Boiling point	145 °C
Vapour pressure	6.67 hPa
Distribution coefficient (log Pow)	2.95
Water solubility	310 mg/L

Absorption and distribution
According to scientific literature, styrene vapours are easily absorbed by humans via inhalation. The absorbed fraction of the substance is app. 100% at concentration levels of 10-200 ppm. For skin contact, the absorption of styrene is considerably lower with an estimated absorption of 2-5% of the applied dose. There is no accessible information regarding the oral ingestion of styrene, but based on the physicochemical properties and compared to data from tests with animals the absorbing fraction is assumed to be app. 100 % (EU RAR, 2008).

Styrene and metabolites of this substance are distributed in the entire body with the highest concentration in the fatty tissue. The concentration of styrene is usually higher in the brain compared to the concentration in the blood. Tests with mice have also demonstrated that the substance can reach the embryo via the placenta. In humans, styrene decomposes rather quickly and is eliminated via the urine. A more detailed description of the metabolism of styrene can be found in the report on styrene by the Danish EPA, which was prepared as a part of the work carried out in relation to the List Of Undesirable Substances (LOUS) (EPA, 2014C).

Local effects: Irritation and allergy
Styrene is classified under CLP as a substance that can cause skin irritation (Skin Irrit. 2) and serious eye irritation (Eye Irrit. 2). The available data on skin irritation after exposure to styrene in liquid form indicates that repeated exposure is required to induce an effect. On the other hand, liquid styrene and styrene vapours can cause eye irritation. The NOAEC value (No Observed Adverse Effect Concentration) has been set to 100 and 216 ppm at 7 and 1-hour of exposure, respectively (EU RAR, 2008). Styrene may also cause irritation of the respiratory tract, but at a higher concentration level than the level that causes eye irritation.

A great amount of data from tests on humans and animals does not give any reason to classify styrene as sensitizing (EU RAR, 2008).

Systemic effects: Acute and chronic effects
The information on acute toxicity in humans in relation to inhalation indicates that styrene has an effect on the central nervous system at a concentration level of 200-400 ppm (for 30-90 minutes). There is no information about other acute effects of styrene in humans, and the available tests on animals are considered invalid, since the acute effect of styrene on mice differs from the effect on humans (EU RAR, 2008). In relation to the risk assessment where no acute effects on the central nervous system are observed the concentration is set to 100 ppm for a 7-hour exposure (EU RAR, 2008). Notifiers of the substance under REACH indicate a systemic DNEL of 174.25 mg/m³ for the acute effect via inhalation. This DNEL has been calculated on the basis of a NOAEC of 863 mg/m^3 and applies a safety factor of 5, which considers differences between individuals[26].

A considerable number of studies exist on humans regarding the toxicity of styrene after a longer period of exposure (chronic) or repeated exposure. Studies on effects of styrene related to the working environment show that the most significant symptoms are irritation of the eyes and nose. However, disturbances of the central nervous system, such as headache and drowsiness, are the most health hazardous effects (EU RAR, 2008). Neurotoxic effects of styrene are also well-documented in animal tests. The effect of styrene on eyesight and especially hearing is regarded to be the most relevant effect in relation to repeated inhalation exposure. A previous report for the Danish EPA also indicates that long-term inhalation exposure to styrene in the working environment may lead to a partial hearing loss (the Danish EPA, 2014C). In 2012, upon request by the Danish EPA, it was concluded by the ECHA risk assessment committee (RAC) that styrene must be classified as STOT SE1 (causes organ damage (auditory organs) after long-term or repeated exposure) (ECHA, 2012A).

Regarding the inhalation effects, the noifiers under REACH determined a chronic DNEL of 10.2 mg/m³ (repeated dose toxicity). That was established according to a NOAEC (No Observed Adverse Effect Concentration) for systemic effect determined at 212 mg/m^3). For the calculation of DNEL, a joint safety factor of 3 is applied, where the variations from workers to the general population are taken into consideration[27].

In connection with the risk assessment carried out by RAC for styrene, the substance was also classified as Repr. 2 (suspected of damaging the unborn child) (ECHA, 2012A). Reproduction toxic effects were demonstrated as development effects (delayed development) in a well-documented two generation rat test, and that study estimated a NOAEC of 120 mg/kg/day (EU RAR, 2008). There is also a large amount of data material on the reproduction toxic effects in humans after exposure in the working environment (e.g., miscarriage, menstrual irregularities, decreased fertility and sperm quality, lower birthweight and mentally underdeveloped children), but no definite conclusions can be made on the bais of these studies (EU RAR, 2008).

There is no evidence of mutagenic effects. Previously, IARC (International Agency for Research on Cancer) evaluated styrene to be potentially carcinogenic for humans, but the current conclusion is that there is no evidence of that effect in humans (EU RAR, 2008).

Identification of critical effect and determination of safe dose
The critical effect (in case of oral exposure) for styrene is the reproduction toxic effect of the substance, where NOAEC has been estimated to be 120 mg/kg/day (RAR, 2008).

According to the RAR report, the NOAEC value is based on inhalation exposure from a well-documented two generation study on rats. In a previous risk assessment for the Danish EPA

[26] https://echa.europa.eu/da/registration-dossier/-/registered-dossier/15565/7/6/3

[27] https://echa.europa.eu/da/registration-dossier/-/registered-dossier/15565/7/1

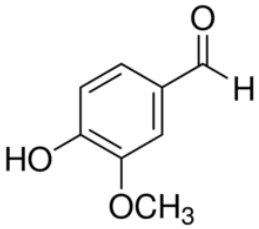
(the Danish EPA, 2015B), a DNEL oral of 0.6 mg/kg BW/day was applied for styrene based on the above-mentioned NOAEC of 120 mg/kg/day. For styrene, the intake and absorption of the substance by inhalation corresponds to intake by oral exposure, and in the previous risk assessment no safety factor was applied in that connection. For the calculation of DNEL, a joint safety factor of 200 was applied, and it takes the differences in exposure duration into account (from sub chronic to chronic, factor 2), the variations between species (allometric scaling from rats to humans, factor 4), a factor 2.5 for the remaining differences between the species as well as the variations between humans (intraspecies, factor 10), as stated in ECHA Guidance on information requirements and chemical safety assessment – Chapter R.8 (ECHA, 2012B). On the other hand, the notifiers of the substance state a considerably higher DNEL oral of 2.1 mg/kg BW/day (repeated dose toxicity), but the background for that value is not clearly indicated in the published part of the registration data. In this report, the lowest of these two DNEL, i.e., a DNEL of 0.6 mg/kg BW/day, is applied.

5.2.4 Vanillin

Identification, classification and physicochemical properties

The physicochemical properties and the classification of the substance from the self-classification by industry as indicated on ECHA's website appears in Table 21.

Table 21. Physicochemical properties stated in ECHA's published registration data for the substance as well as the classification of the substance in ECHA's CLP database.

Chemical name	Vanillin
Synonyms	1-butoxypropan-2-ol 3-hydroxy-4-methoxybenzaldehyde 3-Methoxy-4-hydroxy benzaldehyde 4-hydroksy-3-metoksybenzaldehyd, 4-Hydroxy-3-methoxy-benzaldehyde 4-Hydroxy-3-methoxybenzaldehyd 4-Hydroxy-3-methoxybenzaldehyde 4-hydroxy-3-méthoxybenzaldéhyde Benzaldehyde, 4-hydroxy-3-methoxy- Ester vanilin vanilla VANILLIN Vanillin (4-hydroxy-3-methoxybenzaldehyde) Wanilina
CAS no.	121-33-5
EC no.	204-465-2
Chemical structure	
Classification Self-classification after CLP (aggregated)	Eye Irrit. 2, H319 – Causes serious eye irritation (1085 of 1457 notifiers) Skin Sens. 1, H317 - Can cause allergic skin reaction (226 of 1457 notifiers) Acute Tox. 4, H302 – Harmful if swallowed (91 of 1457 notifiers)

	Skin Irrit. 2, H315 – Causes skin irritation (12 of 1457 notifiers) Aquatic Chronic 3, H412 – Harmful to aquatic life with long lasting effects (1 of 1457 notifiers) Aquatic acute, H400 – Very toxic to aquatic life (1 of 1457 notifiers)
Physical condition	Solid, crystalline powder, colourless to slight yellow
Molecular weight	152.15 g/mol
Melting point	81-83 °C
Boiling point	285 °C
Vapour pressure	1.33 hPa (107 °C)
Distribution coefficient (log Pow)	1.17
Water solubility	9 g/L

Absorption and distribution
100 mg/kg BW vanillin in an oral dosage for male albino rats led to the excretion of most of the metabolites via the urine within 24 hours, primarily as glucuronide and sulphate conjugates, even though vanillin acid is eliminated as free acid and as glycine conjugate. After 48 hours, 94% of the dose was excreted as metabolites. For a human adult, there was an increase in vanillin acid in the urine over a period of 24 hours after a dosage of 100 mg dissolved in water, which corresponds to app. 94% of the vanillin dosage (EFSA, 2005).

Local effects: Irritation and allergy
The substance does not have a harmonized classification, but most notifiers report the substance to be eye irritating (74% state the category Eye Irrit 2).

Vanillin is a known contact allergen in humans. Between 11 and 100 cases have been published in literature, and those cases do not give enough accessible knowledge to determine the threshold values of the sensitizing effect of the substance (SCCS, 2012). In a previous report for the Danish EPA on allergy causing substances in toys, a LOAEL (Lowest Observed Adverse Effect Level) of >12.500 µg/cm^2 is stated, but the background is not evident. The recommendation from SCCS regarding the assessment of allergy causing substances is that when a lack of specific data is encountered, thena general threshold value of 0.8 µg/cm^2 should be applied (based on a concentration of 100 ppm) (SCCS, 2012).

Systemic effects: Acute and chronic effects
Various older studies have been included in the published part of the registration data for this substance, where the conclusions in general indicate no hazard or low hazard for the studied effects. No systemic effects are stated, and the substance does not show CMR effects according to the existing data.[28]

Identification of critical effect and determination of safe dose
The critical toxicological effect of vanillin is considered to be the allergenic effect of the substance. Vanillin is a known allergen, but according to the existing knowledge it has not been possible to determine limit values for elicitation or sensitization. Therefore, the general threshold value recommended by SCCS in relation to risk assessment is applied: 0.8 ug/m^2 (SCCS, 2012).

5.3 Summary of hazard assessment

The table below shows the critical effect of the four selected substances, the most relevant exposure route and the chosen threshold value for the subsequent risk assessment.

[28] https://echa.europa.eu/da/registration-dossier/-/registered-dossier/2209/7/1

Table 22. Summary of hazard assessment

Substance	CAS no.	Critical effect, threshold value	Relevant route of exposure
Acrylic acid	79-10-7	Irritation of skin, 1 mg/cm²	Dermal
		Irritation of respiratory tract, 3.6 mg/m³	Inhalation
n-butyl methacrylate	97-88-1	Irritation of respiratory tract, 66.5 mg/m^3	Inhalation
Styrene	100-42-5	Reprotoxic effect, of 0.6 mg/kg BW/day	Oral, dermal
Vanillin	121-33-5	Sensitizing, 0.8 ug/cm^2	Dermal

6. Exposure and risk assessment

6.1 Background

Based on the results of the analysis, an initial assessment of the risk of the 16 substances was carried out where possible (SECTION 5.1), and subsequently a hazard assessment of four of the substances was carried out. This chapter comprises a risk assessment of whether it can be considered safe to use the four substances in the 3D pens in question. The method used to calculate the risk when using the identified substances in the material for the 3D pen is described below as well as in CHAPTER 3.

6.2 Method for calculation of risk

The calculation method given in the REACH Risk Assessment Guideline (ECHA, 2016) is used to calculate the risk. In each case, it is on the basis of the Risk Characterization Ratio (RCR) assessed whether there is a health risk. RCR is calculated by using the identified threshold values (DNEL), by using the exposure calculated on the basis of the parameters set in CHAPTER 3, and by using the analysis results from CHAPTER 4.

The health risk of exposure to a given concentration of a substance over a given period of time is assessed on the basis of worst case calculations for dermal, inhalation and oral exposure, respectively, and they are compared to the respective DNEL values summarized in Table 22. The risk of an effect is thus assessed from an RCR value calculated by using the following equation:

$$RCR = \frac{D_{Der}}{DNEL} \quad \text{or} \quad RCR = \frac{D_{Inh}}{DNEL} \quad \text{or} \quad = \frac{D_{oral}}{DNEL} \qquad (7)$$

If significant contributions are expected via more than one route of exposure, then the individual contributions can be calculated and a total exposure is used to calculate the RCR. In that case, the result of a total risk should be subject to reservations as the exposure assessments are carried out by using conservative assumptions, e.g. that 100% of the substance is released from the material.

For threshold values given as a concentration, as is the case for irritation of the respiratory tract by acrylic acid with a DNEL of 3.6 mg / m³, the RCR value is calculated on the basis of exposure calculated as concentration (i.e., C_{inh} or C_{der} is used instead of D_{inh} or D_{der}, respectively).

An RCR value above 1 indicates that there is a risk associated with the given substance under the selected conditions. If the value is close to 1, the exposure scenario can be refined and the risk can be assessed on the basis of a more realistic scenario. It is also possible to include parameters from the hazard assessment of the substance, which could be relevant for the setting of a refined DNEL value.

6.3 Results and discussion

6.3.1 Acrylic acid

Irritation by inhalation - acute effect

To calculate the concentration of the substance in the room (C_{inh}) by means of equation 1, the

exposure assessment parameters set in CHAPTER 3 are used. They are summarized in Table 23.

Table 23. Parameters for calculation of exposure level and RCR for irritation by inhalation of acrylic acid.

Parameter	Description	Value for 3-6-year-olds	Value for 6-11-year olds
FCprod	Concentration of substance in the material in mg/g	0.31 mg/g	0.31 mg/g
Qprod	Amount of material in grams	25 g	50 g
Vroom	Volume of the room where exposure takes place, in m^3	20 m^3	20 m^3
Cinh	Concentration of substance in the room, in mg/m^3	0.39 mg/m^3	0.78 mg/m^3
DNEL	Threshold value	3.6 mg/m^3	3.6 mg/m^3
RCR	Risk Characterization Ratio	0.11	0.22

The calculated RCR values are highest for 6 to 11-year-old children, but both RCR values are below 1. The age group recommendation for the 3D pen in question is closer to the age group 6-11 years, and therefore this calculation is considered most relevant. If a room size of 2 m^3 is used instead to simulate that all substance is released locally around the child when playing (and inhaled), then it will result in an RCR of 1.1 for 3-6-year-olds and 2.2 for 6-11-year-olds, respectively. The calculation assumes that 100% of the substance in the material the child is playing with will be released in the room without taking the effect of possible ventilation and dispersion of the substance to the rest of the room into account. This simple model probably provides a worst case assessment of risk by inhalation, but acrylic acid is a volatile substance with a high vapor pressure, which may positively affect the evaporation of the substance from the material. Therefore, the risk assessment cannot rule out that the threshold value of acrylic acid potentially can be exceeded locally, which may cause respiratory irritation when using the 3D pen. However, acrylic acid does tend to bind to plastic, and in this project, it is not possible to verify the risk, as additional data is needed to determine the emission of the substance from the material to the surrounding air, as well as the possible spreading of the substance over time, e.g., by collecting air samples and measuring the concentration of the substance in the samples.

Skin irritation – acute effect

To calculate the amount of substance per surface (L_{der}) by means of equation 3, the parameters for exposure assessment set in CHAPTER 3 are used. They are summarized in Table 24.

Table 24. Parameters for calculation of exposure levels and RCR for skin irritation from acrylic acid.

Parameter	Description	Value for 3-6-year-olds	Value for 6-11-year olds
FCprod	Concentration of substance in the	0.31 mg/g	0.31 mg/g

	material in mg/g		
Qprod	Amount of material in contact with skin in grams	5 g	5 g
Ader	Skin area exposed, in cm^3	46.25 cm^2	63.75 cm^2
Lder	Skin exposure, in mg substance/cm^2	0.034 mg/cm^2	0.024 mg/cm^2
DNEL	Threshold value	1 mg/cm^2	1 mg/cm^2
RCR	Risk Characterization Ratio	0.034	0.024

The calculated RCR values are highest for 3-6-year-old children, but both RCR values are significantly below 1. The age group recommendation for the 3D pen in question is closer to the age group 6-11, and therefore this calculation is considered most relevant. Acrylic acid has a tendency to bind to plastic, and due to the physicochemical properties of the substance it can be expected to evaporate from the material and thereby reduce skin exposure. Therefore, this simple model is expected to provide a worst case assessment of risk through skin contact. The content of acrylic acid is considered safe in relation to the risk of skin irritation under the conditions applied.

6.3.2 n-Butyl methacrylate

Irritation by inhalation - chronic effect

To calculate the concentration of the substance in the room (C_{inh}) by means of equation 1, the exposure assessment parameters set in CHAPTER 3 are used. They are summarized in Table 25.

Table 25. Parameters for calculation of exposure level and RCR for irritation by inhalation of n-butyl methacrylate.

Parameter	Description	Value for 3-6-year-olds	Value for 6-11-year olds
FCprod	Concentration of substance in the material in mg/g	66 mg/g	66 mg/g
Qprod	Amount of material in grams	25 g	50 g
Vroom	Volume of the room, where the exposure takes place, in m^3	20 m^3	20 m^3
Cinh	Concentration of substance in the room, in mg/m^3	82.5 mg/m^3	165 mg/m^3
DNEL	Threshold value	66.5 mg/m^3	66.5 mg/m^3
RCR	Risk Characterization Ratio	1.24	2.48

The calculated RCR values for the systemic effect of the substance by inhalation are high for 6-11-year-olds as well as for 3-6-year-olds. The age group recommendation for the 3D pen in question is closer to the age group of 6-11, and therefore this calculation is considered most relevant. The substance is a volatile organic compound, and therefore the concentration of the

substance in a restricted area is not expected to remain high for very long. Furthermore, as only chronic effects and no acute effects of the substance are registered, it is not considered relevant to assess exposure in the restricted area.

The calculation assumes that 100% of the substance in the material the child is playing with is released, without considering the effect of possible ventilation that will reduce the concentration in the area over time. The simple model provides a worst case assessment of risk by inhalation, but n-butyl methacrylate is volatile, which may positively affect the evaporation of the material from the material, but also cause the substance to be removed more quickly from the room with ventilation. In addition, the model does not consider that the substance may be retained in the material to some extent, and the release will therefore be less than 100%. If instead the calculated concentration in the air is compared to the threshold value for irritation by inhalation (local effect), stated to be 366.4 mg/m³, then it is not exceeded under the conditions applied.

Therefore, based on the calculated RCR values it cannot be ruled out that the content of the substance potentially poses a risk of irritation by inhalation under the conditions applied. However, it has not been possible to verify the risk on the basis of the analyses performed.

6.3.3 Styrene

Reprotoxic effect, chronic

To assess the risk of the reproductive toxicity of styrene, a possible contribution is expected from dermal as well as oral exposure. Therefore, exposure is calculated through both routes of exposure, and total exposure is used to calculate risk.

The oral intake (D_{oral}) is calculated by using equation 5 and the parameters set in CHAPTER 3, which are summarized in Table 26.

Table 26. Parameters for calculation of oral exposure to styrene.

Parameter	Description	Value for 3-6-year-olds	Value for 6-11-year olds
FCprod	Concentration of substance in the material in mg/g	1.1 mg/g	1.1 mg/g
Qprod intake	Amount of product which is consumed, in grams	0.1 g	0.1 g
n	Number of incidents per day	1	1
BW	Body weight in kg	18.6	31.8
Doral	Oral intake in mg/kg BW/day	0.006	0.003

To calculate the dermal contribution to the systemic exposure of styrene, equations 3 and 4 are used with the exposure assessment parameters set in CHAPTER 3, which are summarized in Table 27.

Table 27. Parameters for calculation of dermal exposure to styrene.

Parameter	Description	Value for 3-6-year-olds	Value for 6-11-year-olds
FCprod migr	Concentration of substance in the material in mg/g	1.1 mg/g	1.1 mg/g
Qprod	Amount of material in gram	5 g	5 g
Ader	Skin area that is exposed, in cm^3	46.25 cm^2	63.75 cm^2
N	No. of incidents per day	1	1
BW	Body weight in kg	18.6	31.8
Dder	Dermal exposure in mg substance/kg BW/day	0.296	0.173

Table 28. Total systemic exposure level to styrene.

Parameter	Description	Value for 3-6-year-olds	Value for 6-11-year olds
Doral	Oral contribution to exposure	0.006	0.003
Dder	Dermalt contribution to exposure	0.296	0.173
Sum	Oral + dermal contributions	0.302	0.716
DNEL	Threshold value	0.6 mg/kg BW/day	0.6 mg/kg BW/day
RCR	Risk Characterization Ratio	0.503	0.294

The calculated RCR values are highest for 3-6-year-old children, and the dermal contribution exceeds the oral, which was expected, as the oral intake is considered to be very limited for that age group of children. The age group recommendation for the 3D pen in question is closer to the age group of 6-11, and therefore this calculation is considered most relevant. The model for oral absorption assumes that all of the substance in the material is released and absorbed when consumed (100% migration). This is considered to be realistic based on the physico-chemical properties of styrene and when compared to data from animal experiments (EU RAR, 2008). At the same time, the amount of material used in the calculation for the expected intake is considered to be rather high, and that is considered to be a worst case consideration.

As worst case consideration, the intake of styrene through the skin is set to 100%, which is significantly higher than what can be expected. Data in the available literature indicates that only 2-5% is absorbed through the skin. Therefore, the model for both oral and dermal exposure reflects a worst case assessment of the risk. As both RCR values are below 1, it is unlikely that styrene poses a risk under the conditions applied.

Irritation by inhalation

In addition to the repotoxic effect of styrene, the substance also causes irritation by inhalation. This effect is therefore assessed in relation to children's exposure to the substance when using 3D pens. To calculate the air concentration of the substance in the room (Cinh) by means of equation 1, the exposure assessment parameters set in CHAPTER 3 are used. They are summarized in Table 29.

Table 29. Parameters for calculation of exposure level and RCR for irritation by inhalation of styrene.

Parameter	Description	Value for 3-6-year-olds	Value for 6-11-year olds
FCprod	Concentration of substance in the material in mg/g	1.1 mg/g	1.1 mg/g
Qprod	Amount of material in grams	25 g	50 g
Vroom	Volume of the room, where the exposure takes place, in m^3	20 m^3	20 m^3
Cinh	Concentration of substance in the room, in mg/m^3	1.38 mg/m^3	2.75 mg/m^3
DNEL	Threshold value	10.2 mg/m^3	10.2 mg/m^3
RCR	Risk Characterization Ratio	0.135	0.270

The RCR values are below 1, but if a room size of 2 m^3 is used to simulate that all of the substance is released locally around the child when playing (and is inhaled), then that results in an RCR of 1.3 for 3-6-year-olds and 2.7 for 6-11-year-olds, respectively. Since the headspace analysis of styrene indicates that only a fraction (10-20%) of the substance can be expected to evaporate during use in the 3D pen, the actual exposure will be lower and result in RCR values below 1. Therefore, the content of styrene is considered safe in relation to the risk of irritation by inhalation under the conditions applied.

6.3.4 Vanillin

Allergen effect

To assess the sensitizing effect of vanillin, the calculation of the dermal load stated as the amount of substance per surface (L_{der}) is used, and it is calculated by using equation 3. The parameters for the calculation are set in CHAPTER 3 and summarized in Table 30.

Table 30. Parameters for calculation of exposure level of vanillin for comparison with threshold value set by SCCS.

Parameter	Description	Value for 3-6-year-olds	Value for 6-11-year-olds
FCprod	Concentration of substance in the material in mg/g	0.059 mg/g	0.059 mg/g
Qprod	Amount of material in contact with the skin in gram	5 g	5 g

Ader	Skin area exposed, in cm^2	46.25 cm^2	63.75 cm^2
Lder	Skin exposure, in µg substance/cm^2	6.38 µg/cm^2	4.63 µg/cm^2
SCCS threshold*	General threshold value	0.8 µg/cm^2	0.8 µg/cm^2

* SCCS, 2012.

The concentrations in the analysed samples correspond to a dermal exposure of 6.38 and 4.63 µg/cm^2, respectively. The age group recommendation for the 3D pen in question is closer to the older age group, and therefore this calculation is considered most relevant. As described in Section 5.2.4, there is no clear concentration limit for sensitization or induction of an allergic reaction to vanillin. The calculated skin exposure is above the proposed general limit value for allergens of 0.8 µg/cm^2. The calculations are based on an expected migration of 100%, but the play dough-like material, in which vanillin was detected, has a rather solid texture, so retention of the substance in the material is expected to occur. No data on migration of vanillin was found that could be used to refine the scenario, but migration from the product is expected to be lower than 100%. A direct comparison of the amount of substance per surface and the limit value will be an overestimation of the risk, and no vanillin migration studies have been carried out that can further elucidate the risk.

The simple calculation model assumes that the child is exposed to the total content of vanillin from the amount expected to come into contact with the skin during use. Based on the expectation that vanillin to some extent is retained in the material, a refinement of the scenario can be carried out by assuming that the child is exposed only to vanillin from a layer of 0.01 cm closest to the skin (recommendation from ECHA, 2016). If a density of the material of 1 g/cm^3 is assumed, then that corresponds to the amount of material (Qprod) being reduced to 0.46 g for the 3-6 year olds and 0.64 g for the 6-11 year olds, respectively. That would result in skin exposure of 0.59 µg/cm^2 for both age groups. Therefore, the refinement of the scenario based on these assumptions suggests that an exposure level below the general limit value set by SCCS is likely to be achieved.

Therefore, it is likely that the amount of vanillin does not pose a health risk in the material in question. However, exposure may be close to the general threshold value.

6.4 Summary of risk assessment

The risk assessment was carried out on the basis of a number of realistic worst case assumptions in connection with the development of exposure scenarios for the substances. In general, that means that the real risk of the investigated substances is most likely to be lower than stated in the report, and for all of the examined substances it has been necessary to refine some of the scenarios used.

For acrylic acid, calculations of the air concentration in a restricted area suggest that the threshold value of acrylic acid potentially can be exceeded and cause respiratory irritation when the 3D pen is used. However, the properties of the substance indicate that the risk is overestimated under the conditions applied, and in this project, it has not been possible to verify the risk as that would require additional data.

The calculated RCR values for the systemic effect of n-butyl methacrylate by inhalation are higher than 1 for both 6-11-year-olds and 3-6-year-olds. However, the concentration of the substance in the room is not expected to remain high over longer periods of time as the substance is volatile. High concentrations over longer periods of time determine whether chronic effects are induced, and the simple calculation thus provides a worst case assessment

of the risk of chronic effects by inhalation. If the calculated concentration in the air instead is compared to the threshold value for irritation by inhalation (local effect), reported to be 366.4 mg/m³, then it is not exceeded under the conditions applied. Based on the calculated RCR values, it cannot be ruled out that the content of the substance potentially can pose a risk of chronic effects by inhalation. However, it has not been possible to verify the risk on the basis of the analyses performed.

It is not considered likely that styrene represents a risk in relation to the reprotoxic effects under the conditions applied, as the calculated RCR values are below 1. The RCR is highest for 3-6-year-old children and as expected the dermal contribution exceeds the oral contribution. In addition to the repotoxic effect of styrene, the substance causes irritation by inhalation. If a room size of 2 m^3 is used to simulate that all substance is released locally around the child when playing (and is inhaled) that will result in an RCR over 1 for both age groups. The analyses performed indicate that only a fraction (10-20%) of the substance evaporates when using the 3D pen. If 20% of the substance evaporates, then the actual exposure will be lower and result in RCR values below 1. Therefore, the content of styrene is considered safe in relation to the risk of irritation by inhalation under the conditions applied.

The content of vanillin is high in the product. That results in dermal exposure above the overall threshold value set by SCCS if full migration is assumed from the entire amount expected to come into contact with the skin. It is considered likely that the substance to a certain degree will be retained in the material, which has a play dough-like texture. If instead, migration is calculated from a 0.01 cm thick layer in contact with the skin, then dermal exposure will be below the threshold value. herefore it is considered likely that vanillin does not pose a health risk in the product in question.

7. Conclusion and future perspectives

The survey and analysis of selected materials for 3D pens has provided increased knowledge of the techniques used in 3D pens, of the specific use situation and of the chemical content of the materials used.

Based on the results of the screening analyses of 3D pens nad the knowledge of possible constituents, it was chosen to perform quantitative analyses of the content of 16 selected substances. Among the tested materials, ten of the substances were detected above the detection limit of the method. Acrylic acid, styrene, n-butyl methacrylate and vanillin were subsequently selected for assessment of the health risk during use. Based on the refined exposure scenarios it is estimated that styrene is not expected to pose a risk. For acrylic acid and n-butyl methacrylate, the risk calculations indicate that it cannot be ruled out that the threshold values for inhalation might be exceeded, but at the same time the properties of the substances and the assumption of full migration mean that the calculation is likely to overestimate the risk. It has not been possible to verify the risk in this project due to lack of data. For vanillin, dermal exposure is above the general threshold value set by SCCS if full migration is assumed from the entire amount expected to come into contact with the skin. However, it is considered likely that the substance to a certain extent will be retained in the material that has a play dough-like texture. If instead, migration is calculated from a 0.01 cm thick layer in contact with the skin, then dermal exposure will be below the threshold value. Therefore, it is considered likely that vanillin can be expected to not pose a health risk in the product in question.

The risk assessment does not consider the fact that simultaneous exposure to several different chemical substances may cause combination effects – the so-called cocktail effects. Combination effects change the risk of effects and mean that even if exposure to a single substance in a certain amount does not in itself pose a risk, then there might be a risk if you simultaneously are exposed to other substances. It is a difficult issue, and there is a lack of knowledge regarding how combination effects work. The screening analyses suggested a wide range of possible chemical substances. All of the substances have not been identified or reviewed in detail in this report. The screening confirmed that the UV reactive materials had far more different substances than the materials that harden without a light source, e.g., ABS and PLA. A more detailed review of the 151 identified substances as well as follow-up analyses and a risk assessment of selected substances could provide increased knowledge of other relevant substances than the 16 selected for analysis in this project.

The materials used for 3D pens have proven to be very diverse and, e.g., cover thermoplastics (where the material can melt and harden by cooling) and thermoset plastics (where polymerization takes place under UV light). This means that the analysis of the materials is complex, and the materials must be treated differently. A lot of considerations are necessary in connection with the analysis when the results are to be used for exposure and risk assessments. Data should, as far as possible, reflect the actual use situation, but many parameters are of importance, e.g., that the chemical composition of UV curing materials changes after extrusion because polymerization takes place.

This project focuses on exposure to chemical substances. In previous reports on 3D printing, the problem related to particle generation connected with printing was elucidated. It has not been investigated whether particle generation also could pose a health risk when children use 3D pens. No emission measurements were carried out on volatile substances in climate chambers or in use situations, which could give a true and fair view of the exposure and provide increased knowledge of, for example, concentration levels in the immediate proximity of children during use.

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Enclosure 1. Questionnaire used during survey

The questions in this questionnaire were used as a starting point, and they were adjusted according to who was interviewed: the manufacturer, distributor or event manager.

On your website, we can see that you sell 3D pens (name of the product) and that they are targeted at children.

- Which considerations have you had regarding the sale of 3D pens to children when their content of harmful substances and their use by children are considered?
- Which age group would you in general recommend for each 3D pen (and why)?
- As far as we understand, special measures have been taken for some 3D pens in order to minimize the risk for children; could you explain/elaborate on safety during use?
- Would it be possible to provide us with the safety data sheets (SDS) for the materials that are used for 3D pens?
- According to the REACH regulation we are entitled to receive information about the content of substances of very high concern – the so-called candidate list substances – where the content exceeds 0.1% by weight. Could you inform us about possible contents in the 3D pens or materials that are used?

To help us evaluate the exposure of children when they use 3D pens we would like to know more about the use of the 3D pens. Would you tell us about your experience with the actual use of the products, e.g.:

- Is the extruded polymer soft or sticky when it comes out of the pen and for how long does it remain so?
- Do the materials/the 3D pen emit any odour or smoke during use?
- For how long do children typically play with the 3D pen?
- Do children face special challenges when using 3D pens?
- Which considerations have you had regarding events/courses that are targeted at children (recommended age interval for target group, choice of materials, etc.)?
- Do you have other user-related observations that could have relevance when assessing exposure?

Enclosure 2. Estimate of extrusion rates

To assess the risk when using 3D pens, a realistic estimate is required of the amount of material used by the children when they use of the pen. Therefore, a series of analyses have been carried out on the purchased 3D pens, and the amount of material that is extruded in one minute has been weighed. The extrusion rate for three repetitions per pen was calculated and reported in **Table 31** below.

Furthermore, the amount in each material unit was reported to the extent possible. The weight or volume reported should be used with reservations, as they are not always stated on the unit or the packaging, and for some units they are reported for open containers where part of the material already had been used.

Table 31. Extrusion rates and weight or volume per material unit.

3D pen no.	Weight or volume per material unit	Extrusion rate, g/min – test 1	Extrusion rate, g/min – test 2	Extrusion rate, g/min – test 3	Extrusion rate, g/min – average
4	1.68 g	0.56	0.58	0.59	0.57
8	app. 12 g	1.14	1.18	1.15	1.16
2	0.90 g	0.39	0.39	0.41	0.40
9	app. 12 g	1.01	0.93	0.98	0.97
3	26 ml	2.43	2.44	2.17	2.35
5	20 g	3.37	3.76	2.74	3.29
1	22 ml	1.66	2.37	1.95	1.99
7	app. 14 g	2.65	2.76	2.56	2.65
	Average, g/min				1.67

An average extrusion rate of 1.67 g/min corresponds to extruding 25 g of material in 15 minutes and 50 g of material in 30 minutes.

Survey and Risk Assessment of 3D pens

3D pens are small handheld tools that can extrude plastic material in thin strings and thus used to create figures in 3D. Several types of 3D pens are marketed for children. The Environmental Protection Agency wishes to gain more knowledge about the content of chemical substanc-es in materials used in 3D pens and to assess whether children's use of 3D pens can pose a health risk. The survey shows that the materials used in 3D pens for chil-dren, primary cure do to temperature reduction or UV lighting. Screening analyzes of materials for 3D pens indicated content of a wide range of chemical substanc-es. 16 substances were selected for quantitative analysis, of which 4 (styrene, vanillin, acrylic acid and n-butyl methacrylate) were selected for health risk assessment. Based on the assessment the content of styrene and vanillin was not expected to pose a risk, but the risk calculations for acrylic acid and n-butyl methacrylate content could not exclude that the thresholds for health effects can be exceeded in a worst-case scenario assum-ing full migration. Both substances were identified in liquid materials that cure do to UV lighting. This survey is the first on 3D pens. It focuses on exposure to chemical substances, but it was not possible within the framework of the project to quantify and assess all identified chemi-cal substances in the materials studied. Also, measure-ments have not been made in real-life situations or exam-ined aspects such as combination effects and particle formation in relation to the risk assessment of children's use of 3D pens.

The Danish Environmental
Protection Agency
Haraldsgade 53
DK-2100 København Ø

www.mst.dk